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The Estimation of the Volatile Matter Content of Propellant Explosives

Part I.—The Estimation of Water by an improved Fischer Method

BY

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The Estimation of the Volatile Matter Content of Propellant Explosives

Part I.—The Estimation of Water by an improved Fischer Method

By T. G. BONNER

(Read at the Meeting of the Society on October 2nd, 1946)

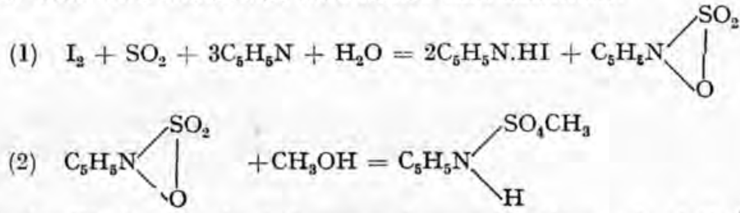
An accurate knowledge of the moisture content of a propellant explosive is of considerable importance in assessing its influence on the ballistic properties of the propellant, particularly in relation to variations in moisture content with changes in temperature and humidity. In the few instances where determinations of the moisture content have been reported in the literature,[1,2] it is apparent that rather arbitrary methods have been employed which are unsatisfactory both for absolute estimations and for the measurement of small variations. It was evident that an accurate routine method was required for estimating quantities of water of the order of a few milligrams in all types of propellant explosives; for this purpose the procedure developed by Fischer[3] was investigated with a view to applying it to propellants.

THE FISCHER REAGENT FOR THE ESTIMATION OF WATER—

The increasing employment of the Fischer reagent for the estimation of the water content of liquids and solids in recent years is an indication of the recognition of its wide applicability and high accuracy. The principle of this method of estimation was discovered by Fischer when attempting to determine the water present in liquid sulphur dioxide and mixtures of this with other solvents. He made use of the fact that sulphur dioxide is oxidised by iodine in presence of water and that decolorisation takes place owing to the disappearance of iodine in the reaction. The reaction was represented by the equation:

$$2H_2O + SO_2 + I_2 \rightleftharpoons H_2SO_4 + 2HI$$

The equilibrium was displaced completely to the right by addition of pyridine, which removed the acid products. For the estimation of water in organic solvents, Fischer employed the reagent now known by his name consisting of a solution of sulphur dioxide, iodine and pyridine in methyl alcohol. The reagent was standardised by titration with known amounts of water dissolved in methyl alcohol, the end point being detected by a change in colour from light yellow (due to the products of the titration) to brown when the whole of the water had reacted and excess of the reagent was present. As the reagent and the titration solution absorb atmospheric moisture very rapidly, Fischer employed the smallest possible vessels (100 ml. Erlenmeyer flasks) for the titrations to reduce the volume of air present. In a detailed study of the method by Smith, Bryant and Mitchell[4] they discovered that the reaction occurred in two distinct stages, and that one molecule of iodine reacted with only one molecule of water and not with two molecules as Fischer had assumed:



(1) $I_2 + SO_2 + 3C_5H_5N + H_2O = 2C_5H_5N.HI + C_5H_5N\langle{}^{SO_2}_{O}$

(2) $C_5H_5N\langle{}^{SO_2}_{O} + CH_3OH = C_5H_5N\langle{}^{SO_4CH_3}_{H}$

In applying the Fischer method these workers and others who followed usually employed methyl alcohol to extract the water from solids, transferring the methyl alcohol solution to a flask and either titrating directly with the Fischer reagent or adding an excess of the latter and titrating back with a standard solution of water in methyl alcohol. Although in general, steps were taken to exclude atmospheric moisture during the titration, the exposure of a large surface area of the hygroscopic methyl alcohol to the atmosphere at one or more stages of the determination was not avoidable. This factor assumes considerable importance when the quantity of water to be estimated is of the order of a few milligrams, but this has not always been emphasised by later workers. Other more obvious limitations were that the end-point colour change was insufficiently sensitive for the accurate determination of such small quantities of water, and coloured solutions, of course, were not titratable. The latter difficulties were overcome by Almy, Griffin and Wilcox,[5] who introduced a potentiometric method of detecting the end-point, which depended on the change of potential of a platinum-tungsten electrode system immersed in the solution. A more sensitive method was reported by Wernimont and Hopkinson[6] by application of the dead-stop end-point technique used by Foulk and Bawden[7] in the detection of the end-point in iodimetric titrations. The dead-stop end-point technique depends on the fact that when a small electromotive force is applied to two platinum electrodes immersed in iodine solution a measurable current will flow while iodine is present to remove the hydrogen which tends to accumulate on the cathode, but immediately the whole of the iodine is removed (by titration) polarisation of the cathode by hydrogen accumulation occurs and a back e.m.f. is set up sufficient to overcome the small applied e.m.f., the current then ceasing to flow through the solution. A sensitive galvanometer included in this circuit registers the change of current and the attainment of the end-point is indicated by the return of the galvanometer needle to the zero of the scale. The technique was adapted to the Fischer method by adding a measured volume of the Fischer reagent in excess to the water solution to be estimated and titrating back the excess with a standard solution of water in methyl alcohol. A more refined technique for the dead stop end-point method was reported by McKinney and Hall[8] employing a "magic eye" electronic tube instrument in place of the sensitive galvanometer.

While studying the application of this modified Fischer method to the estimation of water in cordites and other solid explosives, which involved quantities of water of the order of a few milligrams, it became evident that it was of paramount importance to reduce to a minimum the possibility of interference by atmospheric moisture, and further a solvent less hygroscopic than methyl alcohol for the extraction of the water to be estimated was desirable. Two recent papers have provided details of methods for the estimation of very small quantities of water, in which specially designed apparatus is employed for the exclusion of atmospheric moisture during sampling and titration. Levy and others[9] claim to have estimated 1 to 25 mg. quantities of water with a precision of ±20 to 100 μg., using a small titration vessel completely protected from the atmosphere by means of a tightly fitting rubber cap through which the samples and reagents are introduced by means of a hypodermic syringe. Aepli and Carter[10] report the estimation of 0–60 p.p.m. of water in liquid petroleum fractions, using an all-glass apparatus in which 150 ml. samples are transferred for titration to a 500 ml. four-necked flask fitted with a mercury-seal stirrer, exposure to the atmosphere being avoided during transfer. Both methods appear to be satisfactory for the special purposes for which they were devised, although it should be mentioned that in the first method a maximum error, *i.e.*, ±100 μg. on 1 mg. is an error of ±10 per cent., while in the second method the contents of the flask are transitorily exposed to the atmosphere at the stage immediately following the introduction of the 150 ml. sample.

The need for a simple inexpensive apparatus suitable both for general application and for the accurate estimation of a few milligrams of water is evident, and the apparatus and technique described below have fulfilled all requirements for such estimations in propellants and other explosives, and many other materials. The problem of providing a more suitable solvent than methyl alcohol for extraction of the water to be estimated was solved by use of diethylene dioxide (dioxan). Although pure dry dioxan is non-conducting under the conditions of the dead-stop end-point method and is a non-solvent for the pyridinium salts formed during the titration, it can be rendered sufficiently conducting and a solvent for the pyridinium salts by addition of about 25 per cent. of its volume of methyl alcohol; this condition is fulfilled during a titration by the addition of Fischer reagent (which contains methyl alcohol) provided that the volume added is sufficient. Pure dioxan or, where necessary, mixtures of dioxan with methyl alcohol were invariably used for the extraction of water from solids or the dissolution of solids; the proportion of dioxan in mixtures with methyl alcohol was always maintained as great as possible.

All solutions to be estimated were kept in stoppered measuring cylinders, reducing to a minimum the surface area of solution exposed to the atmosphere during withdrawal of an aliquot portion with a pipette. Using dioxan or mixtures of dioxan and methyl alcohol, it was not found necessary to provide for the exclusion of atmospheric moisture during the very short period of time required for the withdrawal. During the actual titration, however, such provision was essential and was achieved by passing a stream of dry nitrogen continuously into the titration vessel for the whole of the time the apparatus was in use; although the effect on the water content might have been negligible the stream of dry nitrogen was not allowed to bubble into the solution as this would have led to loss of iodine by vaporisation.

In order to increase the accuracy of the method for small quantities of water the use of a more dilute Fischer reagent was investigated and it was found that the reagent recommended by previous workers (including Smith, Bryant and Mitchell[4]) could be diluted without impairing the sensitivity of the method. The final solution adopted had a strength equivalent to about 1·5 mg. water per ml. The standard water solution for back-titration of the excess Fischer reagent was prepared from a 1 : 1 by volume mixture of methyl alcohol and dioxan and was approximately equivalent in strength to the Fischer reagent, *i.e.*, it contained about 1·5 mg. of water per ml.; standard water solutions prepared with a higher proportion of dioxan to methyl alcohol, including pure dioxan were found to be equally satisfactory. For the estimation of larger quantities of water, the stronger Fischer reagent can of course be employed and the water content of the stock water solution correspondingly increased. Finally, it was discovered that an e.m.f. of 200 mv. or even higher could be employed without any apparent decrease in sensitivity; to standardise procedure an e.m.f. of 80 mv. was used. In presence of some highly oxygenated substances the voltage must be kept very low, *e.g.*, not above 20 mv. for tetryl.

METHOD

PREPARATION OF REAGENTS—

Pyridine is dried by allowing it to stand over anhydrous barium oxide for a few weeks, pouring off and distilling. Dioxan is dried by allowing it to stand over freshly heated calcium oxide for 3–4 days and filtering the supernatant dioxan through a sintered glass funnel with atmospheric moisture excluded. Methyl alcohol and iodine are used as AnalaR reagents.

The Fischer reagent is prepared by dissolving 84·7 g. of iodine in 667 ml. of methyl alcohol in a large round-bottomed flask, adding 269 ml. of pyridine and cooling in ice; 64 g. of liquid sulphur dioxide are weighed into a small beaker and carefully added to the iodine solution while shaking gently, the flask being closed after each addition with a bung carrying a calcium chloride tube. The solution is diluted with an equal volume of methyl alcohol and stored in a dark glass bottle.

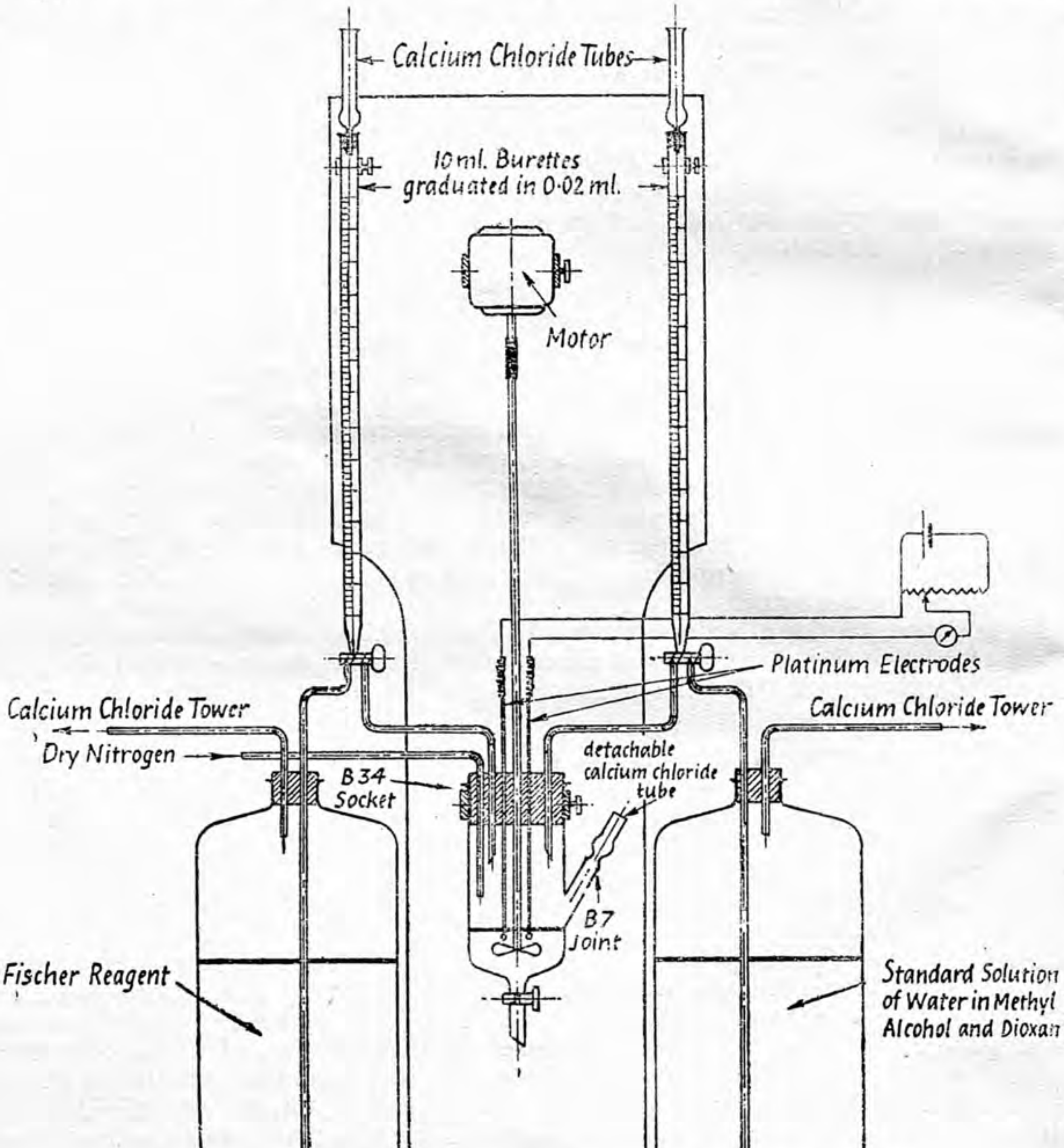
The standard solution of water is prepared by adding about 2·5 ml. of water to a mixture of 1 litre of methyl alcohol and 1 litre of dioxan (each of these solvents obtained as described above contain about 0·02–0·03 per cent. of water).

APPARATUS—

The Fischer reagent and the standard water solution are separately contained in dark-coloured bottles forming part of the apparatus shown in the figure. Both solutions are pumped into the burettes by a hand bellows, the air passing into the bottles being dried by passage through a calcium chloride tower. The burettes are of 10 ml. capacity, graduated in 0·02 ml. and are closed by small calcium chloride tubes having a short length at the top of the tube filled with silica gel to prevent rapid "caking" of the calcium chloride; this involves no danger of loss of water from the standard water solution, which is very dilute. The titration vessel has a ground glass B.34 neck and a capacity of 60–70 ml. It carries a well-fitting bakelite stopper drilled with holes to take the two burettes, the two glass tubes with sealed-in platinum wires, the stirrer and an inlet tube attached to a drying train through which nitrogen from a cylinder of the compressed gas is passed continuously into the vessel; the drying train consists of a calcium chloride tower, two wash bottles containing concentrated sulphuric acid and a phosphorus pentoxide tube. All the tubes passing through the bakelite stopper are treated with sealing wax to give an air-tight seal and the stirrer and stopper are thickly coated with a suitable vaseline. The provision of a tap to allow titrated solutions to be run off and replaced by dry nitrogen avoids the necessity of removing the titration vessel after each titration and the exposure of the dry, hygroscopic solvent on the interior surface of the vessel to atmospheric moisture. The solutions to be estimated are introduced through the narrow side arm which at all other times is closed with a small calcium chloride tube, the end of which is ground to fit the B.7 ground glass neck of the side-arm. The bottles, the burettes, the electric motor for driving the stirrer and the titration vessel are mounted on a wooden stand and baseboard as shown. A self-contained portable potentiometer (Cambridge Instrument Co., No. L.25740) calibrated to 2 mv. was used to apply the e.m.f. of 80 mv. to the platinum electrodes, using a 1·5 v. dry battery as the source of supply. The connection between the platinum electrodes and the potentiometer is made in the usual way by filling the glass tubes with mercury. The pointer galvanometer of the unipivot type included in the output circuit has a sensitivity of 15 mv. per full scale deflection and was quite adequate for detecting the end-point of the titration.

STANDARDISATION OF THE STANDARD WATER SOLUTION—

After passing dry nitrogen into the titration vessel for 15 minutes, deliver 4 ml. of Fischer reagent into the vessel and apply an e.m.f. of 80 mv. to the platinum electrodes. With the galvanometer needle deflected off the scale, stir the solution and add the standard water solution until the colour approaches a yellowish brown. Then continue the addition dropwise until the galvanometer needle "kicks"; stop the stirrer and the return of the needle to the zero point of the scale indicates the end-point of the titration. Run out the solution, deliver another 4 ml. of Fischer reagent into the vessel and titrate as before. Repeat until three successive titrations do not differ by more than 0·01 ml. During the titration the stirrer should not be allowed to rotate too rapidly, since its mechanical action is then liable to sweep away the hydrogen accumulating on the cathode at the end-point and so delay the movement of the galvanometer needle back to the zero of the scale.



Into each of two 50 ml. measuring cylinders provided with stoppers pipette 50 ml. of "dry" dioxan (*i.e.*, dioxan dried to a water content of 0·02–0·03 per cent. as described above) and stopper the flasks immediately. The dioxan should be drawn into the pipette by means of an air or water suction pump with a calcium chloride tower inserted between the pipette and the source of suction. Into one of the measuring cylinders introduce a weighed quantity of water by means of a Lunge Rey pipette. Then titrate each of the two solutions in turn by withdrawing a 5 ml. portion in a pipette, introducing it into the titration vessel through the side arm, adding a measured excess of the Fischer reagent and titrating back the excess of Fischer reagent with the standard water solution as above. Repeat the titration until two successive values do not differ by more than 0·01 ml.

The amount of water in each of the two solutions is then expressible in ml. of the standard water solutions. The actual difference in water content of the two solutions is known since it is equal to the weight of water added to one, and this can be equated to the difference in ml. of standard water solution for the two solutions. The equivalence of the standard water solution to the weight of added water is thus established and its actual water content can be calculated. Usually another solution of a weighed amount of water in 50 ml. of "dry" dioxan was prepared and titrated to provide a check. It was found advisable on all occasions to add sufficient excess of Fischer reagent to give a back titration of at least 1 ml. of the standard water solution. An actual example is given to make this method of standardisation clear and to demonstrate the accuracy of the method.

(1) *Titration of Fischer reagent (F.R.) against standard water solution (S.W.S.):*
1 ml. of F.R. ≡ 1·33 ml. of S.W.S. .. .. (i)

(2) *Titration of 5 ml. of "dry" dioxan:*
F.R. added, 3 ml.; S.W.S. required for back titration, 2·90 ml.

From (i), 3 ml. of F.R. ≡ 3 × 1·33 = 3·99 ml. of S.W.S.
Back titration = 2·90 ml. ,, ,,

∴ Water in 5 ml. of "dry" dioxan ≡ 1·09 ml. ,, ,, ... (ii)

(3*a*) *Titration of 5 ml. of dioxan containing* 0·01396 *g. of added water:*
F.R. added, 8·50 ml.; S.W.S. required for back titration, 1·12 ml.

From (i), 8·50 ml. of F.R. ≡ 8·50 × 1·33 = 11·30 ml. of S.W.S.
Back titration = 1·12 ml. ,, ,,

∴ Total water in the dioxan solution ≡ 10·18 ml. ,, ,,
From (ii), water originally in the dioxan ≡ 1·09 ml. ,, ,,

∴ The added water, 0·01396 g., ≡ 9·09 ml. ,, ,,
Hence **1 ml. of S.W.S.** ≡ 0·01396/9·09 ≡ **0·00154 g. of water**.

(3*b*) A similar titration to (3*a*) but with 0·0151 g. of added water, gave
1 ml. of S.W.S. ≡ 0·00155 g. of water

If at any stage during the standardisation it is found necessary to detach the Fischer titration vessel, *e.g.*, through blockage of a burette, it is essential on replacing the vessel to titrate again 4 ml. portions of the Fischer reagent with the standard water solution as described in the first part of the determination; this titration is repeated until the original relationship between the two solutions is established. Only when this is achieved can the standardisation be resumed at the point where the vessel was detached.

Since the Fischer reagent gradually decreases in strength, it is essential to standardise it by titration against the standard water solution daily, and the latter should be standardised by the procedure described above at least once per week.

Results of estimations of dioxan solutions of known water content prepared by adding weighed quantities of water to "dry" dioxan are given in Table I. The results indicate an accuracy of 2–3 per cent. over the range 3–15 mg. of water.

EFFECT OF ATMOSPHERIC MOISTURE—

The effect of atmospheric moisture in the Fischer method was investigated by (1) standardising the standard water solution as above at two different relative humidities and (2) repeating the standardisation at the same two relative humidities but without passing dry nitrogen into the titration vessel. The two relative humidities were 47 per cent. and 89 per cent. The results are shown in Table II. In the column headed "Factor" is given the volume in ml. of standard water solution equivalent to 4 ml. of Fischer reagent, while the last column, headed "Strength of S.W.S.," is the amount of water per ml. of the standard water solution as found by standardisation. It is clear that with a relative humidity of 47 per cent. no interference from atmospheric moisture occurs when "dry" nitrogen is not passed into the titration vessel. With the relative humidity at 89 per cent., however, the effect of atmospheric moisture, in the absence of the dry nitrogen, is to reduce the effective strength of the Fischer reagent relative to the standard water solution by about 5 per cent. and to result in an error in the estimation of the strength of the standard water solution. Since the apparatus is designed to reduce exposure to atmospheric moisture to a minimum (quite apart from the employment of dry nitrogen) it is evident that any method involving detachment of the titration vessel during a series of estimations is liable to an even greater error, varying with the prevailing humidity.

TABLE I

WEIGHED AMOUNTS OF WATER IN DIOXAN SOLUTION

Weight of water added to 5 ml. of dioxan g.	Weight of water found g.	Error %
0·0155	0·0158	+1·8
0·0153	0·0154	+0·7
0·0128	0·0126	−1·8
0·0103	0·0102	−1·0
0·0101	0·0102	+1·0
0·0095	0·00935	−1·6
0·0052	0·00534	+2·8
0·00364	0·00360	−1·7
0·00314	0·00304	−3·3
0·00294	0·00286	−2·8

TABLE II

EFFECT OF ATMOSPHERIC MOISTURE

	Relative humidity	Factor	Strength of S.W.S.
Passing dry nitrogen ..	47	2·00	0·00266
	89	1·98	0·00264
Not passing dry nitrogen	47	1·99	0·00265
	89	1·89	0·00273

ANALYSIS OF THE WATER CONTENT OF PROPELLANTS

The high viscosity of solutions of nitrocellulose, which is the principal constituent of propellants, precludes the use of nitrocellulose solvents for the dissolution of the water in propellant samples. To overcome this difficulty, attempts were made to free the water by heating under reflux and distilling the sample with dioxan in an all-glass apparatus. The end of the condenser was connected to a 50 ml. measuring cylinder by means of a suitable adapter, to which was attached a calcium chloride tube to exclude atmospheric moisture. 2–3 g. of the propellant sample, prepared by breaking or cutting into small pieces, was added to 50 ml. of dioxan in a 150 ml. conical flask, and refluxed gently in the apparatus for about 20 minutes; the major portion (about 35 ml.) of the dioxan was then allowed to distil over slowly into the measuring cylinder. The procedure was repeated with 50 ml. of dioxan without the sample, and the water content of each of the solutions determined. The method was found to be satisfactory except that occasionally the propellant decomposed with liberation of water. During the distillation it was observed that the propellant grains became slightly swollen in appearance and further investigation revealed that if the sample was allowed to stand in contact with dioxan overnight, the dioxan penetrated into the propellant grains and completely extracted the water without causing dissolution of the propellant (which would have resulted in the formation of a viscous solution). The method finally adopted therefore was to add 25 ml. of "dry" dioxan to a 2–3 g. sample of propellant in a 25 ml. measuring cylinder, which was stoppered and allowed to stand overnight. The water content of the supernatant dioxan was then determined on 5 ml. aliquots. The water content of the "dry" dioxan was also determined and the percentage of water in the sample calculated. The results of determinations on several different types of propellants are given in Table III and are compared with the water content as determined on 25 g. quantities of the samples by an adaptation of the entrainment method of Dean and Stark[11] (*i.e.*, removal of the water by distillation from a solution of the sample in acetophenone with benzene and direct measurement of the volume of water collected). Excellent agreement is evident. The propellants investigated variously contained nitrocellulose, nitroglycerine, diethyldiphenylurea, nitroguanidine, dinitrotoluene, dibutyl phthalate and mineral jelly.

TABLE III

WATER IN PROPELLANTS

Sample 2 g./20 ml. of dioxan	Wt. of water in 5 ml. aliquot of dioxan g.	Water found %	Water found by Dean and Stark method %
NH powder, web size 050	(I) 0·00520 (II) 0·00518 (III) 0·00504	(I) 1·04 (II) 1·04 (III) 1·01	1·05
NH powder, web size 033	(I) 0·0046 (II) 0·00465	(I) 0·92 (II) 0·93	0·95
Cordite WM 130	(I) 0·0020 (II) 0·0020	(I) 0·40 (II) 0·40	0·40
Cordite containing nitroguanidine	(I) 0·0012 (II) 0·0011	(I) 0·24 (II) 0·22	0·25
Solventless cordite	(I) 0·00285 (II) 0·0028	(I) 0·57 (II) 0·56	0·55

Other solid substances that are not as heat-sensitive as propellants can be successfully treated by the method of distilling with dioxan, and substances which dissolve completely in dioxan or methyl alcohol - dioxan mixtures can be titrated directly after dissolution. Direct titration of insoluble substances by introducing a weighed amount of the solid through the side arm of the Fischer titration vessel gave erratic results in the few cases investigated, *e.g.*, starch, but this method may be successful for some substances and should always be investigated. To the group of substances which interfere in the Fischer reaction should be added boric acid, which has been found to esterify the methyl alcohol present with liberation of a nearly quantitative yield of water.

SUMMARY

An improved method and apparatus is described for employing the Fischer reagent for the estimation of quantities of water of the order of a few milligrams. Atmospheric moisture is excluded by passing a stream of dry nitrogen gas into the vessel used for titration, and the value of this innovation is demonstrated by ascertaining the effect of different relative humidities on titrations with and without the employment of dry nitrogen gas. The method has been successfully used for the estimation of water in propellants and other explosives.

In conclusion I should like to thank Mr. G. L. Hutchison, of the Armament Research Department, for his valuable advice on the problem of estimating the water content of propellants and the Chief Scientific Officer, Ministry of Supply, for permission to publish this material.

Acknowledgment is made to the Chemical Inspection Department, Ministry of Supply, whose staff independently suggested the use of the side tube in the reaction vessel as an alternative to a tube through the stopper.

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ARMAMENTS RESEARCH DEPARTMENT
MINISTRY OF SUPPLY
WALTHAM ABBEY, ESSEX

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Discussion

Mr. N. Strafford enquired how the standard water solution was prepared and standardised and whether its water content altered on storage. He also confirmed the experience of American workers (*cf.* G. C. Warren, *Canad. Chem. Process Inds.*, 1945, **29**, 370; *Chem. Abstr.*, 1945, **39**, 3221), who had recommended the use of hydrated sodium acetate ($3H_2O$) as a convenient substance for the standardisation of the Fischer reagent.

Dr. H. E. Cox enquired whether the author had found the method suitable for determining water in fatty oils and whether polyhydroxyl compounds, such as glycols or glycerol or even higher alcohols such as propanol, interfered.

Mr. J. H. High asked if there was any objection to the use of nitrogen to stir the mixture durin titration.

Mr. A. H. Holloway mentioned that the end-point might be approached by titrating the water wit the Fischer reagent, in which case a fading end-point was observed, or by adding an excess of reagent an titrating back with standard water in methanol, in which case a definite end-point, the "dead-stop," v obtained. In the estimation of small quantities of water these end-points in many cases did not ag with one another or with the visual end-point. Had the author any observations on this point, and did he think that the dead-stop end-point was well defined, because it was, in fact, overshot?

Mr. J. Haslam asked if the author had any experience of the Carter and Williamson method (Analyst, 1945, **70**, 369) in which a direct titration of the water was carried out.

Mr. R. C. Chirnside asked the author if he thought the method would be applicable to two of the commoner refrigerants, liquid sulphur dioxide and methyl chloride. The first of these was of course one of the constituents of the Fischer reagent. The quantities of water involved were of the order of 50 parts per million.

In a written communication, Mr. N. L. Allport, who was unable to attend the meeting, said he had been privileged some time ago to visit the author's laboratory and see the procedure for determining moisture actually being carried out. He had been much impressed by the manner in which the defects associated with the Fischer method had been eliminated. Since then his colleagues at the B.D.H. Laboratories had set up the equipment described in this paper and had found the method quite satisfactory. He considered that the modifications proposed effected most significant improvements in the Fischer method and he felt that analysts were indebted to the author for a most useful advance.

Mr. T. G. Bonner, in reply to Mr. Stafford's question, stated that full experimental details of the preparation and standardisation of the standard water solution were given in the paper; solutions of known weights of water in dioxan were employed in place of hydrated salts. In reply to Dr. Cox, he said that the Fischer reagent had been used for pine oil and no difficulties should arise in the case of fatty oils; neither polyhydroxyl compounds nor higher alcohols interfered and he had used the method with diethylene glycol and glycerol in the normal way. Replying to Mr. High, he stated that the only objection to passing the nitrogen directly into the mixture for the purpose of stirring was that the methyl alcohol readily vaporised, leaving a deposit of pyridinium salts on the walls of the titration vessel. Replying to Mr. Holloway and Mr. Haslam, he referred to the fact that many workers had reported the fading end-point when the Fischer reagent was directly titrated against water and in view of this phenomenon it was unwise to expect agreement with the described method of adding excess of Fischer reagent and titrating back the excess with a standard solution of water; in explanation of the fading end-point he suggested that the sensitivity of the Fischer reagent to atmospheric moisture and the general failure of workers to prevent interference were partly responsible, since the gradual take-up of atmospheric by the very slight excess of Fischer reagent present at the end-point of the direct titration would tend to cause fading of the end-point. In the method now described the dead-stop end-point is most well defined and sensitive to 0·01 ml. of the standard solution containing 1·5 mg. of water per ml. In reply to Mr. Chirnside, the author stated that the method had been originally developed by Fischer for the estimation of water in liquid sulphur dioxide and it was doubtless equally applicable to methyl chloride; in 1945, a method had been reported in *Ind. Eng. Chem., Anal. Ed.*, for the estimation of 0–60 parts per million of water in petroleum fractions, in which 150 ml. samples were used.

Notes

THE DETERMINATION OF IRON IN CEREALS

A recent paper gives figures for the iron content of flours of different extraction milled from the same grist of wheat or rye.[1] Wheats vary in their iron content, and during milling the products may pick up traces of iron from the plant.[2] For both reasons, therefore, the iron contents of samples of flour of given extraction are not constant.

Iron is an important nutrient in cereal grains, and work is in progress in these laboratories on its distribution in wheat, oats and other cereals. Meanwhile the analytical method we are at present employing may be of interest.

Reagent—Of the many reagents that have been used for the estimation of small quantities of iron in biological material those containing the cyclic N–C–C–N grouping which form co-ordination complexes with ferrous iron are preferable because of their specificity, the wide *p*H range over which they can be used and their sensitivity. With the introduction of 2:2′-dipyridyl by Hill,[3] 2:2′:2″-tripyridyl by Cooper,[4] 1:10-phenanthroline by Saywell and Cunningham[5] and five new derivatives of 1:10-phenanthroline by Moss, Mellon and Smith,[6] a wide choice has become available. The absorption spectra of the ferrous complexes of these

2.

The Estimation of the Volatile Matter Content of Propellant Explosives

Part 2.—The Estimation of Ethyl Alcohol and Ether

BY

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The Estimation of the Volatile Matter Content of Propellant Explosives

Part 2.* The Estimation of Ethyl Alcohol and Ether

BY T. G. BONNER

IN the manufacture of nitrocellulose powders a mixed solvent of ethyl alcohol and ether is invariably used to facilitate the mixing of constituents and to ensure homogeneity of the product. The removal of these solvents in the final stage of manufacture is never complete, and a small residuum is always tenaciously retained in the propellant. A knowledge of the exact amount of this volatile matter is of considerable importance in the chemistry of propellants, particularly in relation to the effect on ballistic stability of changes in the volatile matter content arising from variations in the temperatures and humidities under which the propellant is stored and used.

Several attempts have been made to estimate this residual volatile matter in simple nitrocellulose powders containing only cellulose nitrate and diphenylamine, but most of the

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* For Part 1, see ANALYST, 1946, **71**, 483–490.

methods described are liable to considerable error. Desmaroux[1] obtained an aqueous solution of the organic solvents by heating under reflux and distilling with aqueous sodium hydroxide solution, and then estimated them by physical methods. The same author[2] later estimated the ethyl alcohol and ether in the aqueous distillate by oxidation with potassium dichromate in acid solution; the ethyl alcohol was separately estimated by the method of Fischer and Schmidt,[3] involving conversion into ethyl nitrite, which was removed by a stream of carbon dioxide and passed into acid potassium iodide solution, the iodine liberated being titrated with thiosulphate. Dalbert[4] also estimated the ethyl alcohol and ether together by dichromate oxidation but replaced the method of Fischer and Schmidt for ethyl alcohol by one depending on surface tension effects. Lalande[5] estimated ether alone by drawing a stream of air through the aqueous distillate, removing the ethyl alcohol in a strongly alkaline solution of potassium permanganate and then absorbing and oxidising the ether to acetic acid with dichromate in diluted sulphuric acid (1+1), the unchanged dichromate being estimated iodimetrically.

A preliminary investigation of these methods indicated that the estimation of mixtures of ethyl alcohol and ether at concentrations of about 0·1 per cent. in aqueous solution was possible with an accuracy to within 1 or 2 per cent. The ethyl alcohol is readily oxidised quantitatively to acetic acid by the method of Szeberenyi[6] by boiling with potassium dichromate in a 1:10 by volume mixture of concentrated sulphuric acid and the aqueous alcohol-ether solution. The ether is not attacked under these conditions and can be estimated by difference after oxidation of another portion of the aqueous solution in a 1:1 by volume mixture of sulphuric acid and solution, which converts both the ethyl alcohol and ether quantitatively to acetic acid; this oxidation is carried out by allowing the mixture to stand at room temperature for 1½ to 2 hours.

In applying this method to the estimation of an aqueous distillate obtained by heating under reflux and distilling a sample of propellant with aqueous sodium hydroxide two major difficulties were encountered. First, a small but appreciable amount of volatile oxidisable matter, from the disintegration of the propellant, distilled with the ethyl alcohol and ether and secondly, in modern nitro-cellulose powders dibutyl phthalate is often present and from it butyl alcohol is formed by the hydrolysing action of the sodium hydroxide; the butyl alcohol distils and interferes in the subsequent dichromate oxidation of the ethyl alcohol and ether.

The first difficulty was met by distilling with sodium hydroxide solution a synthetic mixture of cellulose nitrate, diphenylamine and any other constituents in the amounts present in a 25-g. sample of the propellant and determining the amouut of oxidisable matter in the distillate obtained; a correction was then applied for this amount. The presence of butyl alcohol in the distillate, however, required the development of a method of estimating ethyl alcohol, ether and butyl alcohol together in dilute aqueous solution.

THE ESTIMATION OF ETHYL ALCOHOL, BUTYL ALCOHOL AND ETHER IN DILUTE AQUEOUS SOLUTION

Attempts to effect complete hydrolysis of the dibutyl phthalate and subsequent distillation of the whole of the butyl alcohol were unsuccessful; prolonged hydrolysis and distillation did not achieve more than about 80 per cent. recovery of butyl alcohol from known quantities of dibutyl phthalate. Methods of estimating similar simple aliphatic compounds in dilute aqueous solution have been described by Christiansen and Fulmer[7] for mixtures of ethyl alcohol, butyl alcohol and acetone, by Bayly,[8] who investigated the oxidation of aliphatic alcohols in about 0·5 per cent. aqueous solution with potassium dichromate in 45 per cent. sulphuric acid solution; by Skrabal,[9] who claims that with minor modifications the Fischer and Schmidt method (*loc. cit.*)[3] could be applied to an aqueous solution of any simple aliphatic alcohol with an accuracy to within about 1 per cent.; and by Fresenius,[10] who estimated aqueous butyl alcohol solutions by oxidation with dichromate followed by distillation and titration of the acid products in the distillate with sodium hydroxide solution.

Application of Lalande's method—As a first step, the direct estimation of ether in dilute aqueous solutions containing ethyl and butyl alcohols by Lalande's method (*loc. cit.*)[5] was investigated. It was found that an alkaline potassium permanganate solution absorbed both alcohols, whilst the ether, unaffected by passage through this solution, could be absorbed and oxidised quantitatively to acetic acid by potassium dichromate in a 1:1 by volume mixture of sulphuric acid and water. By drawing a slow stream of air through the aqueous solution of the three constituents at 30° to 40° C. for 5 to 6 hours, then through alkaline potassium permanganate solution and finally through the acid potassium dichromate solution, it was established that a quantity of ether of the order of 50 mg. could be estimated with an error of about 1 to 2 per cent.

Oxidation of butyl alcohol—The oxidation of butyl alcohol was next studied and it was found that, under the conditions that convert ethyl alcohol quantitatively into acetic acid in Szeberenyi's method (*loc. cit.*),[6] 1 molecule of butyl alcohol consumes 3 atoms of oxygen; this oxidation procedure is subsequently referred to as the "mild" oxidation method. Attempts to discover other oxidation conditions giving a simple stoichiometric relation between butyl alcohol and oxygen but not affecting ether were unsuccessful, and it was evident that the only immediate possibilities were the complete combustion of the three constituents to carbon dioxide and water, or the quantitative conversion of all three into acetic acid. The former possibility was rejected when the wet combustion method of Williams,[11] employing potassium dichromate or potassium iodate in concentrated sulphuric acid solution, gave erratic results with aqueous solutions of these constituents. Since the oxidation of ether to acetic acid in diluted sulphuric acid (1+1) appeared to be sensitive to any change in the ratio of acid to water, the investigation of the oxidation of butyl alcohol to acetic acid had to be confined to this acid concentration. Employing a dilute aqueous solution of butyl alcohol of known concentration and this concentration of acid, the oxidation was carried out at different temperatures for varying periods of time, and it was finally established that if the temperature was maintained at 0° C. for 24 hours and then raised to and maintained at room temperature for a further 1½ hours, the oxidation proceeded quantitatively to acetic acid; no further change then took place in the potassium dichromate content of the oxidising solution and the amount of potassium dichromate consumed corresponded to 8 atoms of oxygen per molecule of butyl alcohol. Under these conditions of oxidation ethyl alcohol and ether were both quantitatively oxidised to acetic acid. This oxidation procedure was designated the "total" oxidation method. Results of the direct estimation of synthetic aqueous butyl alcohol solutions by the mild and total oxidation procedures are given in Table I. An accuracy of to within 1 or 2 per cent. is evident.

TABLE I

ESTIMATION OF BUTYL ALCOHOL IN AQUEOUS SOLUTION

Butyl alcohol per 100 ml. of aqueous solution taken g.	Type of oxidation	Potassium dichromate consumed g.	Butyl alcohol found g.	Error per cent.
0·0810	Mild	0·319	0·0802	−1·0
0·1084	,,	0·426	0·1074	−1·0
0·1200	,,	0·482	0·1212	+1·0
0·1170	Total	1·224	0·1154	−1·3
0·1170	,,	1·232	0·1162	+0·6
0·1200	,,	1·260	0·1188	−1·0
0·1200	,,	1·258	0·1187	−1·0

Application of methods above—These oxidation methods were applied to synthetic aqueous solutions of ethyl alcohol, butyl alcohol and ether. Three aliquot portions of the solution were separately treated (1) by the "mild" oxidation method, (2) by the "total" oxidation method and (3) by Lalande's method for ether; the quantity of dichromate consumed in each was determined iodimetrically and calculated to 100 ml. of the original solution. The ether was thus obtained directly while the alcohols were obtained indirectly by the following method of calculation.

For 100 ml. of the aqueous solution, let the amounts of potassium dichromate in grams required in the various oxidations be

M. for the preferential oxidation of the two alcohols by the mild oxidation method.
T. for the total oxidation of the three constituents to acetic acid by the total oxidation method.
A. for the oxidation of ethyl alcohol to acetic acid.
B. for the oxidation of butyl alcohol to acetic acid.
C. for the oxidation of ether to acetic acid.

The amounts of dichromate represented by M, T and C are experimentally determined values; the amount of dichromate consumed by the butyl alcohol in 100 ml. of the aqueous solution in the mild oxidation is 3B/8, since one molecule of butyl alcohol requires 3 atoms of oxygen for the mild oxidation and 8 atoms for the total oxidation.

Then for the mild oxidation of 100 ml. of the solution

$$M = A + (3B/8)$$

and for the total oxidation of 100 ml. of the solution

$$T = A + B + C.$$

From these two equations,

$$5A = 3C + 8M - 3T \quad \text{and} \quad 5B = 8(T - M - C)$$

the amount of dichromate equivalent to both alcohols is therefore obtained. The relationship between potassium dichromate and each of the three constituents is given by

1 g. of potassium dichromate ≡ 0·1886 g. of ether
≡ 0·02344 g. of ethyl alcohol
≡ 0·0944 g. of butyl alcohol,

from which the amount of each constituent present can be calculated. Results of the estimation of synthetic aqueous solutions of ethyl alcohol, butyl alcohol and ether are given in Table II, and indicate an accuracy to within 1 per cent. for the ether estimation and to within about 2 to 3 per cent. for the alcohols.

TABLE II

ESTIMATION OF MIXTURES OF ETHYL ALCOHOL, BUTYL ALCOHOL AND ETHER IN AQUEOUS SOLUTION

Aqueous solution taken contained: g./100 ml.		Type of oxidation	Potassium dichromate		Found, per 100 ml.		
			Calculated equivalent g.	Amount consumed g.	Ether (direct) g.	Ethyl alcohol (indirect) g.	Butyl alcohol (indirect) g.
Ethyl alcohol	0·0499	Mild	0·624	0·626	0·0504	0·0490	0·1051
Butyl ,,	0·1037						
Ether	0·0500	Total	1·576	1·588			
Ethyl alcohol	0·0502	Mild	0·650	0·646	0·0517	0·0491	0·1100
Butyl ,,	0·1095						
Ether	0·0510	Total	1·644	1·648			
Ethyl alcohol	0·0453	Mild	0·597	0·595	0·0625	0·0435	0·1033
Butyl ,,	0·1015						
Ether	0·0620	Total	1·597	1·610			

In applying this method to estimations on aqueous distillates from propellants containing dibutyl phthalate it was necessary to apply corrections for oxidisable impurities in the distillate, in both the mild and the total oxidation, and these increased the error of the method to the order of about 5 per cent. In the absence of any other suitable method, however, this procedure was regarded as satisfactory for providing a preliminary estimate of the true ethyl alcohol and ether contents of nitrocellulose powders. In the wide variety of powders investigated the ether content was invariably higher than the alcohol content, the former usually ranging from about 0·2 to 2 per cent. and the latter from about 0·1 to 1 per cent.; some old types of powders contained over 5 per cent. of residual solvent.

When the necessity arose for an accurate routine method for the estimation of these volatile constituents certain unsatisfactory features of the method described became apparent. These included the large amount of sample required (25 to 50 g.), which is not always available, and the length of time required for an estimation (2 to 3 days); further, certain special investigations required greater accuracy than was possible with this procedure. As an alternative, the possibility was considered of vaporising the ethyl alcohol and ether in a current of air without decomposition of the propellant and subsequently absorbing and differentially oxidising them in acid dichromate solutions of different concentrations.

THE SEMIMICRO-ESTIMATION OF ETHYL ALCOHOL AND ETHER VAPOURS ENTRAINED IN AIR

Somogyi[12] describes a method for estimating mixtures of ethyl alcohol and ether vapours in air by passing the air first through 9 *N* sulphuric acid, which preferentially absorbs the alcohol, and then through a solution of potassium dichromate in diluted sulphuric acid (1+1), in which the ether is absorbed and oxidised to acetic acid; the ethyl alcohol is estimated by subsequently oxidising its solution in sulphuric acid with potassium dichromate. Quantities of the order of 0·25 to 0·025 g. of each constituent were estimated by this method with an accuracy to within about 3 per cent. Komar, Sergunin and Fainberg[13] criticise certain features of this method and apply a slightly modified form of it to the estimation of much smaller quantities of ethyl alcohol and ether in air; their results show that when the amount of ether present is less than 5 mg. the recovery of it is less than 90 per cent., but with larger quantities the method is accurate to within about 3 to 4 per cent.

It was evident that this method might be further modified to include the simultaneous absorption and oxidation of the ethyl alcohol; to this end the conditions necessary for the quantitative oxidation of small amounts of ethyl alcohol (5 to 30 mg.) to acetic acid at room temperatures were investigated. It was found that this could be achieved quite readily with potassium dichromate in diluted sulphuric acid (1+10) in about 1¼ hrs. at ordinary room temperatures. To test the modified method, weighed quantities of ethyl alcohol and ether contained in thin sealed glass tubes were introduced into a 500 ml. flask fitted with an inlet and an outlet tube each carrying a stop cock, the inlet tube reaching to the bottom of the flask. After the stop cocks were closed the tubes were fractured by shaking the flask. The flask was placed in an absorption train similar to that shown in the diagram, in the position occupied in the diagram by the three-necked flask. The first absorption spiral tube contained the acid dichromate solution for the oxidation of the ethyl alcohol, the second absorption spiral tube alkaline potassium permanganate solution (prepared as described later) and the third the usual acid dichromate solution for oxidation of the ether The alkaline potassium permanganate solution was used because in determinations on propellants its presence was effective in absorbing any oxidisable volatile constituents that would not be affected by the weak oxidising solution in the first absorption tube but that might be oxidised by the stronger solution in the third tube. At the head of the absorption train were two conical flasks, the first containing a concentrated chromic acid solution to remove any oxidisable impurities in the air drawn through the train and the second serving as a trap for any acid spray from the first. The last absorption tube in the train was connected to a bottle in which a partial vacuum was maintained by means of a water pump. After all the stop-cocks had been opened a slow stream of air was drawn through the apparatus, carrying the ethyl alcohol and ether vapours into the absorption tubes. After 3 to 4 hours the air flow was stopped, the acid dichromate solutions were washed out and the unchanged potassium dichromate was estimated iodimetrically. Results for several such determinations are given in Table III, and these show that the method is accurate to within about 2 per cent. for quantities of ethyl alcohol and ether not less than about 5 mg.

TABLE III

ESTIMATION OF MIXTURES OF ETHYL ALCOHOL AND ETHER VAPOURS ENTRAINED IN AIR

Taken in mixture					
Ethyl alcohol g.	Ether g.	Ethyl alcohol found g.	Error per cent.	Ether found g.	Error per cent.
0·0365	0·0795	0·0361	−1·1	0·0803	+1·0
0·0343	0·0475	0·0340	−0·9	0·0491	+3·4
0·0227	0·0152	0·0216	−4·8	0·0155	+2·0
0·0187	0·0155	0·0185	−1·1	0·0160	+3·2
0·0097	0·0110	0·0096	−1·0	0·0109	−0·9

APPLICATION TO THE ESTIMATION OF ETHYL ALCOHOL AND ETHER IN PROPELLANTS—

Various methods were considered for removing the ethyl alcohol and ether from nitrocellulose powders free from volatile impurities oxidisable by the acid dichromate solution used in the first absorption spiral tube. It became evident that their complete removal could only be effected by dissolution of the sample of powder in a suitable solvent. Kraus[14] gives a comparison of the solubilities of cellulose nitrates, of nitrogen contents ranging from 10·20 to 12·29 per cent., in 70 different solvents; from this list a selection of the most likely solvents was made and of these, mononitrobenzene proved by far the most suitable.

Dissolution of a 2 to 3-g. sample of a nitrocellulose powder was achieved in about 2 hours at 100° C. Blank determinations on the solvent alone, and also on solutions of the usual constituents of nitrocellulose powders in it, indicated complete absence of interference by volatile oxidisable products. The method adopted therefore was to agitate the sample of powder (2–3 g.) with 25 ml. of nitrobenzene by means of a gas-tight stirrer arrangement in the three-necked flask shown in the diagram. The flask was immersed in a boiling water bath and a stream of air was bubbled through the solution to remove the ethyl alcohol and ether. Other constituents of nitrocellulose powders volatile to some extent at 100° C., *e.g.*, diphenylamine, were almost completely retained by passing the vapours through a condenser before drawing them into the first absorption tube. Acetone and camphor, which are present in some types of powders, were removed by the alkaline potassium permanganate solution (both of these volatile constituents are unaffected by the oxidising solution in the first absorption tube but would be oxidised in the stronger medium in the third absorption tube). To test the method, weighed amounts of ethyl alcohol and ether were dissolved in nitrobenzene and an aliquot portion of the solution was transferred to the three-necked flask; the other constituents of a typical nitro-cellulose powder were added in the amounts present in a 2-g. quantity of sample and the estimation was carried out as indicated above. The time necessary to effect complete removal, absorption and oxidation was about 4 hours. Results given in Table IV indicate errors of 2 to 3 per cent. for both ethyl alcohol and ether. Duplicate results obtained with different types of nitrocellulose powders are given in Table V; excellent reproducibility is evident. The table also includes the result of analysis of one sample containing camphor and one containing acetone in place of ether; the acetone content was 1·10 per cent., but this was completely removed by the alkaline potassium permanganate solution, for no oxidation was found to have occurred in the third absorption tube. The method used for estimating this acetone will be given in Part 3 of this paper. The fact that nitroglycerine does not interfere in the method was demonstrated by carrying out an estimation on a sample of solventless cordite that contained a high percentage of nitroglycerine but no solvent; no oxidation took place in either of the acid dichromate solutions. The method has been found completely satisfactory for all types of propellants. Full details of the solutions and procedure employed are given below.

TABLE IV

ESTIMATION OF MIXTURES OF ETHYL ALCOHOL AND ETHER IN NITROBENZENE SOLUTION

Taken in mixture					
Ethyl alcohol g.	Ether g.	Ethyl alcohol found g.	Error per cent.	Ether found g.	Error per cent.
0·0188	0·0455	0·0186	−1·1	0·0465	+2·2
0·0105	0·0142	0·0105	0	0·0144	+1·4
0·0105	0·0142	0·0104	−1·0	0·0143	+0·7
0·0097	0·0262	0·0097	0	0·0266	+1·6
0·0094	0·0164	0·0093	−1·1	0·0170	+3·7
0·00323	0·0074	0·0031	−3·7	0·0072	−2·7

TABLE V

THE ESTIMATION OF ETHYL ALCOHOL AND ETHER IN PROPELLANT EXPLOSIVES

Sample of propellant	Ethyl alcohol per cent.	Ether per cent.
Modern nitrocellulose powders:		
(1) MA.668	0·08; 0·09	0·57; 0·58
(2) MA.621	0·13; 0·12	0·99; 0·97
(3) Dupont 4825	0·40; 0·40	0·99; 1·01
Neonite (small flake)	0·75; 0·77	0·10; 0·11
German igniter (acetone present)* ..	0·38; 0·39	0·00; 0·00
Celluloid (camphor present)	0·21; 0·20	0·00; 0·00

* Acetone found 1·08 and 1·12 per cent. Estimation to be described later.

DETAILS OF METHOD—

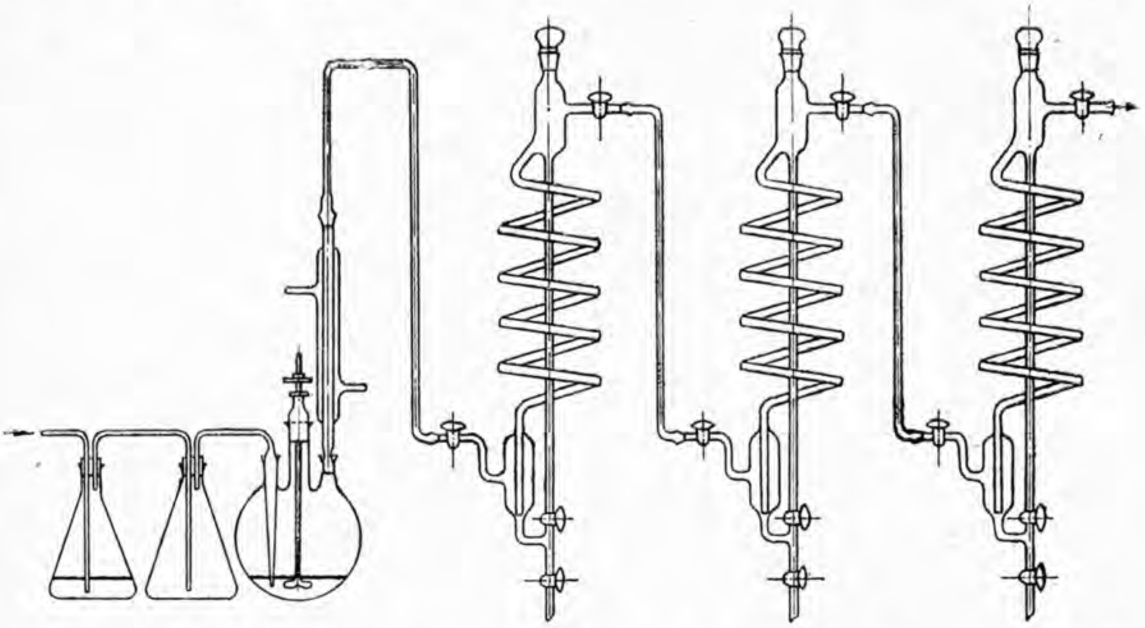
Apparatus—This is shown in the diagram. The absorption spiral tubes have an over-all length of about 18 inches and the diameter of the spiral is about 2 inches; the total internal volume is about 60 ml.

Solutions—To prepare the acid dichromate solution for the oxidation of the ethyl alcohol, transfer 25 ml. of an aqueous solution containing exactly 8 g. of potassium dichromate per litre to a clean dry 100 ml. graduated flask and add 2·5 ml. of concentrated sulphuric acid.

Introduce the bulk of this solution into the first absorption spiral tube shown in the diagram Retain the flask, as the solution is eventually returned to it.

To prepare the acid dichromate solution for the oxidation of the ether, transfer 25 ml. of an aqueous solution containing exactly 16 g. of potassium dichromate per litre to a clean dry 200 ml. flask and add, while cooling, 25 ml. of concentrated sulphuric acid. Introduce this solution into the third absorption spiral tube shown in the diagram and retain the flask.

To prepare the alkaline potassium permanganate solution boil gently under reflux for 10 hours 104 g. of potassium permanganate and 261 g. of potassium hydroxide with 1 litre of water. After cooling, pour off the supernatant solution and introduce about 30 ml. of it into the second absorption spiral tube.



Procedure.—Crush the propellant sample into small pieces (about 3 mm. across) with a steel pestle and mortar, weigh accurately 2 to 3 g. and add it to 25 ml. of nitrobenzene (AnalaR quality) in the 250 ml. three-necked flask shown in the diagram. (The relative effects of crushing and grinding samples will be described in Part 4 of this paper.) Stir the nitrobenzene solution vigorously and, with the flask immersed in a boiling water bath, draw a stream of air through the solution at the rate of 1 to 2 bubbles per second for 5 hours.

Then stop the flow of air, wash the dichromate solutions back into their respective flasks and make up the volumes to the marks with water. Of the 100 ml. of oxidised ethyl alcohol solution add 25 ml. to a solution of 2 to 3 g. of potassium iodide in about 30 ml. of water and, after 2 minutes, dilute the solution to about 100 ml. with water and titrate the liberated iodine with 0·05 *N* sodium thiosulphate solution, using starch solution as indicator. Treat the oxidised ether solution similarly except that, as the acid concentration is much higher, add the 25-ml. aliquot portion to a solution of the potassium iodide in 100 ml. of water and, after 2 minutes, dilute to about 200 ml. with water and titrate. Calculate the amounts of ethyl alcohol and ether present from the relation to the potassium dichromate given previously (p. 50).

SUMMARY

An account is given of the methods of determining the residual contents of ethyl alcohol and ether in nitrocellulose propellants. A new method is described which employs dissolution of a small sample of the propellant in nitrobenzene at 100° C.; the ethyl alcohol and ether vapours are removed in a current of air and are differentially absorbed and oxidised in acid potassium dichromate solutions of different concentrations. The method is suitable for all normal types of nitrocellulose and nitroglycerine powders and is applicable in presence of the usual constituents of propellants including acetone, camphor, dibutyl phthalate, diethyl diphenylurea and diphenylamine. Arising out of the preliminary investigation of the problem a method is described for the estimation of mixtures of ethyl alcohol, butyl alcohol and ether at concentrations of 0·05 to 0·10 per cent. in aqueous solution.

Acknowledgment is made to Imperial Chemical Industries (Explosives Division) for making available a valuable report in which the earlier attempts at estimating ethyl alcohol and ether in simple nitrocellulose powders were reviewed and critically assessed.

In conclusion, the author wishes to thank Mr. G. L. Hutchinson of the Armaments Research Department for his helpful discussion of the problem and the Director-General of Scientific Research (Defence), Ministry of Supply, for permission to publish this material.

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The Estimation of the Volatile Matter Content of Propellant Explosives

Part 3.—The Estimation of Acetone

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Part 3.* The Estimation of Acetone

By T. G. BONNER

ACETONE is widely employed in the manufacture of various types of cordite (*i.e.*, propellants, containing both nitrocellulose and nitroglycerine). The acetone is used in optimum admixture with water to facilitate the formation of a homogeneous solution of the constituents of the cordite, which is necessary to ensure uniformity of product. The presence of the solvent in the final product is, of course, undesirable, and the last stage of manufacture is designed to remove as much of it as possible by "stoving" at an elevated temperature. This removal is never complete and in order to assess the effect of the residual acetone on ballistic properties, particularly in relation to variations in the acetone content with changing temperature and humidity, an accurate method of estimation is of paramount importance.

Various workers[1,2,3] have reported attempts to determine the residual acetone content, but no evidence is advanced that the methods give absolute figures and in general the results are quite arbitrary. Friedmann[4] recommended reducing the sample to shavings, introducing 2 to 5 g. into a U-tube immersed in a bath at 75° C., drawing a stream of carbon dioxide or nitrogen through the U-tube into either 23 per cent. potassium hydroxide solution or water, and determining the absorbed acetone by Messinger's method[5] by conversion to iodoform with excess of iodine in presence of sodium hydroxide and back-titration with sodium thiosulphate. Although this method has useful features, no evidence is adduced to prove that heating at 75° C. removes the whole of the acetone from the sample, a point which is emphasised by Kostevitch[6] in a criticism of the method used by Benesch,[7] and later by Graulich,[8] of heating samples of propellants to release the volatile matter for estimations. It is well known that solvent matter is tenaciously held by nitrocellulose and its quantitative removal by heat alone is only conceivable with ground material or very small grain or flake samples, and the reduction of larger sizes of cordite to such a state of subdivision introduces the difficulty of avoiding loss of solvent during the process.

These methods were not considered reliable either for routine analysis or for special investigations, and an improved technique was sought. Two possibilities were considered for the quantitative removal of the acetone from a propellant; first, dissolution of the cordite in a suitable medium followed by volatilisation and absorption, and secondly, extraction of the acetone from the cordite by an organic solvent. Since the amount of acetone present in cordites rarely exceeds 0·6 per cent. and also a method suitable for 2- to 3-g. samples was considered necessary, the quantity of acetone to be estimated was of the order of a few mg. Methods applicable to the estimation of small quantities of acetone include Messinger's method,[5] which has been investigated in detail by Goodwin[9]; the hydroxylamine hydrochloride method,[10] in which the hydrochloric acid liberated by the formation of acetone oxime is titrated with standard alkali solution; the formation of double salts of acetone with mercuric salts first employed by Dénigès[11]; colorimetric determination based on the condensation of acetone with such compounds as *o*-nitrobenzaldehyde[12,13]; and a micro-diffusion method based on the bisulphite reaction described by Winnick.[14] A very useful critical review of methods of estimating small quantities of acetone in air has been given by Komar,[15] who preferred a modification of Messinger's method. An examination of all the above methods indicated that the first two were the most satisfactory. Further, for a given amount of acetone, the equivalent volume of standard iodine solution required in Messinger's method is nearly four times the volume of standard alkali solution of the same normality required in the hydroxylamine hydrochloride method, and this fact was considered to justify a preference for the former method, which later became a necessity on grounds of compatibility of reagents with other constituents of the propellant present during the estimation. With this method of estimating the recovered acetone, the two procedures outlined above for the quantitative removal of the acetone from cordite were investigated.

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* For Parts 1 and 2, see ANALYST, 1946, **71**, 483; 1947, **72**, 47.

THE QUANTITATIVE REMOVAL OF ACETONE FROM CORDITE BY ENTRAINMENT WITH AIR AND ABSORPTION

The removal of the residual organic solvent matter in a propellant by passing a stream of air through a solution of the sample in nitrobenzene at 100° C. has already been described in the method of estimating ethyl alcohol and ether in nitrocellulose powders, in Part 2 of this series.[16] Cordites dissolve even more readily than nitrocellulose powders in nitrobenzene and this method was therefore adopted for cordites. To absorb the acetone carried over by the air stream, various solvents were investigated; it was found that absorption was incomplete in saturated sodium bisulphite solution, water and dilute sulphuric acid, and concentrated sodium hydroxide solution was not wholly satisfactory. Complete absorption was effected, however, in a 1 : 1 by volume mixture of concentrated sulphuric acid and water. An apparatus was used identical with that described in the method for nitrocellulose powders (see Part 2) except that only one absorption tube was employed in place of the three required in that method. The procedure used in carrying out the separation of the acetone in this way and its subsequent titration was as follows.

ABSORPTION METHOD

About 10 ml. of the sulphuric acid was introduced into the absorption tube, while 2 g. of the cordite sample, cut up into $\frac{1}{4}$-in. lengths, were added to about 25 ml. of pure nitrobenzene in the 250-ml. three-necked flask. The flask was heated in a boiling water bath and a stream of air bubbled through the nitrobenzene solution to carry the acetone vapour into the sulphuric acid in the absorption tube. After 5 hours, the flow of air was stopped and the sulphuric acid run out and carefully neutralised with 30 per cent. sodium hydroxide solution; 1 drop of phenolphthalein was used as indicator and the solution was cooled during neutralisation. Forty ml. of N sodium hydroxide solution were added and, after cooling in ice for 10 minutes, 10 ml. of 0·1 N iodine were slowly run in, the flask being shaken during the addition. After the flask had been replaced in ice for 10 minutes, the iodine that had not reacted was liberated by addition of a slight excess of 2 N sulphuric acid and titrated with 0·05 N sodium thiosulphate, with starch solution as indicator. A blank determination was carried out on 10 ml. of the original diluted sulphuric acid (1 + 1) and the amount of acetone present in the sample calculated. One ml. of 0·1 N iodine ≡ 0·0009675 g. of acetone.

The accuracy of the method was tested by introducing a solution of acetone in nitrobenzene of known concentration into the flask, adding the other ordinary constituents of cordite, *viz.*, nitrocellulose, nitroglycerine, nitroguanidine and diethyldiphenylurea, and carrying out an estimation as described above. No interference by these constituents was observed and the results obtained for various solutions of acetone in nitrobenzene given in Table I indicate an accuracy of 3 to 4 per cent. with a maximum error of 5 per cent. for quantities of acetone of the order of 1·5 to 5 mg. No difficulties were encountered in applying the method to the analysis of cordites. Confirmation of the reliability of the method was obtained by applying it to a sample of solventless cordite; no acetone or other organic solvent is used in the manufacture of this type of cordite and an analysis for its acetone content gave a figure of 0·00 per cent. The only unsatisfactory feature of this method is that it is impracticable for dealing with the large numbers of samples encountered in routine analysis. For this reason the possibility of quantitative extraction of the acetone with an organic solvent was investigated.

TABLE I

ABSORPTION METHOD—WEIGHED AMOUNTS OF ACETONE IN NITROBENZENE SOLUTION REMOVED AT 100° C. AND ABSORBED IN SULPHURIC ACID

Weight of acetone taken mg.	Weight of acetone found mg.	Error per cent.
5·31	5·08	−4·3
2·85	2·95	+3·5
2·62	2·49	−5·0
1·88	1·89	+0·5
1·45	1·50	+3·0

THE QUANTITATIVE EXTRACTION OF ACETONE FROM CORDITE WITH AN ORGANIC SOLVENT

The quantitative extraction of moisture from cordite by means of dioxan has already been described in Part 1 of this series.[17] Of possible solvents for the present purpose, dioxan was unsuitable in that it consumed appreciable traces of iodine, and methyl alcohol had to be rejected owing to its dissolving some nitroglycerine, which by its interaction with sodium hydroxide gave rise to decomposition products interfering in the iodine titration. In point of fact, no single organic solvent was found to be suitable for the quantitative extraction of acetone from cordite; eventually, it was found that a mixed solvent consisting of 3 volumes of nitrobenzene and 2 volumes of chloroform satisfied requirements. Trials were made with solutions of acetone of known strength in this mixed solvent, the estimations being carried out directly by Messinger's method; the acetone solution was vigorously stirred with the aqueous sodium hydroxide and standard iodine solution during the time allowed for the acetone and iodine to react. All solutions except the iodine solution were maintained at 0° C. before being mixed in the reaction vessel, which was kept during the estimation in a Dewar flask containing ice. The measured volume of iodine was added slowly from a burette over a period of 5 minutes. In a series of determinations the factors that were varied were the relative volumes of the mixed organic solvent and the aqueous solution, the strength of the sodium hydroxide solution and the length of time allowed for reaction between the iodine and acetone. From the results given in Table II it can be concluded that (*a*) an increase in the volume of organic solvent relative to the volume of aqueous solution necessitates a longer period of time for completion of the reaction, (*b*) a decrease in the strength of sodium hydroxide solution must be compensated by an increase in the time allowed for reaction, (*c*) quantities of acetone of the order of 5 mg. dissolved in this mixed solvent can be estimated with an accuracy of 2 to 3 per cent. under the optimum conditions. It was ascertained that neither nitrocellulose nor diethyldiphenylurea interfered in the estimation and nitroguanidine is practically insoluble in nitrobenzene and chloroform. A further series of determinations were carried out with nitroglycerine added to the synthetic solutions of acetone. The variation of factors influencing the estimation was modified in relation to the knowledge gained from the first series of determinations and from the results given in Table III it is evident that the extent of interference by nitroglycerine increases with an increase in either the amount of nitroglycerine present or the strength of the sodium hydroxide solution or

TABLE II

ESTIMATION OF ACETONE IN NITROBENZENE - CHLOROFORM SOLUTION

Weight of acetone taken mg.	Volume of organic solvent ml.	Volume of water ml.	Volume of *N* NaOH ml.	Time of reaction min.	Weight of acetone found mg.	Error per cent.
6·36	20	25	15	20	5·05	−20
6·36	20	25	15	40	6·19	−3·0
6·36	20	25	15	40	6·19	−3·0
3·34	15	25	15	20	3·23	−3·3
5·30	15	25	15	10	5·10	−3·9
4·16	15	25	15	20	4·26	+2·4
6·36	15	25	15	25	6·31	−0·9
6·81	15	25	15	25	6·63	−2·9
4·24	15	25	15	25	4·11	−3·1
7·42	15	25	15	30	7·15	−3·6
5·30	15	25	15	35	5·30	0
5·40	10	50	15	15	5·20	−3·7
5·40	10	50	15	20	5·22	−3·3
5·40	10	50	15	27	5·26	−2·6
5·40	10	50	15	30	5·24	−3·0
5·40	10	50	10	15	5·07	−6·1
5·40	10	50	10	20	5·26	−2·6
4·32	10	50	10	20	4·28	−0·9
7·56	10	50	10	20	7·35	−2·8
5·40	10	50	10	25	5·27	−2·4
5·40	10	50	10	25	5·27	−2·4
5·40	10	50	10	25	5·28	−2·2
4·32	10	50	10	25	4·21	−2·5
7·56	10	50	10	30	7·41	−2·0
7·56	10	50	10	40	7·49	−0·9

the length of time allowed for the estimation. As the conditions are approached under which no interference at the end-point occurs, the interval of time between the stage at which the end-point is reached and the return of the blue colour of the starch - iodine complex increases until it is of the same order as that occurring when no nitroglycerine is present, *i.e.*, when the gradual reappearance of the blue colour can be attributed solely to the effect of atmospheric oxygen. The last two results in Table III indicate the optimum conditions; full experimental details based on these conditions are given below. Using this procedure, a sample of solventless cordite which contained no acetone was analysed. This type of cordite has a higher nitroglycerine content than normal cordites, and the amount of nitroglycerine extracted from it by the nitrobenzene - chloroform solvent was obviously much higher than that extracted from ordinary cordites. On two separate samples of this cordite, analyses showed apparent acetone contents of 0·005 and 0·004 per cent. which are negligible. No difficulty was experienced with the end-point and it is clear therefore that the method is quite satisfactory in presence of nitroglycerine. In Table IV is given a comparison of results obtained on some cordites by this method and by the method of entrainment by air from solution in nitrobenzene at 100° C. described above; excellent agreement is evident.

TABLE III

EFFECT OF NITROGLYCERINE ON METHOD OF TABLE II

Volume of nitroglycerine added ml.	Weight of acetone taken mg.	Volume of organic solvent ml.	Volume of water ml.	Volume of N NaOH ml.	Time of reaction min.	Weight of acetone found mg.	Error per cent.
0·30	5·84	15	50	10	20	5·22	−11·0
0·10	5·84	15	25	15	20	5·35	−9·0
0·10	5·84	15	50	10	40	5·55	−5·0
0·10	5·84	10	50	10	25	5·70*	−2·4
0·15	3·34	10	50	10	20	3·25*	−2·7

* No interference at end-point of titration.

TABLE IV

DETERMINATION OF ACETONE IN CORDITE—COMPARISON OF EXTRACTION AND ABSORPTION METHODS

Sample	Acetone per cent.	
	Absorption method	Extraction method
Cordite W 124, lot BS 87	0·09; 0·09	0·10; 0·10
Cordite WM 130, lot WAC 1724 ..	0·33; 0·31	0·34; 0·33
Cordite MD St., lot WA 791 ..	0·32; 0·30	0·30; 0·29

Final confirmation of the accuracy and reliability of the method was provided by the following experiment. Three g. of a sample of a W.M. cordite containing mineral jelly and diethyldiphenylurea was allowed to stand in contact with 20 ml. of the nitrobenzene - chloroform solvent overnight. Exactly 5 ml. of the supernatant solvent was then removed and replaced by 5 ml. of a synthetic solution of acetone in the same solvent, and this was again allowed to stand overnight. The acetone contents of both this final solution and of the 5 ml. aliquot portion originally removed were estimated. The estimation of the acetone content of the 5 ml. aliquot portion enabled the acetone content of the residual 15 ml. to be calculated; to this figure was added the known amount of acetone present in the added 5 ml. of synthetic solution, and this was compared with the result of the direct analysis of the final solution. As the results of the duplicate determination given in Table V show, these figures differ by about 2 per cent. This experiment establishes that complete extraction of the acetone occurs on standing overnight, for no increase in the acetone content of the supernatant solvent is detected after allowing to stand for a second time overnight.

For most purposes this procedure of allowing the sample of propellant to stand in contact with the solvent overnight was convenient, but if results are required more quickly, the time of standing can be reduced to a few hours by increasing the amount of nitrobenzene relative to the chloroform in the mixed solvent. When this modification was used, however, it was found that for each particular type of cordite the altered conditions of the estimation varied slightly. Therefore, before this more rapid method is employed, it is necessary to investigate the optimum ratio of nitrobenzene and chloroform and the time to be allowed for extraction for the type of cordite under analysis.

TABLE V

RECOVERY OF ACETONE ADDED TO AN EXTRACTED CORDITE SAMPLE
3 g. of sample in 20 ml. of nitrobenzene - chloroform solvent

	(*a*) mg.	(*b*) mg.
(1) Weight of acetone found in 5 ml. of supernatant solvent	2·31	2·48
(2) Weight of acetone in residual 15 ml. of solvent from (1)	6·93	7·44
(3) Weight of acetone added to residual 15 ml. of solvent	5·40	5·40
(4) Total weight of acetone present in final solution, *i.e.*, (2) + (3)	12·33	12·84
(5) Total weight of acetone found in final solution ..	12·6	12·6
Error	+2·1%	−1·9%

(*a*) and (*b*) are duplicate estimations.

The method is applicable in the presence of ethyl alcohol and has been used without modification for the estimation of acetone in cordites manufactured with a mixed ethyl alcohol - acetone solvent. Details of the method are given below.

EXTRACTION METHOD

Make up the solvent as required by mixing **3** volumes of AnalaR nitrobenzene and 2 volumes of B.P. chloroform. Cut up the sample of cordite into ¼-in. lengths, and add a weighed 3-g. portion to 20 ml. of the solvent in a 25-ml. cylinder fitted with a ground-glass stopper. Stopper the cylinder and allow to stand overnight. After shaking and allowing to settle, transfer 5 ml. of the supernatant solution to a 200-ml. pear-shaped flask and add 5 ml. of the nitrobenzene - chloroform solvent and 50 ml. of water. After stoppering, place the flask in an ice bath, in which is also maintained a *N*-solution of sodium hydroxide. After 15 minutes in the ice bath remove the flask to a Dewar flask containing ice and clamp it vertically with the lower portion immersed in the ice. Remove the stopper and add 10 ml. of the *N* sodium hydroxide. Introduce a motor driven stirrer into the flask and add 10 ml. of 0·1 *N* iodine dropwise over a period of 5 minutes from a 10-ml. burette, keeping the solution efficiently stirred during the addition. Continue the stirring for a further 20 minutes and then remove the flask and add a slight excess of *N* sulphuric acid immediately. Titrate the liberated iodine without delay, with 0·05 *N* sodium thiosulphate. Near the end-point vigorous shaking is necessary to remove the last traces of iodine dissolved in the nitrobenzene - chloroform layer to the aqueous layer. Carry out a blank determination on 10 ml. of the nitrobenzene - chloroform solvent and, after correcting for the very slight consumption of iodine in this "blank" (usually equivalent to 0·05 or 0·10 mg. of acetone per 10 ml. of solvent), calculate the amount of acetone present from the relationship between the iodine solution and acetone given above (p. 435).

SUMMARY

Existing methods of estimating the residual acetone content of cordite are critically reviewed, particularly from the viewpoint of ensuring quantitative removal of the acetone from the cordite prior to its estimation. A new method is described in which the acetone is extracted with a mixed nitrobenzene - chloroform solvent and estimated by Messinger's method with an accuracy of 2 to 3 per cent. Interference by nitroglycerine has been studied in detail and the conditions established for its complete elimination.

In conclusion, I should like to thank Mr. G. L. Hutchison, of the Armament Research Department for his helpful advice, and the Director-General of Scientific Research (Defence), Ministry of Supply, for permission to publish this material.

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786. *Nitration of Alcohols at Oxygen Centres. Part III.*[1] *The Reaction of Nitric Acid and 2,4-Dinitrobenzyl Alcohol in Acetic Anhydride–Acetic Acid Solvent.*

T.G. BONNER
D.Sc. 1960

By T. G. Bonner.

The rate of conversion of 2,4-dinitrobenzyl alcohol into its nitrate ester by nitric acid in several acetic anhydride–acetic acid mixtures has been measured. The *O*-nitration proceeds to completion and no acetylation of the alcohol is apparent. The reaction is of the second order with respect to the nitric acid, which suggests that dinitrogen pentoxide formed in fractionally small amount is the active nitrating agent. Within the range of media containing 0—10% of acetic anhydride a maximum rate of reaction appears at about 7% acetic anhydride although at a much higher acetic anhydride content the reaction is immeasurably fast.

The various equilibria which may be present in the system are discussed.

The nitrating property of nitric acid in acetic anhydride first demonstrated by Orton [2] in the nitration of aromatic compounds was until fairly recently assumed to be due to the presence of acetyl nitrate, since preparations of this reagent showed similar nitrating behaviour.[3] A kinetic study [4] of the nitration of benzene by benzoyl nitrate in carbon tetrachloride however has established that in the case of this mixed anhydride a small stationary concentration of the more reactive dinitrogen pentoxide is formed in equilibrium with benzoic anhydride according to eqn. (1), and that the *C*-nitration proceeds solely by attack of the dinitrogen pentoxide and not to any detectable extent directly by benzoyl nitrate. The same report suggests that a similar mechanism is operative in the nitration of benzene by nitric acid and acetic anhydride in carbon tetrachloride [5] and includes the qualitative observation that there is an optimum amount of acetic anhydride, excess of which decreases the rate of nitration by reversing the equilibrium in which the dinitrogen pentoxide is formed.

$$2\mathrm{BzO{\cdot}NO_2} \rightleftharpoons \mathrm{N_2O_5} + \mathrm{Bz_2O} \qquad (1)$$

In the conversion of alcohols into nitrate esters, nitric acid in a mixed solvent of acetic anhydride and acetic acid is frequently used as the nitrating medium.[3,6] The experience gained with 2,4-dinitrobenzyl alcohol in *O*-nitration studies in other media [1] made it possible to investigate whether dinitrogen pentoxide was the essential intermediate in promoting *O*-nitration in acetic anhydride–acetic acid. In this reaction, apart from the problem of the nitrating entity, there is the possibility of a competing acetylation.

Preliminary examination of the interaction of nitric acid with 2,4-dinitrobenzyl alcohol in this system showed that a 90% yield of the nitrate ester was readily attained, and that as a preparative method this procedure was superior to that of using a mixture of nitric acid and sulphuric acid. The method of analysing reaction mixtures of 2,4-dinitrobenzyl alcohol in the latter solvent [1] by quantitative oxidation of the alcohol with acidic dichromate and spectrophotometric determination of the nitrate ester after extraction with benzene was found to be applicable to the acetic anhydride–acetic acid solutions without modification. Some preliminary analyses were carried out in a medium containing about 4% of acetic anhydride in acetic acid to establish whether the amount of nitrate ester formed after different times corresponded to the amount of alcohol consumed. A typical result with initial concentrations of *ca.* 0·1M-2,4-dinitrobenzyl alcohol and 0·3M-nitric acid is shown in Table 1. The constancy to within 2% of the sum of the independently determined concentrations of the alcohol and nitrate excludes the possibility that any acetate ester is separately formed in detectable amount concurrently with the nitrate ester. This is in agreement with the failure to detect any acylated product in the nitration of anisole

TABLE 1. *Analysis of an* O-*nitration reaction mixture at 25° in acetic acid containing* 0·39M-*acetic anhydride.*

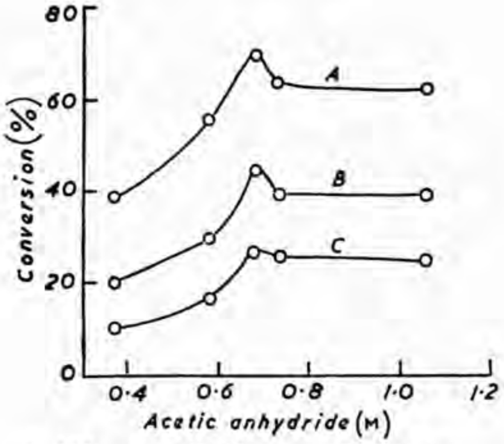
Initial concns.: [ROH] = 0·1020M; $[HNO_3]$ = 0·3212M.

Time (min.)	0	5	10	15	30	60	90	120	150
10^2[ROH] (*A*)	10·20	9·42	8·58	7·87	6·28	4·35	3·05	2·33	1·88
$10^2[RO{\cdot}NO_2]$(*B*)	0	1·06	1·75	2·48	4·01	6·02	6·99	7·82	8·23
A + *B*	10·20	10·48	10·33	10·35	10·29	10·37	10·04	10·15	10·11

with acyl nitrates in acetonitrile.[7] It is clearly unlikely that the acetate ester has the alternative rôle of a highly reactive intermediate. Experiments to confirm this point showed that over several hours (a period much longer than that required for the completion of the *O*-nitration of the alcohol) added acetate ester was not noticeably attacked by nitric acid in the acetic anhydride–acetic acid solvent, the final analysis showing that at least 96% of the acetate ester remained unchanged.

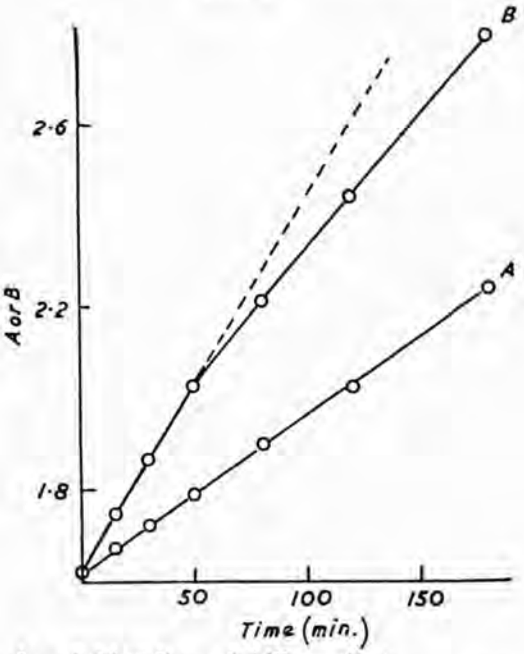
Variation of Rate of O-*Nitration with Acetic Anhydride Concentration.*—Measurements of the extent of conversion of 2,4-dinitrobenzyl alcohol into its nitrate ester in a given time showed that the presence of acetic anhydride was essential for reaction, no change being observed when nitric acid alone was present in the acetic acid solvent. Over the range 0—10% (*i.e.*, 0—1M) acetic anhydride there was an increasing rate of conversion into the nitrate ester with increasing acetic anhydride concentration, a maximum rate appearing in the medium containing 7% of acetic anhydride. This is shown in Fig. 1 in which the percentage conversions of 2,4-dinitrobenzyl alcohol into nitrate ester at three separate time intervals for five different acetic anhydride–acetic acid solvents are plotted against molarity of acetic anhydride. Although the maximum is clearly evident from the curves, there is only a slight fall in rate from this point to that corresponding to a medium containing 10% of acetic anhydride. Rates of reaction at much higher acetic anhydride concentrations, *e.g.*, 40%, were too fast for measurement so that in the range 10—40% an increase in rate with acetic anhydride content reappears. By means of Fig. 1, the maximum obtained at 7% of acetic anhydride is made evident without knowledge of the mechanism of the reaction. It is also evident that, if the *O*-nitration proceeds exclusively through the action of dinitrogen pentoxide formed by dehydration of the nitric acid and regulated by an equilibrium similar to (1), other equilibria will be necessary to maintain

FIG. 1.



A, 100 min.; *B*, 40 min.; *C*, 20 min.

FIG. 2.



$A = 2{\cdot}3 \log \{(a - 2x)/(b - x)\} + 2x(2b - a)/a(a - 2x).$
$B = 2{\cdot}3 \log \{(a - x)(b - x)\} - x(a - b)/a(a - x).$

an effective constancy in the fraction of nitric acid converted into dinitrogen pentoxide in media containing acetic anhydride concentrations from 0·7 to 1·06M. An indication of the equilibria set up in these systems has been provided by reports of studies of the physical properties of various mixtures of nitric acid, dinitrogen pentoxide, acetic anhydride, and acetic acid. Vapour-pressure measurements on nitric acid–acetic anhydride mixtures [8] show a maximum near the 1 : 1 mole mixture corresponding to substantially complete formation of acetyl nitrate according to eqn. (2). With increasing nitric acid content

$$Ac_2O + HNO_3 \rightleftharpoons AcO{\cdot}NO_2 + AcOH \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

above the 1 : 1 mole mixture, the vapour pressure rises to a maximum at a mole fraction of 0·84 corresponding to formation of dinitrogen pentoxide which can be represented by either equation (3) or (4). Further increase in the nitric acid content decreases the vapour

$$AcO{\cdot}NO_2 + HNO_3 \rightleftharpoons AcOH + N_2O_5 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

$$Ac_2O + 2HNO_3 \rightleftharpoons N_2O_5 + 2AcOH \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

pressure until that corresponding to pure nitric acid is finally attained. Raman spectra [9] confirm that, when acetic anhydride is in excess over nitric acid, there is complete conversion of nitric acid into acetyl nitrate and, when nitric acid is in large excess, *i.e.*, >80 moles %, dinitrogen pentoxide is the major product and only traces of acetyl nitrate are present. The formation of acetyl nitrate from nitric acid is represented as the dehydration (4) followed by reaction (5) which is complete when the acetic anhydride is in excess. Mix-

$$N_2O_5 + Ac_2O \rightleftharpoons 2AcO{\cdot}NO_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

tures of nitric acid and acetic anhydride in the mole ratio 2 : 1 and of dinitrogen pentoxide and acetic acid with mole ratio 1 : 2 gave the same spectra, confirming the rapid establishment of the equilibrium (4). The ultraviolet spectra of the system dinitrogen pentoxide–acetic anhydride [10] indicated some instability over the range 12—96%; for nitric acid–acetic anhydride mixtures containing more than 96% of nitric acid, the ultraviolet spectra resembled those of high concentrations of dinitrogen pentoxide in nitric acid, while mixtures containing less than 7% of nitric acid had a spectra similar to those of solutions of low concentration of dinitrogen pentoxide in nitric acid. Although these results led Jones and Thorn to suggest that in both cases, *i.e.*, of high and low nitric acid concentrations in acetic anhydride, the operative equilibrium was (4) lying well to the right, their results do not exclude the possibility that acetyl nitrate may be substantially formed at the lower nitric acid concentration. More recently, measurements of the density, viscosity, and refractive index [11] of the systems acetic anhydride–nitric acid and acetic acid–nitric acid have also shown that a 1 : 1 molar mixture of acetic anhydride and nitric acid gives almost complete conversion into acetyl nitrate according to eqn. (2) and that appreciable amounts of dinitrogen pentoxide are only formed according to (4) when the concentration of nitric acid is very high. The conclusion was also reached that acetyl nitrate is not likely to be an intermediate in the formation of dinitrogen pentoxide.

The Kinetic Order of the O-*Nitration in the Acetic Anhydride–Acetic Acid Solvent.*— Before any use could be made of the above data, it was necessary to determine the kinetic order of the *O*-nitration. Some preliminary experiments were carried out with a solvent containing 0·37M-acetic anhydride in acetic acid, using a fixed initial concentration of 0·04M-2,4-dinitrobenzyl alcohol (*b*) for all runs, and systematically increasing the initial nitric acid concentration (*a*) from 0·2 to 0·8M. Higher concentrations of nitric acid appeared to result in some side reactions to give easily oxidisable products which interfered in the method of analysis. The results, although accurately reproducible for duplicate runs, did not satisfy the rate equation for a second-order reaction (*i.e.*, first-order with respect to the alcohol and to the nitric acid), the plots of log $(a - x)/(b - x)$ against time in all cases giving a smooth curve. For reactions in which the nitric acid concentration was in tenfold or greater excess over the alcohol the results were plotted as for a first-order reaction of the alcohol only. Although there was an evident curvature when log $(b - x)$

was plotted against time, rate constants could be calculated from the straight portion of the curve covering up to about 25% conversion of the alcohol into nitrate ester. The significant feature then appeared that the ratio of the rate constant to the square of the initial nitric acid concentration was a constant independent of the latter. The reaction was therefore of the second order with respect to the nitric acid. These results suggested that *O*-nitration did not take place through attack by acetyl nitrate on the alcohol since this would most probably require first-order dependence on the nitric acid. To derive the simplest kinetic equation on the basis of a reaction of the first order with respect to the alcohol and second order with respect to the nitric acid, it was assumed that the two molecules of nitric acid were initially involved in the formation of dinitrogen pentoxide which then reacted with the alcohol.

Stoicheiometrically, in this reaction a molecule of nitric acid is liberated for each molecule of alcohol consumed, and if the reactions are represented as in (6) with the concentrations of the reactants at time t as shown, the rate equation can be represented

$$\underset{a-2x}{2HNO_3} \longrightarrow N_2O_5;\ \underset{b-z}{ROH} + N_2O_5 \longrightarrow \underset{x}{RO{\cdot}NO_2} + \underset{x}{HNO_3} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

by eqn. (7) from which the kinetic equation (8) is derived:

$$dx/dt = k(a-x)^2(b-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$k(a-b)^2t = 2{\cdot}3 \log \{b(a-x)/a(b-x)\} - (a-b)/a(a-x) \quad . \quad . \quad (8)$$

If however the nitric acid liberated in the *O*-nitration is removed, *e.g.*, by conversion into acetyl nitrate as in eqn. (2), the rate equation then becomes that shown in (9) and the derived kinetic equation is (10):

$$dx/dt = k(a-2x)^2(b-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$kt(a-2b)^2 = 2{\cdot}3 \log \{b(a-2x)/a(b-x)\} + 2x(2b-a)/a(a-2x) \quad . \quad (10)$$

With a fixed initial concentration of 2,4-dinitrobenzyl alcohol of 0·04M and with that of the nitric acid within the range 0·2—0·8M, it was found in all cases that the kinetic equation (10) was obeyed. This is demonstrated in Fig. 2 in which the plot of $2{\cdot}3 \log \{(a-2x)/(b-x)\} + 2x(2b-a)/a(a-2x)$ against t (eqn. 10) is a straight line over the 70% change followed in the reaction while the plot of $2{\cdot}3 \log \{(a-x)/(b-x)\} - x(a-b)/a(a-x)$ (eqn. 8) against t deviates markedly from a straight line. With the reactant concentrations indicated, a constant value of k is obtained from these plots for kinetic measurements in a given medium, as the results shown in Table 2 for the medium containing 0·37M-acetic anhydride demonstrate. The rate constants obtained from eqn. (10) over the range of media investigated show that there is an optimum acetic anhydride concentration at about 0·7M, as mentioned previously. When the initial concentration of the alcohol is altered, the kinetic equation (10) is still obeyed but the value of the rate constant changes slightly. The effect is small in the 0·37M-medium (experiments **44** and **45**) but is more marked in media with a higher acetic anhydride content; a more detailed investigation is necessary to interpret this feature.

Evidently there is more than one reaction scheme which satisfies the kinetic order

TABLE 2. *Rate constants of* O*-nitration of 2,4-dinitrobenzyl alcohol in acetic anhydride–acetic acid.* (*Initial concns. shown.*)

Expt.	$[Ac_2O]$ (M)	$10^2[ROH]$ (M)	$10^2[HNO_3]$ (M)	k	Expt.	$[Ac_2O]$ (M)	$10^2[ROH]$ (M)	$10^2[HNO_3]$ (M)	k
41	0·37	4·06	16·37	0·22	29	0·58	4·13	20·45	0·46
43	,,	4·07	16·26	0·20	30	,,	4·09	15·33	0·46
49	,,	4·06	20·48	0·22					
48	,,	4·15	41·80	0·21	26	0·68	4·16	16·20	0·76
50	,,	4·16	40·95	0·21					
51	,,	4·14	63·30	0·22	22	0·73	4·14	21·15	0·67
52	,,	4·16	79·20	0·19	23	,,	4·18	15·86	0·71
44	,,	6·10	21·70	0·18	18	1·06	4·22	15·84	0·65
45	,,	2·13	22·00	0·17	63	,,	4·04	40·20	0·68

found experimentally and provides for dinitrogen pentoxide as the active nitrating agent. The main possibilities are shown in (i)—(iv):

(i) $Ac_2O + HNO_3 \rightleftharpoons AcO{\cdot}NO_2 + AcOH$ and either (ii), (iii), or (iv)

(ii) $2AcO{\cdot}NO_2 \rightleftharpoons Ac_2O + N_2O_5$

(iii) $AcO{\cdot}NO_2 + HNO_3 \rightleftharpoons AcOH + N_2O_5$

(iv) $Ac_2O + 2HNO_3 \rightleftharpoons 2AcOH + N_2O_5$

Since the nitration of benzene by pure dinitrogen pentoxide in carbon tetrachloride is immeasurably fast and rate measurements are only possible when deactivating substituents are present,[12] the easier *O*-nitration in acetic anhydride–acetic acid can proceed at a measurable rate only if the fraction of nitric acid present as dinitrogen pentoxide in this system is extremely small. Although reaction (ii) provides an obvious means of interpreting the occurrence of an optimum concentration of dinitrogen pentoxide, it does not account for the immeasurably fast rate at a much higher acetic anhydride concentration. This can be accommodated by reactions (iii) or (iv) since the lower relative amount of acetic acid in such media would correspond to a shift in equilibrium to the right in (iii) and (iv). Further, a large increase in the ratio of acetic anhydride to acetic acid in media containing a very low concentration of perchloric acid ($<0{\cdot}1$M) leads to a considerable increase in the acidity of the medium; [13] this would enhance the formation of dinitrogen pentoxide in both cases.

EXPERIMENTAL

Materials and Media.—2,4-Dinitrobenzyl alcohol and its nitrate ester are described in the preceding paper.[1] "AnalaR" acetic acid was distilled to give a product of m. p. 16·5°. Acetic anhydride, distilled twice through a small fractionating column, was weighed in appropriate amount and made up to a known volume at 25° with the acetic acid; allowance was made for the small amount of water in the acetic acid in calculating the composition of each medium.

Kinetic Measurements.—It was established that the acetic anhydride–acetic acid solvent did not interfere with the methods of determination of 2,4-dinitrobenzyl alcohol (by dichromate oxidation) and of its nitrate ester (spectrophotometrically) previously described.[1] The alcohol was weighed into a B24 cap which fitted the neck of the reaction flask containing 20 ml. of the medium at 25°. The cap was inserted into the neck of the reaction flask at zero time and on vigorous shaking the alcohol dissolved almost instantaneously. The flask was returned to the thermostat at 25° and 2 ml. samples were removed at intervals and run into 10 ml. of a solution of 4 g. of potassium dichromate in 1 l. of 6N-sulphuric acid. Next morning the excess of dichromate was determined with potassium iodide and standard thiosulphate solution by the usual procedure. When the 2,4-dinitrobenzyl nitrate ester formed was determined simultaneously, the dichromate solutions after the overnight standing were extracted twice with 10 ml. portions of benzene. The extracts were combined, washed with 0·2N-sodium hydroxide, then with water, filtered into 25 ml. volumetric flasks, and made up to the mark with benzene washings.

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DETECTION OF POLYHYDROXY-COMPOUNDS AND THEIR CARBOXYLATE ESTERS WITH POTASSIUM PERIODATO-CUPRATE

By T. G. Bonner

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Potassium periodatocuprate (KPR), which is widely used in the quantitative analysis[1] of proteins and certain other organic compounds, has now been found to serve as a sensitive reagent for the detection in paper chromatography of a variety of easily oxidisable substances, including sugars, polyhydroxy-compounds, phenols and their ester derivatives. For some compounds which do not give a satisfactory reaction with existing location reagents, KPR provides a superior alternative, e.g. pentaerythritol and methyl α-glucoside are both detected in 5μg. quantities on a paper chromatogram developed with ethanol: butanol: water (4: 5: 1). Glucose, fructose and sucrose give a positive reaction when 1-2μg. quantities are present, and phenols show similar if not greater sensitivity. Mannitol and its hexa-acetate are detected with equal facility and 2,5-*O*-methylene-D-mannitol also gives a positive reaction (but not 1,3: 4,6-di-*O*-methylene- or 1,3: 2,5: 4,6-tri-*O*-methylene-D-mannitol). As expected from its original application to proteins, KPR also detects the presence of a peptide linkage.

When applied to paper, KPR provides a brownish coloured background against which a white spot appears in the place of the oxidised compound (or any ester of it which is readily hydrolysed by the alkaline medium in which KPR is prepared). The distinctive background disappears after a few minutes, presumably owing to the reduction of the reagent by constituents of the paper. A permanent record is obtained either by marking the white spots as they appear or by spraying the paper with a solution of rosaniline base in 10% acetic acid in acetone within one minute of applying KPR, when a permanent red spot appears against a white background at the position occupied by the oxidised compound.

The reagent is prepared[2] by dissolving 12·5g. copper sulphate pentahydrate in 400 ml. boiling water, adding 23g. potassium periodate and then a concentrated solution of 56 g. potassium hydroxide in water. Small portions of potassium persulphate (20 g.) are added to the hot solution at 1 minute intervals and the solution then boiled for 20 minutes. After cooling the solution is decanted, diluted to 500 ml. with water, and 500 ml. 2N potassium hydroxide added. The solution then contains 0·05M potassium periodatocuprate in 2N potassium hydroxide. It can be kept indefinitely without noticeable deterioration in a polythene bottle. The rosaniline solution is prepared by dissolving 0·3 g. rosaniline base in 100 ml. acetic acid and diluting to 1 litre with acetone.

The KPR reagent can be applied to the dry paper either with a fine spray or by the usual dipping technique.

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X919. *The Solvation of Ammonium Ions in Sulphuric Acid.*

By T. G. Bonner.

A method is described for the determination of the solvation number of the ammonium ion in ammonium sulphate–sulphuric acid–water mixtures based upon the direct dependence of the rate constant of cyclodehydration 4-*p*-toluidinopent-3-en-2-one on the ratio of sulphuric acid to hydrogen sulphate (HSO_4) concentrations in the mixtures. The solvation number of one for the ammonium ion appears to be maintained up to 3M-concentration of ammonium sulphate in the presence of 2M-water.

A H_0 acidity scale is evaluated for the range of acid media investigated.

Evidence that the ammonium ion in sulphuric acid has a solvation number of one has been provided by Gillespie *et al.*[1,2] by determinations of depression of freezing point of solutions of ammonium sulphate in nearly anhydrous sulphuric acid. It is assumed that solvation of the hydrogen sulphate anion is negligible and this view has been more fully discussed together with the effect of dissolved salts on the density and viscosity of sulphuric acid.[3] The highest concentration of ammonium sulphate employed in freezing-point determinations was 0·12M, but the probability that the solvation of the ammonium ion is maintained up to a 30-fold higher concentration has already been suggested by kinetic results obtained for the cyclodehydration of 4-*p*-toluidinopent-3-en-2-one to 2,4,6-trimethylquinoline in anhydrous ammonium sulphate–sulphuric acid solvents containing up to 4 moles/litre of the salt.[4] The mechanism of the cyclodehydration then suggested has since been slightly modified,[5] but the validity of the conclusion concerning the solvation of the ammonium ion is not affected. The unique value of the kinetic method is in allowing solvation studies at very much higher concentrations of the solute than is possible by freezing-point studies; in addition, it is evident that the method need not be confined to the anhydrous sulphuric acid media. This feature is important in that it provides a means of discovering whether or not the addition of water desolvates a cation in sulphuric acid. Accordingly, kinetic measurements have now been carried out in ammonium sulphate–sulphuric acid–water mixtures containing up to 3 moles per litre of ammonium sulphate and 2 moles per litre of water.

The interpretation of the results is based on the knowledge that, in the aqueous acid in the range 85—97% sulphuric acid, the kinetic results satisfy the relation[6] $\log k + H_0 =$ constant, where k is the rate constant of cyclodehydration for a given medium and H_0 is the corresponding value of the Hammett acidity function. Since an anil formed from primary aromatic amines and acetylacetone is almost certainly completely converted into its conjugate acid (AH^+) in these media,[5] it can be concluded that the cyclohydration proceeds through a diprotonated form (AH_2^{++}) present in fractionally small amount. The equilibrium set up by these species can be represented by (1) The cyclodehydration

$$AH^+ + H_2SO_4 \rightleftharpoons AH_2^{++} + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is a first-order reaction with a rate constant k_1 evaluated from (2), where [A] is the stoicheio-

$$-d[A]/dt = k_1[A] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

metric concentration of the anil. The theoretical rate equation based on the Brönsted

$$-d[A]/dt = k[AH_2^{++}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

treatment is given by (3), in which k represents the product of the theoretical rate constant and the ratio of the activity coefficients of AH_2^{++} and the transition complex.

on the molal volumes of these solutions has led to a revised value of 0·4. A recalculation of (*b*) with this value instead of unity gave a smaller but still significantly pronounced variation in the log ratio (from 1·72 to 1·56 in 97·9% sulphuric acid, and 1·77 to 1·61 in 98·44% sulphuric acid). It is possible that the hydroxonium ion is desolvated as the concentration of ammonium ion is increased, so that the values of B gradually approach those of A. In the absence of ammonium sulphate the log ratio $[H_2SO_4]/[HSO_4^-]$ in 97·9% sulphuric acid changes from 1·68 to 1·72 for a change of solvation number of the hydroxonium ion from 1 to 0·4, and the difference in the value of the log ratio is even less in 98·44% sulphuric acid. The possibility of desolvation of the ammonium ion in changing from pure sulphuric acid to aqueous acids containing up to 2M-water is clearly inadmissible. The fact that the relation between the ratio $[H_2SO_4]/[H_2O]$ and k_1 continues to hold up to a concentration of 3M-ammonium sulphate in the aqueous media suggests that the solvating power of the sulphuric acid is unimpaired by the presence of the water. This has a bearing on the problem of why the rate of nitration of aromatic compounds by the nitronium ion initially increases as water is added to pure sulphuric acid, in spite of accompanying decrease in the acidity of the medium.[8] In a discussion of this problem,[9] the explanation put forward, that the solvating power of the medium decreased on addition of water with a consequent decrease of energy of activation of the nitration reaction, now seems less acceptable than the alternative description which the authors provide by applying the theory of solvent effects [10] to this medium in which addition of water produces a decrease in dielectric constant.

It is significant that it has been found previously [4,5] that log k_1 bears a linear relationship both to log $[H_2SO_4]/[HSO_4^-]$ and to $-H_0$ and that in each case the slope of the line is approximately -1. This indicates that values of H_0 for these sulphuric acid–ammonium sulphate–water mixtures parallel those of log $[H_2SO_4]/[HSO_4^-]$ and could be derived from them by the addition of a constant term, as in equation (6). Evaluation of the ratio

$$H_0 = \text{constant} - \log([H_2SO_4]/[HSO_4^-]) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$[H_2SO_4]/[HSO_4^-]$ is based solely on the composition by weight of the mixtures and the assumption that there is complete conversion of the water present into hydroxonium ion and of the ammonium sulphate into the monosolvated ammonium ion, both species providing the corresponding quantity of hydrogen sulphate anion; if the stoicheiometric concentrations of sulphuric acid, water, and ammonium sulphate are represented by M, m_1, and m_2, respectively, it can be shown that the ratio is given by equation (7),

$$[H_2SO_4]/[HSO_4^-] = m - 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$m = (M - m_2)/(m_1 + 2m_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Brand [11] has already shown that, in the range 89—99·8% sulphuric acid, H_0 can be calculated from an equation of the type (6), in which the empirical constant is $-8·36$. With this constant, H_0 values have now been calculated for all media included in the Table, the equation being used in its more general form (9).

$$H_0 = -8·36 - \log(m - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Values H_0 are given in the last column of the Table. The plot of log k against $-H_0$ for these results is shown in the Figure. The slope of the straight line obtained is almost exactly unity as required by theory. The assumption that sulphuric acid molecules involved in solvation in solutions of high acidity are effectively removed from participation in equilibrium (1) and hence make no contribution to the acidity function, H_0, has some similarity to the contention [12] that in more aqueous sulphuric acid–water mixtures the water molecules involved in hydration of hydrogen ions do not contribute to the activity of the water present in these media.

Until further results are available, it cannot be assumed that the evaluation of H_0 for the sulphuric acid–ammonium sulphate–water system by means of equation (9) can be

If the anil is almost entirely present as its conjugate acid and $[AH^+] \gg [AH_2^{++}]$, equations (4) and (5) are obtained

$$k_1 = k[AH_2^{++}]/[AH^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$= kK[H_2SO_4]/[HSO_4^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where K represents the product of the thermodynamic equilibrium constant of eqn. (1) and the activity coefficient ratio $f_{AH^+}f_{H_2SO_4}/f_{AH_2^{++}}f_{HSO_4^-}$. Both k and K are assumed to be constant over the range of strongly acid media studied.

Two different sulphuric acid–water mixtures were investigated containing 97·90% and 98·44% of sulphuric acid severally, and in both cases the rate of cyclodehydration of 4-*p*-toluidinopent-3-en-2-one was measured in the presence of ammonium sulphate up to 3M-concentration. The ratio $[H_2SO_4]/[HSO_4^-]$ was calculated from the total weight of reactant solution (50 ml.) containing the ammonium sulphate at 25° before addition of the anil (*ca.* 0·5 g.). It was assumed that, in all media, the water present was quantitatively converted into hydroxonium and hydrogen sulphate ions. If the sulphuric acid molecules involved in solvation are effectively removed from participation in equilibrium (1), then the residual sulphuric acid concentration is reduced by n moles for each g.-ion of cation present with a solvation number of n. The calculated value of $[HSO_4^-]$ is independent of n, from which it follows that, if a direct dependence of k_1 on the ratio $[H_2SO_4]/[HSO_4^-]$ expressed in eqn. (5) is found for any one value of n, the experimental results cannot satisfy any other value of n. Three possibilities for cation solvation were considered, based on the following solvation numbers: (*a*) ammonium ion, 1; hydroxonium ion, 0; (*b*) ammonium ion, 1; hydroxonium ion, 1; and (*c*) ammonium and hydroxonium ions both zero. The calculated values of $[H_2SO_4]/[HSO_4^-]$ for each of these three cases are designated A, B, and C respectively in the Table. The results previously reported[4] for pure sulphuric acid were recalculated, account being taken of the subsequent discovery[5] that the dissolved anil is almost completely converted into its conjugate acid by an equimolecular quantity of sulphuric acid with the formation of hydrogen sulphate ion. It is evident that equation (5) is only satisfied by the first proposition (*a*). The values of $\log(A/k_1)$ for this case are constant within each of the three media, and the mean values 1·66, 1·68, and 1·70 for these media are in good agreement. No constancy is apparent in the case of (*b*) or (*c*). The value of one for the solvation number of the hydroxonium ion was suggested on the basis of cryoscopy data on sulphuric acid solutions, but later work[3]

Correlation of the rate constant k, and the ratio $[H_2SO_4]/[HSO_4^-]$ *for the cyclodehydration of* 4-p-*toluidinopent-3-en-2-one.*

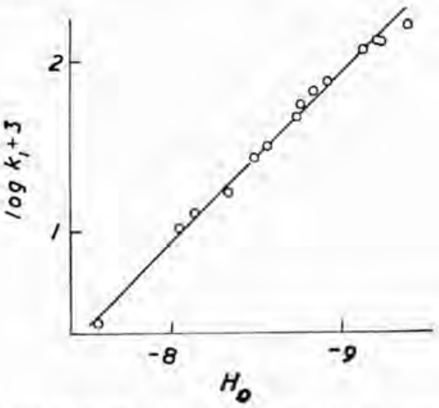
Initial concn. of 4-toluidinopent-3-en-2-one, 0·05M; Temp. 25°.

	Stoicheiometric concn.							
H_2SO_4 (%)	$[(NH_4)_2SO_4]$ (M)	$[H_2SO_4]_T$ (M)	$[H_2O]$ (M)	10^3k_1 (min.$^{-1}$)	$\log A/k_1$	$\log B/k_1$	$\log C/k_1$	$-H_0$
97·9	0	18·29	2·14	131	—	1·68	1·75	9·24
,,	1	17·13	2·00	68	1·65	1·57	1·73	8·84
,,	2	15·78	1·83	27	1·69	1·58	1·87	8·49
,,	3	14·36	1·68	10·4	1·65	1·38	2·08	8·04
98·4	0	18·46	1·59	165	—	1·75	1·79	9·39
,,	0·5	17·76	1·53	116	1·70	1·65	1·72	9·13
,,	1	17·08	1·48	76	1·67	1·62	1·73	8·92
,,	1·5	16·55	1·43	47	1·70	1·64	1·81	8·74
,,	2	15·87	1·37	35	1·66	1·58	1·82	8·56
,,	3	14·52	1·25	125	1·66	1·51	2·05	8·13
100	1	17·32	—	131	1·71	—	1·78	9·21
,,	2	16·04	—	55·4	1·65	—	1·80	8·76
,,	2·5	15·37	—	31·4	1·69	—	1·90	8·56
,,	3	14·70	—	17·2	1·73	—	2·05	8·34
,,	4	13·26	—	2·98	1·71	—	2·59	7·56

A = $[H_2SO_4]/[H_2O]$, monosolvation of the NH_4^+ ion only being assumed.
B = ,, ,, ,, both NH_4^+ and H_3O^+ ions being assumed.
C = ,, no solvation of either NH_4^+ of H_3O^+ ions being assumed.

extended to media more aqueous than those here examined. Its importance, however, is that within the range of compositions studied it covers a scale of acidity in H_0 units equal to that extending from 85% to 98% sulphuric acid.

Considerable difficulty might arise in attempting to measure H_0 by the usual method [6] of determination of the extent of ionisation of an indicator B to its conjugate acid BH^+, because of the shift of spectrum which would be likely to occur with increasing concentration of ammonium sulphate.



In the above evaluation of the H_0 acidity scale, it is assumed that any substrate is present in such low concentrations that it has a negligible effect on the concentration of either sulphuric acid or hydrogen sulphate ion. Any appreciable change in these concentrations due to the added substrate would necessitate appropriate correction of the H_0 values indicated.

Experimental.—Materials and media. Sulphuric acid solutions were prepared and standardised as reported previously.[4] 4-*p*-Toluidinopent-3-en-2-one was crystallised from light petroleum (b. p. 40—60°) and had m. p. 68°.

Kinetic measurements. The ammonium sulphate (" AnalaR ") was weighed into a tared 50 ml. volumetric flask, the sulphuric acid medium added, and after dissolution of the salt, the solution was made up to the mark at 25°. The flask was reweighed and then drained into a 100 ml. reaction vessel having a B24 neck. The residue (0·5 ml.) which remained in the 50 ml. flask was neglected. *p*-Toluidinopent-3-en-3-one (0·47 g.) was weighed into a B24 cap which fitted to the reaction vessel. Zero time was taken from the moment when vigorous shaking was started to effect dissolution of the anil in the medium. Solution was complete in *ca.* 1—2 min.; 2 ml. samples were withdrawn at appropriate intervals of time and run into 20 ml. of water. The acetylacetone liberated from the residual anil was determined as previously described.[5]

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9.

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D.Sc. 1960

The Absorptiometric Determination of Acetylacetone with Ferric Iron

BY

T. G. BONNER and Miss M. THORNE

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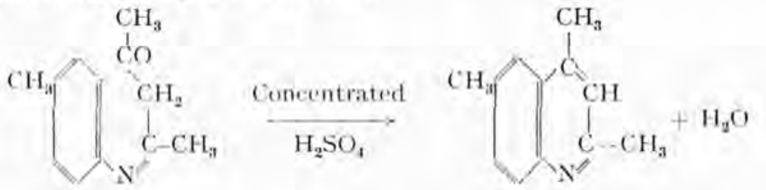
The Absorptiometric Determination of Acetylacetone with Ferric Iron

By T. G. BONNER and Miss M. THORNE

An absorptiometric method is described for the determination of acetylacetone in aqueous solution by converting it to the soluble red ferric salt. The influence of acidity and sodium sulphate on the colour intensity was investigated and the method was shown to be applicable to the determination of a Schiff's base of acetylacetone.

A CONVENIENT method of synthesising 2 : 4-dimethylquinolines in concentrated sulphuric acid by cyclisation of Schiff's bases prepared from primary aromatic amines and acetylacetone was developed by Combes,[1,2] and later the influence of nuclear substituents in the anilino portion of the Schiff's base on the yield and course of the cyclisation reaction was studied by Turner and Roberts.[3]

The cyclisation reaction is an electrophilic substitution, and a method was sought for following the rate of cyclisation in sulphuric acid - water mixtures of those Schiff's bases, such as methyl β-(*p*-toluidino)propenyl ketone (**I**), that are converted to the corresponding quinoline compound in nearly 100 per cent. yield.



(**I**)

As the Schiff's base (**I**) is quantitatively hydrolysed to acetylacetone and *p*-toluidine in dilute sulphuric acid, the reaction mixture can be examined by determining the acetylacetone liberated when an aliquot portion is run into water.

Pulsifer[4] showed that the red-coloured compound formed by acetylacetone and ferric iron could be used for the colorimetric determination of small quantities of ferric iron in aqueous solutions; this method has been recommended as one of the most satisfactory by Wenger and Duckert.[5] The intensity of the colour developed was shown to depend on the acidity of the solution, but not on the presence of small amounts of salts.

When the method was adapted for the determination of acetylacetone, the influence of acidity and of concentration of ferric salt and sodium sulphate was investigated, and so the optimum conditions for the determination were established.

EXPERIMENTAL

REAGENT—

Ferric ammonium sulphate solution—A 6·5 per cent. w/v solution in 0·1 *N* sulphuric acid.

PROCEDURE FOR THE DETERMINATION OF ACETYLACETONE IN AQUEOUS SOLUTION—

To 5 ml of the ferric ammonium sulphate solution, add a measured volume (1 to 15 ml) of the acetylacetone solution, which must be 0·1 *N* with respect to sulphuric acid, and then add an appropriate volume of 0·1 *N* sulphuric acid so that the final volume is 20 ml. Allow the solution to stand for 15 minutes, when the colour develops its full intensity. Prepare a blank solution by substituting an equal volume of 0·1 *N* sulphuric acid for the acetylacetone solution. Measure the colour in a Spekker photo-electric absorptiometer, using an Ilford No. 603 blue-green filter. There should be no alteration of colour intensity after the solution has stood for a further hour.

ABSORPTION SPECTRUM OF THE FERRIC - ACETYLACETONE COMPOUND—

This was studied with a Uvispek spectrophotometer. The colour was developed as described above, except that only 1 ml of the reagent was used; the final solution contained

1·75 mg of acetylacetone in 20 ml ($8·73 \times 10^{-4}$ moles per litre). The results are shown graphically in Fig. 1, the maximum absorption being at 484 mμ.

INFLUENCE OF THE ACIDITY AND AMOUNT OF REAGENT ON COLOUR PRODUCTION—

By the procedure described above and with the final solution always containing 2·00 mg of acetylacetone, the acidity was varied over the range 0·001 to 0·300 *N* with respect to sulphuric acid; the optical density of the different solutions was found to decrease continuously from 0·832 to 0·477 with increase of acidity. It is therefore essential to maintain the acidity at some arbitrarily chosen value for the standard procedure, and 0·1 *N* sulphuric acid was used for this purpose.

The optical density depends on the concentration of the ferric reagent. In preliminary experiments with a 5 per cent. w/v ferric ammonium sulphate solution in 0·1 *N* sulphuric acid, variations in the volume of reagent solution used, between 1 and 9 ml in a total volume of 20 ml, resulted in a change of optical density from 0·260 to 0·656. The variation was least marked in the region of 6 to 6·5 ml of this ferric solution. These experiments led to the use of 5 ml of a 6·5 per cent. w/v ferric ammonium sulphate solution in a total volume of 20 ml for the proposed procedure.

TABLE I

EFFECT OF ADDED SODIUM SULPHATE ON COLOUR PRODUCTION

	Optical density		
Acetylacetone, mg	No added sodium sulphate	1·04 g of sodium sulphate in 20 ml of final solution	0·39 g of sodium sulphate in 20 ml of final solution
2·45	0·768	0·748	
2·25	0·719	0·689	0·689
2·04	0·650	0·632	
1·83	0·584	0·574	0·573
1·63	0·524	0·511	
1·43	0·461	0·452	0·452
1·23	0·395	0·388	
1·02	0·325	0·327	

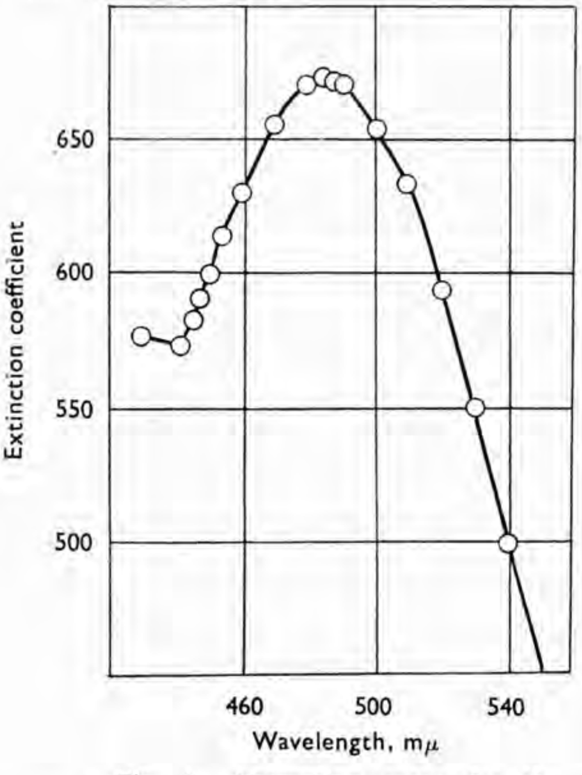


Fig. 1. Absorption curve for the ferric - acetylacetone complex

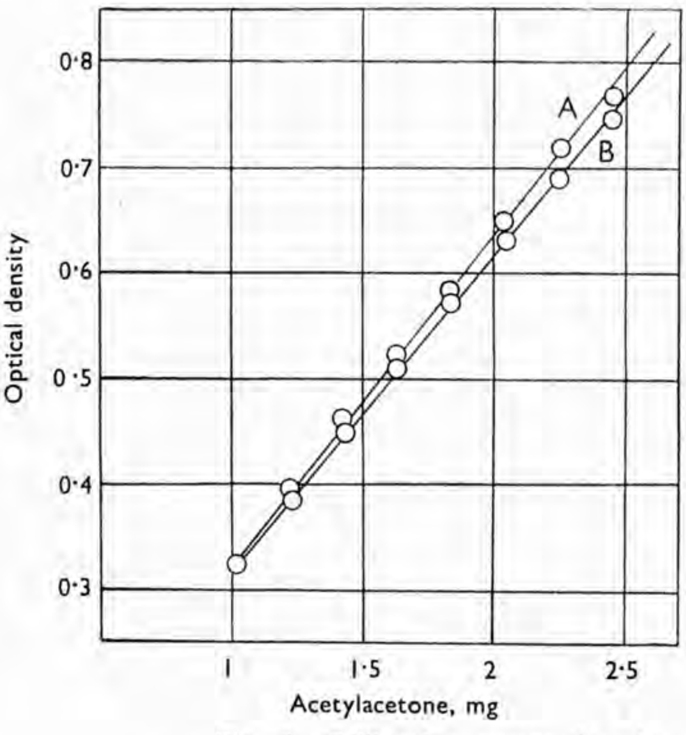


Fig. 2. Calibration curves for the ferric salt of acetylacetone: curve A, no added sodium sulphate; curve B, 1·04 g of sodium sulphate in 20 ml of final solution

EFFECT OF SODIUM SULPHATE ON COLOUR PRODUCTION—

As the acidity of the acid solutions of acetylacetone used in the kinetic experiments had to be adjusted by the addition of sodium hydroxide solution, the final solution to be examined absorptiometrically contained considerable amounts of sodium sulphate (about 0·5 g of sodium sulphate per 5-ml aliquot of the acetylacetone solution).

The effect of the presence of this salt on the colour production is shown in Fig. 2. The linear relationship between the optical density and concentration of acetylacetone is maintained, but with a slightly altered slope. Further, as indicated in Table I, it appears that the influence of the sodium sulphate is constant within the range of 0·40 to 1·00 g of salt per 20 ml of final solution.

TABLE II

DETERMINATION OF THE SCHIFF'S BASE (I) BY HYDROLYSIS

Aliquots used, ml	Amount of Schiff's base (I), g	Acetylacetone Calculated, mg	 Found, mg	Recovery, %
5	0·3485	1·84	1·84	100
10	0·2003	2·12	2·10	99·1
15	0·1006	1·60	1·56	97·5

APPLICATION OF THE METHOD TO THE DETERMINATION OF METHYL β-(*p*-TOLUIDINO)PROPENYL KETONE (I)—

Various weights of the Schiff's base (I) were dissolved in 100-ml portions of *N* sulphuric acid and the solutions were allowed to stand for 2 hours to effect complete hydrolysis to acetylacetone. The acid solutions were neutralised by titration with *N* sodium hydroxide solution, universal indicator paper being used to establish the end-point. Then 50 ml of *N* sulphuric acid were added and the solution was diluted to 500 ml with water. Aliquot portions were removed for the determination of acetylacetone; the results are shown in Table II and indicate that the method is applicable to the analysis of Schiff's bases of acetylacetone.

In kinetic experiments 1 g of the Schiff's base was dissolved rapidly in 25 ml of the concentrated sulphuric acid medium at 25° C at zero time and 2-ml aliquots were withdrawn at fixed time intervals and run into 20 ml of water. This dilution reduced the acidity to about 2 *N* and, on standing for 2 hours, complete hydrolysis of the unchanged Schiff's base occurred. The solution was neutralised as described above and, after filtration, was diluted exactly to 100 ml with water after the addition of 10 ml of *N* sulphuric acid, to give an exactly 0·1 *N* acid solution. A 5-ml or 10-ml aliquot portion of this solution was then removed and its acetylacetone content was determined by the standard procedure. The rate constants determined by this method were satisfactory.

Acknowledgments are made to Imperial Chemical Industries Limited and to the Central Research Fund for financial assistance.

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June 8th, 1954

10.

THE CYCLODEHYDRATION OF ANILS. PART I. KINETICS OF CYCLODEHYDRATION OF 2-ANILINO- AND 2-*p*-TOLUIDINO-PENT-2-EN-4-ONE IN SULPHURIC ACID

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The Cyclodehydration of Anils. Part I. Kinetics of Cyclodehydration of 2-Anilino- and 2-p-Toluidino-pent-2-en-4-one in Sulphuric Acid.

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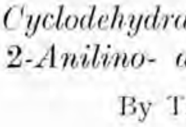
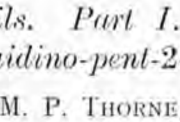
The rates of cyclodehydration of 2-anilino- and 2-*p*-toluidino-pent-2-en-4-one have been measured in aqueous sulphuric acid in the range 84·5—97·3% H_2SO_4. The first-order rate constants (k_1) for a fixed initial 0·1M-concentration of condensation product are related to the acidity function, H_0, by Hammett's equation $\log k_1 + H_0 = \text{constant}$. An approximately linear relation is found between k_1 and the molar ratio $[H_2SO_4]/[HSO_4^-]$. This relation also applies to the rate constants determined in ammonium sulphate–sulphuric acid if it is assumed that the NH_4^+ ion has a solvation number of 1 in sulphuric acid.

THE formation of 2 : 4-dimethylquinolines when the condensation products of acetylacetone and primary arylamines are heated in sulphuric acid was first investigated by Combes (*Compt. rend.*, 1887, **106**, 142; *Bull. Soc. chim.*, 1888, **49**, 90). The influence of substituent groups in the aromatic nucleus on this cyclodehydration reaction was examined by Turner and Roberts (*J.*, 1927, 1836), and their results, together with subsequent work on cyclodehydration, have been summarised by Bradsher (*Chem. Rev.*, 1946, **38**, 447).

The condensation products are usually represented as tautomeric ketimine (I or II) and enamine (III) structures; *e.g.*, the last is 2-anilinopent-2-en-4-one. From a study of the


(I)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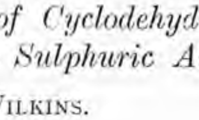
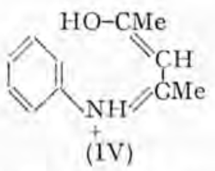

(III)

molecular refractivity of this anil, using both the pure compound and its solution in methylnaphthalene, von Auwers and Susemihl (*Ber.*, 1930, **63**, 1072) obtained exaltations of 3·5 for the pure compound and 3·35 for the solution above the value calculated for structure (III). They concluded that the anil has this structure, since there exists conjugation between the C=C bond and C=O group and between the nitrogen atom and the benzene ring. However, comparison of the calculated molecular refractivities of the forms (II) and (III) shows that they differ only in the contribution of the nitrogen and the oxygen atoms which are differently bound in the two structures. The molecular refractivity values for these contributions are shown below [values taken from von Auwers and Susemihl (*loc. cit.*) and Gilman's " Organic Chemistry," John Wiley & Sons, Ltd., 2nd Edn., 1943, Vol. II, p. 1751]. The difference of only 0·135 therefore does not permit a decision between the two structures.

$C_6H_5\cdot NH\cdot\underset{CH_3}{C}\colon CH\cdot\underset{CH_3}{C}=O$	Secondary N atom =O	2·499 2·211	4·710
$C_6H_5\cdot N\colon\underset{CH_3}{C}\cdot CH\colon\underset{CH_3}{C}\cdot OH$	–N= –O–	3·05 1·525	4·575

The ketimine structure has been proposed in cases where failure to cyclise under the usual conditions has been observed; *e.g.*, since the products from aniline and formylacetone (Thielpape, *Ber.*, 1922, **55**, 127) and from *p*- and *o*-chloroaniline and acetylacetone (Turner and Roberts, *loc. cit.*) could not be cyclised in acidic media, it was suggested that they exist in the *trans*-form of the ketimine, which is sterically unsuited to cyclisation. Edwards and Petrow (*J.*, 1954, **2853**) recently dealt with this point and from infrared-spectral studies concluded that the products from *o*-, *m*-, and *p*-chloroaniline and acetylacetone are in the ketimine form; of these only the *m*-compound cyclises in sulphuric acid (Turner and Roberts, *loc. cit.*).

It is reasonable to assume that in the acid media employed for cyclodehydration the reacting form is cationic, and the same cationic resonance structures (IV)—(VI) can be derived from structure (II) or (III) by proton uptake.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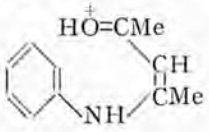
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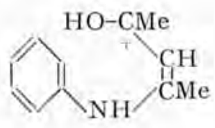
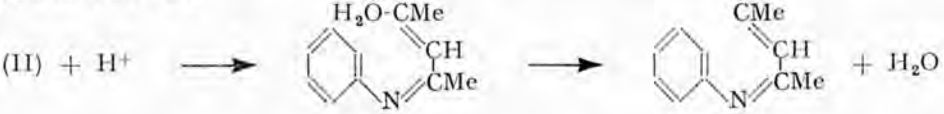

(VI)

Similar cationic structures in other cyclisations in acid media have been suggested by Petrow (*J.*, 1942, 693), Berliner (*J. Amer. Chem. Soc.*, 1944, **66**, 533), and Morley and Simpson (*J.*, 1948, 2024).

An alternative but more remote possibility is that the anil in the form (II) ionises in sulphuric acid as follows:


(VII)

A decision between the alternative cationic species represented by (IV)—(VI) and (VII) can be made by examining the relations between the rate constant of the cyclodehydration and Hammett's acidity function H_0 and the J_0 function defined by Gold and Hawes (*J.*, 1951, 2102). Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1932, **54**, 2721) showed that if a reaction in sulphuric acid is of the first order and the reacting species is formed by uptake of a single proton from the medium without further modification of the cation which results, then, provided there is only a relatively small fraction of the compound present in its cationic form, the experimental rate constant k_1 and the acidity function H_0 are related by the equation $\log k_1 + H_0 = \text{constant}$, where $H = -\log \alpha_{H^+} f_B/f_{BH^+} = pK + \log [B]/[BH^+]$, K representing the acid dissociation constant, and $[B]$ and $[BH^+]$ the concentration of un-ionised and ionised form of a base indicator ionising in the medium by simple proton uptake. This is in effect equivalent to demonstrating the constancy of the sum of $\log k_1$ and the logarithm of the ionisation ratio $[B]/[BH^+]$ of a simple basic indicator ionising over the range of media for which kinetic data are obtainable.

If on the other hand the cyclisation occurs in the cationic species represented by structure (VII), then a similar type of relation can be deduced between k and the ionisation ratio $[ROH]/[R^+]$ of a triphenylmethanol-type indicator which ionises according to the sequence

$$\mathrm{ROH} \overset{H^+}{\rightleftharpoons} \mathrm{ROH_2^+} \rightleftharpoons \mathrm{R^+ + H_2O} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let $[A]_T$ represent the concentration of the total amount of " anil " present, $[A^+]$ that present as the cation (VII), and $[A]$ that of the residual " anil." The theoretical rate equation (for a first-order reaction) is given by $k_0[A^+]f_{A^+}/f_{tr}$, where f_{tr} is the activity coefficient of the transition complex. Assuming that the activity coefficient ratio f_{A^+}/f_{tr} is constant over the range of media investigated, and equating with the experimental rate equation, we have:

$$k_1[A]_T = k[A^+] \text{ where } k = k_0 f_{A^+}/f_{tr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$\log k_1 + \log [A]_T/[A^+] = \log k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For alcohols ionising in the form of equation (1) it has been shown (Murray and Williams, *J.*, 1950, 3318) that the difference between the logarithms of the ionisation ratios of two such compounds over narrow ranges of sulphuric acid–water media is a constant. If the same relation holds for an " anil " ionising as in (1) we can write:

$$\log [A]/[A^+] - \log [ROH]/[R^+] = \text{constant (independent of medium)} \quad . \quad (4)$$

where ROH represents a triphenylmethanol indicator ionising in the range of media in which the rates of cyclisation have been measured. If the extent of conversion of the compound A into its cation A^+ is very small, *i.e.*, $[A^+] \ll [A]$ so that [A] is approximately the same as $[A]_T$, we have by combining (3) and (4) :

$$\log k_1 + \log [\mathrm{ROH}]/[\mathrm{R^+}] = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

A correlation of this kind between the rate of nitration of benzene and the ionisation ratio for 4 : 4′ : 4″-trinitrotriphenylmethanol in sulphuric acid, found by Westheimer and Kharasch (*J. Amer. Chem. Soc.*, 1946, **68**, 1871), provided evidence that the nitric acid ionised according to (1) to produce the nitronium NO_2^+ ion. A more general form of equation (5) is :

$$\log k_1 + J_0 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where J_0, as defined by Gold and Hawes (*loc. cit.*), is given by $J = -\mathrm{p}K_{\mathrm{ROH}} + \log [\mathrm{ROH}]/[\mathrm{R^+}]$. Equation (6) has been shown to apply to the nitration of the p-$C_6H_4Me{\cdot}NMe_3^+$ ion in sulphuric acid (Lowen, Murray, and Williams, *J.*, 1950, 3318) and to the decarbonylation of triphenylacetic acid in sulphuric acid (Deno and Taft, *J. Amer. Chem. Soc.*, 1954, **76**, 244, from results obtained by Dittmar, *J. Phys. Chem.*, 1929, **33**, 533). In the present paper, equation (5) is preferred to equation (6) as a test of this mechanism, since an agreed scale of J_0 values over a sufficient range of media is not yet available (see Williams and Bevan, *Chem. and Ind.*, 1955, 171, and Gold, *ibid.*, p. 172).

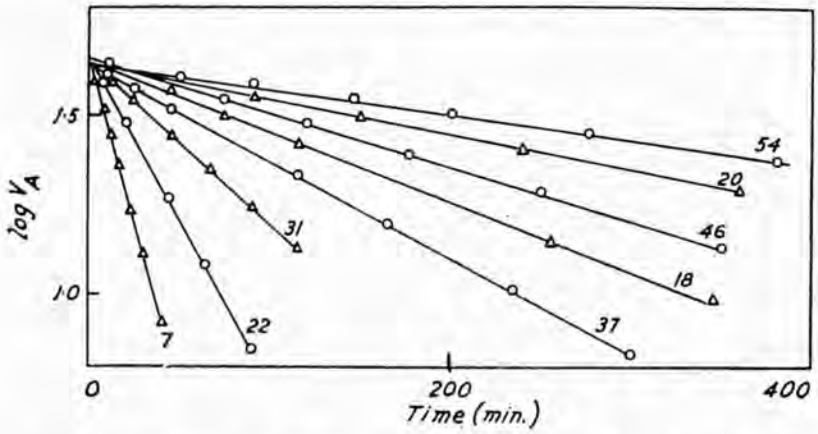


FIG. 1.
○ 2-*Anilinopent-2-en-4-one.*
△ 2-p-*Toluidinopent-2-en-4-one.*

Kinetics of the Cyclodehydration.—The rates of conversion of 2-anilino- and of 2-*p*-toluidino-pent-2-en-4-one into 2 : 4-dimethyl- and 2 : 4 : 6-trimethyl-quinoline in aqueous sulphuric acid were followed by hydrolysis of the unchanged compound at known intervals of time to the aromatic amine and acetylacetone, and colorimetric estimation of the latter by conversion into ferric acetylacetone in aqueous acid. Excellent first-order rate constants were obtained for both compounds in the range of media studied as shown in Fig. **1.** The rate constant depends to a slight extent on the initial concentration of the " anil "; this is a feature of other reactions in sulphuric acid, *e.g.*, nitration, and will form the subject of a separate study. All results quoted in this paper have been obtained with an initial 0·1M-concentration of organic reactant. The results for the anilino- and the *p*-toluidino-compounds are shown in Table 1. The H_0 values were taken from a curve obtained by plotting the experimental H_0 values (quoted by Deno and Taft, *loc. cit.*) against percentage of sulphuric acid, and the log $[\mathrm{ROH}]/[\mathrm{R^+}]$ values were similarly obtained from the results of the investigation of the ionisation of 4 : 4′ : 4″-trinitrotriphenylmethanol (Murray and Williams, *loc. cit.*). It is clear that the $(\log k + H_0)$ values are reasonably constant for both compounds, while there is a marked variation in the $(\log k + \log [\mathrm{ROH}]/[\mathrm{R^+}])$ values. It can be concluded that the products cyclise in the form of simple cationic structures resulting from uptake of a single proton without further change in the ionic species.

First-order rate constants were obtained in the decarbonylation of aromatic aldehydes (Schubert and Zahler, *J. Amer. Chem. Soc.*, 1954, **76**, 1) and in the decarboxylation of aromatic acids (Schubert, Donohue, and Gardner, *ibid.*, p. 9) in sulphuric acid, but the authors concluded that the Hammett unimolecular mechanism does not apply to these reactions. In both reactions studied, extensive conversion of the aromatic compound (B) into its conjugate acid (BH^+) occurs in relatively aqueous acids (60—80% sulphuric acid) and a modified form of the Hammett equation was used, *viz.*,

$$\log k + H_0 - \log [B]/[B]_{\text{stoich.}} = \text{constant}$$

where [B] represents the concentration of un-ionised form and $[B]_{\text{stoich.}}$ the total concentration (all forms) of the aromatic compound. Since their results did not fit this equation, alternative bimolecular and termolecular mechanisms were considered and for the decarboxylation evidence was obtained for a bimolecular reaction between the aromatic compound and molecular sulphuric acid. A similar bimolecular mechanism was put forward by Sommer, Barie, and Gould (*ibid.*, 1953, **75**, 3765) for the formation of methane from β-trimethylsilylpropionic acid in sulphuric acid; the ratio of the first-order rate constant for the evolution of methane to the concentration of molecular sulphuric acid was shown to be constant over the range 89—97% sulphuric acid, and Deno and Taft (*loc. cit.*) later established that the constancy of this ratio was maintained down to 85% sulphuric acid. There is no evidence of any such correlation in the cyclodehydration, and this particular bimolecular mechanism can be rejected for this reaction.

TABLE 1. *Rates of cyclodehydration in sulphuric acid–water media.*

2-Anilinopent-2-en-4-one					2-*p*-Toluidinopent-2-en-4-one				
Medium, % H_2SO_4	Expt. no.	10^2k_1 (min.$^{-1}$)	$\log k_1 + H_0$	$\log k + \log [ROH]/[R^+]$	Medium, % H_2SO_4	Expt. no.	10^2k_1 (min.$^{-1}$)	$\log k_1 + H_0$	$\log k + \log [ROH]/[R^+]$
97·3	22	2·11, 2·09	−10·79	—	95·5	95	8·49, 8·45	− 9·89	—
95·7	71	1·24, 1·22	−10·76	—	93·1	7	4·29, 4·28	− 9·91	−2·57
95·5	97	1·20, 1·21	−10·74	—	91·1	11	2·12, 2·12	− 9·98	−2·32
95·2	26	1·14	−10·72	—	89·2	13	1·22, 1·23	−10·00	−2·05
93·3	37	0·614, 0·622	−10·77	−3·46	89·0	31	1·06, 1·05	−10·01	−2·02
91·2	46	0·343, 0·341	−10·79	−3·15	87·6	24	0·742, 0·741	−10·05	−1·83
89·2	75	0·211, 0·210	−10·77	−2·80	86·3	18	0·445, 0·450	−10·10	−1·63
88·6	54	0·166, 0·163	−10·80	−2·75	85·5	27	0·330, 0·330	−10·13	−1·50
					84·5	20	0·238, 0·239	−10·14	−1·32

Relation between the Rate Constant and the Ratio $[H_2SO_4]/[HSO_4^-]$.—Brand (*J.*, 1950, 1002) has shown that Hammett's acidity function H_0 in the range 89—99·8% sulphuric acid can be calculated with the empirical equation

$$H_0 = -8{\cdot}36 + \log [HSO_4^-]/[H_2SO_4] \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

if the reaction

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

is assumed to be complete. Deno and Taft (*loc. cit.*) later showed that equation (7) is applicable in the range of media 83—89% sulphuric acid if a value of 50 is assigned to the equilibrium constant, *K*, of reaction (8). As a consequence of the validity of this method of calculating H_0 values, these authors conclude that the activity coefficient ratio $f_{H_3O^+}f_{HSO_4^-}/f_{H_2O}f_{H_2SO_4}$ is constant over the range 83—100% sulphuric acid. From the constancy of the $\log k_1 + H_0$ addition in the cyclodehydration, it follows that for this reaction

$$\log k_1 - \log [H_2SO_4]/[HSO_4^-] = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

A simple derivation of equation (9) is possible from the following considerations. If the compound A is involved in the equilibrium

$$A + H_2SO_4 \rightleftharpoons AH^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

with an equilibrium constant K' given by

$$K' = \frac{[AH^+][HSO_4^-]}{[A][H_2SO_4]} \frac{f_{AH^+}f_{HSO_4^-}}{f_A f_{H_2SO_4}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

then from equation (11) and the appropriate form of equation (3) in which $[A^+]$ is replaced by $[AH^+]$, assuming that $[AH^+] \ll [A]$ (*i.e.*, $[A]$ is approximately equal to $[A]_T$), we have

$$k_1 = kK'[H_2SO_4]/[HSO_4^-] \times \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

since the activity coefficient term is similar to that for the equilibrium (8) and can be expected to show the same constancy. The direct relation between the rate constant, k_1, and the ratio $[H_2SO_4]/[HSO_4^-]$ indicated in equation (12) is evident in Fig. 2, in which the curve represents the variation of $[H_2SO_4]/[HSO_4^-]$ with percentage of sulphuric acid; the values of the rate constants for both condensation products plotted (on suitable ordinate scales) against the percentage of sulphuric acid in the media in which they are determined lie very close to the curve. No parallelism is found with the curves of the variation of $[H_2SO_4]$ or $[HSO_4^-]$ with the percentage of sulphuric acid.

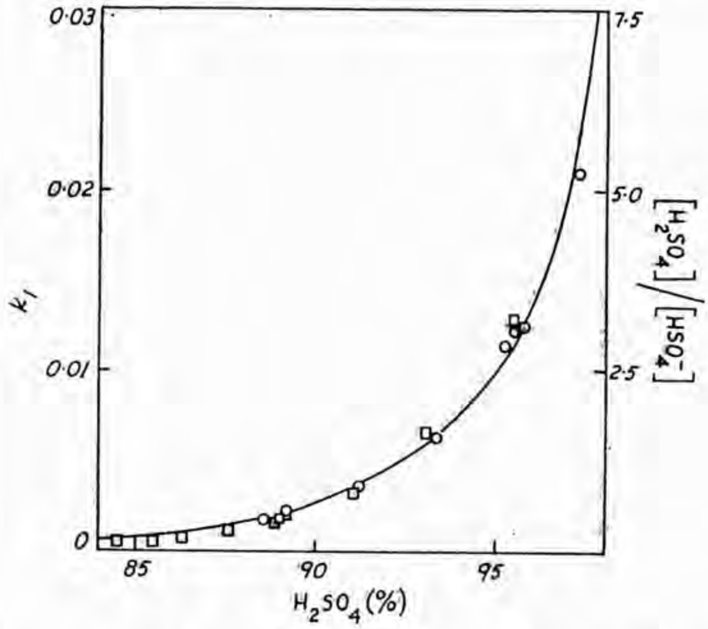


FIG. 2.
○ 2-*Anilinopent-2-en-4-one.*
□ 2-p-*Toluidinopent-2-en-4-one.*

A more stringent test of equation (12) is the demonstration that the plot of k_1 against $[H_2SO_4]/[HSO_4^-]$ is a straight line. This is shown in Fig. 3 and for both compounds reasonable linearity is evident. Also included in this Figure is the plot of k_1 against $[H_2SO_4]/[HSO_4^-]$ for the cyclodehydration of the *p*-toluidino-compound in water-free $(NH_4)_2SO_4$–H_2SO_4 media. The relevant results are shown in Table 2, where $[H_2SO_4]_T$ represents the stoicheiometric concentration of sulphuric acid, and $[H_2SO_4]$ the residual molecular sulphuric acid concentration. Each mole of ammonium sulphate requires 1 mole of sulphuric acid according to the equation $(NH_4)_2SO_4 + H_2SO_4 = 2NH_4^+ + 2HSO_4^-$. Although no simple correlation is found between k_1 and $[H_2SO_4]/[HSO_4^-]$ if this represents the sole interaction, yet the linear relation is obeyed if it is assumed that each ammonium ion binds 1 molecule of sulphuric acid by solvation. Evidence that this solvation occurs is provided by the freezing-point–composition data for $(NH_4)_2SO_4$–H_2SO_4 mixtures (Kendall and London, *J. Amer. Chem. Soc.*, 1920, **42**, 2135), which indicate the existence of a stable compound $(NH_4)_2SO_4,3H_2SO_4$, and the interpretation of the depression of freezing point

TABLE 2. *Rates of cyclodehydration of* 2-p-*toluidinopent-2-en-one in* $(NH_4)_2SO_4$–H_2SO_4 *media.* (All concns. in moles/l.)

$(NH_4)_2SO_4$	k_1	$[HSO_4^-]$	$[H_2SO_4]_T$	$[H_2SO_4]$	$\frac{[H_2SO_4]}{[HSO_4^-]}$	$\log k_1 - \log [H_2SO_4]/HSO_4^-]$
1	0·131	2	17·42	14·42	7·21	−1·74
2	0·0554	4	16·14	10·14	2·54	−1·67
2·5	0·0314	5	15·47	7·97	1·59	−1·70
3	0·0172	6	14·80	5·80	0·97	−1·75
4	0·00298	8	13·36	1·36	0·17	−1·76

of pure sulphuric acid by small amounts of ammonium sulphate by Gillespie, Hughes, and Ingold (*J.*, 1950, 2487) in terms of a solvation number of unity for the ammonium ion.

The constancy of the term in the last column of Table 2 is another expression of the relation given by equation (12) and shows in effect that the Hammett equation is obeyed although it cannot be tested directly since H_0 values have not been determined for $(NH_4)_2SO_4$–H_2SO_4 media.

The gradient of each line in Fig. 3 represents the product of the constant terms in equation (12), and the ratio of the gradients for the two anils is the ratio of the kK products for each. The ratio kK(*p*-toluidino-compound)/kK(anilino-compound) obtained for the results in aqueous sulphuric acid is approximately 7, while the same ratio, from the results obtained for the *p*-toluidino-compound in ammonium sulphate–sulphuric acid, is *ca.* 5. The *p*-toluidino-compound cyclises more rapidly than the anilino-compound as a result of (i) the activating effect of the methyl group at the *meta*-position where ring closure occurs and (ii) the greater basicity of the nitrogen atom which is in the *para*-position to the methyl group. The rate of electrophilic substitution in aromatic compounds at the *meta*-position to a methyl group is about 2·5—3 times faster than in the unsubstituted benzene ring; this would account for about half the kK ratio found experimentally, the remainder presumably being the result of the greater basicity of the *p*-toluidino-compound.

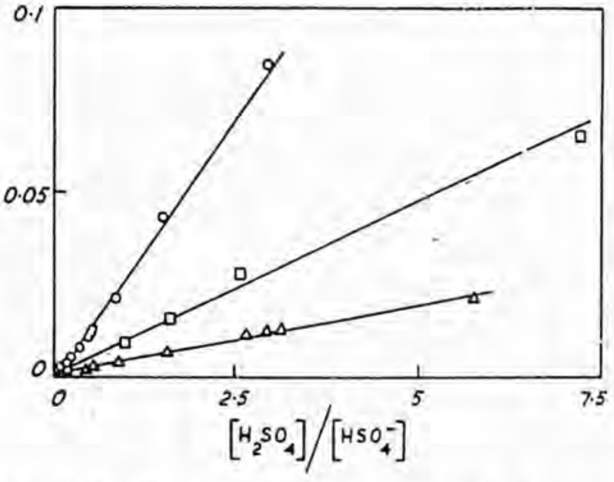


FIG. 3.

○ 2-p-*Toluidinopent-2-en-4-one in* H_2SO_4–H_2O.
△ 2-*Anilinopent-2-en-4-one in* H_2SO_4–H_2O.
□ 2-p-*Toluidinopent-2-en-4-one in* $(NH_4)_2SO_4$–H_2SO_4 ($k_1 \times 0·5$).

EXPERIMENTAL

Materials.—Aniline and acetylacetone were distilled before use, and *p*-toluidine was crystallised twice from aqueous alcohol. The condensation products were prepared by Turner and Roberts's method (*loc. cit.*) and were recrystallised twice from light petroleum (b. p. 40—60°); 2-anilinopent-2-en-4-one had m. p. 50—52°; 2-*p*-toluidinopent-2-en-4-one had m. p. 65—66°.

Media.—Sulphuric acid–water mixtures were prepared by adding water or redistilled oleum to "AnalaR" concentrated sulphuric acid and standardised against N-sodium hydroxide referred through N-hydrochloric acid to potassium iodate. 100% Sulphuric acid was obtained by adjustment of a weak oleum to maximum freezing point. Water-free ammonium sulphate–sulphuric acid mixtures were prepared directly for each kinetic experiment by weighing the required amount of ammonium sulphate into a tared 50-ml. volumetric flask, adding 100% sulphuric acid to dissolve the solid, and making up to the mark at 25°; the flask was then reweighed to obtain the weight of pure sulphuric acid present.

Conversion into Quinoline Compounds.—To establish that the cyclodehydration is practically quantitative under the conditions used for rate measurements, 1 g. of 2-anilinopent-2-en-4-one was rapidly dissolved in 10 ml. of 97·9% sulphuric acid (this corresponds to 5 times the concentration of organic reactant used in kinetic experiments) and kept at room temperature for 2 hr. The solution was poured into ice-cold water (100 ml.) and left for 2 hr. to ensure complete hydrolysis. The solution at 5° was treated with an ice-cold solution of sodium nitrite (0·05 g.) in water (5 ml.) to diazotise any aniline resulting from the hydrolysis, and then warmed to convert the diazonium salt into phenol. After cooling, sodium hydroxide (15 g.) was added to make the solution alkaline. The 2 : 4-dimethylquinoline was extracted with ether, and the ether extracts were washed with water and dried (Na_2SO_4). After filtration and evaporation, the crude product was obtained as a yellow liquid (yield 92%) (Found : C, 82·9; H, 7·2; N, 9·0. Calc. for $C_{11}H_{11}N$: C, 84·0; H, 7·05; N, 8·9%)

In a similar experiment, 2-*p*-toluidinopent-2-en-4-one (1 g.) was dissolved in a solution (10 ml.) of 1 mole/l. of ammonium sulphate in 100% sulphuric acid and kept for 2 hr. 2 : 4 : 6-Trimethylquinoline was recovered in 93% yield by the method described above (m. p. of crude product 40—41·5°; m. p. of pure compound 43—45°) (Found: C, 84·2; H, 8·0; N, 7·6. Calc. for $C_{12}H_{13}N$: C, 84·2; H, 7·65; N, 8·2%).

Analytical Method.—The condensation products could be determined by hydrolysis in *ca.* 2N-sulphuric acid to the aromatic amine and acetylacetone, followed by conversion of the latter into its soluble ferric complex; this is red and its solution obeys Beer's law (cf. Bonner and Thorne, *Analyst*, 1954, 79, 759). The reagent is a 6·5% w/w solution of "AnalaR" ferric ammonium sulphate in 0·1N-sulphuric acid to which an aliquot portion of acetylacetone (1—2·5 mg.) in 0·1N-sulphuric acid is added. The colour is fully developed after 15 min., and the optical density of the solution is then determined on a "Hilger Spekker" photoelectric absorptiometer, a sodium filament lamp and a blue-green filter (No. 603) being used to confine the incident light to a wavelength band of 4700—5000 Å. The amount of acetylacetone present is read off from a standard curve obtained from measurements on solutions of known concentration. No interference occurs with aniline, *p*-toluidine, or the corresponding quinoline compounds, and the effect of sodium sulphate present in solutions from the kinetic experiments can be eliminated by obtaining the standard curve with acetylacetone solutions containing this salt. The results of analysis of pure 2-anilinopent-2-en-4-one are shown below. After hydrolysis with 2N-sulphuric acid each solution was made up to 500 ml., and the acidity adjusted to 0·1N. A suitable aliquot part was taken for the acetylacetone determination.

Reactant taken (g.)	Aliquot taken (ml.)	Acetylacetone in aliquot : Calc. (mg.)	Found (mg.)
0·2222	5	1·27	1·27
0·1295	10	1·48	1·50
0·0796	15	1·36	1·37

Procedure for Measuring the Rate of Cyclodehydration.—Kinetic measurements were carried out at 25° in a thermostat controlled to ±0·02°. The reaction vessel was a 100-ml. round-bottomed flask with a B24 neck. The organic reactant was weighed into a B24 socket cap, the amount taken providing a 0·1M-solution when dissolved in 50 ml. of the medium. The medium, previously made up to the mark in a tared 50-ml. volumetric flask at 25°, was transferred to the reaction vessel; 30 sec. were allowed for drainage, and the flask was reweighed to allow a correction to be made for incomplete transfer. To start the reaction, the reaction vessel was removed from the thermostat, and the filled socket cap inserted. The medium and reactant were brought into contact at zero time by vigorous shaking; and after complete dissolution had occurred (1—2 min.) the flask was returned to the thermostat. Air bubbles formed during the shaking were rapidly removed by replacing the socket cap with a B24 cone connected to a suction pump. As soon as the liquid was clear (1—2 min.) the cone and pump were detached and the flask was restoppered. Six to eight 2-ml. samples were taken from the reaction mixture in the course of a run. Each sample was drawn into 2-ml. pipette, having a wide delivery jet and previously standardised for delivery of sulphuric acid, and run into 20 ml. of ice-cold water. This dilution stopped the reaction and also provided an approximately 2N-sulphuric acid. After the mixture had been kept for 2 hr. at room temperature to ensure complete hydrolysis of unconverted anil, 2·5 g. of pellet sodium hydroxide were added to the ice-cold solution to neutralise the bulk of the acid present. The solution was finally adjusted to neutrality by successive titration with N-sodium hydroxide, N-sulphuric acid, and 0·1N-sodium hydroxide (B.D.H. Universal Indicator paper); the proximity of the end-point is indicated by the separation of the quinoline. 5 Ml. of N-sulphuric acid were added, and the solution filtered into a 50-ml. volumetric flask and made up to the mark with washings. The solution, now 0·1N with respect to sulphuric acid, was analysed by adding a 5-, 10-, or 15-ml. aliquot portion to 5 ml. of the ferric ammonium sulphate reagent and dilution to a final volume of 20 ml. with 0·1N-sulphuric acid. The optical density was measured as described above against a blank prepared in the same way from 2 ml. of the pure medium. Reactions were followed up to about 80% change. Rate constants were obtained from the first-order rate equation $k_1t = 2·303 \{\log a - \log (a - x)\}$; k_1 (min.$^{-1}$), was obtained graphically from the plot of log V_a against t, where V_a is the volume of the standard acetylacetone solution equivalent to the amount of acetylacetone in each 2-ml. aliquot portion of the reaction mixture removed. Duplicate determinations were carried out and these rarely differed by more than 1%.

Test for Surface Catalysis Effects.—The rate of cyclodehydration of 2-anilinopent-2-en-4-one in 95·5% sulphuric acid at 25° was unaltered within the limits of experimental accuracy by the addition of a quantity of small glass balls (with and without this addition, rate constant = 0·0123 and 0·0121 min.$^{-1}$, respectively). The reaction thus occurs entirely in the homogeneous liquid phase.

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THE CYCLODEHYDRATION OF ANILS. PART II. THE HYDROGEN ISOTOPE EFFECT IN THE CYCLODEHYDRATION OF 2-ANILINOPENT-2-EN-4-ONE

BY
T. G. BONNER
AND
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The Cyclodehydration of Anils. Part II. The Hydrogen Isotope Effect in the Cyclodehydration of 2-Anilinopent-2-en-4-one.*

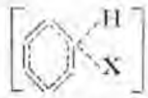
By T. G. BONNER and J. M. WILKINS.

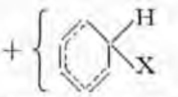
[Reprint Order No. 6170.]

The ratio of the rates of cyclodehydration of 2-(2 : 4 : 6-trideuteroanilino)-pent-2-en-4-one and its protium analogue is found to be approximately 2 : 3 in both 95·5% and 89·2% sulphuric acid–water. It is suggested that although fission of the C–H bond is not the kinetically decisive factor in the cyclodehydration, some weakening of the bond occurs in the rate-determining step.

IN a detailed discussion of the mechanism of aromatic electrophilic substitution, Melander (*Arkiv Kemi*, 1950, **2**, 211) considered the hydrogen isotope effect in the two alternative S_E2 processes—the single step replacement with the activated complex (I), and the two-stage process with an intermediate addition compound (II) regarded as having rather greater stability than the activated complex. In (I) the π-electrons of the benzene ring do not take part in the formation of π-bonds, although they may be polarised by the positive charge;

(I)





(II)

but in (II), two of these electrons are used for the addition of the cation resulting in the appearance of four bonds of the sp^3 type at the nuclear carbon atom. If, experimentally, identical rates of substitution for hydrogen isotopes are found, this implies that the step-wise reaction occurs with a rate-determining first step, since this step does not involve hydrogen loss; if a substantially slower rate is observed for the heavy isotope the substitution may occur either by the stepwise reaction with the second step rate-determining, or by the single-step replacement. The isotopic rate ratio k_T/k_H for the rates of replacement of tritium and protium may be found to have any value from unity to about 0·05. In nitration and bromination experiments, Melander obtained minimum values of 0·74—0·85 for k_T/k_H and concluded that these results established that the hydrogen loss in both substitution reactions was kinetically insignificant. The result for the nitration was confirmed by Bonner, Bowyer, and Williams (*J.*, 1953, 2650) who obtained values of 0·99 and 0·95 for k_D/k_H by direct determination of the rates of nitration of nitrobenzene and pentadeuteronitrobenzene in sulphuric acid solution. For sulphonation a significantly lower isotope ratio of 0·55 for k_T/k_H has been reported by Berglund-Larsson and Melander (*Arkiv Kemi*, 1953, **6**, 219) and their interpretation of this result favours the step-wise reaction with the second step rate-determining.

Rates of cyclodehydration at 25°.

Initial concn. of organic reactant 0·1M. k in min.$^{-1}$.

Medium, % H_2SO_4	Expt. no.	k_H	Expt. no.	k_D	k_D/k_H
95·7	71	0·0124, 0·0122	72	0·00811, 0·00811	0·66
89·2	75	0·00210, 0·00211	78	0·00148, 0·00149	0·71

The Isotope Effect in Cyclodehydration.—The ratio k_D/k_H in cyclodehydration was determined by measuring the rates of conversion of 2-anilino-(k_H) and 2-(2 : 4 : 6-trideutero-anilino)-pent-2-en-4-one (k_D) to the corresponding quinoline derivatives by the method described in Part I. The first-order rate constants obtained are shown in the Table.

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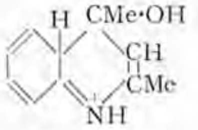
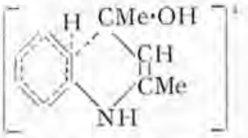
* Part I, preceding paper.

A definite isotope effect is evident, but the ratio is sufficiently close to unity to exclude the possibility that the fission of the C–H bond is the sole rate-determining factor. The reaction is an intramolecular electrophilic substitution within the cation formed by proton uptake from the medium and differs from a bimolecular electrophilic substitution in that the formation of the product requires the elimination of a molecule of water instead of a proton. In a mechanism corresponding to the formation of the intermediate addition compound (II) the cation would assume the structure (III). Elimination of a molecule of

(III)





(IV)

water from this intermediate in strongly acidic media should be rapid. Further, if interaction with sulphuric acid were kinetically significant, then the simple relation between the rate constant and the ratio $[H_2SO_4]/[HSO_4^-]$ found experimentally (Part I), *viz.*, $k = \text{const.}[H_2SO_4]/[HSO_4^-]$, could hardly be expected; the derivation of this equation assumes that the only interaction between the organic reactant (A) and the solvent species is that involved in the equilibrium, $A + H_2SO_4 \rightleftharpoons AH^+ + HSO_4^-$. It follows that if the reaction occurs by a two-step process through the intermediate compound (III), it is the formation of this compound which is the rate-determining step, and the small isotope effect must be accepted as a feature of this mechanism. The alternative single-step mechanism represented by the transition complex (IV) is less likely since the difference in zero-point energies of the C–H and C–D bonds should lead to a much lower k_D/k_H ratio than that found experimentally. The effect might not be so pronounced if a proton-acceptor participates in the transition state, but this would almost certainly lead to a more complex relation between k and the solvent species than that found experimentally. Hammond (*J. Amer. Chem. Soc.*, 1955, **77**, 334), in a discussion of Melander's results for bromination and nitration has suggested that, although they show that the breaking of the C–H bond makes little progress in the attainment of the first transition state leading to the formation of the intermediate (II), they do not establish that the C–H bond is not broken in the rate-determining step of the reaction, since the removal of a proton from the intermediate (II) may require only a very slight weakening of the C–H bond to yield the second transition state preceding the formation of the products. The further observation is made that some loosening of the C–H bond might be expected in the formation of the intermediate in the change from the trigonal to the tetrahedral configuration of the nuclear carbon atom, although Melander (*loc. cit.*, p. 246) does not hold this view. It is probable that some stretching and bending of the C–H bond is more likely to occur in cyclodehydration than in nitration or bromination during the formation of a transition state (whether this leads to the intermediate or directly to the products) since the electrophilic attack of the side-chain is sterically hindered as a result of its attachment to the ring; a small isotope effect would then be the expected result.

EXPERIMENTAL

Preparation of 2-(2 : 4 : 6-*Trideuteroanilino*)*pent*-2-*en*-4-*one*.—2 : 4 : 6-Trideuteroaniline was prepared by Best and Wilson's method (*J.*, 1946, 2391). Aniline hydrochloride (13 g.) was heated with heavy water (20 g.) in a sealed tube in boiling water for 24 hr. This treatment was repeated five times, the water being removed by vacuum-distillation and replaced by a fresh sample each time. The first five treatments were carried out with heavy water containing 99·73 atoms % of deuterium and the last with a sample containing 99·95 atoms % of deuterium. The deuteroaniline was removed by making the residue alkaline and extracting it with ether. After removal of the ether, the liquid was distilled and the fraction boiling at 180° was collected. It was condensed with a slight excess of acetylacetone as described in Part I. Colourless crystals, m. p. 51—53°, of the *deutero-compound* were obtained from light petroleum (b. p. 40—60°). We are greatly indebted to Dr. R. I. Reed and Mr. A. Macdonald, of the University of Glasgow, for a mass-spectrographic examination of the water formed by combustion of this product (and of the quinoline compound obtained from it, referred to in the next paragraph). Their analysis gave 5·71 ± 0·02% D_2O by wt. from 0·0427 g. of the deuteroanilino-ketone diluted with 0·1416 g. of the protium-analogue (Calc. : 5·82% D_2O).

Test for Deuterium Exchange during Cyclodehydration.—The 6 : 8-dideutero-2 : 4-dimethylquinoline formed in the kinetic experiments in 95·7% sulphuric acid was separated by addition of sodium hydroxide and extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and filtered, and the ether was removed. Mass-spectrographic examination of the water obtained by combustion gave 4·68 ± 0·02% D_2O by wt. from 0·1060 g. of sample (Calc. : 4·78% D_2O). Deuterium exchange with the medium during the cyclodehydration was therefore not significant.

Kinetic Measurements.—The rates of cyclodehydration of the protio- and deutero-compounds in the two sulphuric acid media were measured by the method described in Part I.

We thank Professor Gwyn Williams for his interest in this work, the Central Research Fund for a grant for the purchase of heavy water, and this College for a postgraduate studentship (to J. M. W.).

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841. *The Cyclodehydration of Anils. Part III.* The Alternative Hydrolytic Reaction.*

By T. G. Bonner and Mary Barnard.

Anils of acetylacetone are slowly hydrolysed in aqueous sulphuric acid at acidities slightly lower than those which bring about cyclodehydration to the corresponding quinoline compound.[1] A correlation between the rate of the hydrolysis and the activities of the hydrogen ion and water in the medium has been found for 4-(2 : 3-dimethylanilino)pent-3-en-2-one which suggests a simple bimolecular mechanism.

It is concluded that cyclodehydration proceeds through the diprotonated anil, and hydrolysis through the neutral anil.

Anils of acetylacetone are very rapidly hydrolysed to the primary aromatic amine and ketone in dilute aqueous acids and use is made of this fact to stop cyclodehydration of the anil to a substituted quinoline in concentrated sulphuric acid by diluting the mixture with water.[1] At some intermediate acidity, therefore, a change occurs in the nature of the reaction between the anil and its acid environment. The two most important solvent properties affecting the point at which the transition from cyclodehydration to hydrolysis can occur are (i) the activity of protons measured by Hammett's acidity function H_0 and (ii) the activity of water, obtained from the ratio of the vapour pressure of pure water to the vapour pressure of water over the sulphuric acid–water mixture (p/p_0). The medium or range of media where the change of reaction takes place should vary with the particular anil selected since proton-accepting capacity and reactivity (whether in cyclodehydration or hydrolysis) will depend on the constitution of the anil.

Previous work on the hydrolysis of anils appears to be confined to aqueous-alcoholic solutions. It has been shown [2] that hydrolysis of 4 : 4'-disubstituted benzylideneanilines in acetate-buffered 50% aqueous methanol is a first-order reaction with respect to the benzylideneaniline. Catalysis by water or bases was negligible in comparison with acid-catalysis and at pH 3 the rate of hydrolysis became immeasurably fast. The abnormally slow acid hydrolysis of *N*-(*p*-dimethylaminobenzylidene)aniline was attributed to the formation of its less reactive conjugate acid. Another study [3] of the hydrolysis of benzylideneaniline over the pH range 6—13 indicated that below pH 11 catalysis by the hydroxyl ion was negligible, the only effective catalyst being the H_3O^+ ion; the formation of an intermediate, *N*-(α-hydroxybenzyl)aniline was postulated and evidence for it from ultraviolet and infrared absorption spectra was claimed. Measurement [4] of the rates of hydrolysis and formation of the product of condensation of a substituted benzaldehyde and *p*-toluidine has shown that practically all substituents in the *m*- and the *p*-position in the benzaldehyde portion of the anil reduce the rate of hydrolysis relatively to that of benzylidene-*p*-toluidine. This is typical of a side-chain reaction dependent mainly on the inductive effect of nuclear substituents in which either attack by an electrophilic reagent or proton addition to the side chain takes place before reaction.

Preliminary work on the anils of acetylacetone showed that hydrolysis was immeasurably rapid in 2—3N-sulphuric acid. The more acidic ranges were therefore explored for a measurable rate of hydrolysis since at the point where cyclodehydration becomes significant the hydrolysis must be relatively slow. It was found that 4-(2 : 3-dimethylanilino)pent-3-en-2-one gave a measurable rate of cyclodehydration in the range 70—81% sulphuric acid. Below 70% H_2SO_4 the cyclodehydration was too slow for measurement. It was shown that this anil did not remain stable in the more aqueous media below 70% sulphuric acid since when the acidity was increased considerably above this strength by

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* Part II, *J.*, 1955, 2358.

rapid addition of pure sulphuric acid the yield of cyclodehydration product, 2 : 4 : 7 : 8-tetramethylquinoline was very much less than that obtained when the anil was treated directly with concentrated sulphuric acid. This result was also obtained with other anils and was fully investigated to confirm that it meant a slow hydrolysis of anil to re-form 2 : 3-dimethylaniline and acetylacetone.

EXPERIMENTAL

Media.—Pure sulphuric acid and sulphuric acid–water mixtures were prepared and standardised as described in Part I.[1]

Materials.—4-(2 : 3-Dimethylanilino)pent-3-en-2-one, prepared from 2 : 3-dimethylaniline and acetylacetone by the method of Turner and Roberts [5] and recrystallised twice from light petroleum (b. p. 60—80°), had m. p. 83—84°. An 89% yield of 2 : 4 : 7 : 8-tetramethylquinoline was obtained when 1 g. of this was treated with 10 ml. of concentrated sulphuric acid; [1] the m. p. of the product after crystallisation twice from light petroleum (b. p. 40—60°) was 30—31° (Found: C, 84·3; H, 8·3; N, 7·6. Calc. for $C_{13}H_{15}N$: C, 84·3; H, 8·1; N, 7·6%)

Behaviour of 4-(2 : 3-*Dimethylanilino*)*pent*-3-*en*-2-*one in Acid.*—In 2N-sulphuric acid hydrolysis to the amine and acetylacetone was virtually complete in a few minutes, colorimetric analysis of the acetylacetone by the method described in Part I indicating a 99·3% recovery. A much slower hydrolysis in 60% sulphuric acid was established by maintaining overnight at 25° a solution of 0·2 g. of anil in this medium and then adding 15 ml. of pure sulphuric acid to convert the unchanged anil very rapidly into the quinoline derivative. (It was confirmed that the cyclodehydration of this anil is immeasurably fast in the medium formed under these conditions.) 2 ml. portions of the solution were removed at hourly intervals: the acetylacetone content remained constant and corresponded to 71% hydrolysis at equilibrium. When the solution in 60% sulphuric acid was kept at 25° for 1½ hr. instead of overnight before addition of the 100% sulphuric acid, only 20% hydrolysis occurred.

Both the acetylacetone and the 2 : 3-dimethylaniline in separate solution in 60% sulphuric acid were quantitatively recoverable on dilution with water. If a mixture of these solutions, however, is kept at 25° overnight and then pure sulphuric acid added, the recovery of acetylacetone is only 74%, indicating that some anil had been formed. No product other than quinoline compound was found. In order to establish that the acetylacetone and amine form the anil only in the 60% sulphuric acid and do not condense together on addition of the pure sulphuric acid, the following experiments were carried out on a 10 ml. sample of a solution of acetylacetone in 60% sulphuric acid:

(*a*) 2 ml. of the solution were made up to 10 ml. with pure sulphuric acid; (*b*) 0·5 g. of 2 : 3-dimethylaniline was added to the remaining 8 ml. of the original solution; a 2 ml. aliquot portion was immediately removed, made up to 10 ml. with pure sulphuric acid, and kept at room temperature for 24 hr.; (*c*) the residual solution of acetylacetone and amine in 60% sulphuric acid from (*b*) was kept at room temperature for 24 hr., and a 2 ml. aliquot portion then removed and made up to 10 ml. with pure sulphuric acid. On analysis of these three solutions, 100% recovery of the acetylacetone was evident in (*a*) and (*b*) but only 67% in (*c*). The anil is therefore formed in (*c*) but not in (*b*).

Measurement of the Rate of Hydrolysis.—Kinetic measurements were carried out at 25° in a thermostat controlled within ±0·02°. The reaction vessel was a 50 ml. conical flask with a B24 neck. The anil was weighed into a B24 socket cap, the amount taken providing a 0·1M-solution when dissolved in 25 ml. of the medium. The medium was contained in a tared 25 ml. graduated flask and after being made up to the mark in the thermostat at 25° it was transferred to the reaction vessel in the thermostat. The 25 ml. flask was weighed in order to calculate the exact volume of medium used. To start the reaction, the reaction vessel was removed from the thermostat and the filled socket cap inserted. The medium and reactant were brought into contact at zero time by vigorous shaking and after complete dissolution had occurred (1—2 min.) the flask was returned to the thermostat. Six to eight 2 ml. samples were removed from the reacting mixture in the course of each experiment. Each sample was run into 7 ml. of pure sulphuric acid in a 10 ml. graduated flask cooled in ice, and the solution made up to the mark at room temperature with pure sulphuric acid. This was left for 2 hr. to ensure complete conversion of unhydrolysed anil into the quinoline derivative. A 2 ml. sample was then run into 20 ml. of ice-cold water, neutralised, and made up to 50 ml. in 0·1N-sulphuric acid, and its acetylacetone content determined colorimetrically. The rate constant, k, was obtained from the kinetic equation for a reversible reaction in which a first-order hydrolysis is opposed by a second-order recombination of the products

$$kt(2a - x_e) = 2{\cdot}3x_e \log [ax_e + x(a - x_e)]/a(x_e - x)$$

where a is the initial concentration of anil, and x and x_e are the concentrations of anil at time t and at equilibrium respectively. The plot of $\log [ax_e + x(a - x_e)]/a(x_e - x)$ against t was a good straight line for all experiments. A typical duplicate result is shown in Fig. 1. Rates of hydrolysis over the range 52—62% sulphuric are given in the Table.

FIG. 1.

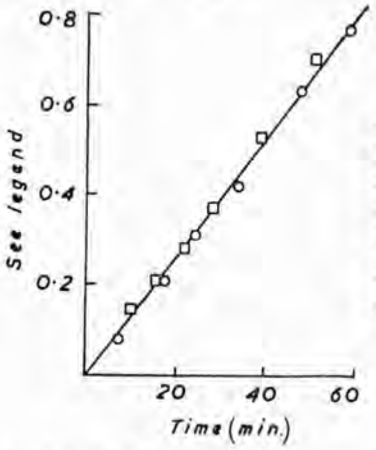


FIG. 2.

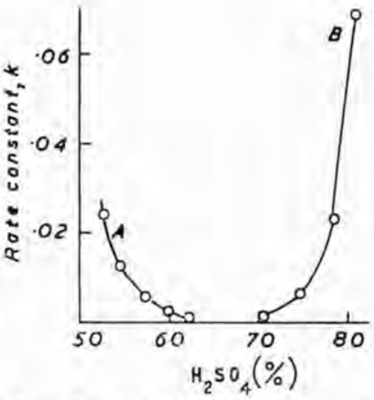


FIG. 1. *Hydrolysis of* 4-(2 : 3-*dimethylanilino*)*pent*-3-*en*-2-*one in* 52·8% H_2SO_4. $k = 0{\cdot}0241$ min.$^{-1}$. *Ordinate*: $\log [ax_e + x(a - x_e)]/a(x_e - x)$.

FIG. 2. 4-(2 : 3-*Dimethylanilino*)*pent*-3-*en*-2-*one*: *A*, *hydrolysis*; *B*, *cyclodehydration*.

Rates of hydrolysis of 4-(2 : 3-*dimethylanilino*)*pent*-3-*en*-2-*one* (*initial concn.* 0·1M) *at* 25°.

H_2SO_4 (%)	10^3k (min.$^{-1}$)	$\log k + H_0$	$\log p/p_0$	$\log k - H_0 - \log p/p_0$
62·4	0·962, 0·973	−7·63	−0·88	2·49
60·1	2·25, 2·27	−6·96	−0·76	2·46
57·7	5·34	−6·34	−0·66	2·46
54·9	12·7, 12·4	−5·64	−0·58	2·42
52·8	24·1, 24·1	−5·14	−0·50	2·40
60·1 *	5·33, 5·38			

* M-$(NH_4)_2SO_4$ present.

RESULTS AND DISCUSSION

Ionisation of Anils in Sulphuric Acid.—Previous investigation[1] of the cyclodehydration of the acetylacetone anils from aniline and *p*-toluidine in the range 85—97% sulphuric acid established that the kinetic results satisfied the relation[6] $\log k + H_0 =$ Constant, where k is the rate constant for the cyclodehydration and H_0 the Hammett acidity function for the corresponding medium. Accordingly, it was concluded that reaction proceeded through a positively charged anil formed in fractionally small amount. The cyclodehydration of 4-(2 : 3-dimethylanilino)pent-3-en-2-one conforms with this result, since rates of cyclodehydration measured over the range 70—80% sulphuric acid fitted the above equation (see Fig. 2 and following paper). It is evident however that in these strongly acid media, an anil may be almost entirely present in the monoprotonated form,[7] and in this case the result obtained would suggest that the cyclodehydration occurs in a diprotonated anil present in fractionally small amount, the bulk of the anil being present in a stable monoprotonated form. The relation deduced[1] would then be $\log k + H_+ =$ Constant, where H_+ is an acidity function evaluated in the same way as H_0 but by means of bases carrying a single charge which form a doubly positively charged conjugate acid. As the H_+ acidity function had not then been evaluated, this equation could not be tested but recently[8] it has been shown that H_0 and H_+ are parallel functions of medium composition. The original result therefore satisfies both the above equations. Evidence in favour of complete monoprotonation of anils in these media was sought by determining the lowering of freezing point of a solution of an anil in pure sulphuric acid. The anil selected was 4-*p*-chloroanilinopent-3-en-2-one which was found [5] to be stable but incapable of cyclisation in the concentrated acid. A spectroscopic examination of this anil in pure sulphuric acid showed that it remained unchanged during the time taken to determine the freezing point. No special apparatus was employed for the f. p. determination and the method used [9] of comparing the *i*-factor with that of a neutral compound known to form its conjugate acid quantitatively in pure sulphuric acid was found to be adequate. The neutral compound used was benzoic acid and a satisfactory value of 2·07 was found for the *i*-factor for this solution. The *i*-factor for the depression of f. p. by the anil under the same conditions was found to be 2·05. If this result is general for anils of this type, it can be concluded that over the range of sulphuric acid media where measurable rates of cyclodehydration are found, the anil is almost entirely present as a stable monoprotonated form, the ring closure occurring through a diprotonated form. The decrease in rate of this reaction as the acidity of the medium is reduced is due to the decreasing degree of formation of this species from the monoprotonated form. Further decrease in acidity will eventually result in the appearance of the neutral anil and at that point it is likely that very little, if any, of the diprotonated species will be present. An alternative mechanism to the rate-determining ring closure which would give the same correlation of log k and H_+ is one in which a rate-determining elimination of water from the diprotonated anil is followed by rapid ring closure. There are however no theoretical grounds for assuming that the diprotonated anil would eliminate water at a measurable rate. Any species directly formed by elimination of water would be highly unstable and likely to give rise to products other than the quinoline derivative. No evidence has been found for any other product.

Mechanism of Hydrolysis of Anils.—The results in the Table show that the highest acidity at which a measurable rate of hydrolysis is obtained is about 63% sulphuric acid and that the hydrolysis becomes more rapid as the acidity of the medium is decreased by further addition of water. Ammonium sulphate is also known to decrease the acidity of sulphuric acid solutions and its addition in molar concentration to one of the media more than doubles the rate of hydrolysis. Since this salt reduces acidity without increasing the water content of the medium, its effect corresponds to altering an equilibrium in the direction of forming a large proportion of the species actually undergoing the hydrolysis. Increasing the water content of the solution could have the same effect but it is difficult to separate the extent of this effect on the rate from that due to the increasing concentration of water as a reactant in the hydrolysis. If it is assumed that the species undergoing hydrolysis is the neutral anil the marked increase in rate of hydrolysis shown in Fig. 2 would follow from the rapid change which is known to occur in the ionisation ratio $[AH^+]/[A]$ for a base A and its conjugate acid AH^+ in the appropriate range of sulphuric acid–water mixtures.

Hydrolysis of the neutral anil by water to form the amine and acetylacetone would lead to the following kinetic analysis:

Let A and AH^+ represent the neutral anil and its conjugate acid respectively. Assuming that these are the only forms of the anil present and that $[AH^+] \ll [A]$ in the media in which measurable rates of hydrolysis are obtained, we have by the Brønsted treatment:

$$\text{Theoretical rate} = k_0 K(\text{A})(\text{H}_2\text{O})/f_\ddagger$$

where k_0 is the theoretical rate constant, K is the equilibrium constant for the equilibrium between the reactants and the transition complex, $f_\ddagger$ is the activity coefficient of the latter, and the parentheses denote activities

$$\text{Experimental rate} = k[\text{A}]_\text{T}$$

where $[A]_T$ is the stoicheiometric concentration of anil. Equating the two rate equations we have

$$k[A]_T = k_0K[A](H_2O)f_A/f_\ddagger$$

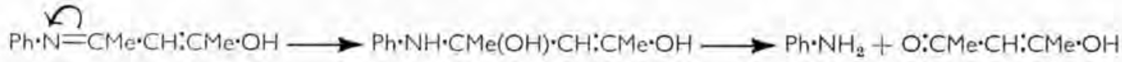
and since $[A]_T \simeq [AH^+]$

$$k[AH^+]/[A] = k_0K(H_2O)f_A/f_\ddagger$$

Taking logarithms and substituting for the term log $[AH^+]/[A]$ from the equation $H_0 = pK_a - \log [AH^+]/[A]$, it follows that

$$\log k - H_0 - \log (H_2O) = \log k_0Kf_A/f_\ddagger - pK_a$$

which is a constant if the activity coefficient ratio $f_A/f_\ddagger$ is constant over the range of media employed. Since the two species concerned, *i.e.*, the anil and the transition complex, are both neutral this is a reasonable expectation. The above equation was tested by using the known values [6] of H_0 and of log (H_2O) (ref. 10) at 25°. The results given in the Table indicate the constancy attained and at the same time show that the simpler relation $\log k + H_0$ = Constant is not obeyed for the hydrolysis. The reaction can be readily represented as a nucleophilic attack by water on the carbon atom of the azomethine bond as shown:



$$\mathrm{Ph{\cdot}N{=}CMe{\cdot}CH{:}CMe{\cdot}OH \longrightarrow Ph{\cdot}NH{\cdot}CMe(OH){\cdot}CH{:}CMe{\cdot}OH \longrightarrow Ph{\cdot}NH_2 + O{:}CMe{\cdot}CH{:}CMe{\cdot}OH}$$

The stability of the monoprotonated anil can be attributed to the loss of resonance represented in structures (I) and (II) by any similar bonding with a water molecule.

(I) $\mathrm{Ph{\cdot}\overset{+}{N}H{:}CMe{\cdot}CH{:}CMe{\cdot}OH}$ $\qquad$ $\mathrm{Ph{\cdot}NH{\cdot}CMe{:}CH{\cdot}CMe{:}\overset{+}{O}H}$ (II)

(III) $\mathrm{Ph{\cdot}\overset{+}{N}H{:}CH{\cdot}C_6H_4{\cdot}NMe_2}$ $\qquad$ $\mathrm{Ph{\cdot}NH{\cdot}CH{=}C_6H_4{\cdot}\overset{+}{N}Me_2}$ (IV)

An analogous case is provided by the abnormal behaviour on hydrolysis of *N*-(*p*-dimethylaminobenzylidene)aniline previously referred to.[2] Hydrolysis in dilute aqueous acid would require the loss of resonance energy corresponding to the two resonance structures (III) and (IV) of its stable conjugate acid, and in consequence this reaction is extremely slow.

The conjugate acid of the parent benzylideneaniline will only have one stable resonance structure, *i.e.*, that corresponding to (III), and the carbon atom of the azomethine bond will be an electron-deficient centre for attack by water, giving a much faster rate of hydrolysis, as found experimentally.

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T.G. BONNER
D.Sc. 1960

842. *The Cyclodehydration of Anils. Part IV.*[1] *Substituent Effects.*

By T. G. Bonner and Mary Barnard.

Substituent effects have been studied in the cyclodehydration of substituted 4-anilinopent-3-en-2-ones to the corresponding 2 : 4-dimethylquinolines in strongly acidic aqueous media. The *m*-halogeno-derivatives all cyclise faster than the unsubstituted compound, in accord with stabilisation of the transition complex by electron-release from the halogen atom.

Additivity of substituent effects has been studied for both cyclodehydration and hydrolysis of disubstituted 4-anilinopent-3-en-2-ones and compared with the additivity of pK_a values of the anilinium ions. The enhanced interaction of the substituents in 2 : 3-disubstituted derivatives in particular is noted and discussed.

The correlation reported previously[2] between the rate constant, k, for cyclodehydration of acetylacetone anils to 2 : 4-dimethylquinolines and Hammett's acidity function, H_0, given by the equation:

$$\log k + H_0 = \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

was established for the anils of aniline and *p*-toluidine over the range aqueous 85—97% sulphuric acid. The ratio of the rate constants for these two anils k_{Me}/k_H is reasonably constant over the range of medium common to both compounds. This is expected since the mechanism of ring closure should be independent of the constitution of the anil. The ratio is most conveniently evaluated from the difference in the mean values of the sum, $\log k + H_0$, for the cyclodehydration of each compound over the range of media studied. This gives $k_{Me}/k_H = 6$ which is in accord with the activating effect of a methyl group *meta* to the point of electrophilic substitution in the benzene ring. A much greater activating effect with measurable rates of cyclodehydration requiring more aqueous sulphuric acids should be found for 4-*m*-toluidinopent-3-en-2-one where the methyl group is *para* to the point of ring closure. The most acid medium in which the cyclodehydration of the *m*-methylanilino-compound could be accurately measured was 83% sulphuric acid. The ratio k_{Me}/k_H calculated from the corresponding $\log k$ and H_0 values was then *ca.* 700. The 3 : 4- and 2 : 3-dimethylanilino-compounds similarly gave high values for this ratio (k/k_H = 1180 and 430 respectively). As the latter anil proved to be the most convenient for a study of the hydrolysis,[1] it was used also for a more extensive study of the cyclodehydration. The rate of cyclodehydration of this anil was measured in the range 70—80% aqueous sulphuric acid and also in aqueous perchloric acid. The results given in Table 1 show that equation (1) is obeyed in these more aqueous solutions and that the lack of

TABLE 1. *Rates of cyclodehydration of* 4-(2 : 3-*dimethylanilino*)*pent*-3-*en*-2-*one* (*initial concn.* 0·05M) *at* 25°.

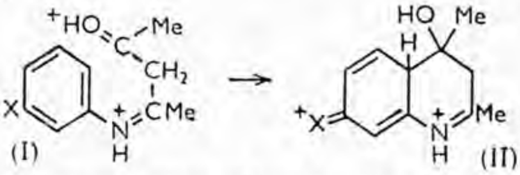
H_2SO_4 (%)	10^2k (min.$^{-1}$)	$\log k + H_0$	$\log k + C_0$	$HClO_4$ (%)	10^2k (min.$^{-1}$)	$\log k + H_0$
80·8	6·92, 6·97	−8·31	−15·54	71·4	11·1, 11·5	−9·02
78·6	2·26, 2·23	−8·31	−15·42	69·4	6·52, 6·52	−9·03
74·8	0·592, 0·586	−8·36	−15·03	66·7	1·09, 1·07	−8·92
70·5	0·135, 0·140	−8·39	−14·54	63·6	0·164, 0·164	−8·91

correlation between the rate constant and the acidity function, C_0 (ref. 3) (or J_0; ref. 4), previously noted[1] is confirmed. The plot of log k against H_0 was a good straight line for both media with a slope of $-1{\cdot}09$ for sulphuric acid and of $-0{\cdot}92$ for perchloric acid. It can be concluded that over a considerable range of aqueous acidic media (from $H_0 = -5{\cdot}5$ to $-9{\cdot}1$) the cyclodehydration proceeds by a rate-determining internal electrophilic substitution of the diprotonated form of the anil which is present in fractionally small amount.[1]

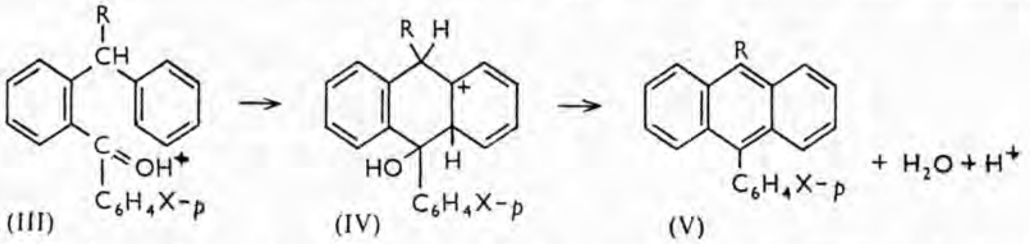
Halogen Substituents.—It has been noted[5] that while 4-*m*-chloroanilinopent-3-en-2-one cyclises in concentrated sulphuric acid to 7-chloro-2 : 4-dimethylquinoline the corresponding *p*-chloro- and 3 : 5-, 2 : 5-, and 2 : 4-dichloro-anils fail to react. Since halogen deactivates the benzene nucleus to attack by electrophilic reagents, the rate of cyclodehydration for the *m*-chloroanil should be less than for the unsubstituted anil. However, this was not found to be the case, as the results in Table 2 show. The experimental result for 4-anilinopent-3-en-2-one is halved to allow for the fact that there are two identical points of ring closure in this compound compared with one only in its *meta*-substituted derivatives. In all four *m*-halogenoanils, the halogen atom activates the *para*-position relative to hydrogen, the order being F > I > Cl > Br > H. Activation is readily explicable in terms of the stabilisation of the transition complex by operation of the electromeric effect of halogen. The diprotonated side chain in the anil (I) can transfer one of its positive charges to the halogen atom, X, in forming the intermediate (II) which must resemble closely the transition state in the reaction. The quinoline produced results from loss of a molecule of water and a proton from this intermediate. The inhibitory inductive effect is clearly still operative since the rate of cyclodehydration of the corresponding *m*-toluidine anil is several hundred times greater still. The inductive effect, however, is secondary to the polarisability of the halogen atoms under the influence of the strong electrical field in the cyclic transition state.

TABLE 2. *Rates of cyclodehydration of* m-*halogenoanils in* 93·8% *sulphuric acid at* 25°.

4-Anilinopent-3-en-2-one	*m*-F	*m*-I	*m*-Cl	*m*-Br	H
10^2k (min.$^{-1}$)	4·16	1·90	0·83	0·696	0·371

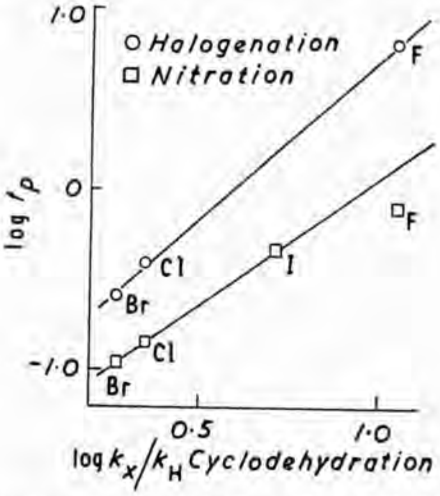


Another cyclisation in which the effect of halogen has been studied is the conversion of 2-benzyl-4′-halogenobenzophenones to 9-*p*-halogenophenylanthracenes (V) in hydrobromic–acetic acid.[6] Here the rate of cyclisation is hardly affected by *p*-halogeno- (or even *p*-methyl) substituents and this is in accord with the formation of a transition state in which the electromeric effect cannot operate, as shown in (III) and (IV).



The similarity in operation of the polarisability effect of halogens in other electrophilic substituents is shown by a comparison of the rates of cyclodehydration with the partial rate factors for *para*-substitution in nitration and halogenation of the corresponding halogenobenzenes.[7] As shown in the Figure a linear relation exists between log k (cyclodehydration) and log f_P in both cases, the sole exception being the fluorine substituent in nitration. This is further evidence for the efficacy of the nitronium ion as an electrophilic reagent, since it does not evoke the full operation of the polarisability of the fluorine atom. The view that halogenation by means of the less effective halogen molecule is more powerfully electron-demanding [8] clearly applies to the cyclodehydration.

A recent example of activation by a *p*-fluorine substituent has been found in the solvolysis of halogenobenzyl toluene-*p*-sulphonates in aqueous acetone.[9] The sequence of decreasing rate constants, *p*-F $>$ H $>$ *p*-Cl $>$ *p*-I $>$ *p*-Br, demonstrates the superior conjugating effect of fluorine in stabilising the transition state in this reaction, but it is evident that for the other halogens the balance of conjugative and inductive effects is not identical with that of the cyclodehydration. In the correlation found between the rate constants of the solvolysis and of nitration of the corresponding halogenobenzenes, only the *p*-fluoro-substituent showed a considerable deviation. It was suggested that this was due to the decreased availability of the non-bonding electrons of the fluorine atom in the nitration by hydrogen-bonding with the highly acidic medium. The similar deviation evident in the correlation of the rates of cyclodehydration and nitration shown in the Figure does not support this proposal since in this case the medium is the same for both reactions.



Comparison of rates of halogenation, nitration, and cyclodehydration at the para-*position to halogen.*

The complete failure of 4-*p*-chloroanilinopent-3-en-2-one to cyclise was confirmed and it is evident that in this compound and the dichloroanils referred to above the deactivating inductive effect of halogen *meta* to the point of ring closure predominates.

Additivity of Substituted Effects.—Before considering the effects of substituents in the cyclodehydration of disubstituted anils, it is convenient to review the additivity of these effects in the acid dissociation constants of the corresponding anilinium ions. Substituent effects will be additive if the experimental value for $pK_a^{X,Y}$ fits equation (2):

$$pK_a^{X,Y} = pK_a^{X} + pK_a^{Y} - pK_a^{H} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Previous results [10,11] show that the biggest deviation from additivity occurs with 2 : 6-xylidine where the lower pK_a value indicates that the amine is less basic than if the effects of the two methyl groups were strictly additive. In contrast, the 2 : 3-xylidine is a stronger base than expected. Steric hindrance of resonance in the base is frequently invoked to account for the increased basicity of an aromatic amine when bulky substituents such as methyl are introduced in the *ortho*-positions [12] but the lower basicity of *o*-toluidine compared with aniline and the *m*- and *p*-toluidines is in contradiction to the operation of this factor; in this case, the difference has been attributed to a sterically hindered solvation of the *o*-toluidinium ion.[13] The latter effect would account for the decreased basicity of 2 : 6-xylidine and the former for the increase in 2 : 3-xylidine but it is difficult to predict which of the two effects would predominate in any given compound. Similar differences in behaviour have also been observed between 2 : 5- and 2 : 3-dimethyl derivatives of benzene of the type XYC_6H_3R where $R = NO_2$[14] or CO_2H,[15] in that the introduction of the 3-methyl but not the 5-methyl substituent increases the influence of the 2-methyl substituent on the interaction between the group R and the benzene ring. For the remaining compounds in Table 3 it is evident that the substituent effects are reasonably additive.

The test of additivity in the cyclodehydration reaction is obtained by replacing the pK_a terms in equation (2) by the logarithms of the rate constants of cyclodehydration and assuming that the value of the acid dissociation constant of the diprotonated anilinoanil AH_2^{++} is not greatly affected by nuclear substituents. The results in Table 4 show that an additivity of substituent effects in the cyclodehydration is found only for the 2 : 4-dimethylanilino-anil and the 3-chloro-4-methylanilino-anil. The largest deviations occur in the 2 : 3- and the 3 : 4-dimethyl compound, and are in the direction of greatly decreased rates of reaction. In both cases this effect can be interpreted as steric inhibition by the adjacent methyl group of the full operation of the electromeric effect of the 3-methyl substituent. This would reduced to some degree the stabilisation of the transition complex by the resonance structure corresponding to (II).

TABLE 3. pK_a *values of disubstituted anilines.*

Aniline	Found	Calc.	Diff.	Aniline	Found	Calc.	Diff.
2 : 6-Dimethyl	3·95	4·26	−0·31	3 : 4-Dimethyl	5·17	5·23	−0·06
2 : 3-Dimethyl	4·70	4·57	+0·13	2 : 5-Dimethyl	4·53	4·57	−0·04
2 : 4-Dimethyl	4·89	4·91	−0·02	5-Chloro-4-methyl ...	4·05	4·09	−0·04

The peculiarity of the 2 : 3-disubstituted anils is analogous to the unusual effect on the basicity of the adjacent methyl groups in 2 : 3-xylidine, to which reference has been made above. This effect is also evident in the hydrolysis of the anils. The hydrolysis rates given in Table 4 show that while the effects of methyl groups in the 2- and the 4-position are additive, the rate of hydrolysis of the 2 : 3-dimethylanilino-compound is less than expected. It has been suggested that the enhanced effect of the 2-methyl substituent on an adjacent side chain due to the repulsion of a 3-methyl substituent operates by reducing the coplanarity of the side chain with the benzene ring.[15] This would clearly result in the increased basicity of 2 : 3-xylidine. The slower hydrolysis of the 2 : 3-dimethylanilino-compound found experimentally would also be expected since the greater electron-density in the neighbourhood of the azomethine bond would hamper the nucleophilic attack by water. The reduced rate of cyclodehydration of 4-(2-chloro-3-methylanilino)pent-3-en-2-one has a similar explanation if it is assumed that there is an increase in the repulsion between the chlorine and the methyl substituent due to the side chain which decreases the conjugation of the 3-methyl group with the ring and reduces the contribution of the resonance structure corresponding to (II).

TABLE 4. *Additivity of substituent effects.*

			Cyclohydration			
4-Anilinopent-2-en-2-one	log k^X	log k^Y	log k^H	Calc.	log $k^{X,Y}$ Found	Diff.
2 : 3-Dimethyl	−1·99	0·41	−2·43	0·85	0·20	−0·65
2 : 4-Dimethyl	−1·99	−1·58	−2·43	−1·14	−1·14	0
3 : 4-Dimethyl	0·41	−1·58	−2·43	1·26	0·64	−0·62
3-Chloro-4-methyl	−2·08	−1·58	−2·43	−1·23	−1·27	−0·04
3-Chloro-2-methyl	−1·99	−2·08	−2·43	−1·64	−2·00	−0·36

			Hydrolysis			
4-Anilinopent-3-en-2-one	log k^X	log k^Y	log k^H	Calc.	log $k^{X,Y}$ Found	Diff.
2 : 3-Dimethyl	−2·17	−1·56	−1·34	−2·39	−2·65	−0·26
2 : 4-Dimethyl	−2·17	−1·74	−1·34	−2·57	−2·57	0
3 : 4-Dimethyl	−1·56	−1·74	−1·34	−1·96	−1·90	+0·06

Rates of cyclodehydration were determined in 93·8% sulphuric acid at 25°, except those of the *m*-methyl, 2 : 3-dimethyl, and 3 : 4-dimethyl compounds. The last three were measured in 74·8% sulphuric acid and the values in the 93·8% acid calculated from equation (1). All rates of hydrolysis were determined in 60·1% sulphuric acid at 25°.

In the hydrolysis methyl groups in all positions reduce the rate, in contrast to their activating effect in cyclodehydration, and this is in accord with the mechanism proposed in the preceding paper of nucleophilic attack by water on the carbon atom of the side chain adjacent to the nitrogen atom. As might be expected in a side-chain reaction, the results for the hydrolysis of both the monosubstituted and the disubstituted anils (except the 2 : 3-dimethylanil) fit the Hammett equation:[16]

$$\log k/k_0 = \rho\sigma$$

where k and k_0 are the rate constants for the substituted and unsubstituted anils respectively, ρ is a constant characteristic of the reaction, and σ a constant characteristic of the substituent. The plot of log k/k_0 against Hammett's original σ values is a straight line and the value of ρ from the slope is 1·91. The fact that ρ is positive indicates a reaction facilitated by a low electron-density at the reaction site. No similar correlation of rate constant with the σ values recently proposed[17] for electrophilic aromatic substitution was found for the cyclodehydration.

TABLE 5. *Activation energies (± ca. 300 cal.) in cyclodehydration.*

	4-*p*-Toluidinopent-3-en-2-one		4-Anilinopent-3-en-2-one	
H_2SO_4 (%)	E_A (cal.)	$\log_{10} A$	E_A (cal.)	$\log_{10} A$
94·9	15,900	10·4	17,400	10·9
91·2	16,500	10·4	15,600	9·1
86·8	17,300	10·5	—	—

Constants of the Arrhenius Equation.—Rates of cyclodehydration of both anilino- and *p*-toluidino-anils were measured over the range 0—50° in different media to evaluate the constants, A and E, of the equation $\log k = \log A - E/\boldsymbol{R}T$ which are given in Table 5. Reproducible results could not be obtained for the anilinoanil in 86·8% sulphuric acid, possibly because of some hydrolysis in this medium.

EXPERIMENTAL

Media.—Pure sulphuric acid and sulphuric acid–water mixtures were prepared and standardised as described in Part I.[2] Perchloric acid–water mixtures were prepared from "AnalaR" perchloric acid and similarly standardised.

Materials.—Acetylacetone was dried over potassium carbonate and distilled. The majority of aromatic amines were obtained from B.D.H. or Light and Co. and were recrystallised or distilled under reduced pressure. *m*-Iodoaniline was obtained by reduction of *m*-nitroaniline. 3-Chloro-4-methylaniline was prepared from 2-methyl-5-nitroaniline by diazotisation and treatment with cuprous chloride.[18] 4-Chloro-3-methylaniline was obtained by the action of sodium chlorate and concentrated hydrochloric acid on aceto-*m*-toluidide.[19]

The anils were prepared by boiling under gentle reflux a 1 : 1·1 mixture[5] of the aromatic amine and acetylacetone. Most anils were obtained in 60—70% yield by this method and were crystallised from light petroleum (b. p. 40—60°). The following substituted 4-anilinopent-2-en-4-ones do not appear to have been described previously: *m*-fluoro-, m. p. 35—36°; *p*-fluoro-, m. p. 44°; *m*-bromo-, m. p. 37—38°; *m*-iodo-, m. p. 56—57°; 2 : 4-dimethyl-, m. p. 38—40°; 3 : 4-dimethyl-, b. p. 190°/20 mm.; *3-chloro-4-methyl-*, m. p. 67—68·5° (Found: N, 6·5; Cl, 16·1. $C_{12}H_{14}ONCl$ requires N, 6·3; Cl, 15·9%); *4-chloro-3-methyl-*, m. p. 46—47° (Found: N, 6·5; Cl, 15·6. $C_{12}H_{14}ONCl$ requires N, 6·3; Cl, 15·9%); 3-chloro-2-methyl-, m. p. 81—82°.

The corresponding quinoline compounds were obtained from these anils in 89—99% yields by dissolving 1 g. of the anil in 10 ml. of 98% sulphuric acid and keeping the solution at room temperature for several hours before isolating the product.[2] The following substituted quinolines do not appear to have been reported previously: 7-fluoro-2 : 4-dimethyl-, m. p. 45—46°; 7-bromo-2 : 4-dimethyl-, m. p. 46—47°; 7-iodo-2 : 4-dimethyl-, m. p. 54—55°; 2 : 4 : 6 : *7-tetramethyl-*, m. p. 79—80° (Found: C, 84·4; H, 8·1; N, 7·7. $C_{13}H_{15}N$ requires C, 84·3; H, 7·9; N, 7·6%); *7-chloro-*2 : 4 : *6-trimethyl-*, m. p. 81—82° (Found: N, 7·1; Cl, 17·3. $C_{12}H_{12}NCl$ requires N, 6·8; Cl, 17·2%); 5-chloro-2 : 4 : 8-trimethyl-, m. p. 54—55°; 6-chloro-2 : 4 : 7-trimethyl-, m. p. 89—90°; *7-chloro-*2 : 4 : *8-trimethyl-*, m. p. 68—69° (Found: N, 6·8; Cl, 17·9. $C_{12}H_{12}NCl$ requires N, 6·8; Cl, 17·2%).

Measurement of Reaction Rates.—Rates of cyclodehydration in sulphuric acid–water and perchloric acid–water were determined as described in Part I.[2] It was established that neither sodium perchlorate nor any of the amines or quinoline compounds investigated interfered with analysis of the mixtures, in which the acetylacetone obtained from unchanged anil is converted into its ferric salt which is determined colorimetrically. A small refinement was introduced to obtain the reference curve for standard solutions of acetylacetone prepared from the pure ketone. Two reference curves were obtained, the prepared solutions for analysis in one case containing 1·62 g. of sodium sulphate per 40 ml., and in the other case 3·24 g. of sodium sulphate per 40 ml. These are the lower and the upper limit of sodium sulphate concentrations in the solutions obtained for colorimetric analysis from reaction mixtures. While the difference in slopes of the straight lines obtained by plotting the logarithms of the optical density ratio against concentration of acetylacetone was almost negligible, the gradients in both cases were about 3% less than the slope of the reference curve obtained in the absence of added sodium sulphate. The new reference curves were therefore preferred for the evaluation of the experimental results.

Rates of hydrolysis were determined as described in the preceding paper.[2]

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14.

T. G. BONNER
D.Sc. 1960

THE H_0 ACIDITY SCALE IN AQUEOUS PERCHLORIC ACID

BY
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AND
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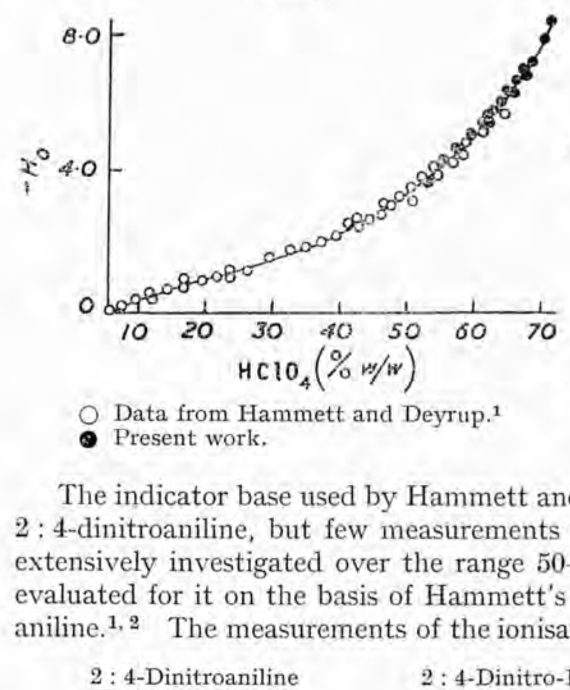
552. *The H_0 Acidity Scale in Aqueous Perchloric Acid.*

By T. G. BONNER and J. C. LOCKHART.

ALTHOUGH aqueous perchloric acid is readily available in concentrations up to 72% w/w, the H_0 acidity function has not been measured above 64% $HClO_4$. Hammett and Deyrup [1] did not proceed beyond this point because of the danger of explosion; they also found that some indicators, which were stable in concentrated sulphuric acid, decomposed irreversibly in solutions of perchloric acid.

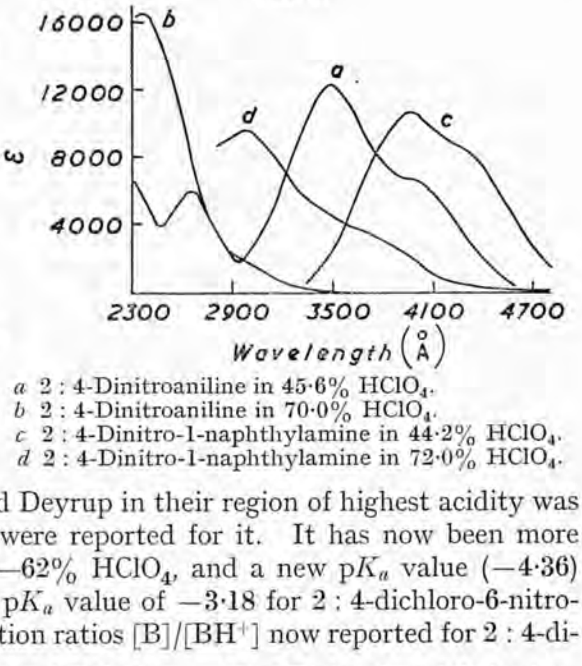
2 : 4-Dinitro-1-naphthylamine is not attacked by perchloric acid up to 72% concentration and is thus a suitable indicator for extending the H_0 scale. Indicators which had to be rejected were benzylideneacetophenone, which decomposed on irradiation with the ultraviolet light used in the spectrophotometric analysis of its solutions, and 2 : 4-dinitrodiphenylamine which, although behaving normally in concentrated sulphuric acid to give a pale yellow solution, appeared to decompose in perchloric acid, to a deep brown solution similar to that reported [1] for 4-nitrodiphenylamine.

FIG. 1.



○ Data from Hammett and Deyrup.[1]
● Present work.

FIG. 2.



a 2 : 4-Dinitroaniline in 45·6% $HClO_4$.
b 2 : 4-Dinitroaniline in 70·0% $HClO_4$.
c 2 : 4-Dinitro-1-naphthylamine in 44·2% $HClO_4$.
d 2 : 4-Dinitro-1-naphthylamine in 72·0% $HClO_4$.

The indicator base used by Hammett and Deyrup in their region of highest acidity was 2 : 4-dinitroaniline, but few measurements were reported for it. It has now been more extensively investigated over the range 50—62% $HClO_4$, and a new pK_a value (−4·36) evaluated for it on the basis of Hammett's pK_a value of −3·18 for 2 : 4-dichloro-6-nitroaniline.[1, 2] The measurements of the ionisation ratios [B]/[BH⁺] now reported for 2 : 4-dinitroaniline and 2 : 4-dinitro-1-naphthylamine permit the calculation of accurate values of the acitity function H_0 over the range 50—71% $HClO_4$ from the usual equation $H_0 = \mathrm{p}K_a + \log [B]/[BH^+]$, where [B] and [BH⁺] represent the concentrations of the un-ionised

2 : 4-Dinitroaniline
(pK_a = −4·36)

$HClO_4$ (%)	log [B]/[BH⁺]	$-H_0$
49·6	1·27	3·09
50·3	0·80	3·56
53·0	0·55	3·81
54·2	0·31	4·05
55·5	0·04	4·32
57·2	−0·28	4·64
59·5	−0·78	5·14
62·2	−1·25	5·61

2 : 4-Dinitro-1-naphthylamine
(pK_a = −6·37)

$HClO_4$ (%)	log [B]/[BH⁺]	$-H_0$
59·6	1·25	5·12
61·4	0·90	5·47
62·0	0·84	5·53
62·7	0·58	5·79
64·0	0·25	6·12
65·0	−0·03	6·40
65·3	−0·05	6·42
66·4	−0·39	6·76

2 : 4-Dinitro-1-naphthylamine
(pK_a = −6·37)

$HClO_4$ (%)	log [B]/[BH⁺]	$-H_0$
67·3	−0·60	6·97
67·5	−0·69	7·06
68·3	−0·87	7·24
70·2	−1·58	7·95
71·3	−2·09	8·46

and ionised forms of the indicator in a medium of acidity H_0, and K_a the acidity constant of the acid BH^+. These values are given in the Table. Fig. 1 shows that H_0 values for acids stronger than 61% perchloric acid form a curve continuous with that previously reported for acids below this strength.

Experimental.—*Materials.* 2 : 4-Dinitroaniline was crystallised from alcohol to a constant spectrum, $\varepsilon_{\text{max.}} = 12{,}300$ at 3480 Å in dilute aqueous perchloric acid ($\varepsilon_{\text{max.}} = 12{,}800$ at 3480 Å has been reported in aqueous sulphuric acid [3]), and had m. p. 180°. 2 : 4-Dinitro-1-naphthylamine was prepared by nitration of acetnaphthalide in acetic acid and hydrolysis of the dinitro-derivative.[4] The brown product was boiled with charcoal and crystallised from alcohol to a constant spectrum, $\varepsilon_{\text{max.}} = 10{,}600$ at 3960 Å in dilute aqueous perchloric acid; it had m. p. 244°.

Absorption spectra. These were measured on a Hilger " Uvispek " spectrophotometer and the indicator ionisation ratio was obtained from the equation $[B]/[BH^+] = (\varepsilon_{BH^+} - \varepsilon)/(\varepsilon - \varepsilon_B)$, where ε_{BH^+} and ε_B are the extinction coefficients at any selected wavelength of the ionised and un-ionised forms of the indicator respectively, and ε is the extinction coefficient at the same wavelength for a particular medium containing the concentrations $[B]$ and $[BH^+]$ of the two forms. The absorption spectra of the ionised and un-ionised forms of 2 : 4-dinitroaniline and 2 : 4-dinitro-1-naphthylamine in perchloric acid are shown in Fig. 2. As the absorption curves were very slightly displaced to higher wavelengths with increasing acidity of the media, $[B]/[BH^+]$ was calculated at several different wavelengths on either side of the peak, and the mean value taken.

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15.

THE PARALLELISM OF THE ACIDITY FUNCTIONS H_0 AND H_+

BY
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AND
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Preprinted from the
Journal of the Chemical Society, January, 1957, pages 364—367.

65. *The Parallelism of the Acidity Functions H_0 and H_+.*

By T. G. Bonner and J. C. Lockhart.

The Hammett acidity functions H_0 and H_+ are shown to be parallel functions of medium composition in aqueous sulphuric acid over the ranges 30—55% and 75—95% sulphuric acid.

Hammett[1] has suggested that while the value of the acidity function H_0, given by

$$H_0 = -\log a_{\mathrm{H}^+} . f_{\mathrm{B}}/f_{\mathrm{BH}^+} = \mathrm{p}K_a^{\mathrm{BH}^+} + \log[\mathrm{B}]/[\mathrm{BH}^+] \quad . \quad . \quad . \quad (1)$$

measures the tendency of a solution to transfer a proton to a neutral indicator base, B, to form the conjugate acid BH^+, it does not at all measure the tendency to do the same thing to a base of any other electrical charge. A proton transfer to a univalent cation base AH^+ to form the conjugate acid AH_2^{++} corresponds to an acidity function H_+ defined by

$$H_+ = -\log a_{\mathrm{H}^+} . f_{\mathrm{AH}^+}/f_{\mathrm{AH}_2^{++}} = \mathrm{p}K_a^{\mathrm{AH}_2^{++}} + \log[\mathrm{AH}^+]/[\mathrm{AH}_2^{++}] \quad . \quad . \quad (2)$$

The difference between H_+ and H_0

$$H_+ - H_0 = \log f_{\mathrm{B}} f_{\mathrm{AH}_2^{++}}/f_{\mathrm{BH}^+} f_{\mathrm{AH}^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

has been calculated[2] for pure sulphuric acid and is only *ca.* 0·28 log unit; H_0 in this medium is $-10{\cdot}60$, and since the value of the acidity function changes rapidly with medium composition in this region, the difference may not be significant.

Coryell and Fix[3] state that all Hammett acidity functions are parallel functions of medium composition, and refer to the constant difference of 0·8 log unit between H_0 and H_- found in the range of 4—6M-sulphuric acid and to the close parallelism[4] between H_0 and the Michaelis acidity function G (measured up to 11M-sulphuric acid with substituted thiazine indicators which take up variously from one to three protons). Any two acidity functions will be parallel functions of medium composition if the activity-coefficient ratio corresponding to eqn. (3) is unity or constant over the range of media studied. It would follow for H_+ and H_0 that

$$\log[\mathrm{B}]/[\mathrm{BH}^+] - \log[\mathrm{AH}^+]/[\mathrm{AH}_2^{++}] = \mathrm{p}K_a^{\mathrm{BH}^+} - \mathrm{p}K_a^{\mathrm{AH}_2^{++}} = \mathrm{const.} \quad . \quad (4)$$

since the K's are thermodynamic acidity constants.

Hammett and Deyrup[5] demonstrated the parallelism of the plots of the log ionisation ratios $[B]/[BH^+]$ against medium composition for different neutral indicator bases and concluded that the ratio f_B/f_{BH^+} has the same value for all bases of this type in the same medium. In the course of measurements of H_0 for H_2SO_4–SO_3 media, the *m*-nitroanilinium ion was used[2] as one of the indicators and the plot of the log ionisation ratio for this cation base and its conjugate acid against medium composition was parallel to those for neutral indicator bases in the same range of media, indicating that, for oleum, eqn. (4) is valid. The present work has shown that this validity holds for aqueous sulphuric acid media. The indicators used were 4-nitro-1 : 2-phenylenediamine over the range 30—55% sulphuric acid and 4-aminoacetophenone over the range 75—95% acid, and the ratios $[AH^+]/[AH_2^{++}]$ for these indicators were determined from spectrophotometric data.

Experimental

Materials.—4-Nitro-1 : 2-phenylenediamine was obtained by reduction of 2 : 4-dinitroaniline with aqueous ammonium polysulphide[6] (some 2-nitro-1 : 4-phenylenediamine was also formed but this remained dissolved in the aqueous medium); it was recrystallised from water to a constant spectrum $\varepsilon_{\mathrm{max.}} = 7920$ at 2470 Å in 72% perchloric acid and had m. p. 204°. 4-Aminoacetophenone was boiled in aqueous solution with charcoal and recrystallised from water to a constant spectrum $\varepsilon_{\mathrm{max.}} = 16470$ at 3110 Å in water; m. p. 106°.

Ultraviolet Absorption Measurements.—These were made on a Hilger Uvispek spectrophotometer. Solutions were prepared separately by weight and diluted to give the optimum range of absorption for measurement. The ionisation ratio was obtained from the equation

$$[AH^+]/[AH_2^{++}] = (\varepsilon_{AH_2^{++}} - \varepsilon)/(\varepsilon - \varepsilon_{AH^+})$$

where $\varepsilon_{AH^{++}}$ and ε_{AH^+} are the extinction coefficients at the selected wavelength for the diprotonated and monoprotonated form as indicated by the curves in Fig. 1 (for 4-nitro-1 : 2-phenylenediamine at 3600 Å, $\varepsilon_{AH_2^{++}} = 150$ and $\varepsilon_{AH^+} = 12{,}010$, and for 4-aminoacetophenone at 2440 Å $\varepsilon_{AH_2^{++}} = 4210$ and $\varepsilon_{AH^+} = 11{,}900$), and ε is the extinction coefficient corresponding to the presence of both forms of the given indicator in a particular medium. The isobestic-point method [7] was used for 4-aminoacetophenone.

FIG. 1. *A, 4-Nitro-1 : 2-phenylenediamine at* 3600 Å. *B, 4-Aminoacetophenone at* 2440 Å.

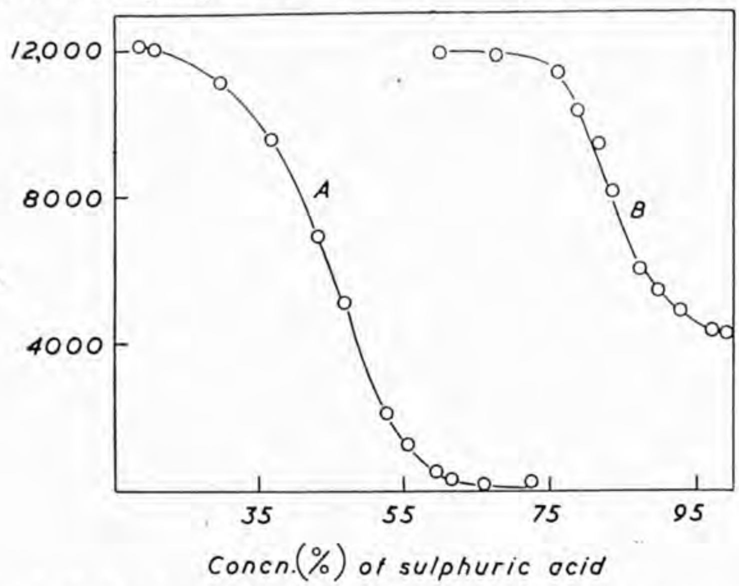


FIG. 2. 4-*Nitro*-1 : 2-*phenylenediamine in* 20·0% H_2SO_4 (*C*), 43·2% H_2SO_4 (*D*), *and* 73·0% H_2SO_4 (*E*).

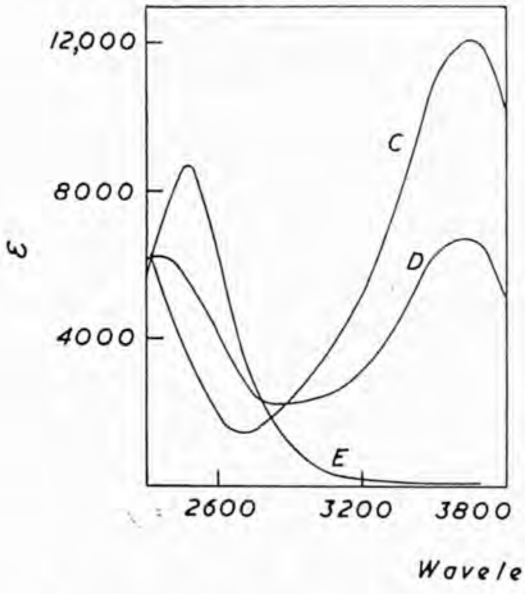
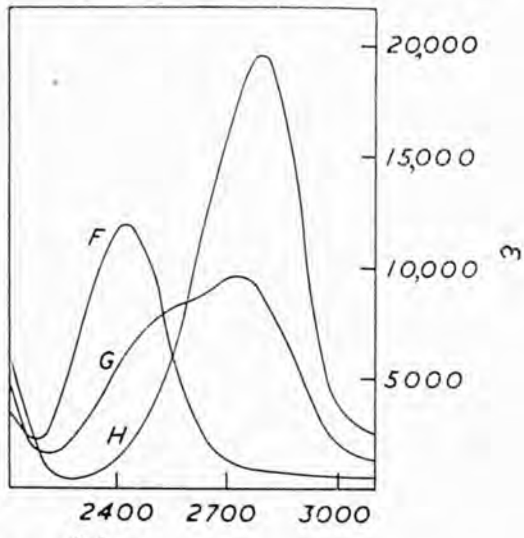


FIG. 3. 4-*Aminoacetophenone in* 59·9% H_2SO_4 (*F*), 83·8% H_2SO_4 (*G*), *and* 98·5% H_2SO_4 (*H*).



Results

Spectra of the Indicators in Sulphuric Acid–Water Media.—(a) 4-*Nitro*-1 : 2-*phenylenediamine.* The absorption curves corresponding to the pure monoprotonated form (curve *C*) and pure diprotonated form (curve E) are shown in Fig. 2. As expected, curve C resembles that of p-nitroaniline in water[8] ($\varepsilon_{\text{max.}}$ *ca.* 11,500 at 3850 Å, taken from the graph in ref. 8), and curve E that of p-nitroaniline in acid solution ($\varepsilon_{\text{max.}}$ *ca.* 7600 at 2580 Å also taken from ref. 8).

(b) 4-*Aminoacetophenone*. The absorption curve of the monoprotonated form (curve F, Fig. 3) is similar to that of acetophenone ($\varepsilon_{\text{max.}}$ 11,700 at 2500 Å, from ref. 7) and that of the diprotonated form (curve H, Fig. 3) resembles that of the conjugated acid of acetophenone ($\varepsilon_{\text{max.}}$ 10,500 at 2900 Å, from ref. 7).

The Parallelism of H_+ and H_0.—The log ionisation ratios $[AH^+]/[AH_2^{++}]$ for both indicators in their respective ranges of media are plotted in Fig. 4 against concentration of sulphuric acid, together with the corresponding figures reported by Hammett and Deyrup[5] for the ratios of $[B]/[BH^+]$ for neutral indicator bases ionising in the same ranges of media. The parallelism of the two types of curves is evident and it can be concluded that H_+ and H_0 either differ by a small constant value or are identical. H_0 as defined is identical with pH in very dilute aqueous acids and this identity should also apply to H_+. Any divergence between these acidity functions, if it occurs at all, must therefore appear in the lower ranges of acidity and the difference would have to reach a constant value in order to attain the parallelism found above 30% sulphuric acid.

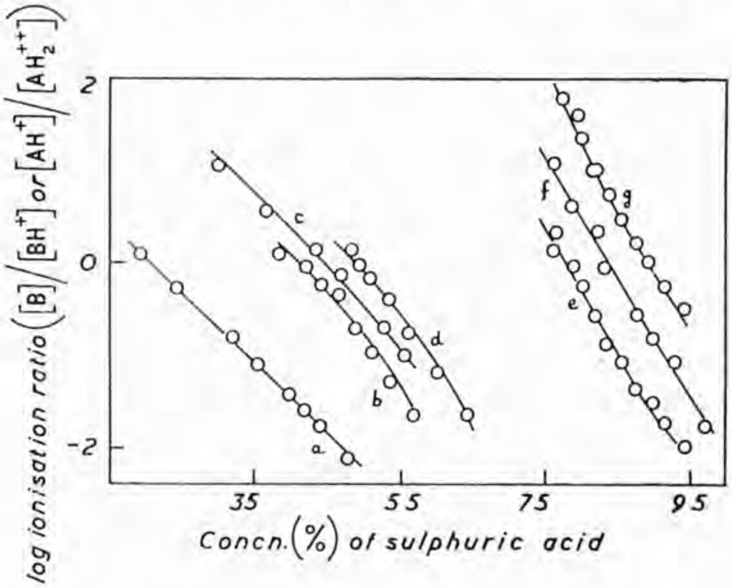


FIG. 4. *a*, 4-*Chloro-2-nitroaniline*; *b*, 4-*nitrodiphenylamine*; *d*, 2 : 4-*dichloro-6-nitroaniline*; *e*, 6-*bromo-2* : 4-*dinitroaniline*; *g*, *anthraquinone* (*results of Hammett and Deyrup*[5]); *c*, 4-*nitro-1* : 2-*phenylenediamine*; *f*, 4-*aminoacetophenone* (*this paper*).

If the identity of H_+ and H_0 is assumed, the pK_a values for the diprotonated forms of 4-nitro-1 : 2-phenylenediamine and 4-aminoacetophenone can be calculated by means of eqn. (3); they are $-2{\cdot}67 \pm 0{\cdot}07$ and $-7{\cdot}36 \pm 0{\cdot}06$ respectively.

Acidity Function and Reaction Mechanism.—The relation

$$\log k + H_0 = \text{Constant} \quad \quad (5)$$

between rate constant and H_0 has hitherto only been applied to test whether a reaction in strongly acidic media proceeds through a reacting species formed in relatively small amount by a single proton uptake on an uncharged molecule. Since H_0 can now be replaced by H_+ in equation (5) without affecting the constancy of the quantities indicated, the equation can be used to decide if a reaction proceeds through a diprotonated form present in relatively small amount, provided that all of the remaining substrate is in the monoprotonated form. An example of this use of eqn. (5) is provided by the denitration of the univalent nitroguanidinium cation in sulphuric acid solution.[9] The plot of log k against H_0 has a gradient of $-1{\cdot}4$, which is sufficiently far removed from unity to indicate that the denitration is not likely to proceed through the relatively small amount of the conjugate acid of the nitroguanidinium ion which may be present.

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[*Received, August 2nd*, 1956.]

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T.G. BONNER
D.Sc. 1960

783. *The Denitration of Nitroguanidines in Strong Acids. Part I. The Correlation of Rate Constants with the Acidity Function, H_0, and Activities of Solvent Entities.*

By T. G. Bonner and J. C. Lockhart.

The rates of denitration of some nitroguanidines have been measured in an extensive range of strongly acidic media, and a difference in mechanism has been detected in sulphuric acid and perchloric acid. The empirical relation between rate constant, the acidity function H_0, and the activities of solvent species previously reported [1] for the denitration of *N*-methyl-*N'*-nitroguanidine in sulphuric acid has been confirmed for several other nitroguanidines and a new interpretation of this relation put forward. The occurrence of a minimum in the extent of denitration at equilibrium confined to the range 85—88% sulphuric acid for all the nitroguanidines investigated is discussed.

Nitration of guanidine in concentrated aqueous acid solution is reversible,[2] and rates of the reverse reaction, *i.e.*, denitration, were first obtained by Simkins and Williams.[3] Reliable measurements of the denitration rate were limited by an unfavourable equilibrium position but *N*-methyl-*N'*-nitroguanidine gave [1] accurately measurable rates in the range 71—81% of sulphuric acid. These investigations established that denitration is a first-order reaction (opposed by the second-order nitration). A parallelism was found [1,3] between the rate of the nitration and the ionisation of triarylmethanols in the same range of media which established that the nitrating entity was the nitronium ion.[4] The importance of the part played by the solvent in these equilibria is shown by the occurrence of a minimum in the extent of denitration of nitroguanidine and its *N*-methyl derivative in the same medium, *viz.* 88% sulphuric acid.

Since nitroguanidine and its *N*-methyl derivative are completely converted into their conjugate acids in below 40% sulphuric acid and are quite stable at very much higher acidities, it was assumed that denitration took place only after the addition of a second proton.[1] The mechanism first suggested [2] represented the denitration as a rate-determining ejection of the nitronium ion from the doubly-charged nitroguanidine cation

$$PH^+ + H^+ \underset{}{\overset{\text{fast}}{\rightleftharpoons}} PH_2^{++} \overset{\text{slow}}{\rightleftharpoons} GH^+ + NO_2^+$$

where P and G represent nitroguanidine and guanidine, respectively. The species PH_2^{++} can only be present in relatively minute amount but the extent of its formation is difficult to assess. It has been shown that the stronger base, guanidine, forms detectable amounts of its doubly protonated derivative only in sulphuric acid stronger than 99% [5] but urea, a base of similar strength to nitroguanidine, does appear to become doubly charged in concentrated sulphuric acid.[6] The essential point, however, is whether the reaction proceeds uniquely through this species. This can be tested over the range of media studied by means of a relation of the type

$$\log k + H_0 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the rate constant for denitration and H_0 is Hammett's acidity function.[7] Since the reactant is envisaged as carrying two positive charges, the acidity function required is H_+ rather than H_0 but in the absence of a scale of H_+ values similar to that evaluated by Hammett for H_0, the relation can be tested only with the latter. This is acceptable, since it has been recently established that H_0 and H_+ are parallel functions of medium composition over a wide range of sulphuric acid–water mixtures.[8] The test of the mechanism proposed is that the plot of log k against H_0 should be a straight line of slope -1. In fact, the slopes so far reported have been considerably removed from -1, being $-1{\cdot}42$ for nitroguanidine [3] and $-1{\cdot}50$ for *N*-methyl-*N'*-nitroguanidine. Bimolecular reactions were considered,[1] similar to those suggested for decarbonylation of alkylbenzaldehydes in sulphuric acid,[9] but no simple bimolecular mechanism appeared to be operative. A useful empirical relation, however, was found [1] in the reasonable constancy over the range 71—82% sulphuric acid of the summation of terms in equation (2)

TABLE 1. *Denitration in sulphuric acid–water at* 25° (initial concn. 0·01M; k in 10^3 min.$^{-1}$).

% H_2SO_4	A	B	2-Nitramino-1 : 3 : 4-triazole			2-Nitrimino-1 : 3-diazacyclohexane			*NN*-Dimethyl-*N'*-nitroguanidine		
			k	C	D	k	C	D	k	C	D
67·0	4·36	9·52	0·42	8·80	13·16	—	—	—	—	—	—
68·0	4·46	9·67	—	—	—	0·274	8·77	13·23	—	—	—
69·7	4·59	10·03	—	—	—	0·546	8·70	13·31	0·468	8·81	13·40
70·5	4·67	10·28	1·13	8·56	13·23	0·834	8·69	13·36	—	—	—
71·8	4·78	10·54	2·09	8·44	13·22	—	—	—	—	—	—
72·8	4·84	10·76	—	—	—	2·84	8·48	13·33	1·84	8·65	13·49
74·8	4·98	11·14	12·43	8·07	13·29	7·38	8·29	13·29	4·37	8·52	13·50
76·1	5·08	11·41	—	—	—	11·8	8·29	13·39	—	—	—
78·6	5·24	11·91	63·0	7·87	13·11	36·4	8·12	13·36	—	—	—
70·2	5·27	12·05	—	—	—	—	—	—	36·4	8·22	13·49
81·9	5·33	12·45	—	—	—	—	—	—	121	8·04	13·37

% H_2SO_4	A	B	4-Methyl-2-nitrimino-1 : 3-diazacyclopentane			2-Nitrimino-1 : 3-diazacyclopentane *		
			k	C	D	k	C	D
76·1	5·08	11·41	0·514	9·62	14·70	0·302	9·84	14·92
78·6	5·24	11·91	—	—	—	1·33	9·54	14·78
79·2	5·27	12·05	1·86	9·49	14·76	—	—	—
81·2	5·33	12·37	5·16	9·33	14·66	3·99	9·34	$14{\cdot}7_6$
81·9	5·33	12·45	5·95	9·36	14·69	5·98	9·34	$14{\cdot}6_7$
83·3	5·38	12·72	13·6	9·21	14·60	12·07	9·27	$14{\cdot}6_5$
85·1	5·42	12·99	26·0	9·15	14·57	24·3	9·20	$14{\cdot}6_2$
87·5	5·40	13·31	91·9	8·95	14·35	74·0	9·04	$14{\cdot}4_4$
89·9	5·30	13·51	—	—	—	191·1	8·93	$14{\cdot}2_3$
92·6	5·10	13·57	—	—	—	526	8·75	13·85

A = $\log\{H_2SO_4\} + \log\{H_2O\}$; B = $-(H_0 - \log\{H_2SO_4\} - \log\{H_2O\})$; C = $-(\log k + H_0)$; D = $-(\log k + H_0 - \log\{H_2SO_4\} - \log\{H_2O\})$.

* Initial concn. 0·008M.

Values of log $\{H_2SO_4\}$ were obtained from ref. 26 and of log $\{H_2O\}$ from ref. 27.

TABLE 2. *Denitration in aqueous perchloric acid and in sulphuric acid–acetic acid at* 25° (initial concn. 0·01M; k in 10^3 min.$^{-1}$).

Perchloric acid–water			Sulphuric acid–acetic acid	
	N-methyl-*N'*-nitroguanidine	2-nitrimino-1 : 3-diazacyclohexane		2-nitrimino-1 : 3-diazacyclohexane
% $HClO_4$	k	k	% H_2SO_4	k
59·6	0·038	0·186	52·7	0·736
63·6	—	1·67	55·8	0·894
64·6	0·316	3·46	59·1	1·50
66·4	2·02	—	64·6	2·07
67·0	—	12·7	65·5	3·78
69·0	10·2	—	71·1	10·5
72·0	63·2	—	—	—

$$\log k + H_0 - \log\{H_2O\} - \log\{H_2SO_4\} = \text{constant} \quad . \quad . \quad . \quad (2)$$

where the quantities in braces represent activities. Considerable difficulty is apparent in the attempts to reconcile equation (2) with a simple mechanism of denitration.[10]

It appeared desirable to examine denitration of other substituted nitroguanidines with sufficient variety of structure to ensure an extension of the range of acidity over which the reaction takes place, and also to employ strongly acid media other than aqueous sulphuric acid. A few compounds (detailed in Table 1) were suitable for measurements of rate and equilibria in aqueous sulphuric acid. 2-Nitrimino-1 : 3-diaza*cyclo*hexane (II) and *N*-methyl-*N'*-nitroguanidine were studied in aqueous perchloric acid and the former in anhydrous sulphuric acid–acetic acid also (see Table 2).

EXPERIMENTAL

Materials.—Sulphuric acid and perchloric acid solutions were prepared by dilution of the "AnalaR" acid with distilled water and analysed as previously reported.[2a] 100% Sulphuric acid was obtained from a weak oleum by dilution to maximum freezing point with "AnalaR" sulphuric acid. Sulphuric acid–acetic acid solutions were obtained by mixing the required weights of 100% sulphuric acid and 100% acetic acid.

Nitroguanidine was obtained by nitration of guanidine in sulphuric acid.[11] Methylnitroguanidine, m. p. 160—161°, was made from nitroguanidine as described by McKay and Wright.[12] *NN'*-Dimethyl-*N''*-nitroguanidine, m. p. 171—172°, was obtained from the mother liquor of this reaction by Hardy-Klein's method.[1] *NN*-Dimethyl-*N'*-nitroguanidine, m. p. 194—195°, was made from *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine and dimethylamine.[12]

2-Nitrimino-1 : 3-diaza*cyclo*pentane, m. p. 220—221°, 4-methyl-2-nitrimino-1 : 3-diaza*cyclo*pentane, m. p. 170—171°, and 2-nitrimino-1 : 3-diaza*cyclo*hexane, m. p. 249—250°, were prepared by the method used for methylnitroguanidine.[12] 2-Nitramino-1 : 3 : 4-triazole was made by refluxing formamidonitroguanidine with sodium carbonate.[13]

All these nitroguanidines were purified by recrystallisation to constant spectrum for kinetic work. Spectral data are given in the following paper. A commercial specimen of guanidine nitrate was recrystallised from water, then six times from water containing 10% of alcohol.

Recovery of Denitration Products.—*NN*-Dimethyl-*N'*-nitroguanidine and the diaza-*cyclo*hexane and -*cyclo*pentanes were tested by Holstead and Lamberton's method to demonstrate the formation of nitric acid. The yield in all cases was within 71—73% of theory, as had been previously found for potassium nitrate and nitroguanidine. The nitration mixture from 2-nitrimino-1 : 3-diaza*cyclo*pentane was also treated to yield the guanidine as nitrate,[2b] needles, m. p. 112—113°, identified as 2-amino-1 : 3-diaza*cyclo*pentane nitrate by conversion into the carbonate and picrate.[14]

Measurement of Reaction Velocity and Equilibrium Composition.—The optical density of a sample suitably diluted with water was measured at the absorption maximum for the particular nitroguanidine.

The absorptions of guanidine,[15] alkylguanidines,[1] and 2-aminotetrahydropyrimidine [16] are known to be negligible at 2600—2900 Å. The absorption of 2-amino-1 : 3-diaza*cyclo*pentane nitrate also was found to be negligible in this region. The nitrate ion has an extinction coefficient of ε, 2 in this region and can be neglected [1] as long as denitration is less than 95% complete.

Rate constants were obtained graphically from the kinetic equation previously employed,[1] *i.e.* $kt(2a - x_e) = 2{\cdot}3x_e \log_{10}\{a(x_e - x)/[ax_e + x(a - x_e)]\}$ where a is the initial concentration of reactant, x the concentration of the denitrated reactant at time t, and x_e the concentration of the latter at equilibrium. A plot of the log term against time was a straight line to about 80% of the conversion for all compounds and media studied.

RESULTS AND DISCUSSION

The Relation between Rate Constant and Acidity Function, H_0.—The rapid increase in rate of denitration with increasing acidity [1,3] was also found for all the compounds in Table 1. Rate constants increase approximately one-hundred fold over a 10% range of acid, for both sulphuric acid and perchloric acid solutions. The influence of acidity is only slightly less marked in sulphuric acid–acetic acid. The plots of log k against H_0 for aqueous sulphuric acid [17] are shown in Fig. 1; the slopes for all the compounds lie between $-1{\cdot}41$ and $-1{\cdot}49$. In aqueous perchloric acid [18] the two compounds studied, 2-nitrimino-1 : 3-diaza*cyclo*hexane and *N*-methyl-*N'*-nitroguanidine, give slopes of $-0{\cdot}97$ and $-1{\cdot}09$, respectively. These results imply that denitration in perchloric acid proceeds through a diprotonated species formed in fractionally small amount[17] but that a more complex reaction occurs in sulphuric acid. Since rates in the latter are faster than required by theory, it is possible that in this medium, (*a*) catalysis occurs by some species not present in aqueous perchloric acid, or (*b*) the transition state of the reactant associates with solvent species in a manner not paralleled by the conjugate acids of the Hammett bases used to evaluate H_0.

A mechanism basically similar to that in perchloric acid cannot be excluded for sulphuric acid since previous investigators have often found justification for interpreting slopes of from $-0{\cdot}7$ to $-1{\cdot}5$ in terms of the simple mechanism associated with a slope of -1.[19-22] However, application of the results reported here to equation (2) showed an excellent fit in the range 67—85% sulphuric acid for all the nitroguanidines in Table 1, except 2-nitrimino-1 : 3-diaza*cyclo*pentane. With the latter the constancy is not so marked, but considerable divergence from constancy occurs only above 85% sulphuric acid. It may be significant that this medium is very close to that corresponding to the 1 : 1 mole ratio of sulphuric acid to water and possibly a change of mechanism occurs at the higher acidities. As the results in Table 1 show, the sum of the terms log $\{H_2SO_4\}$ + log $\{H_2O\}$ increases continuously with acidity as does that of the terms log k and H_0. It is the difference between these two sets of values which remains constant. The constancy of the terms in equation (2) is consistent with a rate constant represented by equation (3)

FIG. 1. *Variation of* log k (*denitration*) *with* H_0.

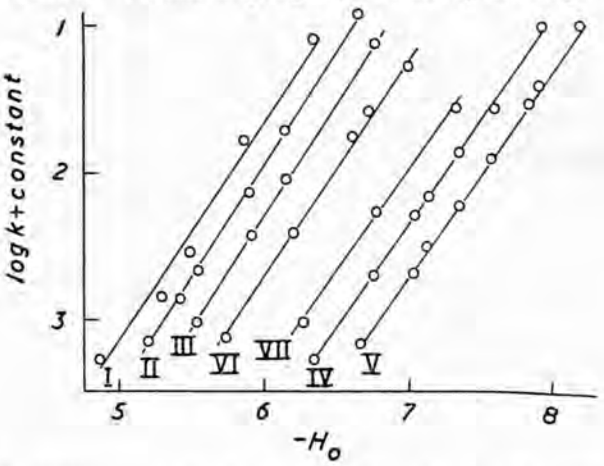
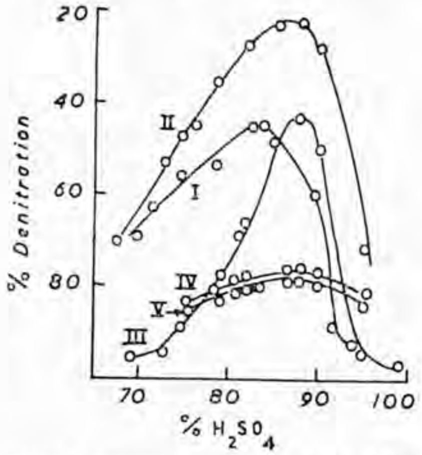


FIG. 2. % *Denitration of equilibrium.*



I, 2-Nitramino-1 : 3 : 4-triazole ($-1{\cdot}44$); II, 2-Nitrimino-1 : 3-diaza*cyclo*hexane ($-1{\cdot}46$); III, *NN*-Dimethyl-*N'*-nitroguanidine ($-1{\cdot}46$); IV, 4-Methyl-2-nitrimino-1 : 3-diaza*cyclo*pentane ($-1{\cdot}41$); V, 2-Nitrimino-1 : 3-diaza*cyclo*pentane ($-1{\cdot}44$); VI, *N*-Methyl-*N'*-nitroguanidine (from ref. 1) ($-1{\cdot}49$); VII, Nitroguanidine (from ref. 3) ($-1{\cdot}46$).

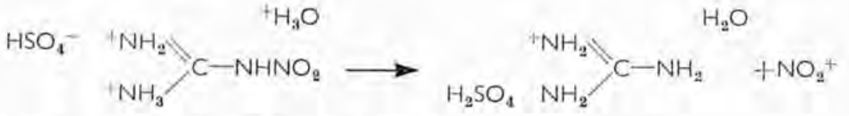
Values in parentheses are of (log k)/H_0.

$$k = \text{constant}\ \{H_2SO_4\}\,\{H^+\}\,\{H_2O\}\,f_B/f_{BH^+} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and this in turn implies a transition complex formed from a nitroguanidine cation PH^+ and the solvent species H_3O^+ and H_2SO_4. If molecular sulphuric acid is absent from the more aqueous sulphuric acid solutions used for denitration, the same transition complex could equally well be formed from the diprotonated nitroguanidine PH_2^{++} and the solvent species HSO_4^- and H_3O^+, both of which should be present in excess in most, if not all, of the media studied. The absorption spectra indicate that addition of a proton to nitroguanidine occurs at the nitrimino-nitrogen atom (see following paper). Denitration of this ion would lead to the formation of a guanidinium ion and a nitronium ion, a process which requires an additional proton

$$(NH_2)_2C{=}\overset{+}{N}HNO_2 + H^+ \rightleftharpoons (NH_2)_2C{=}\overset{+}{N}H_2 + NO_2^+$$

The proton will be supplied by either of the acid species present, H_3O^+ or H_2SO_4, but bimolecular reaction of either with the nitroguanidinium ion can be excluded, as the previously reported failure[1] of the experimental results to conform to a bimolecular mechanism of this type was confirmed for all compounds now studied. If the additional proton becomes attached to the nitroguanidinium ion in any initial fast step, it will almost certainly be located on one of the two amino-groups and the denitration of the bivalent ion so formed through a transition complex which includes a bisulphate and oxonium ion could be represented as shown



The Brönsted rate equation for this reaction is

$$\text{rate} = k_0\{PH_2^{++}\}\{H_3O^+\}\{HSO_4^-\}/f_‡$$

and the experimental rate $= k[PH^+]$ where PH^+ and PH_2^{++} represent the monoprotonated and diprotonated nitroguanidine respectively, and $f_‡$ is the activity coefficient of the transition complex:

$$k = k_0\{PH_2^{++}\}\{H_3O^+\}\{HSO_4^-\}/[Ph^+]f_‡$$

From the equilibria $H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$; $PH^+ + H^+ \rightleftharpoons PH_2^{++}$ which have the thermodynamic equilibrium constants K_{H_2O} and $K_{PH_2^{++}}$, respectively, we have

$$k = k_0K_{PH_2^{++}}K_{H_2O}\{H^+\}\{H_2O\}\{H_2SO_4\}f_{PH^+}/f_‡$$

and since
$$H_0 = -\log\{H^+\}f_B/f_{BH^+}$$

$$\log k = \log k_0K_{PH_2^{++}}K_{H_2O} - H_0 + \log\{H_2O\} + \log\{H_2SO_4\} + \log f_{PH^+}f_{BH^+}/f_Bf_‡$$

which agrees with the empirical equation 2 if the activity coefficient term remains constant.

The range of media in which this combination of reactant and solvent species could be expected to be formed most readily is from that of the 1 : 1 molar ratio of water to sulphuric acid (84·5%) to that of the 2 : 1 molar ratio (72·5%) since within this range it is probable that H_3O^+ is the strongest proton donator and HSO_4^- the strongest proton acceptor. This range largely coincides with that found experimentally for the application of equation 2. The aqueous perchloric acid used corresponds in acidity to the aqueous sulphuric acid range below the 2 : 1 molar ratio of water to sulphuric acid. While H_3O^+ is the strongest acid present, there is no base equivalent to the HSO_4^- ion in aqueous perchloric acid and this may be the reason for the slower reaction and the operation of a different mechanism of denitration with the rate depending mainly on the acidity.

Effect of Change of the Initial Concentration of Reactant on the Rate Constant.—The slight decrease in the rate constant of denitration with increase in initial concentration of the nitroguanidine previously[1,3] observed was confirmed for 2-nitrimino-1 : 3-diaza*cyclo*hexane and *NN*-dimethyl-*N'*-nitroguanidine but the effect was dependent on the particular medium in which the rates were measured. In more aqueous media the effect was virtually eliminated. The rate constant for 2-nitrimino-1 : 3-diaza*cyclo*pentane was independent of initial concentration of reactant over a twenty-fold range from $4·5 \times 10^{-3}$ to 10^{-1} mole/l.; a similar result was found for the 4-methyl analogue. No conclusion has been reached on this difference in behaviour of nitroguanidines.

The Extent of Denitration at Equilibrium.—Although rates of denitration become immeasurably fast above 90% sulphuric acid for all but one of the compounds in Table 1, data on the equilibria attained in all media up to *ca.* 95% sulphuric acid were obtained by determining the equilibrium concentration of the nitroguanidine spectroscopically. Equilibrium concentrations were also measured for the denitration of the diaza*cyclo*hexane and of N-methyl-N'-nitroguanidine in perchloric acid and for the same equilibrium attained by guanidine nitrate in sulphuric acid–acetic acid. The variation in the extent of denitration in aqueous sulphuric acid with medium composition is shown in Fig. 2; a minimum for all compounds occurs at 85—88% sulphuric acid. With sulphuric acid–acetic acid there is a similar minimum at 73% sulphuric acid. In both sulphuric acid–water and sulphuric acid–acetic acid, the composition of the media where the minimum occurs is such that the mole ratio of sulphuric acid to the other component is greater than 1 but in the strongest perchloric acid used (72%) this ratio is much less than 1. A minimum is therefore not observed in the latter because a sufficiently high mole ratio of acid to water cannot be attained.

Since the percentage denitration is a measure of the ratio of the rate of denitration to rate of nitration, it is evident that as the acid strength increases, the rate of nitration at first increases more rapidly than that of denitration, but as the point of minimum denitration is approached this difference is not maintained. The rate of denitration increases sharply above this point as the results for 2-nitrimino-1 : 3-diaza*cyclo*pentane (Table 1) indicate; if the nitration shows the same phenomenon of attaining a maximum rate in *ca.* 90% sulphuric acid as already established for aromatic nitration [23] the occurrence of a minimum is to be expected. The corresponding maximum amount of nitration has been found in the equilibria attained in the nitration of tetraethylguanidine in sulphuric acid, the maximum occurring when the water content of the medium is 10—15%.[24]

A relation between the equilibrium constant and the activity of water has been adduced by Simkins and Williams,[2] given by

$$\log K_0 = \log K + \log \{H_2O\} + \log (f_{PH^+}/f_{GH^+} f_{HNO_3})$$

where K_0 represents a thermodynamic equilibrium constant, K the ratio of equilibrium concentrations $[PH^+]/[GH^+][HNO_3]$, $\{H_2O\}$ the activity of water, and f_{PH^+}, f_{GH^+}, and f_{HNO_3} the activity coefficient of the nitroguanidine ion, the guanidinium ion, and nitric acid, respectively. This has been tested by plotting log k against log $\{H_2O\}$, for sulphuric acid–water (the only medium for which the necessary data are available). With 2-nitrimino-1 : 3-diaza*cyclo*hexane and NN-dimethyl-N'-nitroguanidine good straight lines were obtained for media up to that corresponding to minimum denitration with slopes of $-0{\cdot}99$ and $-1{\cdot}23$, respectively. 2-Nitrimino-1 : 3-4-triazole gives an initial straight-line plot of slope $-0{\cdot}90$, but this falls off rapidly above 80% sulphuric acid. For 2-nitrimino-1 : 3-diaza*cyclo*pentane and its 4-methyl derivative, the extent of denitration is more than 80% in most media, and the back reaction occurs to such a slight extent that it is not possible to deduce reliable values for K.

Rates, k_2, of the nitration can be calculated from the equilibrium constant K and the rate of the forward reaction k, since $K = k_2/k_1$. Reliable values are only possible for 2-nitramino-1 : 3 : 4-triazole, 2-nitrimino-1 : 3-diaza*cyclo*hexane, and NN-dimethyl-N'-nitroguanidine since the equilibrium is displaced too far in favour of the forward reaction for the other two compounds in Table 1.

Comparison of the rates of nitration for these three compounds with the acidity function J_0[25] confirms that nitration of guanidines occurs through the nitronium ion; in each case log k_2 is a linear function of J_0 with slope approximately as indicated: 2-amino-1 : 3 : 4-triazole (0·97), 2-imino-1 : 3-diaza*cyclo*hexane (0·83), and NN'-dimethylguanidine (0·94).

Some attempt was made to measure the rate of nitration of guanidine in sulphuric acid–acetic acid but although preliminary results suggest 99% conversion of the guanidine, substantial decomposition to products other than nitroguanidine was evident, and further investigation of these side-reactions is necessary.

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17.

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784. *The Denitration of Nitroguanidines in Strong Acids. Part II.* Absorption Spectra and* pK_a *Values of Certain Nitroguanidines.*

By T. G. Bonner and J. C. Lockhart.

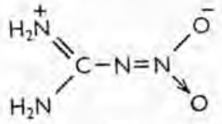
The structure of certain nitroguanidines and their conjugate acids is discussed and ultraviolet absorption spectra data are adduced to support the nitrimino-form of the free base and the nitramino-form for the ion. Differences in absorption spectra and basicity of the nitroguanidines investigated are interpreted in terms of the resonance structures of the free bases and their conjugate acids.

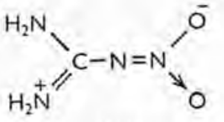
Some controversy has existed over the structure of nitroguanidine, the choice being between two tautomers, the nitramino-form (Ia) and the nitrimino-form (Ib).

$NH{:}C(NH_2){\cdot}NH{\cdot}NO_2$ (Ia) $NH_2{\cdot}C(NH_2){:}N{\cdot}NO_2$ (Ib)

Wright[1] favoured structure (Ib) since no reaction occurs between nitroguanidine and diazomethane or acetyl chloride, both of which react readily with nitramines; the same is true of 2-nitrimino-1 : 3-diaza*cyclo*pentane. Other evidence for the nitrimino-structure comes from dipole-moment measurements[2] but absorption spectra have been interpreted as evidence for both forms.[2, 3]

An *X*-ray study[4] of nitroguanidine showed the molecule to be almost planar with the carbon atom practically equidistant from the three nitrogen atoms to which it is directly attached. This implies that all three carbon–nitrogen bonds have the same bond order, which is not consistent with either form (Ia) or (Ib). The authors have represented the molecule by eight resonance structures of which the positions of the nuclei are those of the nitrimino-form (Ib), and an attempt was made to weight these structures so that a symmetrical electron distribution exists around the carbon atom. However, equal contributions from the covalent structure (Ib) and the ionic structures (II) and (III) would produce the symmetry found.


(II)


(III)

Recent evidence for the nitramino-structure has been provided by an investigation by proton magnetic resonance of nitroguanidine.[5] The curve obtained does not give any indication of the two single protons present in structure (Ia) and is characteristic of proton pairs only, in accordance with structure (Ib).

This conclusion is now confirmed by the ultraviolet absorption spectra of nitroguanidine and its conjugate acid which, although previously investigated, have now been more extensively studied together with several derivatives. In all these nitroguanidines the existence of a strong absorption band at 2600—2700 Å has been observed, the exact position and intensity of which depends on the substituent groups. The absorption spectrum of nitramide[6] is quite different with a broad band at 2250 Å (ε 5900; in water), which suggests that nitroguanidines do not exist in the nitramino-form (Ia). The absorption band characteristic of nitramide appears in the spectra of nitroguanidines in

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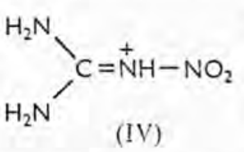
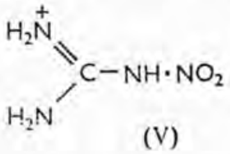
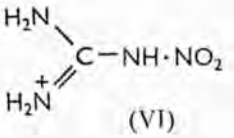
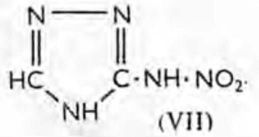
* Part I, preceding paper.

strongly acid solution and reaches maximum intensity in 40—50% sulphuric acid corresponding to complete conversion of the nitroguanidine into its conjugate acid. The change is accompanied by the disappearance of the absorption band characteristic of the free base. A typical example of this change is that of 2-nitrimino-1 : 3-diaza*cyclo*pentane shown in Fig. 1. A nitramino-structure would be readily acquired by the conjugate acid by proton uptake on the nitrimino-nitrogen atom. Three principal resonance structures (IV)—(VI) can represent the nitroguanidinium ion thus formed.


(IV)

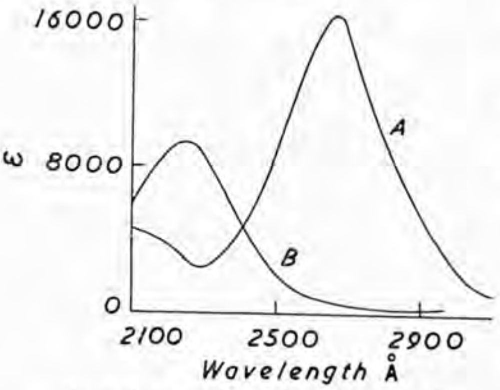

(V)


(VI)


(VII)

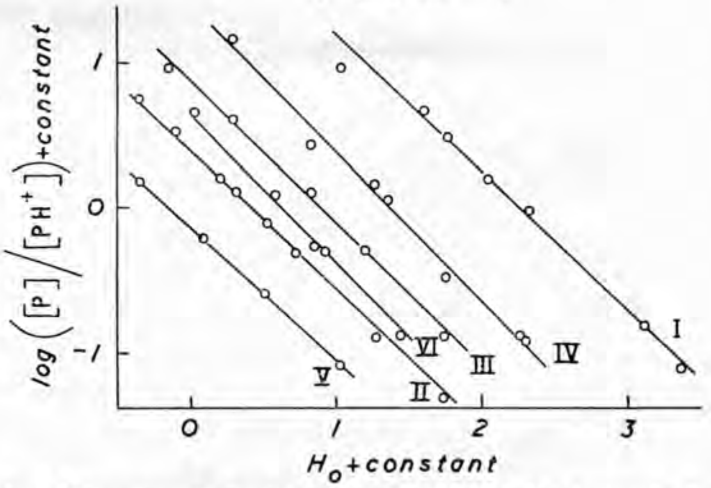
As shown in the Table, the majority of nitroguanidine derivatives undergo this characteristic change of spectrum on conversion into their conjugate acids in sulphuric acid. The only exception is 2-nitramino-1 : 3 : 4-triazole, which shows the same hypsochromic shift but to a lesser extent. Evidently the triazole has structural features which modify its absorption characteristics. An aromatic structure for the triazole ring requires the nitramino-form (VII) and the characteristic spectrum of nitramine will be modified by conjugation of the nitramino-group with the ring. Protonation in strongly acid solution will occur at one of the nitrogen atoms, probably at either of the tertiary atoms, and this will reduce conjugation of the nitramino-group with the ring but not sufficiently to produce the spectrum of nitramine.

FIG. 1. *Spectrum of 2-nitrimino-1 : 3-diaza-cyclopentane in sulphuric acid.*



A, in 0·1N-acid; *B*, in 69% acid.

FIG. 2. *Variation of log* ([P]/[PH⁺]) *with* H_0.



I, 2-Nitramino-1 : 3 : 4-triazole (0·97); II, 2-Nitrimino-1 : 3-diaza*cyclo*hexane (0·96); III, *NN*-Dimethyl-*N'*-nitroguanidine (1·00); IV, 2-Nitrimino-1 : 3-diaza*cyclo*pentane (1·01); V, *N*-Methyl-*N'*-nitroguanidine (0·93); VI, Nitroguanidine (1·02).

Values in parentheses are of log ([P]/[PH⁺])/H_0.

The lower extinction coefficient of *NN*-dimethyl-*N'*-nitroguanidine is clearly an example of steric inhibition of conjugation. If the transition corresponding to the intense absorption of nitroguanidine bases at 2600—2700 Å is from the homopolar ground state (Ib) to the predominantly dipolar excited state (II), the presence of two methyl groups on one amino-nitrogen atom will restrict rotation about the bond linking this nitrogen atom to the central carbon atom and hinder the molecule's attaining the planar configuration necessary for maximum resonance. As the intensity of absorption only is reduced, $\lambda_{max.}$ remaining unchanged, the steric hindrance is relatively weak and is possibly associated with transitions between non-planar ground state and near-planar excited states.[7] The relatively smaller fall in intensity of the symmetrical *NN*′-dimethyl-*N*″-nitroguanidine may be the result of a weaker operation of this effect. The greatest intensity of absorption occurs in the diaza*cyclo*pentane and diaza*cyclo*hexane derivatives, and this can be attributed to the rigidity of these ring systems facilitating the formation of the planar configuration of the dipolar excited state.

pK_a *Values of Nitroguanidines.*—pK_a values are given in the Table. As the absorption spectra of the nitroguanidium ions (except the triazole derivative) indicate a nitramino-structure (IV) corresponding to proton uptake on the nitrimino-nitrogen atom, the relative basicities will depend on the resonance stabilisation achieved by contributions from structures (V) and (VI). The slight increase in basicity (pK_a increases from $-0{\cdot}93$ to $-0{\cdot}86$) produced by the introduction of a single methyl group on the amino-nitrogen atom is in accord with the inductive effect of this group but the considerable decrease in basicity which follows the substitution of a second methyl group on the same nitrogen atom ($pK_a = -1{\cdot}20$) is evidence of the greater strain involved in attaining the planar configuration necessary for appreciable contributions in the ground state from the resonance structures of the type (V).

Absorption spectra data, pK_a *values, and relative rates (RR) of denitration, in aqueous sulphuric acid.*

Compound	Free base		Conjugate acid		pK_a	*RR*
	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$		
2-Nitramino-1 : 3 : 4-triazole	12,400	2820	6700	2470	$-2{\cdot}5$	16·6
2-Nitrimino-1 : 3-diaza*cyclo*hexane	15,450	2680	9700	2315	$-0{\cdot}71$	8·5
NN-Dimethyl-*N*′-nitroguanidine	11,350	2710	8010	2250	$-1{\cdot}30$	6·6
NN′-Dimethyl-*N*″-nitroguanidine	13,200	2675	—	—	—	6·3 [a]
N-Methyl-*N*′-nitroguanidine	14,040	2670	8700	2260	$-0{\cdot}86$	3·8 [a]
Nitroguanidine	14,400	2640	9940	2250	$-0{\cdot}93$ [b]	1 [c]
4-Methyl-2-nitrimino-1 : 3-diaza*cyclo*pentane	17,140	2660	—	—	—	0·41
2-Nitrimino-1 : 3-diaza*cyclo*pentane	16,170	2655	9440	2260	$-1{\cdot}36$	0·33

[a] Ref. 9. [b] The pK_a obtained for nitroguanidine above agrees with that obtained in dilute hydrochloric acid,[11] recalculated on an H_0 basis. [c] Ref. 10.

The markedly higher basicity of the diaza*cyclo*hexane ($pK_a = -0{\cdot}71$) than of the diaza*cyclo*pentane ($pK_a = -1{\cdot}36$) can be related to the relative stability of these ring systems with respect to the exocyclic double bond. Since a double bond which is exocyclic to a five-membered ring is more stable than one which is exocyclic to a six-membered ring,[8] it is possible that greater contributions to the resonance stabilisation from the equivalent structures corresponding to (V) and (VI) will be made in the case of the conjugate acid of the diaza*cyclo*hexane than in that of the diaza*cyclo*pentane.

The notably weak basic character of 2-nitramino-1 : 3 : 4-triazole is characteristic of aromatic bases (cf. aniline, pyridine) and originates in the decrease in resonance which results from proton addition to a nitrogen atom.

A significant feature of the ionisation of each nitroguanidine is that a plot of log ([P]/[PH$^+$]) (where P represents the uncharged nitroguanidine and PH$^+$ its conjugate acid) against H_0 is a straight line of slope 1, as shown in Fig. 2. These compounds are therefore indistinguishable in their ionisation behaviour from the aromatic bases used by Hammett in the evaluation of the H_0 scale.

Relative Rates of Denitration.—The mechanism of denitration of nitroguanidines in strong acids (previous paper) envisages the expulsion of a nitronium ion from the di-protonated base accompanied by proton transfer involving acid and base species present in the medium. An important factor in this process is the ease of proton uptake, with the second protonation more important than the first. Thus although the triazole is the weakest base, its conjugate acid has the largest number of basic centres for the second protonation, and if this second protonation occurs more readily than with the other nitroguanidinium ions, the relatively high rate of nitration found experimentally would be expected. The order of denitration rates for nitroguanidine and its monomethyl and dimethyl derivatives is also in accord with the expected basicity of their conjugate acids, if this is assumed to depend mainly on the inductive effect on the methyl group. The difference in rates of denitration of the diaza*cyclo*hexane derivative and its *cyclo*pentane analogue may be attributed to differences in ring stability, the faster rate for the former corresponding to a greater flexibility of the six-membered ring compared with the five-membered ring in the diprotonated derivatives (the second proton being assumed to add to a ring nitrogen atom).

EXPERIMENTAL

Materials.—These were as in the preceding paper.

Absorption Spectra.—These were measured on a Hilger Uvispek spectrophotometer calibrated with potassium chromate.[12]

Measurement of Ionisation Ratios.—The method developed by Flexser, Hammett, and Dingwall [13] was used. Indicator ionisation ratios were obtained from the equation $[B]/[BH^+] = (\varepsilon_{BH^+} - \varepsilon)/(\varepsilon - \varepsilon_B)$, where ε_B and ε_{BH^+} are the extinction coefficients of the un-ionised base B and its conjugate acid BH^+ at any selected wavelength and ε is that of the mixture of the same wavelength. pK_a values were obtained from the relation $pK_a = H_0 - \log([B]/[BH^+])$, where $[B]$ and $[BH^+]$ are the concentrations of the base and its conjugate acid in a medium of acidity H_0. The results recorded in the Table are the mean of several values obtained at different H_0 values and different wavelengths.

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797. *Comparative Reaction Rates in Solid and in Liquid Sulphuric Acid–Water Mixtures.*

By T. G. BONNER and J. C. LOCKHART.

Rate constants of two different reactions have been measured in liquid and in solid sulphuric acid–water mixtures at 0°. The occurrence in both cases of a more rapid reaction in the solid medium is discussed.

During a study of rate measurements on the cyclodehydration of anils of acetylacetone to 2,4-dimethylquinolines [1] in sulphuric acid at temperatures below 10° it was found that where solidification of the medium inadvertently occurred the reaction still proceeded to completion. In consequence, a comparative study was made of the rates of this reaction in the solid and in corresponding supercooled liquid media at the same temperature, 0°, with two anils, 2-*p*-toluidinopent-2-en-4-one and 2-anilinopent-2-en-4-one and two different acid–water mixtures. In all cases, the cyclodehydration in the solid media was approximately twice as fast as in the liquid medium (Table 1*a*). Rates in solid and in liquid sulphuric acid media of the denitration of nitroguanidines to guanidine and nitric acid [2] were compared similarly; those in the solid media were about four times greater than in the liquid for both 2-nitrimino-1,3-diazacyclopentane and 4-methyl-2-nitrimino-1,3-diazacyclopentane as shown in Table 1*b*. Variation of the initial concentration of 2-nitrimino-1,3-diazacyclopentane did not markedly change the ratio k_S/k_L of the rate constants for the solid and the liquid state (Table 2). As these initial studies were confined to measurements at 0° the sulphuric acid–water mixtures were restricted to the range 81—86% sulphuric acid over which the freezing points have values between 2 and 8°.[3] The only other range in which freezing points are above 0° is 98—100% sulphuric acid, but denitrations were too fast for measurement in these acids while the cyclodehydrations which proceeded at fast but measurable rates did not give satisfactory results, largely owing to the tendency of the solid samples to melt partially during reaction. Lower temperatures, *e.g.*, −10° to −20°, might avoid this difficulty, but will introduce the hazard of spontaneous solidification of the supercooled liquid.

TABLE 1. *Rate constants* (*min.*$^{-1}$) *at* 0° *in solid* (k_S) *and supercooled liquid* (k_L) *sulphuric acid–water mixtures.*

(*a*) Cyclodehydration of anils (0·025M)

Compound*	I	I	II	II
%H_2SO_4	85·5	84·0	85·5	84·0
10^4k_S......	6·4, 6·2	3·4	0·93	0·72
10^4k_L ...	3·2, 3·0	1·7	0·47	0·31

(*b*) Denitration of nitroguanidines (0·0074M)

Compound*	III	III	III	IV
%H_2SO_4 ...	86·4	85·7	84·5	84·5
10^3k_S	7·15	6·72	5·23	5·80
10^3k_L.........	1·78	1·60	1·27	2·12

* I, 2-*p*-Toluidinopent-2-en-4-one; II, 2-anilinopent-2-en-4-one; III, 2-nitrimino-1,3-diazacyclopentane; IV, 4-methyl-2-nitrimino-1,3-diazacyclopentane.

TABLE 2. *Denitration of* 2-*nitrimino*-1,3-*diazacyclopentane at different initial concentrations in* 84·5% *sulphuric acid at* 0°.

10^2 × Initial concn. (M)	0·74	0·89	2·90
10^3k_S (min.$^{-1}$)	5·13, 5·34, 5·23, 5·32	5·07	5·12
10^3k_L (min.$^{-1}$)	1·27	1·18	1·54

A feature common to both the cyclodehydrations and denitrations is that they proceed through protonated forms of the substrate. In cyclodehydration this is a doubly charged species [4] which reacts by a rate-determining closure of the side chain to either *ortho*-position, followed by rapid loss of a proton. The medium is involved in maintaining the equilibrium concentration of the fractionally small amount of diprotonated anil and in the subsequent removal of the proton from the reaction intermediate, but both these proton transfers are presumably as fast in solid media as in the liquid and in any case are not rate-determining. The more rapid ring closure in a solid medium may then be due to entropy; the " caged " anil molecule has a very limited translatory motion but the greater flexibility of the side chain leads to a higher proportion of collisions with the *ortho*-positions at which the closure is affected. This effect would be similar to that discussed by Fairclough and Hinshelwood [5] for bimolecular reactions in solution where the solute molecule is larger than the solvent molecule and the solvent has a high density. Under these conditions the solvent can assume a close-packed structure from which the solute molecules tend to be squeezed out in groups with a consequent large increase in the number of repeated collisions between pairs of solute molecules at the expense of fresh encounters.

Although the denitration of nitroguanidines in sulphuric acid–water mixtures has a more complex mechanism than the cyclodehydration, it is basically similar in that the ionic form of the substrate requires assimilation of a second proton for reaction to occur. The transition state appears to require the presence of the solvent species,[2] H_3O^+ and HSO_4^-, which are involved only in proton transfer to, and proton withdrawal from, the bivalent nitroguanidinium ion during its conversion into the guanidinium and nitronium ion. A significant difference between the liquid and the solid environment could arise as a result of this participation of solvent acid and base species in the denitration. In the liquid the doubly positively charged nitroguanidinium ion will have a preponderantly negatively charged ionic atmosphere while, in the solid state, the solid phase in this range of media is the monohydrate [3] H_2O,H_2SO_4 (or H_3O^+,HSO_4^-) which provides the most favourable balance of the acid and base catalysts as the environment of the reacting ion.

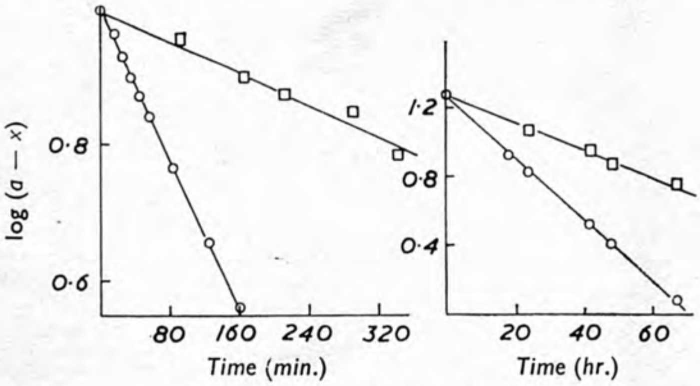
Evidently the study of bimolecular reactions in solid sulphuric acid–water mixtures will provide results of even greater interest than the two reactions reported here. Some preliminary investigations on the nitration of guanidine using guanidine nitrate to provide both reactants showed that the reaction was too fast for measurement even at 0° in the optimum range of sulphuric acid–water mixtures. The measurements did reveal, however, that the equilibrium was more rapidly attained in the solid than in the liquid medium.

EXPERIMENTAL

Materials and Media.—These were prepared as previously described.[1,2]

Kinetic Measurements.—For both cyclodehydration and denitration reactions, the reactant was weighed into a short tube made from a B24 cone. At zero time this tube was inserted into the neck of the flask containing the liquid sulphuric acid medium at 0° and shaken vigorously to dissolve the reactant as rapidly as possible. The flask was shaken in the bath at 0° for about 1 min. To ensure similarity of experimental conditions for both solid- and liquid-phase measurements, 2 ml. aliquot portions were successively removed without delay from the reaction solution and introduced into stoppered tubes, equal numbers of which were immersed in liquid air (to effect rapid solidification) and in a large vacuum flask containing ice and water. Each tube in the liquid-air bath was transferred to the ice-bath after complete solidification of the solution (which required about 1 min.) had occurred. In each experiment 5—8 samples each for the solid and liquid kinetic measurements were thus removed. At fixed time intervals, the stoppered tubes were taken from the ice-baths, and the contents diluted with water to stop further reaction and analysed in the usual way for the amount of unchanged reactant.[1,2] On rare occasions in the cyclodehydration, the supercooled sulphuric acid medium began to solidify during the initial mixing with the reactant. In such cases the experiment was repeated with the medium kept at about 5° before the addition of the reactant, and after complete dissolution of the latter the temperature of the solution was reduced rapidly to 0° by shaking for a few minutes in an ice-bath before removing the 2 ml. aliquot portions to the stoppered tubes. Since all reactions were extremely slow, this procedure did not introduce any detectable error.

Simkins and Williams[6] have shown that the reversible denitrations in liquid sulphuric acid can be treated as a simple first-order change up to about 20% conversion of the nitroguanidine, and this procedure was followed here of plotting log ($a - x$) against time; for liquid media good straight lines were obtained up to about 20% conversion, and for reactions in the solid media the straight line plot continued up to 50% conversion of the nitroguanidine. The cyclodehydration reaction was followed up to about 80% conversion. Typical results are shown in the Figure.



A, Denitration of 2-*nitrimino*-1,3-*diazacyclopentane in* 85·7% *sulphuric acid; B, cyclodehydration of* 2-p-*toluidinopent*-2-*en*-4-*one in* 85·5% *sulphuric acid.*

☐ Liquid, ○ solid medium.

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19.

ESTERIFICATION BY THE NITRONIUM ION IN AQUEOUS PERCHLORIC ACID

By Dr. T. G. BONNER and D. E. FRIZEL

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(*Reprinted from Nature, Vol. 179, p. 1022 only, May 18, 1957*)

Esterification by the Nitronium Ion in Aqueous Perchloric Acid

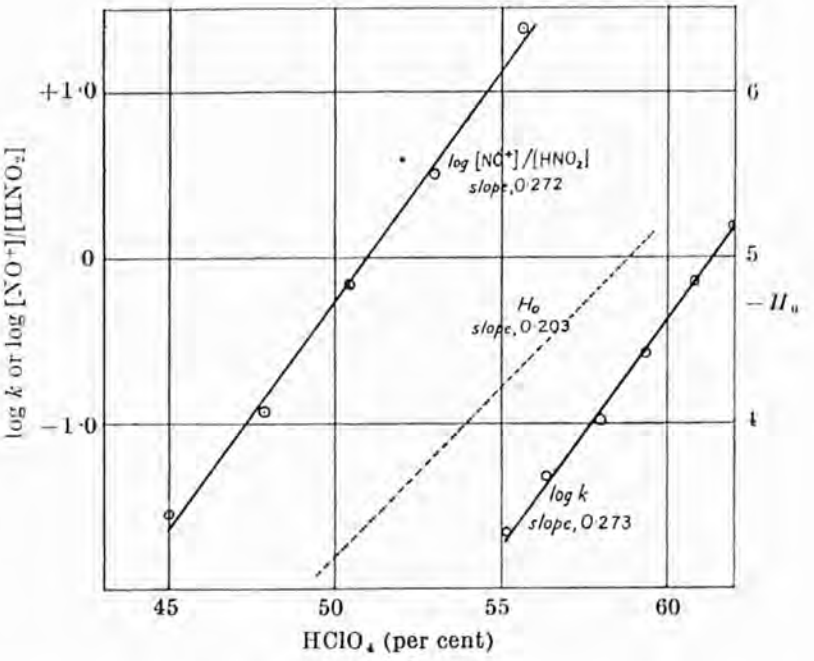
THE nitronium ion, NO_2^+, has been shown to be the active nitrating entity in the O-nitration of certain alcohols in organic solvents[1] in which nitric acid is present in large excess. Kinetic studies in progress on the esterification of *iso*amyl alcohol with nitric acid in 55–62 per cent aqueous perchloric acid have now indicated that here also O-nitration proceeds through the nitronium ion, although only a very small fraction of the nitric acid can be present in this cationic form in media of such high water-content. Rate measurements at 25° C. made by ultra-violet spectrometric analysis of the unchanged nitric acid after dilution of aliquots with water and extraction of the *iso*amyl nitrate product show that the rate equation (1) is obeyed :

$$d[iso\text{-AmNO}_3]/dt = k[iso\text{-AmOH}]\,[\text{HNO}_3] - k'[iso\text{-AmNO}_3] \quad (1)$$

In the range of media studied, about 30–55 per cent conversion to the nitrate ester occurs. Interaction of the medium with *iso*amyl alcohol is negligible. The identification of the nitronium ion as the esterifying agent follows from the demonstration of parallelism over a range of media of $\log k$ and $\log R$ where R is the ionization ratio $[R^+]/[R\text{OH}]$ for a base ROH which ionizes to form R^+ by the same process as that which converts nitric acid to the nitronium ion[2]. The relationship between $\log k$ and $\log R$ has been tested in the form of equation (2) :

$$d \log k/d \text{ percentage HClO}_4 = d \log R/d \text{ percentage HClO}_4 \quad (2)$$

in which R is the ratio $[NO^+]/[HNO_2]$ for the ionization of nitrous acid to the nitrosonium ion, NO^+, in aqueous perchloric acid[3], and as shown in Fig. 1, the rate of change of $\log k$ and of $\log [NO^+]/[HNO_2]$ with the medium are the same. The lack of parallelism of $\log k$ with the Hammett acidity function[4] $\boldsymbol{H}_0$ indicates that the esterifying agent is unlikely to be the nitracidium ion $H_2NO_3^+$.



Fg. 1

Equation 2 in its appropriate form was first used for aqueous sulphuric acid media[5] to verify that nitration of aromatic compounds proceeds through the nitronium ion over a wide range of media; R values used were those for the ionization ratio for a triphenylcarbinol indicator, and appreciable deviations were found from equation 2 in certain ranges. We have found that log R for 4-trimethylammonium triphenylcarbinyl methyl ether perchlorate plotted over the range 50–60 per cent perchloric acid gives a straight line of slope of 0·304, which is 10 per cent higher than those for the esterification rate and the $[NO^+]/[HNO_2]$ ratio given in Fig. 1. This suggests that correlations between rate and ionization ratio are dependent on the size of the molecules and ions concerned.

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20.

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D. Sc. 1960

784. *Nitration of Alcohols at Oxygen Centres. Part I. Criteria for the Nitronium-ion Mechanism in Aqueous Solutions of Strong Acids.*

By T. G. BONNER and D. E. FRIZEL.

The correlation of nitration rates in aqueous sulphuric acid with the acidity function, C_0, as a criterion of nitronium-ion mechanism is discussed. A new criterion for this mechanism in aqueous perchloric acid is put forward based on the ionisation of nitrous acid to the nitrosonium ion in this medium and its extension to sulphuric acid is considered. Comparison is made with the ionisation of certain triphenylmethanol-type indicators and in one case ionisation measurements in perchloric acid are reported for the first time.

THE elegant test for the operation of the nitronium mechanism in *C*-,[1] *N*-, and *O*-nitration [2,3] based on the demonstration of zeroth-order kinetics for sufficiently reactive substrates is decisive in the case of nitration by excess of nitric acid in a relatively weak acidic environment. Under such conditions the rate-controlling step becomes the dissociation of the nitric acidium ion $H_2NO_3^+$ to nitronium ion, NO_2^+ (nitryl cation), which is consumed rapidly and completely by the substrate. In a strongly acidic solvent this test is inapplicable as the nitronium ion is formed in a rapidly established equilibrium, and although its presence can be inferred and its potency assumed there is the necessity of proving that it is the active nitrating agent in this particular situation, particularly since it may be present in such minute concentrations that direct detection by physical methods is impossible.

A valuable criterion for the nitronium-ion mechanism in aromatic *C*-nitration in 80—90% sulphuric acid is the parallelism existing between the experimental rate constant of nitration, *k*, and the ionisation of a triphenylmethanol, ZOH, to its carbonium ion Z^+, which is based on the similarity in the mode of ionisation of nitric acid and triphenylmethanol:[4]

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \quad . \quad . \quad . \quad (1)$$

$$ZOH + 2H_2SO_4 \rightleftharpoons Z^+ + H_3O^+ + 2HSO_4^- \quad . \quad . \quad . \quad (2)$$

This method was extended to a wider range of sulphuric acid–water mixtures by means of eqn. (3) which applies to any single sulphuric acid solvent in which each base is present

$$pK_{ZOH} - pK_{HNO_3} = \log([Z^+]/[ZOH]) - \log([NO_2^+]/[HNO_3]) + \log(f_{Z^+}f_{HNO_3}/f_{NO_2^+}f_{ZOH}) \quad . \quad (3)$$

only in the cationic and neutral forms indicated.[5] K_{HNO_3} and K_{ZOH} are the thermodynamic equilibrium constants for the ionisations (1) and (2) and the *f* terms represent activity coefficients. The derivation of a useful relationship between *k* and the ionisation ratio $[Z^+]/[ZOH]$ depends on the constancy of the activity-coefficient ratio in (3) over a sufficiently wide range of sulphuric acid–water mixtures. Although direct demonstration of this constancy is not impossible since there is no analytical method of determining the ratio $[NO_2^+]/[HNO_3]$ independently, it was shown that the plots of $\log([Z^+]/[ZOH])$ for four different triphenylmethanol indicators against the percentage of sulphuric acid gave approximately straight lines which were reasonably parallel[6] and covered the range 65—90% sulphuric acid. This implies that the variation of $\log(f_{Z^+}/f_{ZOH})$ with composition of the medium is the same for each indicator. If it is assumed that the variation of $\log(f_{NO_2^+}/f_{HNO_3})$ with medium composition would be very similar, it follows that the difference in the log (ionisation ratio) terms in (3) is constant and independent of the medium and that in the region of acidity where the extent of ionisation of nitric acid to nitronium ion is small (*i.e.*, below about 86% sulphuric acid[7]), k is related to $[Z^+]/[ZOH]$ by eqn. (4).

$$\log k - \log ([Z^+]/[ZOH]) = \text{Constant} \qquad . \; . \; . \; . \; . \; . \qquad (4)$$

The application of eqn. (4) to *C*-nitration of the trimethyl-*p*-tolylammonium ion,[5] and to *N*-nitration of guanidine[8] and of methylnitroguanidine,[9] covering the range 71—82% sulphuric acid resulted in gradients of −1·20, −1·06, and −0·93 respectively for the plots of log k against log $([Z^+]/[ZOH])$. Although there is some spread of values around the theoretical value of unity, they are taken to prove that these reactions proceed through the nitronium-ion mechanism. The nitric acidium ion $H_2NO_3^+$ was excluded in all cases since there was no evidence for the correlation of k with the Hammett acidity function H_0 according to eqn. (5) which would be applicable in this event.

$$\log k + H_0 = \text{Constant} \qquad . \; . \; . \; . \; . \; . \; . \; . \qquad (5)$$

More useful general forms of eqn. (4) are based on the definition of acidity functions, *viz.*, H_R,[5] J_0,[10] and C_0[11] related to the ionisation of triphenylmethanol indicators. They are of the type shown in eqn. (6), which appears to have received the widest application.

$$\log k + C_0 = \text{Constant} \qquad . \; . \; . \; . \; . \; . \; . \; . \qquad (6)$$

where

$$C_0 = \mathrm{p}K_{\mathrm{ZOH}} - \log ([Z^+]/[ZOH]) \qquad . \; . \; . \; . \; . \; . \; . \qquad (7)$$

C_0 has been evaluated for the almost complete range of sulphuric acid–water mixtures by using a large number of indicators ionising according to eqn. (2), not all of which are triphenylmethanol derivatives. In applying this acidity function to the examination of nitration data, Deno and Stein tested eqn. (6) in the differentiated form (8):

$$\mathrm{d}\, C_0/\mathrm{d}\, \%H_2SO_4 = -\mathrm{d} \log k/\mathrm{d}\, \%H_2SO_4 \qquad . \; . \; . \; . \; . \; . \qquad (8)$$

or alternatively

$$\mathrm{d} \log Q/\mathrm{d}\, \%H_2SO_4 = \mathrm{d} \log k/\mathrm{d}\, \%H_2SO_4 \qquad . \; . \; . \; . \; . \; . \qquad (9)$$

where $Q = [Z^+]/[ZOH]$ with the implication that the gradients in (8) and (9) are determined for overlapping ranges of indicator ionisation and nitration measurement. In testing eqn. (8), Deno and Stein[12] found some serious weaknesses in this general method of analysing nitration results. $\mathrm{d}\, C_0/\mathrm{d}\, \%H_2SO_4$ changes from 0·12 in mixtures containing up to 25% sulphuric acid to a value of 0·26 over the range 60—90% sulphuric acid. Above 90% sulphuric acid, the value increased still further to 0·34. This variation in itself would not be objectionable provided that (*a*) the value of $\mathrm{d}\, C_0/\mathrm{d}\, \%H_2SO_4$ over the fixed range in which nitration rates are being measured is independent of the indicator selected for evaluation of C_0 in this range, and (*b*) over fixed ranges of medium composition, *e.g.*, 0—10%, 10—20%, 20—30%, etc., sulphuric acid, the gradient maintained a characteristic value not varying by more than, say, ±5%.

The evidence concerning condition (*a*) is conflicting. Table 1 gives the value of

TABLE 1.

Indicator	$\%H_2SO_4$	$\mathrm{d} \log Q/d\, \%H_2SO_4$
(I) 2-Phenylborneol[a]	58—68	0·25
(II) 3,3′,3″-Trichlorotriphenylmethanol[a]	64—72	0·25—0·26
(III) Chloro-4,4′-dinitrotriphenylmethane[a]	70—78	0·26—0·27
(IV) 4,4′,4″-Trinitrotriphenylmethanol[a]	84—92	0·26
(V) Methyl 4-trimethylammoniumphenylmethyl ether perchlorate[b]	58—66	0·26
(VI) 4,4′-Bis(trimethylammonium)triphenylmethyl methyl ether diperchlorate[c]	66—74	0·29
(VII) 4-Chloro-4′,4″-bis(trimethylammonium)triphenylmethyl methyl ether diperchlorate[b]	67—76	0·33
(VIII) Methyl 4,4′,4″-tris(trimethylammonium)triphenylmethyl ether triperchlorate[c]	79—85	0·34
(XI) 4,4′,4″-Tris(trimethylammonium)triphenylmethyl triperchlorate[c]	79—85	0·37
(IV) 4,4′,4″-Trinitrotriphenylmethanol[c]	83—91	0·30

[a] Ref. 11. [b] Ref. 13. [c] Ref. 6.

d log Q/d %H_2SO_4 for four indicators (I—IV) reported by Deno *et al.*[11] and six (IV–IX) by Williams *et al.*[6,13] which collectively cover the range 60—90% sulphuric acid. The differences in the values of the gradients between the two groups are apparent; in addition, the results for (IV) which is common to both groups differ appreciably. In a detailed examination of the applicability of eqn. (8) to nitration data, Deno and Stein[12] found that the equality of the gradients for log k and C_0 was maintained up to 62% sulphuric acid but above this acidity considerable divergence ensued, *e.g.*, for the nitration of nitrobenzene in 80—87·5% sulphuric acid the value of d log k/d %H_2SO_4 is 0·39 while d C_0/d %H_2SO_4 is 0·26. The previously employed test of the nitronium-ion mechanism with eqn. (4) or (6) would give a satisfactory result of 1·18 for the slope of log k against log Q for indicator (VIII) but the less acceptable result of 1·50 for the similar plot of log k against C_0. Differences in ionisation characteristics of the type evident in Table 1 are usually attributed to a difference in the activity coefficient functions d log (f_{Z^+}/f_{ZOH})/d %H_2SO_4 arising from variation in charge type or molecular size. The difficulty of prediction in this matter is evident from the fact that while there are marked differences between the singly, doubly, and triply charged types of the lower group there are none between the uncharged types of the upper group and the singly charged indicator (V). It is possible that this factor may depend on the range of media in which comparisons are made and it has been pointed out that activity coefficients of a variety of oxygen-containing compounds change rapidly over the range 65—80% sulphuric acid.[12] This may be a particularly vulnerable region but the deviations are also apparent in higher acidities and it has been recently shown for certain compounds that d (log f)/d %H_2SO_4 changes very rapidly above 80% sulphuric acid.[14]

A closer examination of the published data on the ionisation of the indicators (IV), (VI), (VII), and (IX) in the lower group of Table 1 suggests that the other condition (*b*) is also not very satisfactorily fulfilled. The plots of log Q against the percentage of sulphuric acid all show a distinct curvature corresponding to a marked change in gradient over even smaller ranges of media than the arbitrarily chosen 10% range. The variation in gradient with range of media is shown in Table 2. In the case of (VIII) the marked curvature evident at very low ionisation has been dismissed as insignificant[5] but although this view may be erroneous this part of the curve has not been used in calculating the data for (VIII) in Table 2. The greater precision which has been achieved[15] in the determination of $[Z^+]/[ZOH]$ values confirms the conclusions implicit in Table 2. Although the limited results reported[11] for indicators used in the evaluation of the C_0 scale do not show the same wide variations it was noted that certain indicators showed a lack of constancy in this property and these were rejected as unsuitable.

TABLE 2.

Indicator	(VI)		(VIII)		(IX)		(IV)	
%H_2SO_4	65—71	70—74	80—82	82—85	80—82	82—85	83—87	87—90
d log Q/d %H_2SO_4	0·26	0·34	0·33	0·36	0·36	0·39	0·33	0·26

The failure of d log Q/d %H_2SO_4 to possess the same value for different indicators, or even to maintain for many individual indicators the constancy required to provide a useful test for the nitronium-ion mechanism, indicates the uncertainty involved in assuming that d log (f_{R^+}/f_{ROH})/d %H_2SO_4 is the same for all compounds ionising according to eqns. (2) or (3). The degree of success of equations (4), (6), (8), or (9) in diagnosing a nitronium-ion mechanism is clearly controlled by the choice of compound for the measurement of $[Z^+]/[ZOH]$ ratios over the range where nitration rates have been measured.

The need to compare nitration rates with the ionisation of a compound as closely similar in size and structure as possible to nitric acid is evident. This became possible with reports of the determination of the extent of ionisation in aqueous perchloric acid of nitrous acid to the nitrosonium (nitrosyl) ion NO^+ according to eqn. (10)[16] and similarly in

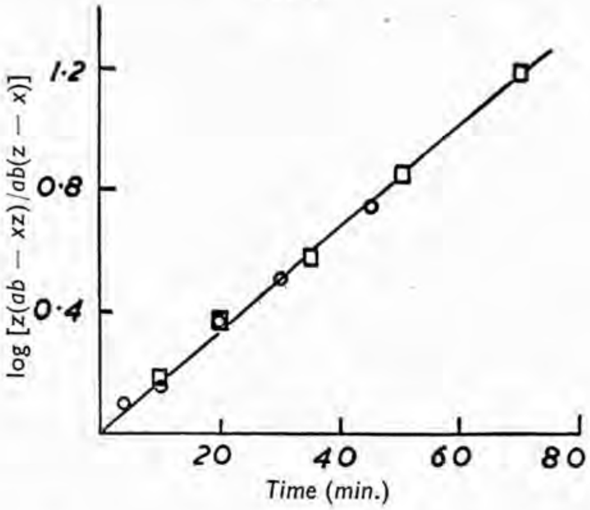
$$HNO_2 + 2HClO_4 \rightleftharpoons NO^+ + H_3O^+ + 2ClO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

aqueous sulphuric acid.[17] As a result of these reports, data were available on the ionisation ratio $[NO^+]/[HNO_2]$ over the range 45—56% perchloric acid and 50—75% sulphuric acid. Several alcohols were investigated to select a suitable one for measurement of *O*-nitration rates in a near or overlapping range of media, and isopentyl alcohol was found to be the most satisfactory. It is rapidly and almost quantitatively converted into its nitrate ester with a mixture of nitric and sulphuric acid at 0° with no apparent oxidation.[18] At 0° and 25° measurable rates of nitration were obtained within the range of 57—75% sulphuric acid with attainment of an unchanging equilibrium in a reasonably short time. The comparable range for perchloric acid at 25° was 55—62·5% acid. In both media, the extremely small amount of oxidation of the alcohol which was detected was eliminated by addition of 0·001M-sulphamic acid. With fixed initial concentrations of isopentyl alcohol (0·07M) and nitric acid (0·15M) the experimental rate equation corresponded to a second-order forward reaction (the *O*-nitration) opposed by a first-order reverse reaction (hydrolysis of isopentyl nitrate). The nitration rate constant, k, was calculated from eqn. (11) where

$$kt\,(ab - z^2) = 2{\cdot}3\,z \log\,[z(ab - zx)/ab\,(z - x)] \quad . \quad . \quad . \quad (11)$$

a and b are the initial concentrations of nitric acid and isopentyl alcohol and x and z are the concentrations of isopentyl nitrate at time t (minutes) and at equilibrium respectively.

FIG. 1.



In all rate measurements the plot of $\log\,[z(ab - zx)/ab(z - x)]$ against t was a straight line from the slope of which k was calculated (see Fig. 1 for a duplicated typical experi-

TABLE 3. *Rates of* O-*nitration of isopentyl alcohol.*

Initial [isopentyl alcohol] = 0·07M; $[HNO_3]$ = 0·15M

Perchloric acid at 25°.							
$\%HClO_4$	62	60·8	59·3	58·0	56·3	55·2	
k	1·56	0·71	0·275	0·100	0·051	0·0222	
	1·58	0·72	0·267	0·102	0·049	0·0225	
Ester (%)	54	46	38	34	28	25	
Sulphuric acid at 25°.							
$\%H_2SO_4$	67·0	66·0	65·3	63·5	62·4	60·0	57·7
k	0·312	0·254	0·218	0·095	0·051	0·0170	0·0074
	0·318	0·249	0·221	0·093	0·049	0·0174	0·0072
Ester (%)	65	68	66	56	48	42	38
Sulphuric acid at 0°							
$\%H_2SO_4$	74·6	72·7	71·4	69·7	68·0	64·6	
k	1·53	0·59	0·343	0·088	0·0351	0·0059	
	1·46	0·60	0·348	0·086	0·0340	0·0060	
Ester (%)	66	63	62	59	55	49	

k is the rate constant obtained graphically from eqn. (11). Ester (%) refers to the percentage conversion of isopentyl alcohol into isopentyl nitrate at equilibrium.

ment). The rate constants obtained for O-nitration in aqueous perchloric acid and sulphuric acid are given in Table 3 together with the percentage conversion of the alcohol into nitrate at equilibrium. The test for the nitronium-ion mechanism in perchloric acid is that equation (12) should be satisfied,

$$d \log k/d \,\%HClO_4 = d \log (NO^+/HNO_2)/d \,\%HClO_4 \quad . \quad . \quad . \quad (12)$$

it being assumed that d log ($f_{NO_2^+}/f_{HNO_3}$)/d $\%HClO_4$ and d log (f_{NO^+}/f_{HNO_2})/d $\%HClO_4$ are closely similar. The plots of log k and of log ($[NO^+]/[HNO_2]$) against percentage of perchloric acid are shown in Fig. 2. The best line through each set of points being taken, both gradients are 0·27. It is possible to discern a slight curvature in the plot of log k, and if this is assumed to be real an increase in gradient from 0·27 to 0·30 with increasing acidity is evident. Discounting the highest point on the log $[NO^+]/[HNO_2]$ line, since it corresponds to more than 95% ionisation and is therefore liable to considerable inaccuracy, we cannot decide, with the limited data, whether any similar curvature occurs in this case. It is clear, however, that in the absence of more accurate ionisation measurements the correspondence required by eqn. (12) and by the similar equations (4), (6), (8), and (9) may not be closer than 10% even in the most favourable circumstances.

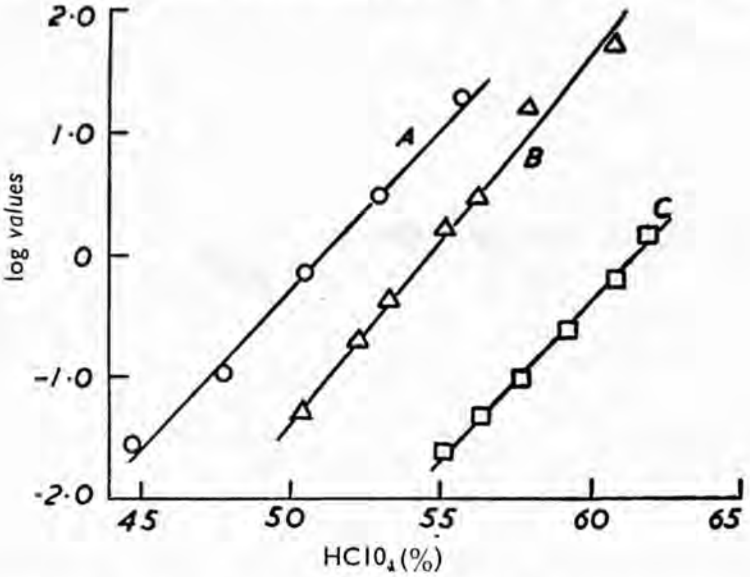


FIG. 2.

A, Plot of log ($[NO^+]/[HNO_2]$); slope 0·27.
B, Plot of log ($[Z^+]/[ZOH]$); slope 0·31.
C, Plot of log k; slope 0·27.

For comparison, some ionisation ratios for indicator (V) (Table 1) were measured in 50—56% perchloric acid and log ($[Z^+]/[ZOH]$) is included in Fig. 2. Again, more data are desirable bnt the best line has a gradient of 0·31 which is close enough to that of the log k value to provide an acceptable proof of the nitronium-ion mechanism. Divergences of this order have been recognised for some time in applications of eqn. (5).[19]

The application of a similar equation to (12) to the results obtained in sulphuric acid is more complicated. Bayliss and Watts[17] do not mention the difficulties noted in this medium by Singer and Vamplew[16] of (i) a large shift in the position of the maximum in the absorption spectrum of the nitrosonium ion with change in acidity, and (ii) appreciable loss of nitrous acid in aqueous acid solutions; these difficulties led the latter authors to abandon sulphuric acid in favour of perchloric acid for their studies. Further, although the latter authors found no evidence in perchloric acid for a third entity such as $H_2NO_2^+$, since the sum of the nitrosonium ion and molecular nitrous acid concentrations corresponded to the initial amount of nitrous acid determined by chemical analysis, Bayliss and Watts found a discrepancy between the two amounts which rose to a maximum between 50% and 65% sulphuric acid which they accounted for by postulating the existence of the $H_2NO_2^+$ ion. In view of this uncertainty about the composition of nitrous acid solutions in sulphuric acid, two different procedures have been employed to obtain d log (NO^+/HNO_2)/d $\%H_2SO_4$; first, values of log $[NO^+]/[HNO_2]$ were calculated in which $[HNO_2]$ was the figure quoted as the concentration of molecular nitrous acid found directly by absorption spectra measurement. Secondly, log $([NO^+]/[HNO_2]_T)$ was evaluated, where $[HNO_2]_T$ is the sum of the values given for $[HNO_2]$ and $[H_2NO_2^+]$, *i.e.*, the figure obtained by subtracting the spectroscopically determined NO^+ from the initial total nitrous acid concentration; this is in effect what the molecular nitrous acid concentration would be if no $H_2NO_2^+$ or any other third form of nitrous acid were present. As shown in Fig. 3, in both cases the plot of log (ionisation ratio) against the percentage of sulphuric acid follows the same course; a straight line is obtained over the range 50—62% sulphuric acid over which the ionisation to nitrosonium ion increases to 60%, followed by a sharp change of slope at higher acidities where the rapid increase in conversion of nitrous acid into nitrosonium ion increases the error in evaluating the ionisation ratio. The significant result is that over the range 50—62% sulphuric acid the gradients for log $([NO^+]/[HNO_2])$ and log $([NO^+]/[HNO_2]_T)$ are 0·19 and 0·17 respectively while d log k/d %H_2SO_4 is 0·19. Although there may be some uncertainty in the interpretation of the ionisation data, the closeness of these values is acceptable evidence of the nitronium-ion mechanism for this region of sulphuric acid–water mixtures. A comparison of the nitration rates with the ionisation ratios of triphenylmethanol type indicators shows that much greater divergences exist, since both d C_0/d %H_2SO_4 and d log Q/%H_2SO_4 for indicator (V) have a value of 0·26; otherwise expressed, a plot of log k against C_0 [or log Q for (V)] would have a gradient of 0·64 instead of unity. It is a coincidence that at 0° d log k/d %H_2SO_4 is 0·25, and this large difference from the value at 25° underlies the necessity, often disregarded, of comparing kinetic and ionisation data at the same temperature.

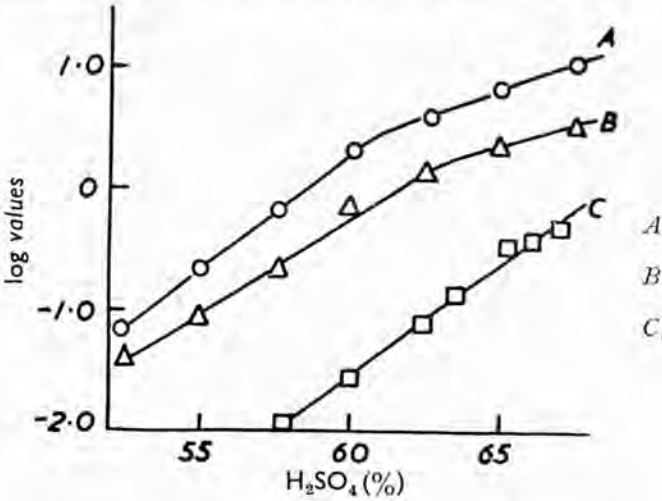


Fig. 3.

A, Plot of log $([NO^+]/[HNO_2])$; slope 0·19 (52—60% H_2SO_4).
B, Plot of log $\{[NO^+]/[H_2NO_2^+] + [HNO_2]\}$; slope 0·17 (52—60% H_2SO_4).
C, Plot of log k; slope 0·19.

One conclusion which may be drawn from the diagnostic value of equations (4), (6), (8), and (9) in perchloric acid as compared with the large divergences in sulphuric acid is that effects of the medium operate much more strongly in the latter. This difference in behaviour of the solvent has already been observed in the denitration of nitroguanidines in the two acids, and led to the view that in sulphuric acid alone solvent species participated in the transition state of denitration.[20] The shifting of absorption bands characteristic of the nitrosonium ion with change of medium in sulphuric acid and the absence of this effect in perchloric acid [16] is further evidence of the contrast between these solvents. A comparison of the ionisation characteristics of a number of triphenylmethanol-type indicators in perchloric acid would obviously be useful in comparing the extent of the variation of log (f_{Z^+}/f_{ZOH}) with medium composition with that in sulphuric acid.

EXPERIMENTAL

Materials and Media.—Commercial isopentyl alcohol was repeatedly distilled (b. p. 130°). Isopentyl nitrate was prepared by the gradual addition of isopentyl alcohol to a 1 : 3 (v/v) mixture of concentrated nitric acid and concentrated sulphuric acid at 0°. After the separation of an oily layer in a few minutes, the mixture was poured into a large volume of water. The oil was extracted with ether and the ether solution dried and distilled. The yield of isopentyl nitrate was 95%, and the b. p. 147°.

Sulphuric and perchloric acid media were obtained by dilution of the " AnalaR " concentrated solutions and standardised with N-sodium hydroxide referred through N-hydrochloric acid to potassium iodate and to potassium hydrogen phthalate as standards. The strengths of the acids are given to the nearest 0·1%. Anhydrous nitric acid was prepared as required by distillation under reduced pressure from a 2 : 3 (v/v) mixture of concentrated nitric and concentrated sulphuric acid.

Analysis of Reaction Mixtures.—Measurements with a Hilger Uvispek instrument in aqueous solution showed that absorption by isopentyl alcohol was negligible while with isopentyl nitrate the absorption steadily decreased from $\varepsilon = 33$ at 2400 Å to $\varepsilon = 1·54$ at 3800 Å with no maxima. Isopentyl nitrate could be virtually completely extracted from a dilute aqueous acid solution in one operation by hexane and the residual solution analysed for nitrate ion ($\varepsilon = 7·1$ at 2940 Å). Solvent interaction with isopentyl alcohol only became noticeable in very strongly acid solutions and was not detectable in the time taken to attain nitration equilibrium in the strongest acids used for rate measurement, *viz.*, 75% sulphuric acid and 62·5% perchloric acid. Very slight oxidation of the alcohol in those acids was detected by small changes in absorption and was completely eliminated without side effects by the addition of 0·001M-sulphamic acid. The rate constants for *O*-nitration in 75% sulphuric acid in the presence and in the absence of sulphamic acid were 1·46 and 1·55 respectively.

To confirm that the reaction being followed was an uncomplicated *O*-nitration one preparative experiment was carried out at 0° in 72·7% sulphuric with initial concentrations of 1M-nitric acid and 0·5M-isopentyl alcohol, *i.e.*, 7 times larger than those used in kinetic measurements. After 15 min. (the time indicated in the kinetic run for the attainment of equilibrium the mixture was added to 200 ml. of water and the oily product extracted with hexane. After drying and removal of the hexane, the residual oil corresponded to a 65% yield of isopentyl nitrate; the yield indicated by analysis of the equilibrium mixture in the kinetic run was 63%. On distillation the whole of the oil distilled at 145°. The failure of hexane to extract isopentyl alcohol from the aqueous acid solution was shown by separately shaking a solution of 1 g. of isopentyl alcohol in 50 ml. of 25% sulphuric acid with 10 ml. of hexane and drying and distilling the hexane extract. The residue weighed less than 50 mg.

Kinetic Measurements.—All rates were determined at 0° and 25° for sulphuric acid and at 25° for perchloric acid solutions with initial concentrations of 0·07M-isopentyl alcohol and 0·15M-nitric acid. Solutions of 0·001M-sulphamic acid and 0·3M-nitric acid were separately prepared in the acid medium at the thermostat temperature (0° or 25°). 20 ml. of the sulphamic acid solution were transferred to the reaction vessel, and the required amount of isopentyl alcohol was added. The reaction was started by delivering 20 ml. of the nitric acid solution from a pipette into the alcohol solution, zero time corresponding to the moment the addition started. 5 ml. samples of the reaction mixture were removed at appropriate intervals and quenched by running them into 10 ml. of distilled water cooled in ice. The solution was shaken with 10 ml. of hexane, and the aqueous layer separated and analysed by measuring the absorption at 2940 Å with the Hilger Uvispek instrument. The amount of nitric acid present was found by comparing this reading with that obtained by treating 5 ml. of the original nitric acid solution in the same way. A check was provided by similar absorption measurement of a solution of potassium nitrate in 70% sulphuric acid diluted in the same manner.

Ionisation of Methyl 4-Methylammoniumtriphenylmethyl Ether Perchlorate in Perchloric Acid.—A pure sample was available.[13] The extent of ionisation to the carbonium ion was about 5% in 50% perchloric acid and was complete in the 64·2% acid with maximum absorption at 4420 Å (ε 34,000). The ionisation ratios $[Z^+]/[ZOH]$ at intermediate acidities were evaluated by the usual procedure [6] and the log Q values are plotted in Fig. 2.

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785. *Nitration of Alcohols at Oxygen Centres. Part II.*[1] *The Equilibria established in Aqueous Sulphuric and Perchloric Acids and the Mechanism of Hydrolysis of the Nitrate Ester.*

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D.Sc. 1960

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The extent of conversion of 2,4-dinitrobenzyl alcohol into its nitrate and sulphate esters in *O*-nitration experiments in a wide range of sulphuric acid–water mixtures has been measured. Similar experiments with isopentyl alcohol have indicated a mechanism for the hydrolysis of isopentyl nitrate in both aqueous sulphuric and perchloric acid. A relationship between the equilibrium constant, K_N, for *O*-nitration and functions which are a measure of the acidity of the media is deduced and tested.

THE conversion of alcohols into their nitrate esters in high yields can frequently be accomplished by means of nitric acid–sulphuric acid–water mixtures.[2] Numerous studies on hydroxy-compounds have demonstrated both the influence of solvent composition on the yield of nitrate ester and the occurrence of the oxidation and sulphation side reactions.[3] The sulphation in the absence of nitric acid has recently been the subject of a detailed kinetic study in which 2,4-dinitrobenzyl alcohol and ethyl alcohol have been employed.[4] 2,4-Dinitrobenzyl alcohol was suitable for *O*-nitration since unlike ethyl alcohol it was completely resistant to oxidation in the mixed acid. Preliminary experiments on the composition of the equilibrium mixture formed by 0·1M initial concentrations of the alcohol and nitric acid in the range 79—93% sulphuric acid showed that the amount of alcohol consumed was only slightly greater than that converted into the sulphate ester.[4] It was therefore necessary to determine the nitrate ester independently and this was achieved by first oxidising the unchanged alcohol quantitatively with acidic dichromate [3] and then extracting the nitrate ester with an organic solvent for analysis. The concentration of the nitrate ester was thus determined directly and the sulphate ester was obtained by difference from the total 2,4-dinitrobenzyl alcohol consumed. Analyses of reaction mixtures showed that the rates of *O*-nitration were too fast for measurement even at 0° in 70% sulphuric acid and at lower acidities than this the yield of nitrate ester was negligible unless the nitric acid was present in considerable excess over the alcohol. Results at 0° for the range 55—93% sulphuric acid are given in Table 1. These show that with equimolecular initial concentrations of the alcohol and nitric acid in the more concentrated

TABLE 1. *O-Nitration and sulphation of 2,4-dinitrobenzyl alcohol at* 0°.

% H_2SO_4	[HNO_3] (M)	[Alcohol] (M)	[Nitrate ester] (M)	Time (min.)	Nitrate ester (%)	Sulphate ester (%)
93	0·1	0·1	—	7	3·7	86
				240	4·1	85
87	0·1	0·1	—	6	19	43
				180	4	80
73	0·1	0·1	—	7	7	3
				240	8	8
70	0·1	0·1	—	7	6	1
				240	5	4
65	0·1	0·1	—	7	0	0
				240	2	0
65	2·0	0·08	—	4	2	—
				30	17	—
				120	17	—
65	4·0	0·1	—	45	55	—
				75	60	—
55	4·0	0·1	—	20	23	—
				35	34	—
				50	43	—
87	—	—	0·1	6	10	74
				180	9	78
77	—	—	0·1	100	9·7	18
75	—	—	0·1	210	5·6	25

sulphuric acids the nitrate ester is initially formed much more rapidly than the sulphate ester but the latter is finally in large excess in the equilibrium mixture. The nitronium ion is clearly much more reactive than the sulphating entity but the *O*-nitration is reversed as the alcohol is gradually solvolysed; in addition, there may be direct conversion of the nitrate into sulphate ester. Attempts to follow the rate of hydrolysis of the nitrate failed because of the considerable time required for dissolution of the ester in all media except the most strongly acidic where reaction was too fast for measurement. The few analyses of mixtures obtained by starting with nitrate ester are included in Table 1 and they confirm the ultimate predominance of the sulphate ester.

The result of these investigations suggested that a larger proportion of nitrate ester might result even in the stronger acids if a higher initial concentration of nitric acid relative to the alcohol was used for all experiments at 25°; therefore a threefold excess of nitric acid were used. The composition of these equilibrium mixtures are expressed in terms of the equilibrium constants K_N and K_S for nitration and sulphation respectively. K_S, as previously defined,[4] is represented by (1) and K_N by (2), in which the bracketed quantities represent the experimentally determined concentrations at equilibrium. The constancy

$$K_S = [RSO_4]/[ROH] \quad (1)$$

$$K_N = [RO{\cdot}NO_2]/[ROH][HNO_3] \quad (2)$$

during several hours of the equilibrium composition once attained and the reproducibility of the analytical measurements are shown by the typical set of results for two duplicated experiments recorded in Table 2*a*. Errors in the alcohol and nitrate determinations are magnified in calculating K, but the largest difference between duplicate values of the latter is not more than 5%. Results for the range 75—85% sulphuric acid at 25° are given in Table 2*b*. The falling K_S and K_N values with decreasing acidity reflect the lower yields of both esters. The variation of K_S with composition of the medium in fact is in excellent accord with that obtained in the same range of media in the absence of nitric acid by Williams and Clark.[4]

TABLE 2. O-*Nitration and sulphation of 2,4-dinitrobenzyl alcohol at 25°.*

(*a*) Analyses of equilibrium mixtures in duplicate experiments in 80·7% H_2SO_3.

Initial concns.: [Alcohol] = 0·100M; $[HNO_3]$ = 0·318M.

Time (hr.)	10^2 [Alcohol] (M)		10^2 [Nitrate ester] (M)		10^2 [Sulphate ester] (M)		K_N		K_S	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1	4·00	4·07	2·03	2·01	3·97	3·92	1·71	1·66	0·99	0·96
2	4·07	4·10	2·01	2·02	3·92	3·88	1·66	1·66	0·96	0·95
3	4·11	4·11	2·05	2·01	3·84	3·88	1·68	1·64	0·94	0·95
4	4·03	4·03	2·01	2·04	3·96	3·93	1·67	1·76	0·98	0·97

K_N (mean) = 1·67; K_S (mean) = 0·96.

(*b*) Variation of K_N and K_S with composition of the medium. Initial concns.: [Alcohol] = 0·100M; $[HNO_3]$ = 0·300M.

H_2SO_4%	84·9	82·5	80·7	78·6	76·8	74·6
K_N	2·87	2·08	1·67	1·23	0·95	0·71
K_S	2·22	1·41	0·96	0·76	0·55	0·46
$\log K_N - H_0 + C_0$...	−7·39	−7·23	−7·13	−7·10	−6·92	−6·75

Acid Hydrolysis of Nitrate Ester.—It is reasonable to assume that in either reverse reaction, the hydrolysis of the ester if it could be measured directly would be of the first order with respect to the ester. If, for nitration, the rate constants of the esterification reaction and the hydrolysis are k_2 and k_1 respectively, then at equilibrium

$$k_2[ROH][HNO_3] = k_1[RO{\cdot}NO_2] \quad (3)$$

and hence

$$k_1 = k_2/K_N \quad (4)$$

It was possible to measure K_N only for 2,4-dinitrobenzyl alcohol in these media and not k_2. For isopentyl alcohol however rates of esterification were measurable at 25° both in sulphuric acid and in perchloric acid solutions.[1] Isopentyl nitrate, like 2,4-dinitrobenzyl nitrate, dissolved too slowly in media in which rates of hydrolysis would have been measurable, and k_1 could not be determined directly. Calculated values of k_1 were however obtained from eqn. (4) and are recorded in Table 3. In the strongest acid employed, 75% sulphuric acid, equilibrium was attained in 15 minutes and during this time sulphation of isopentyl alcohol is negligible.

TABLE 3. *O-Nitration of isopentyl alcohol* (k_2) *and hydrolysis of isopentyl nitrate* (k_1) *at* 25°.

(*a*) In perchloric acid

$HClO_4$%	10^2k_2	K_N	$k_1 = k_2/K_N$	$\log K_N - H_0 - \log([Z^+]/[ZOH])$
62·0	157	10·0	0·157	4·29
60·8	71	7·39	0·096	4·27
59·3	27	5·93	0·0457	4·33
58·0	10·1	4·10	0·0246	4·31
56·3	5·0	3·24	0·0155	4·39
55·2	2·23	2·43	0·0092	4·38

(*b*) In sulphuric acid

H_2SO_4%	10^2k_2	K_N	$k_1 = k_2/K_N$	$\log K_N - H_0 + C_0$
67·0	31·5	19·5	0·0162	−4·28
66·0	25·2	22·4	0·0113	−4·07
65·3	21·9	20·2	0·0108	−4·01
63·5	9·4	13·5	0·0070	−3·97
62·4	5·04	8·3	0·0061	−4·00
60·0	1·72	5·6	0·0031	−3·87
57·7	0·73	3·71	0·0020	−3·73

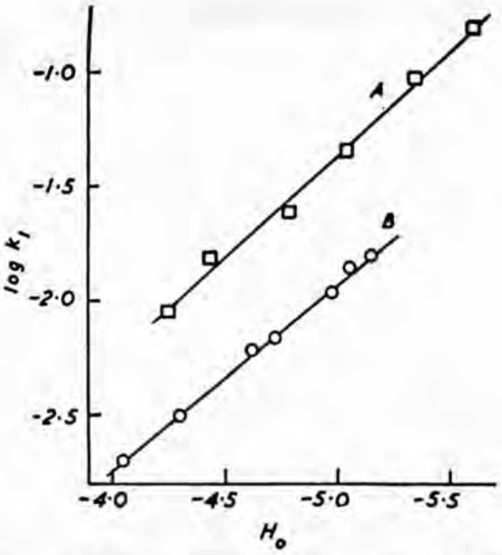


FIG. 1. *A*, $HClO_4$. *B*, H_2SO_4.

The calculated values of k_1 show that in both sulphuric and perchloric acid the rate of hydrolysis of isopentyl nitrate increased with acidity but only about half as rapidly as the forward esterification. Since the rate constant of esterification shows an approximate parallelism[4] with the acidity function, C_0, which increases about twice as rapidly as the Hammett acidity function, H_0, with increasing acid strength of the medium the possibility of a direct dependence of the hydrolysis rate constant on H_0 was evident. This was tested by plotting values of log k_1 at 25° against H_0 for both acids. Fig. 1 shows that reasonably good straight-line plots are obtained; the gradients of —0·92 for perchloric acid and of —0·85 for sulphuric acid are sufficiently close to unity to suggest that hydrolysis proceeds through the protonated nitrate ester formed in fractionally small amount.[5] This result also implies that the transition state involves only the protonated ester and does not include a molecule of water.[6] Protonation of a nitrate ester followed by release of a nitronium (nitryl) ion appears to occur in the concentrated acid since such solutions are nitrating media and in pure sulphuric acid there is cryoscopic evidence [7] of the production of five entities per molecule of added nitrate ester which can be represented by equations (5) and (6).

$$\mathrm{RO{\cdot}NO_2 + H_2SO_4 \rightleftharpoons ROH + NO_2^+ + HSO_4^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$
$$\mathrm{ROH + 2H_2SO_4 \rightleftharpoons RO{\cdot}SO_3H + H_3O^+ + HSO_4^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In aqueous ethanol it has been reported that the hydrolysis of nitrate esters is not catalysed by acids [8] and this is attributed to the loss of resonance stabilisation which would result from protonation of the nitrate group. The hydrolysis of methyl nitrate in aqueous solution also proceeds without any detectable catalysis by the nitric acid formed.[9] However in strongly acidic solutions the existence of a small fraction of the nitrate ester in the form of its conjugate acid is feasible and the extent of conversion into this form would increase with the acidity. The lower stability resulting from loss of resonance stabilisation would be relieved by the loss of a nitronium ion.

Dependence of K_N on the Acidity of the Media.—From the mechanisms which have been deduced for the esterification [1] and the hydrolysis, the equilibrium set up in strongly acidic media between an alcohol and its nitrate ester can be represented by eqn. (7):

$$\mathrm{ROH + NO_2^+ \rightleftharpoons RO{\cdot}NO_2 + H^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If K_0 represents the thermodynamic equilibrium constant, then by combining eqns. (7) and (2) we have

$$K_0/K_N = [\mathrm{HNO_3}](\mathrm{H^+})f_{\mathrm{RONO_2}}/[\mathrm{NO_2^+}]f_{\mathrm{ROH}}f_{\mathrm{NO_2^+}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where square brackets represent concentrations, parentheses activities, and f activity coefficients. Taking logarithms and combining this with eqn. (9) [5] and (10),[10]

$$H_0 = -\log\,(\mathrm{H^+})f_{\mathrm{B}}/f_{\mathrm{BH^+}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$
$$\mathrm{p}K_{\mathrm{HNO_3}} - \mathrm{p}K_{\mathrm{ZOH}} = \log\,([\mathrm{NO_2^+}]/[\mathrm{HNO_3}]) - \log\,([\mathrm{Z^+}]/[\mathrm{ZOH}]) \quad . \quad . \quad (10)$$

where B represents a Hammett-type base and ZOH a triphenylmethanol-type compound, we can derive (11):

$$\log K_N - H_0 - \log\,([\mathrm{Z^+}]/[\mathrm{ZOH}]) = \Sigma\mathrm{p}K - \Sigma \log f \quad . \quad . \quad . \quad (11)$$

where $\Sigma\mathrm{p}K = \mathrm{p}K_{\mathrm{HNO_3}} - \mathrm{p}K_{\mathrm{ZOH}} - \mathrm{p}K_0$

and $\Sigma \log f = \log\,(f_{\mathrm{RONO_2}}f_{\mathrm{BH^+}}/f_{\mathrm{ROH}}f_{\mathrm{B}}f_{\mathrm{NO_2^+}})$

If the $\log f$ term is not subject to considerable change over short ranges of media, the left-hand side of eqn. (11) should show some evidence of constancy. For perchloric acid, use of $\log\,([\mathrm{Z^+}]/[\mathrm{ZOH}])$ values for the indicator methyl 4-trimethylammoniumtriphenylmethyl ether perchlorate [1] makes the expected constancy quite evident, the sum of the three terms over the range 55—62% perchloric acid being $4{\cdot}33 \pm 0{\cdot}06$. For sulphuric acid, values of C_0 were used in place of the term $\log\,([\mathrm{Z^+}]/[\mathrm{ZOH}])$ since by definition [11] these terms only differ by the constant $\mathrm{p}K_{\mathrm{ZOH}}$; when eqn. (11) is tested in this form it is apparent that constancy is attained over the range 62—66% sulphuric acid for isopentyl alcohol and, less definitely, over the range 79—82% sulphuric acid for 2,4-dinitrobenzyl alcohol (see Fig. 2), although these ranges are considerably narrower than in perchloric acid (they correspond to *ca.* $0{\cdot}5H_0$ unit for both sulphuric acid ranges compared with the $1{\cdot}3H_0$ units for perchloric acid).

Previous discussion [1] has indicated that this difference in the two solvents is probably due to a greater diversity in the variation of activity coefficient ratios with composition of the medium in sulphuric acid. It would be useful to extend these studies to other alcohols to see if greater accord between the behaviour of the two solvents is possible in other ranges of media. For this purpose it would suffice to determine the equilibrium composition since eqn. (11) only requires evaluation of K_N and not of individual rate constants; the rapidity with which equilibrium is established is unimportant. In addition, the concurrent sulphation in sulphuric acid does not present any problem provided that analyses can be carried out as in the case of 2,4-dinitrobenzyl alcohol.

In the related equilibria set up when guanidines are nitrated or nitroguanidines denitrated in aqueous strong acids,[12] a direct dependence of the equilibrium constant K on the activity of water present has been found on the assumption that water participates in the equilibrium. The relationship is tested by a plot of log K against log (H_2O) which should give a straight line of negative unit slope. This has not been found to apply to the esterification reported here.

It has been assumed in this discussion that if any protonation of isopentyl alcohol or dinitrobenzyl alcohol occurs in the range of media investigated, this is limited for both compounds to a small amount. The arguments in favour of this view have already been considered for 2,4-dinitrobenzyl alcohol [4] and undoubtedly would apply to isopentyl alcohol. Any extensive change of protonation of either alcohol with increasing acidity in the ranges of media studied would have been revealed in the kinetic analysis.

EXPERIMENTAL

Materials and Media.—The preparation and standardisation of acids and the procedures used for isopentyl alcohol and nitrate have been described.[1] 2,4-Dinitrobenzyl alcohol was prepared [13] from 2,4-dinitrobenzyl chloride by conversion into acetate and hydrolysis of this with 50% sulphuric acid at 120°. The product, crystallised successively from water (with charcoal present), methanol, and benzene, had m. p. 115—116°. 2,4-Dinitrobenzyl nitrate was obtained in excellent yield by the action of freshly prepared anhydrous nitric acid on the alcohol. 15 g. of anhydrous nitric acid were added slowly to 5 g. of 2,4-dinitrobenzyl alcohol with shaking at 0°. After a few minutes, the solution was poured on ice and the yellow oil which separated was allowed to solidify. Recrystallisation gave 4·5 g. (70% yield) of 2,4-dinitrobenzyl nitrate, m. p. 39·5°.

Analysis of Reaction Mixtures.—The residual 2,4-dinitrobenzyl alcohol was determined by oxidation with dichromate in 6N-sulphuric acid by Williams and Clark's [3] method; neither nitric acid nor 2,4-dinitrobenzyl nitrate interfered. In preliminary experiments to find the relative extent of nitration and sulphation, the residual nitric acid was determined by the standard method [14] of reduction with excess of ferrous ammonium sulphate and back-titration with dichromate; the nitrate ester which would have interfered in this determination was first removed by extraction with carbon tetrachloride. In the experiments in which the presence of excess of nitric acid made this method unsuitable, the carbon tetrachloride extract of nitrate ester was evaporated to dryness and the residual oil dissolved in concentrated sulphuric acid and analysed for nitrate by direct titration with ferrous sulphate solution.[15]

FIG. 2. *A*, *2,4-Dinitrobenzyl alcohol; B, Isopentyl alcohol.*

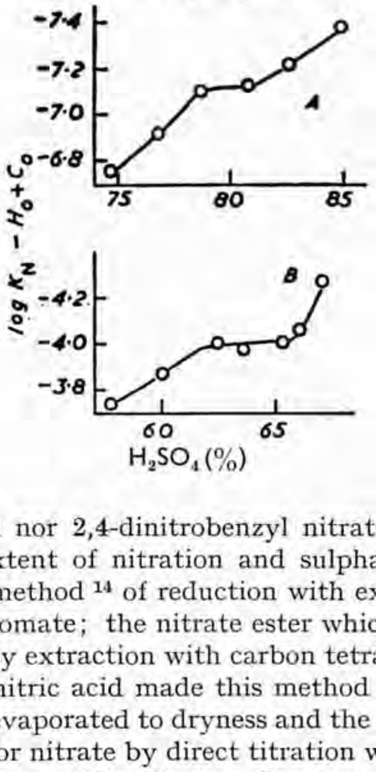
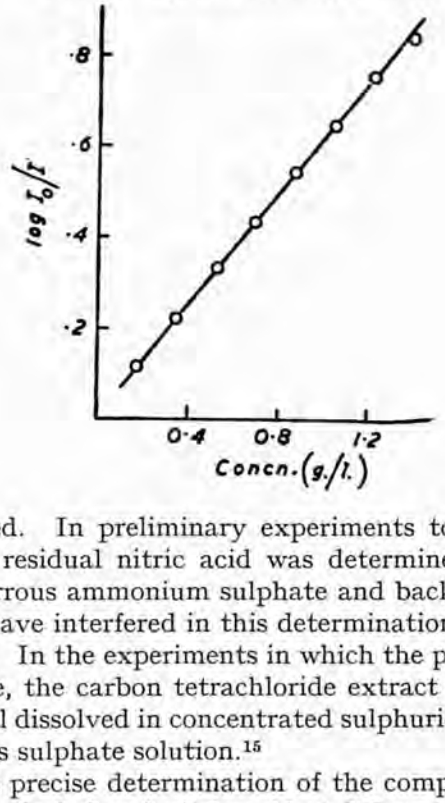


FIG. 3. *2,4-Dinitrobenzyl alcohol.*



Evaluation of Equilibrium Constants.—For the precise determination of the composition of equilibrium mixtures formed by 2,4-dinitrobenzyl alcohol and nitric acid at 25° a new absorptiometric method was devised for the direct determination of 2,4-dinitrobenzyl nitrate. A 2 ml. sample of the equilibrium mixture was diluted to 6N-sulphuric acid and after oxidation of the unchanged alcohol with dichromate the solution was extracted twice with 10 ml. portions of benzene; this extraction removed both the nitrate ester and the oxidation product, 2,4-dinitrobenzoic acid. The latter was removed by washing the combined benzene extracts twice with 5 ml. portions of 0·2N-sodium hydroxide, and once with water, and then filtering into a 25 ml. flask and making up to the mark with benzene. The absorption of this solution was measured on a Spekker photoelectric absorptiometer having 1 cm. cells with H 556 filters, which give a high transmission of ultraviolet light. The concentration of nitrate ester were obtained from a standard curve previously prepared by using a series of solutions of known concentration in benzene (see Fig. 3). By this method, alcohol and nitrate ester determinations were carried out on the same sample of the equilibrium mixture; for each experiment, samples were removed at four half-hourly or hourly intervals to confirm that a true equilibrium had been established.

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D.Sc. 1960

577. *The Mechanism of the Reaction of Boron Trichloride with Cyclic Acetals of Hexitols.*

By T. G. BONNER and N. M. SAVILLE.

The function of boron trichloride as a reagent for the cleavage of cyclic acetals of hexitols has been studied. It appears that co-ordination of the boron trichloride with an acetal oxygen atom is followed by ring opening to produce an α-chloro-ether group, the presence of which has been proved by reduction to a methoxyl group.

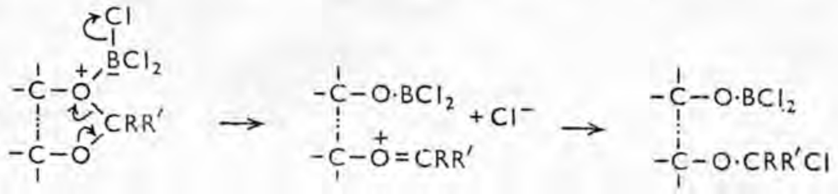
Investigation of the complex between boron trichloride and a tri-*O*-methylenehexitol by analysis and infrared absorption spectra shows that ring opening occurs in the complex with formation of chloroboronate and α-chloro-ether groups.

IN a brief report,[1] an account was given of the efficacy of boron trichloride in opening the rings of cyclic acetals of hexitols, in demethylation and deacylation of sugar derivatives, and in degradation of polysaccharides. Invariably, although yields are not quantitative, the major product isolated after treatment of the reaction mixture with aqueous methanol is the unsubstituted polyhydroxy-compound. The attack of the boron trichloride is directed towards oxygen centres in these molecules and more detailed studies have now been made, particularly of the cyclic acetals of hexitols, to discover the nature of the interaction at these sites and of the subsequent heterolysis of the C–O bonds.

Trimethylene derivatives of hexitols, in addition to regenerating mainly the parent hexitol, always give small quantities of the partially degraded derivatives, *e.g.*, 1,3:2,4:5,6-tri-*O*-methylene-D-glucitol gives, in addition to glucitol (61% yield), a detectable amount of 2,4-*O*-methylene-D-glucitol, the surviving ring in which is the most readily formed when glucitol is converted into its methylene derivatives [2] and is the most stable to aqueous acid,[3] to sulphuric acid in acetic anhydride–acetic acid solution (acetolysis),[4] and to acyl trifluoroacetate.[5] This monomethylene derivative alone with boron trichloride is largely converted into glucitol but even under vigorous conditions a residue of unchanged acetal remains. In contrast, the acetal ring in 2,5-*O*-methylene-D-mannitol, which preferentially survives only in the acetolysis of 1,3:2,5:4,6-tri-*O*-methylene-D-mannitol,[6] is completely destroyed by boron trichloride, the monomethylenemannitol being converted in 94% yield into mannitol without a detectable quantity of the acetal remaining. The lability of this ring is also evident in acid-hydrolysis [7] (which preferentially opens the 2,5-ring in the trimethylenemannitol) and is confirmed by treatment of the trimethylene compound with one mol. of boron trichloride instead of the excess normally used; none of the products obtained except a trace of unchanged acetal, contained the 2,5-ring. The explanation that the survival of this ring in acetolysis is due to a preference of the reagent for attack at a methylene group engaged at a primary rather than a secondary carbon atom suggests that the orientation and steric factors which determine this preference are not operative in the case of boron trichloride. Since both boron trichloride and the acetolysis reagent are essentially electrophilic, it is unlikely that polar factors underlie the difference in the mode of attack of the two reagents. Other cyclic acetals of D-mannitol which gave high yields (55—85%) of mannitol with excess of boron trichloride were the tri-*O*-ethylidene, -benzylidene, -isopropylidene, and -cyclohexylidene derivatives. Bis-*O*-(trifluoroisopropylidene)-D-mannitol yielded only a trace of mannitol under the usual conditions, but when the reaction was prolonged at higher temperatures more extensive ring opening occurred; the inductive effect of the trifluoromethyl groups in this acetal creates an exceptional resistance to attack by acidic and electrophilic reagents.[8] Other compounds which yield the unsubstituted polyhydric alcohol as the chief product are di-*O*-methylene- and mono- and di-*O*-benzylidene-pentaerythritol and the methyl ethers and carboxylic esters of D-glucitol and D-mannitol. The only exception so far discovered is the 1,6-ditoluene-*p*-sulphonate of 2,4-*O*-methylene-D-glucitol which gave only a very small yield of the hexitol. Under all conditions employed it was established that the parent polyols were not affected and could be recovered unchanged.

The Mechanism of Attack of Boron Trichloride at Oxygen Centres.—In extensive studies of the interaction of excess of boron trichloride with oxygen-containing organic compounds, Gerrard and his co-workers[9] have proposed mechanisms for the fission of C–O–C bonds in aliphatic and cyclic ethers, *i.e.*, in compounds closely resembling the cyclic acetals of polyols. In most ether fissions studied it appeared that the alkyl group with the greater electron-releasing properties is found in the alkyl halide produced, suggesting initial formation of a carbonium ion by alkyl–oxygen fission.

In a complex formed between boron trichloride and a cyclic acetal, the –O–C–O– group provides an effective system for stabilisation of the central carbon when the bond with either oxygen atom undergoes heterolysis to give a carbonium ion. The dichloroboronite


. . . . (1)

group contains the still strongly electrophilic boron atom which can co-ordinate with an oxygen centre of an adjacent acetal ring. This undoubtedly occurs when a 1 : 1 molar ratio of boron trichloride to a triacetal compound is used, with formation of the stable cyclic chloroboronate grouping; the absence of any chlorodeoxy-derivative of a polyol in the products of the reaction of its cyclic acetal with boron trichloride also suggests that this intermediate is formed. The α-chloro-ether group $-O\cdot CRR'Cl$ formed in reaction (1) could, by analogy with the known reactions of α-chloro-ethers, give with excess of boron trichloride either a chlorodeoxypolyol or a dichloroboronite, the latter being accompanied by the product $RR'CCl_2$. With methylene acetals this dichloro-derivative would be dichloromethane, already employed as the solvent; benzylidene derivatives, however, were found to give a product with the properties of benzylidene chloride, indicating formation of a dichloroboronite from an α-chloro-ether substituent.

Detection of an α-Chloro-ether Group by Replacement of Chlorine.—Since an α-chloromethyl ether group, if formed in the reaction of boron trichloride with a cyclic methylenedioxy-compound, would be subsequently hydrolysed during the treatment with aqueous methanol, the conversion of this group into a less labile derivative by nucleophilic replacement of the chlorine was investigated, *i.e.*, $-O\cdot CH_2Cl \longrightarrow -O\cdot CH_2X$. Two suitable reagents of this type are the acetate ion[10] and the methoxide ion.[11] In both cases, chlorine attached to boron would also be replaced, but the mild hydrolysis of the complex with aqueous methanol should remove the boron and its attached groups leaving the free hydroxyl groups. In the experimental investigation, anhydrous sodium acetate in suspension in chloroform was added to the products obtained by treating tri-*O*-methylene-D-mannitol and -D-glucitol with excess of boron trichloride after removing the excess of the latter under reduced pressure. After treatment with aqueous methanol, the residue was extracted first with chloroform which removes highly substituted hexitols, and then with pyridine which is a solvent both for these derivatives and for hexitols. Examination by paper chromatography showed that both extracts contained a mixture of fast-moving products (*i.e.*, highly substituted hexitols) while the pyridine solution contained in addition unsubstituted hexitol. Trisacetoxymethylhexitol, in which the three rings have been opened, and bisacetoxymethylmethylene- and monoacetoxymethyldimethylene-hexitols in which only partial ring opening has occurred, would provide fast-moving products while the slower-moving derivatives and the hexitol itself could result either from partial hydrolysis of the acetoxymethyl groups or from incomplete replacement of the chlorine. A similar result was obtained by treating the same trimethylenehexitol–boron trichloride reaction products with sodium methoxide in methanol. After removal of the sodium chloride formed and adjustment to pH 8, evaporation left a residue in which paper chromatography showed the presence of fast-moving substances. Slower-moving, less highly substituted derivatives together with the parent hexitol also indicated partial hydrolysis or incomplete formation of the expected unsymmetrical acetal. The reaction mixtures in both cases were too complex for separation of the acetoxymethyl or unsymmetrical acetal derivatives to be attempted. Attention was, therefore, directed to the possibility of replacing the chlorine by hydrogen, giving a methoxyl group in place of the α-chloro-ether. As the methyl ethers of the hexitols are known to be stable and to resist hydrolysis, it was assumed that their isolation and characterisation would present less difficulty.

The reducing agent used was lithium aluminium hydride, to which ether and acetal groups appear to be stable. It was expected that chloroboronates would give the same products as were obtained with sodium borohydride,[12] with the probability that the subsequent hydrolysis removes any borate ester groups, leaving only a methyl ether group in place of each α-chloro-ether group initially present. Initial investigations of the reaction in tetrahydrofuran of lithium aluminium hydride with the boron trichloride–methylenedioxy-complexes were evaluated by paper chromatography. Tri-*O*-methylene-D-mannitol yielded a mixture and it was significant that no hexitol was detected; the omission of the reduction step as indicated above leads to a substantial yield (53%) of the hexitol. More conclusive evidence was obtained with 2,4-*O*-methylene-D-glucitol, the products from which were separated on a Celite column. One fraction contained the unchanged acetal in relatively small amount together with a larger quantity of a product of closely similar constitution which was converted by boron trichloride into D-glucitol in high yield and had a methoxyl content of 11·8% (calc. 15·8% for monomethylglucitol). By the above sequence of reactions, 2,4-*O*-methylene-D-glucitol could afford the 2- and the 4-methyl ether or both—a model indicates that the two ring-oxygen atoms are equally accessible to attack by boron trichloride. In fact chromatography indicated formation of two similar methyl ethers. To overcome this difficulty, 2,5-*O*-methylene-D-mannitol was used for subsequent investigations. The reduction products from this acetal would be either 2-*O*- or 5-*O*-methylmannitol, which are identical. Also, as the acetal is quantitatively converted into mannitol on reaction with excess of boron trichloride and aqueous methanol, the reduction products should contain no unchanged acetal.

Reaction of Lithium Aluminium Hydride with the 2,5-O-Methylene-D-mannitol–Boron Trichloride Complex.—Treatment of 2,5-*O*-methylenemannitol with excess of boron trichloride followed by lithium aluminium hydride gave two fractions separable on a carbon–Celite column. One fraction yielded mannitol only (1·1% yield) and the other an oil (E; yield, 59% calc. as $C_7H_{16}O_6$). Examination of the oil by paper chromatography indicated a single product and a chromotropic acid determination of its acetal content showed a negligible amount (0·1%). The R_m value of the substance E was less than that of the monomethylenemannitol but on ionophoresis in a borate buffer it migrated further; both observations suggest the formation of a more stable borate complex than that formed by the monomethylene derivative. Treatment with boron trichloride and aqueous methanol yielded only mannitol, confirming that the compound is a mannitol derivative. The position of the single substituent was investigated by periodate oxidation. One mol. (calc. on $C_7H_{16}O_6$) consumed 3 mol. of periodate with the production of 1·02 mol. of formaldehyde and 1·90 mol. of formic acid. The only monomethylhexitol which can give a result of this type is the 2-methyl derivative:

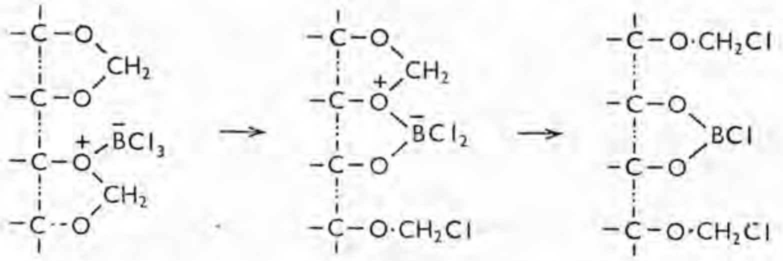
$$\mathrm{HO{\cdot}CH_2{\cdot}CH(OMe){\cdot}[CH(OH)]_3{\cdot}CH_2{\cdot}OH} \xrightarrow{\mathrm{3NaIO_4}} \mathrm{HO{\cdot}CH_2{\cdot}CH(OMe){\cdot}CHO + CH_2O + 2H{\cdot}CO_2H} \quad . \quad (2)$$

Analysis of the substance *E* for carbon and hydrogen agrees with that of a monomethyl ether, but the Zeisel analysis for methoxyl, while indicating a monomethyl ether, gave varying values for the methoxyl content all of which were higher than that calculated for a monomethyl ether. However, the completely acetylated derivative gave carbon, hydrogen, and methoxyl values in accord with those for the penta-acetate of a monomethylhexitol.

While other monomethyl ethers of mannitol are known, the 2-methyl ether has not previously been synthesised. 2-*O*-Methyl-D-mannose, however, had been reported [13] although the evidence for the position of the substituent was known not to be conclusive. This compound was prepared from a sample of methylated D-mannose dibenzyl mercaptal (kindly supplied by Professor Pacsu [13]) by first treating it with mercuric chloride to remove the mercaptal group; the product obtained contained mannose and a faster-moving derivative, and the latter gave an indication of being a 2-methylmannose by its failure to react with triphenyltetrazolium chloride which does not give a positive reaction when there is a substituent adjacent to the reducing group, *i.e.*, at the 2-position in this case.[14] Both products were reduced to the hexitol by potassium borohydride,[15] and paper chromatography then showed that no reducing sugars remained. The monomethylmannitol was separated on a carbon–Celite column and the migration of this compound and of the substance *E* were compared in several solvents. In all cases, including ionophoresis in borate and molybdate buffers, the rates of movement were the same. The penta-acetates were identical (m. p., mixed m. p. and infrared spectra at 5000—666 cm.$^{-1}$). A peak for the pentacetate at 2836 cm.$^{-1}$ was attributed to the carbon–hydrogen stretching frequency of the methoxyl group (anisole and methyl 2-naphthyl ether had peaks at 2837 cm.$^{-1}$). Other workers have shown the spectra of methyl ethers to contain characteristic shoulders on the side of carbon–hydrogen absorption bands in the range 2815—2832 cm.$^{-1}$ which have been correlated with vibration of the methoxyl group: [16] substance *E* gave an absorption peak at 2847 cm.$^{-1}$, *i.e.*, sufficiently close to be acceptable evidence for the presence of the methoxyl group. The failure of the Zeisel method to provide a satisfactory analysis of 2-*O*-methylmannitol while giving a satisfactory result for its penta-acetate is apparently a feature of the hexitol structure, since mannitol and glucitol give apparent methoxyl contents of 11·8% and 12·7% respectively owing to the production of volatile ethyl and vinyl iodide.[17]

Addition Complex of Boron Trichloride and a Cyclic Methylenedioxy-derivative.—The problem remained of whether the cyclic acetal ring is opened by the boron trichloride before, or as a result of, attack of a nucleophilic reagent. A similar uncertainty arises in the reaction of certain non-cyclic acetals and ketals [18] and ethers [19] with a mixture of aluminium chloride and lithium aluminium hydride; reduction occurs readily with the mixed reagent but the compounds are unreactive to lithium aluminium hydride alone. The operative mechanism for the boron trichloride reaction became evident in a study of the complex formed between this reagent and 1,3:2,5:4,6-*O*-trimethylene-D-mannitol. Attempts to analyse quantitatively the complex formed by treatment of weighed amounts of the acetal with excess of boron trichloride and evaporation to constant weight under reduced pressure were not wholly successful.

The suspected ring fission during interaction of the boron trichloride and cyclic acetal was confirmed by a comparison of the infrared spectra of the complex with the 1 : 1 addition compound formed by 1,4-dioxan and boron trichloride. This is a very stable compound which regenerates 1,4-dioxan readily on treatment with pyridine or hydroxylic solvents. Decomposition products of dioxan are only obtained on heating. The spectra of dioxan itself and its compound with boron trichloride were recorded and strong absorptions at 789 and 761 cm.$^{-1}$ were found only in the addition compound; these were correlated with the stretching vibration of the boron–chlorine bonds. In boron trichloride alone, the asymmetric stretching vibrations of these bonds give rise to absorption peaks at 995 (due to ^{10}B–Cl) and at 954 cm.$^{-1}$ (due to ^{11}B–Cl).[20] The lower frequency in its compound with dioxan is attributed to the increase in electron density on the boron atom; this decreases the electron-accepting power of the boron, back-co-ordination of the chlorine atoms is therefore less than in pure boron trichloride, and the consequent reduction in the double-bond character of the boron–chlorine bonds in the addition compound leads to absorption at a lower frequency. If ring opening occurs in the boron trichloride–trimethylenemannitol complex, the products would be dichloroboronites or chloroboronates. The spectra of compounds of this type have been reported;[21] absorptions of methyl dichloroboronite at 997 and 960 cm.$^{-1}$ were correlated with the asymmetric boron–chlorine vibration while in methyl chloroboronate strong absorption at 630 cm.$^{-1}$ was assigned to the boron–chlorine vibration. The spectra of the trimethylenemannitol complex showed strong absorption at 663 cm.$^{-1}$ also attributed to boron–chlorine vibration. This frequency is much lower than in the dioxan–boron trichloride compound and if attributed to the same cause would imply that the trimethylenemannitol complex is even more stable than that of dioxan. This is very unlikely and it is more probable that ring opening has occurred with the formation of a chloroboronate group giving an absorption (663 cm.$^{-1}$) close to that of methyl chloroboronate. The evidence is therefore that the following sequence of reactions (3) occurs with boron trichloride–cyclic methylenedioxy-complexes:



. . . . (3)

Water converts the complex into the polyhydroxy-derivative, while treatment with lithium aluminium hydride followed by hydrolysis produces a methoxyl group in place of an α-chloro-ether group and hydroxyl groups at all other positions.

EXPERIMENTAL

Materials.—Boron trichloride, b. p. 12·5°/760 mm., was obtained in sealed bottles (B.D.H.). These were cooled in acetone–solid carbon dioxide (*ca.* −80°), the contents were transferred to a distillation flask cooled to −80°, and the boron trichloride was distilled by allowing it to warm to room temperature.[22] Small portions of the distillate also at −80° were rapidly transferred to weighed, stoppered test-tubes, each of which had been drawn out to provide a constriction near the mouth, and cooled to −80°. The tubes were sealed off at the constriction and reweighed.

Dichloromethane was washed with 5% sodium carbonate solution and then water, dried ($CaCl_2$), and stored in the dark over calcium chloride.

Paper Chromatography.—Whatman No. 1 paper was used with the following solvents: (*a*) butan-1-ol saturated with water at 0°; (*b*) acetone–water (4 : 1 v/v); (*c*) butan-1-ol–pyridine–water–saturated aqueous boric acid (6 : 4 : 2 : 1 v/v). The usual spray reagents were employed.[23-26] The positions of the compounds are recorded either as R_F values related to the distance of the solvent front from the base line or as R_X values related to the distance travelled by a standard substance X. Paper ionophoresis was carried out on Whatman No. 3 paper with a borate buffer (pH 9·8).[27]

Reactions of Polyol Derivatives with Boron Trichloride.—1,3:2,4:5,6-Tri-*O*-methylene-D-glucitol (0·81 g.) in dichloromethane (40 ml.) was added during 30 min. to boron trichloride (3·0 g., 6·9 mol.) in dichloromethane (30 ml.) at −80°. After attaining room temperature the flask was connected through a trap at −80° to a water-pump to remove the solvent and excess of boron trichloride. The temperature was finally raised to 40° and a brown glass (1·69 g.) was obtained. Methanol (containing *ca.* 0·05% of water) was added and the solution evaporated; this treatment with methanol was continued until no detectable amount of boron remained (indicated by the absence of a red colour on turmeric paper in warm acid solution). Examination of the residual oil (1·10 g.) by paper chromatography with solvent (*b*) showed the presence of a hexitol, R_{glucitol} (R_g) 1·00, a second product, R_g 1·45 (2,4-*O*-methylene-D-glucitol, R_g 1·36), and a third, R_g 1·90. The oil was refluxed for 30 min. with sodium acetate (6·4 g.) and acetic anhydride (20 ml.), and the product shown to be glucitol hexa-acetate (0·76 g.), m. p. 94—97°, mixed m. p. 95—96°. Chloroform-extraction of the filtrate gave a less pure specimen of glucitol hexa-acetate (0·35 g.), m. p. 92—93°; the total yield corresponded to 61% based on the trimethyleneglucitol. The mother-liquor from the crystallisation of the second crop of hexa-acetate was deacetylated with one drop of 0·2N-sodium methoxide in methanol–chloroform; examination by paper chromatography in solvent (*b*) showed the presence of glucitol, R_g 1·00, and a second compound, R_g 1·27 (2,4-*O*-methylene-D-glucitol, R_g 1·25).

1,3:2,5:4,6-Tri-*O*-methylene-D-mannitol, when similarly treated, gave mannitol (53%) and a second product, R_{mannitol} (R_m) 1·43 (2,5-*O*-methylene-D-mannitol, R_m 1·28; 1,3-*O*-methylene-D-mannitol, R_m 1·40).

1,3:2,5:4,6-Tri-*O*-ethylidene-D-mannitol and its isopropylidene, benzylidene, and cyclohexylidene analogues were converted into mannitol in yields of 67%, 84%, 85%, and 55% respectively. Small amounts of substituted mannitol were also detected.

2,4-*O*-Methylene-D-glucitol gave mainly glucitol (61%). 2,5-*O*-Methylene-D-mannitol gave a 94% yield of mannitol. 1,5,6-Tri-*O*-benzoyl-2,4-*O*-methylene-D-glucitol and mannitol hexa-acetate both gave the parent polyol in substantial yield. Di-*O*-methylenepentaerythritol gave a 76% yield of pentaerythritol and a small amount of a second product; both di-*O*-benzylidene- and mono-*O*-benzylidene-pentaerythritol were converted in 91% yield into pentaerythritol. The pentaerythritol (m. p. and mixed m. p. 258—260°) in each case was left as a residue after chloroform-extraction of the product obtained from the methanol-treatment. The chloroform extract in the case of the benzylidenepentaerythritols contained an oil which on treatment with aqueous sodium hydrogen carbonate yielded benzaldehyde, identified as its 2,4-dinitrophenylhydrazone.

1,2:5,6-Bis-*O*-(trifluoroisopropylidene)-D-mannitol gave only a small amount of mannitol on treatment with boron trichloride, but ring scission appeared to occur to a greater extent when the ketal was kept in contact with the reagent in a sealed tube for 6 days at room temperature. 2,4-*O*-Methylene-1,6-di-*O*-toluene-*p*-sulphonyl-D-glucitol was also resistant to the reagent and only a small yield of the hexitol was obtained. D-Glucitol and D-mannitol were not affected by the reagent and after treatment could be recovered as hexa-acetate in 80—90% yield.

Reaction of 1,3:2,5:4,6-tri-*O*-methylene-D-mannitol (0·48 g.) with boron trichloride (0·26 g., 1 mol.) gave a product which was separated on a Celite column into D-mannitol (0·1 g.), 1,3:4,6-di-*O*-methylene-D-mannitol (0·05 g.), m. p. and mixed m. p. 200—209° (Found: C, 46·2; H, 6·9. Calc. for $C_8H_{14}O_6$: C, 46·6; H, 6·9%), and an oil (0·09 g.); paper chromatography with solvent (*a*) showed that the last product had R_m 2·66 (1,3-*O*-methylene-D-mannitol, R_m 2·66); with acetic anhydride (0·5 ml.) in pyridine (2 ml.) it gave 2,4,5,6-tetra-*O*-acetyl-1,3-*O*-methylene-D-mannitol (0·04 g.), m. p. 138—140° (lit.,[28] 143—144°) (Found: C, 49·8; H, 6·4. Calc. for $C_{15}H_{22}O_{10}$: C, 49·7; H, 6·1%). This derivative was deacetylated with 0·2M-sodium methoxide in methanol, and the periodate uptake of the monomethylenemannitol was determined [29] by addition of standard sodium metaperiodate solution and measurement of the optical density of the solution at 223 mμ: the decrease in periodate concentration corresponded to reaction of 2·03 mol. of periodate (theor. for 1,3-*O*-methylene-D-mannitol 2·00, and for 2,5-*O*-methylene-D-mannitol 1·00).

Successive Treatment of 2,5-O-*Methylene*-D-*mannitol with Boron Trichloride and Lithium Aluminium Hydride.*—The acetal (2·91 g.) was treated with boron trichloride (32 g., 18 mol.) to give, after evaporation, a glass (6·25 g.), whose solution in tetrahydrofuran (100 ml.; dried and distilled over sodium) was added slowly to lithium aluminium hydride (6 g., 15·5 mol.) in ether (200 ml.; dried over sodium). The mixture was refluxed for 1 hr., then cooled in ice, water (150 ml.) was added, and the pH adjusted to 4 by addition of hydrochloric acid. The organic solvents were removed under reduced pressure and the aqueous residue was concentrated. The product was centrifuged and the supernatant liquid was passed down a Biodeminrolit ion-exchange column. The eluate, after freeze-drying, was repeatedly refluxed with methanol, acidified with hydrochloric acid, and evaporated to dryness to remove residual boric acid. The neutral residue was finally extracted with pyridine, and the solution concentrated to give a dark oil (1·98 g.). Paper chromatography with solvent (*c*) showed the presence of mannitol, R_m 1·0, and a second product, R_m 1·4 (2,5-*O*-methylene-D-mannitol, R_m 2·0). The oil was dissolved in a small amount of water and run on to a column prepared from equal amounts of charcoal and Celite. Elution was with water containing ethanol, so that the ethanol content increased continuously from 0 to 10%, and fractions of 25 ml. were collected. Examination by paper chromatography with solvent (*a*) showed that fractions 55—100 contained a product (*E*), R_m 2·6. These fractions were concentrated and the solution was passed through an asbestos filter (Ford's Sterimat) to remove any fine particles of Celite. Evaporation to dryness gave colourless, oily 2-*monomethylmannitol* (1·70 g.) (Found: C, 43·4; H, 8·2; OMe, 26·5. $C_7H_{16}O_6$ requires C, 42·9; H, 8·2; OMe, 15·8%). Examination by paper chromatography with solvent (*a*) and ionophoresis in borate buffer established that the substance *E* was not unchanged 2,5-*O*-dimethylene-D-mannitol, while similar examination of the product of its reaction with boron trichloride indicated this to be mannitol only (m. p. and mixed m. p. 168—168·5°). Confirmation that the substance *E* was not a methylene derivative was obtained by attempted acid-hydrolysis to give formaldehyde; determination of the latter with chromotropic acid indicated less than 0·1% of a formal present.

Periodate oxidation of the substance *E* determined by ultraviolet measurement at 223 mμ of the fall in periodate concentration showed that for one sample (6·84 mg.), 2·94 mol. of periodate were consumed, of 4 mol. initially present, and for a second sample (3·34 mg.), 3·06 mol. from 8 mol. initially present. The products of the periodate oxidation, formaldehyde and formic acid, were also determined. For the former, erythritol which gives 2 mols. of formaldehyde per mol. consumed was used as the standard [30] for the preparation of a calibration curve for the chromotropic acid method of determination of formaldehyde.[31] Two samples of the substance *E* (each *ca.* 3 mg.) gave values of 1·07 and 0·96 mol. of formaldehyde. The formic acid simultaneously produced was determined (1·81—1·90 mol.).

Substance *E* (0·103 g.) was refluxed for 1 hr. with acetic anhydride (2·0 ml.) and sodium acetate (0·1 g.); pouring the mixture into water gave an oil (0·22 g.) which was isolated by chloroform-extraction. This crystallised from ethanol, to give 1,3,4,5,6-*penta*-O-*acetyl*-2-O-*methyl*-D-*mannitol* (0·12 g.), m. p. 102—102·5° unchanged by further crystallisation (Found: C, 50·1; H, 6·4; OMe, 8·0. $C_{17}H_{26}O_{11}$ requires C, 50·3; H, 6·5; OMe, 7·6%), $[\alpha]_D^{22}$ +29·5 (*c* 0·87 in $CHCl_3$).

Synthesis of 2-O-*Methyl*-D-*mannitol*.—2-*O*-Methyl-D-mannose dibenzyl mercaptal (0·65 g.) was demercaptalised by the standard procedure.[13] The oily product was shown by chromatography to contain mannose and a compound moving almost twice as fast as mannose, which was not the unchanged mercaptal. The products were reduced to hexitols with potassium borohydride (0·16 g. in 7·5 ml. of water). By next morning gas evolution had stopped and Amberlite ion-exchange resin IR-120(H) was added to decompose the excess of borohydride. Sodium hydrogen carbonate was added to raise the pH from 2 to 5, the resin was filtered off, and the filtrate and washings were concentrated under reduced pressure, giving a white solid. The residue after removal of boric acid was an oil (0·17 g.). Chromatography in solvent (*a*) showed the presence of a hexitol, R_{mannitol} 0·92, and a second product, R_m 1·84. No reducing sugar was detected by the *p*-anisidine hydrochloride spray. The two products were separated on a charcoal–Celite column by elution, first with water (300 ml.) and then with 2% aqueous ethanol. 10 ml. fractions were collected; paper chromatography with solvent (*a*) showed only mannitol, R_m 1·0, and a product, R_m 1·9. After concentration of the appropriate fractions, filtration through asbestos and evaporation gave an oil (0·09 g.) presumed to be 2-*O*-methylmannitol. Sodium acetate (0·1 g.) and acetic anhydride (2·0 ml.) gave a product which after two crystallisations from aqueous ethanol was 1,3,4,5,6-penta-*O*-acetyl-2-*O*-methyl-D-mannitol (0·06 g.), m. p. 102—102·5°. The mixed m. p. with the penta-acetate of the product *E* described above was 101·5—102·5°. The product *E* and 2-*O*-methyl-D-mannitol showed identical behaviour on paper chromatography and ionophoresis. Infrared spectra (in Nujol) of the penta-acetates over the range 5000—666 cm.$^{-1}$ were identical. A diffraction grating spectrometer (third-order spectrum) was used for the fine spectrum between 3158 and 2727 cm.$^{-1}$, in which the symmetrical C–H stretching frequency of the methoxyl group is located.

Analysis and Examination of the Boron Trichloride–Tri-O-methylenemannitol Complex.—The complex was obtained by adding excess of boron trichloride to a known weight of 1,3:2,5:4,6-tri-*O*-methylene-D-mannitol, complete dissolution being allowed to occur in a closed vessel and the excess of boron trichloride then removed under reduced pressure in anhydrous conditions. Determination of the molar ratio, boron trichloride: acetal, was made uncertain by the dependence of the final weight of residue on the extent to which the pressure is reduced; the average value with an oil-pump was 1·8, and with a water-pump 2·3. On analysis of the residue for chlorine no conclusive and reproducible results could be obtained, the values being dependent on the pH of the hydrolysate.

The infrared spectrum of the complex was measured on a sample prepared by distilling boron trichloride (1·99 g.) in a closed system and condensing it on the trimethylenemannitol (0·02 g.); the latter was contained in a narrow tube having a constriction at its upper end and cooled to −80°. The acetal did not dissolve at this low temperature but allowing the mixture to attain room temperature caused complete dissolution. Excess of boron trichloride was removed by evacuation at a water-pump (protected to prevent back-diffusion of moisture). The tube containing the complex (0·06 g.) was sealed off at the constriction. The complex formed by 1,4-dioxan and boron trichloride was prepared by adding dioxan (7·2 g.; distilled from sodium) to dichloromethane (10 ml.), cooling the whole to −80°, then adding boron trichloride (2·3 g., 0·25 mol.). After 15 min., the mixture was allowed to warm to room temperature. After 1 hr., volatile matter was removed at room temperature, first by a water-pump and then at 2 mm. The residue of white crystals (3·74 g.) was recrystallised from dichloromethane–light petroleum (b. p. 60—80°) under anhydrous conditions. The infrared spectra of both complexes were measured in carbon disulphide solution (see above).

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288. *Medium Effects in the Prototropy of Ketones. Kinetics of the Bromination of Acetone and Acetophenone in Aqueous Acetic Acid.*

By TREVOR G. BONNER, DAVID P. EVANS, and H. B. WATSON.

A kinetic study of the bromination of acetone and of acetophenone in different mixtures of water and acetic acid (ranging from pure water to 90% acetic acid) has shown that the changes in velocity are to be ascribed to simultaneous variations in the energy of activation and the *PZ* term of the equation $k = PZe^{-E/RT}$. A similar phenomenon has been observed in a number of other reactions by Hinshelwood and his co-workers. For the base-catalysed change the relationship between *E* and log *PZ* is approximately linear. In both base- and acid-catalysed prototropy the values of the parameters fall and finally rise again as the acetic acid content of the medium is increased.

EARLIER measurements of the speeds of prototropy of acetone, acetophenone, and nuclear-substituted acetophenones in aqueous acetic acids (Watson *et al.*, J., 1931, 3318; 1932, 1207; 1933, 217) indicated that the acid-catalysed change becomes more rapid as the proportion of acetic acid in the solvent increases; *e.g.*, for acetone in presence of M-hydrochloric acid, the relative velocities of bromination in water, 50% acetic acid, and 75% acetic acid were 1 : 2·1 : 4·8. Since the catalytic influence of the acetic acid was almost negligible in comparison with that of the added mineral acid, the observed variations in speed were clearly due to a medium effect, and they appeared sufficiently interesting to merit further investigation.

It has recently been observed (Fairclough and Hinshelwood, J., 1937, 538, 1573; 1938, 236; compare Hinshelwood, *Trans. Faraday Soc.*, 1938, 34, 138) that changes in the medium frequently lead to simultaneous variations in the energy of activation and the non-exponential term of the Arrhenius equation, and this gave added interest to a fuller kinetic study of prototropic changes in a continuously varying solvent.

We have therefore determined the velocities of bromination of acetone and of acetophenone (0·1M) catalysed by 0·5M-hydrochloric acid and also by 0·147M-sodium

Acetophenone.

$CH_3{\cdot}CO_2H$, %, in medium.	Base-catalysed. *E*(cals.).	log *PZ*.	Acid-catalysed. *E*(cals.).	log *PZ*.
25	—	—	19,400	9·4
50	20,300	9·4	19,200	9·4
75	18,400	8·0	20,100	10·4
90	19,300	8·7	19,800	10·9

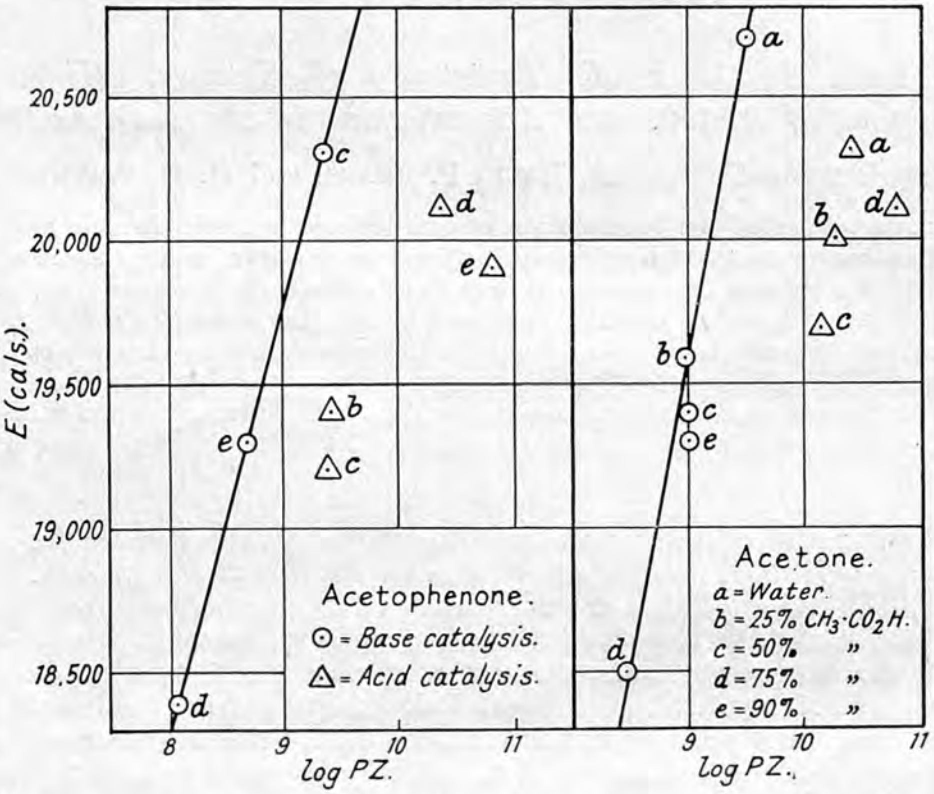
Acetone.

$CH_3{\cdot}CO_2H$, %, in medium,	Base-catalysed. *E*(cals.).	log *PZ*.	Acid-catalysed. *E*(cals.).	log *PZ*.
0	20,700	9·5	20,300	10·4
25	19,600	8·9	20,000	10·3
50	19,400	9·0	19,700	10·2
75	18,500	8·4	20,100	10·8
90	19,300	9·0	—	—

acetate, at different temperatures, in aqueous mixtures having an acetic acid content varying over a range from zero to 90%. In each case the plot of log k against $1/T$ gave a good straight line, and the values of E and log PZ in the equation $k = PZe^{-E/RT}$ are recorded on the previous page.

The following generalisations can be made with regard to the base-catalysed changes. (1) The variations in the medium lead to appreciable changes in both E and PZ; the values of the former cover a range of 2000 cals., and those of the latter vary over more than a ten-fold range. (2) E and PZ rise or fall together, the plot of E against log PZ being roughly linear (see figure). (3) Increase in the acetic acid content of the medium from zero to 75% results in a more or less steady fall of both E and PZ, but further increase causes both to rise again.

For the acid-catalysed reactions the differences are on the whole small, and it is not possible to attach very great significance to them, but here also there appears to be a tendency for E and PZ to fall and then rise again. The increase in the values of both parameters when the medium changes from 50% to 75% acetic acid must certainly be regarded as real, particularly in the case of acetophenone.



We do not yet attempt any interpretation of the observations, but reference may be made to the following points. First, the results provide a further instance of the simultaneous variation of E and PZ which has been noted for other reactions by Hinshelwood and his collaborators. Secondly, they differ somewhat from observations which have been made upon the hydrolysis of benzoic esters, where a consistent variation of the Arrhenius parameters is found as the proportion of alcohol in alcohol–acetone–water media increases (Fairclough and Hinshelwood, *loc. cit.*), and where also changes in the medium have opposite effects upon alkaline and acid hydrolysis (Timm and Hinshelwood, J., 1938, 862). Hegan and Wolfenden's results for the alkaline hydrolysis of valerolactone (this vol., p. 508) resemble ours, however, in that the value of E falls somewhat from water to 21% alcohol and then rises as the alcohol content of the medium increases further.

EXPERIMENTAL.

Acetophenone was purified by distillation in a vacuum and freezing; m. p. 19·6°. Acetone was treated by the sodium iodide method and distilled, b. p. 56·9°; identical results were obtained with a specimen of " AnalaR " acetone, kindly provided by Dr. Dippy, which had been dried and distilled through a 4-ft. column filled with glass beads. Acetic acid, water, and bromine were as used in earlier work. Aqueous acetic acids were made up by volume.

The measurements were carried out as described previously (Evans, Morgan, and Watson, J., 1935, 1167; Evans and Gordon, J., 1938, 1434), 10 c.c. N.P.L.-standardised burettes graduated in 0·02 c.c. being used. For temperatures of 25° and higher, the thermostats were electrically controlled by a toluene regulator in conjunction with a Sun Vic vacuum tube switch. Lower temperatures (0°, 5°, 15°) were obtained by means of a refrigerating system coupled with a number of heating lamps similarly controlled and all contained in a well-lagged copper bath filled with a mixture of water and glycol (compare Smith, J., 1936, 1827; we are indebted to Dr. Smith for the details). Temperatures were constant within 0·02°.

The acid-catalysed reactions were of zero order, and a typical example is given below; this gives an indication of the degree of accuracy in the determinations of the energy of activation.

Bromination of acetophenone in 50% acetic acid.

[HCl] = 0·5M. [Ph·COMe] = 0·1M. Titres and values of k are in terms of c.c. of N/50-thiosulphate for 20 c.c. of reaction mixture; time is in mins.

Temp.	Time.	Titre.	Fall.	k.		E.
25°	0	10·50	—			
	20	8·31	2·19	0·110	0·110	
	40	6·11	4·39	0·110		
	60·5	3·83	6·67	0·110		
35°	0	9·81	—			19,300
	7	7·55	2·26	0·323	0·323	
	14	5·27	4·54	0·324		
	21	3·06	6·75	0·321		
45°	0	9·48	—			19,100
	2·5	7·30	2·18	0·872	0·876	
	5	5·07	4·41	0·882		
	7·5	2·93	6·55	0·873		

Accepted value of E = 19,200 cals.; $\log_{10} PZ$, from equation $k = PZe^{-E/RT}$, is 9·36.

In the base-catalysed changes, however, the velocity coefficients increased as the reaction proceeded, by a factor which varied in different media and was always greater for acetone than for acetophenone. This increase was doubtless due to further bromination. The velocity coefficient at zero time was computed by extrapolation of the straight line obtained by plotting the values of k against time; " zero time " was the moment of mixing the reagents. The following examples are typical; they refer to the bromination of acetone in 75% acetic acid in presence of 0·147M-sodium acetate.

	Temperature 35°.				Temperature 55°.			
Time (mins.)	0	59	119	164	2	9	17	26
Titre (N/50-$Na_2S_2O_3$) ...	10·45	8·30	5·93	3·99	9·77	8·07	5·93	3·35
Fall in titre	—	2·15	4·52	6·46	—	1·70	3·84	6·42
$k \times 100$	(3·48)	3·64	3·80	3·95	(22·7)	24·2	25·6	26·8

The velocity coefficients obtained by this method were reproducible within 1—1·5%, and are more accurate than those recorded by Morgan and Watson (J., 1935, 1173).

The velocity coefficients for the acid- and base-catalysed reactions are summarised below, as fall of N/50-thiosulphate titre per minute for 20 c.c. of reaction mixture. Each is the mean of three concordant determinations. The values of E and log PZ, determined in the usual way, have been recorded in the text.

Bromination of acetophenone.

[Ph·COMe] = 0·1M.

$CH_3 \cdot CO_2H$, %, in medium.	[HCl] = 0·5M.				[NaOAc] = 0·147M.		
	$10^2k_{15°}$.	$10^2k_{25°}$.	$10^2k_{35°}$.	$10^2k_{45°}$.	$10^2k_{35°}$.	$10^2k_{45°}$.	$10^2k_{55°}$.
25	—	8·55	25·6	69·2	—	—	—
50	—	11·0	32·4	88·0	1·54	4·30	11·9
75	7·50	24·4	75·4	218·0	1·74	4·43	11·2
90	44·6	144·0	12·6*	—	1·57	4·23	11·1

Bromination of acetone.

$[Me_2CO] = 0{\cdot}1$M.

$CH_3{\cdot}CO_2H$, %, in medium.	[HCl] = 0·5M. $10^2k_{0°}$.	$10^2k_{15°}$.	$10^2k_{25°}$.	$10^2k_{35°}$.	[NaOAc] = 0·147M. $10^2k_{35°}$.	$10^2k_{45°}$.	$10^2k_{55°}$.
0	1·53*	5·54	18·4	62·0	1·07	3·09	8·45
25	—	6·87	22·2	69·1	1·85	5·19	13·4
50	1·37	9·21	29·9	—	2·84	7·69	20·2
75	2·72	19·6	63·3	—	3·50	9·20	22·6
90	—	—	—	—	3·38	9·00	23·7

* Temperature = 5°.

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THE DEGREE OF IONIZATION OF NITRIC ACID TO THE NITRONIUM ION IN SULPHURIC ACID SOLUTION

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By T. G. Bonner and Gwyn Williams

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Triarylcarbinol indicators[1] and nitric acid ionize similarly in sulphuric acid-water media.

$$Ar_3COH + 2H_2SO_4 \rightleftharpoons Ar_3C^+ + OH_3^+ + 2HSO_4^- \quad ..(1)$$
$$NO_2OH + 2H_2SO_4 \rightleftharpoons NO_2^+ + OH_3^+ + 2HSO_4^- \quad ..(2)$$

Since the speed of nitration of deactivated aromatic molecules (e.g. $PhNMe_3^+$, $PhNO_2$, p-$Cl.C_6H_4.NO_2$)[2] in 90% to 80% sulphuric acid falls parallel to the diminishing extent of ionization of the indicator 4 : 4′ : 4″-trinitrotriphenylcarbinol (I) in the same medium range,[3] it seems probable (*a*) that, within this range, changing medium composition reduces nitration speed *mainly* by its effect upon the prevailing nitronium ion concentration, and (*b*) that the degrees of ionization of nitric acid and of (I) are not very far apart in a given medium. It is the purpose of this note to show that, with certain assumptions, it is possible, in principle, to make a quantitative estimate of the degree of ionization of nitric acid in equation (2), by a combination of indicator and nitration measurements (with *small* reagent concentrations), without exact knowledge of the molecular composition of the medium.

In a given medium, for *small* concentrations of indicator (Ar_3COH = ROH) and of nitric acid,[4]

$$\frac{K_{ROH}}{K_{NO_2OH}} = \frac{[R^+]}{[ROH]} \cdot \frac{[NO_2OH]}{[NO_2^+]} \cdot \frac{f_{R^+} \cdot f_{NO_2OH}}{f_{ROH} \cdot f_{NO_2^+}} \quad \ldots\ldots\ldots \quad (3)$$

The K's are thermodynamic equilibrium constants defined in terms of the ratio a_{R^+}/a_{ROH} and not its reciprocal.

If the *f*-product is unity throughout the medium range, then equation (4) holds, with *b* independent of medium :

$$[NO_2]/[NO_2OH] = b \,.\, [R^+]/[ROH] = b \,.\, R \quad \ldots\ldots\ldots \quad (4)$$

If, in a given medium, *r*, the rate of nitration of ArH, is given experimentally by (5) and theoretically by (6), with k_2° independent of medium, then (7) holds, since

$$[HNO_3] = [NO_2^+] + [NO_2OH].$$
$$r = k_2\,[ArH]\,[HNO_3] \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$
$$r = k_2^\circ\,[ArH]\,[NO_2^+] \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$
$$k_2 = k_2^\circ\,[NO_2^+]/([NO_2^+] + [NO_2OH]) \;.. \quad (7)$$

It is assumed throughout that the ion $H_2NO_3^+$ is not present in appreciable concentration.

For nitrations in media in which $[NO_2OH] \gg [NO_2^+]$, equations (4) and (7) give :

$$\log k_2 = \log k_2^\circ + \log R + \log b \quad \ldots\ldots\ldots\ldots \quad (8)$$

which has already been approximately verified[4] (with the aid of an acidity function for carbinol ionization, not here required) for the nitrations of the p-$Me.C_6H_4.NMe_3^+$ and $PhNMe_3^+$ ions in 76—82% and 82—85% sulphuric acid respectively.

More generally, however, (4) and (7) give :

$$1/R = k_2^\circ\, b \,.\, 1/k_2 - b \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Fig. 1 shows a test of equation (9) in 85—90% sulphuric acid, using 1/R for indicator (I)[5] and $1/k_2$ for the nitration of the $PhNMe_3^+$ ion[2] with 0·025M. reagents. The line in Fig. 1 is drawn to a gradient, $k_2^\circ b = 2{\cdot}40$, and an intercept, $-b = 0{\cdot}56$ (giving $k_2^\circ = 4{\cdot}3$), calculated by the method of least squares. The factor *b* being now known, the fraction $[NO_2^+]/([NO_2^+] + [NO_2OH])$ may be calculated for 85—90% sulphuric acid. The results form the full line in Fig. 2, which is extrapolated to less acid media with slightly less certain values of R.

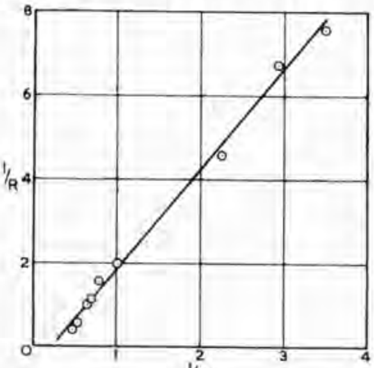

FIG. 1

The reliability of this calculation depends on the invariance of *b* and k_2° with medium, in equations (4) and (7) ; and on the accuracy of the indicator measurements. For the indicator (I), the latter are most accurately measurable in 85—90% sulphuric acid. Any variations of *b* and k_2° should reveal themselves as a curvature of the line in Fig. 1 (unless mutually compensating). The only relevant observations at present available[4] indicate that the gradient in Fig. 1 may not vary by more than ± 25%. Only a curve *concave* to the $1/k_2$ axis, with this change in gradient, can be plausibly fitted to the points in Fig. 1. With this curvature, and (to test the possible range of error) allowing an arbitrary variation of $k_2^\circ = 5{\cdot}4 - 3{\cdot}2$ for 86—90% sulphuric acid, the derived values of *b* define the upper boundary ($H_2SO_4 >$ 87%) of the shaded area in Fig. 2. A steeper fall in k_2° with rising acidity would raise the boundary further ; but other

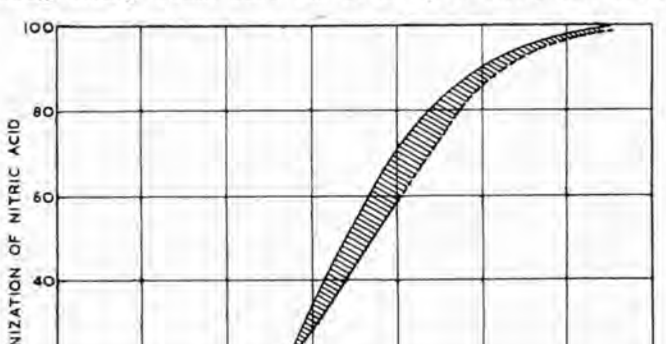

FIG. 2

likely simultaneous variations of k_2° and b (consistent with the same curvature) give ionization curves lying mainly within the shaded area.

A product of the form (10)

$$[NO_2^+[a_{H_2O} / [NO_2OH] h_0 = K_{NO_2OH} \dots\dots\dots \quad (10)$$

has been defined by V. Gold and B. W. V. Hawes[6] as a " secondary " basicity constant for carbinol-like ionization (a_{H_2O} is derived from vapour-pressure measurements[6] ; and -log h_0 = H_0, Hammett's acidity function[7]). From Fig. 1, for the best range (87·9 — 90·1% sulphuric acid) $K_{NO_2OH} = (2{\cdot}49\text{—}2{\cdot}58) \times 10^{12}$, giving $pK_{NO_2OH} \sim 11{\cdot}59$ for 0·025 M. nitric acid in this medium range, for which $pK_{ROH} \sim 11{\cdot}3$ for indicator (I). (From the upper boundary line $pK_{NO_2OH} \sim 11{\cdot}4$). By an undoubtedly hazardous extrapolation, K_{NO_2OH} for 88—90% sulphuric acid may be used (with the appropriate values of a_{H_2O} and h_0) to calculate the degree of ionization in media more acid than 90% sulphuric acid, for which equation (9) cannot be used, because nitration speed is here greatly influenced by solvent factors other than those affecting the ionization of nitric acid. The results are given as the broken continuation of the ionization curve in Fig. 2.

Equation (9) could evidently be applied to other cationic substituting agents,[8] if comparable reaction velocity and indicator measurements were available.

The line in Fig. 2 is an ionization curve for nitric acid which is consistent with the experimental information at present available. The shaded area is a region in which the true ionization curve may lie. A fuller calculation will be published elsewhere when further indicator measurements have been completed.

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NITRATION IN SULPHURIC ACID

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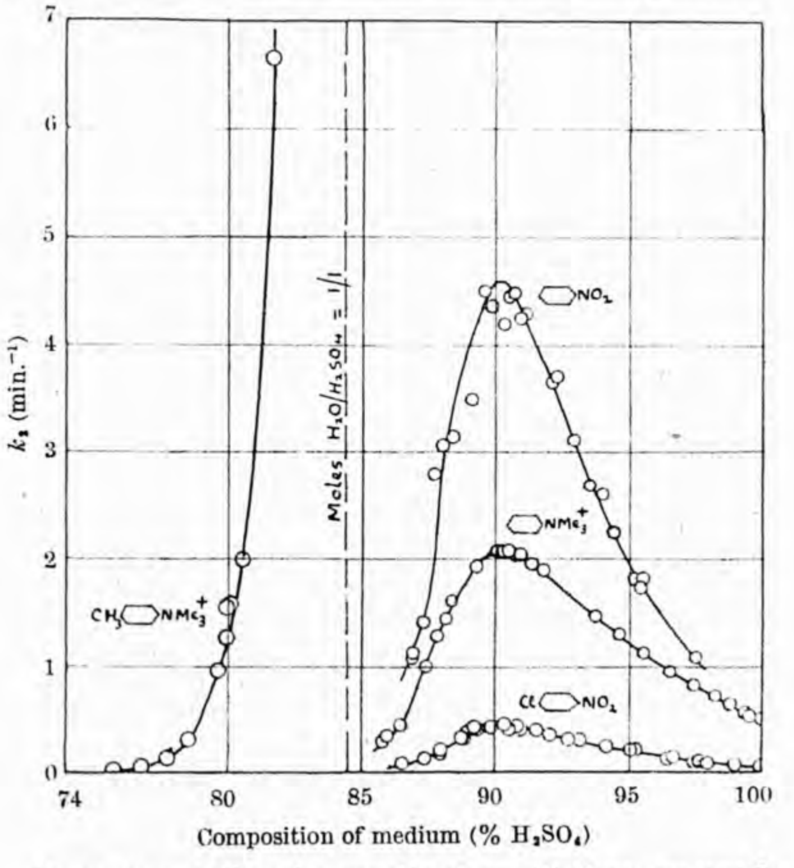
Nitration in Sulphuric Acid

In the nitration of 2 : 4-dinitrotoluene in homogeneous solution in 87–100 per cent sulphuric acid media[1], the effective nitrating agent is the nitronium (NO_2^+) ion[2]. The velocity coefficient k_2 of the equation

$$d[ArNO_2]/dt = k_2\,[ArH]\,[HNO_3]$$

(which is valid for fixed initial conditions only) has a maximum (first discovered by Martinsen[3]) in 92·0 per cent sulphuric acid at 90°.

We have now extended the experiments to the nitration of (*a*) nitrobenzene, (*b*) *p*-chloronitrobenzene, and (*c*) the trimethylphenylammonium ion (introduced as its nitrate), all at 25°. The diagram shows the variations of k_2 with medium composition.



Experimentally, the results show (i) that, as nearly as can be judged, all three substances are nitrated most rapidly, at 25°, in the same optimum medium of approximately 90·4 per cent sulphuric acid; (ii) that relative rates of nitration for these compounds do not vary greatly with medium composition[10].

Medium, % H_2SO_4	97·0	96·0	94·0	92·0	90·0	89·0	87·0
$k_2(a)/k_2(b)$	9·1	9·3	10·3	10·4	10·2	10·6	9·4
$k_2(c)/k_2(b)$	6·5	6·1	5·7	5·0	4·8	5·2	5·6

These kinetic features are consistent with the previous supposition[1] that, in the equation

$$NO_2^+ + ArH + B = ArNO_2 + BH^+,$$

an acceptor molecule B, furnished by the medium, plays a part in determining the rate of nitration in a highly acid environment; but doubt is thrown on the validity of this hypothesis by Melander's demonstration[11] that a tritium atom and a protium atom are replaced at the same rate in the nitration of toluene to dinitrotoluene.

The trimethyl-*p*-tolylammonium ion, which stands structurally to the trimethylphenylammonium ion as *p*-nitrotoluene does to nitrobenzene, is rapidly nitrated (see diagram) in media in which the molar ratio H_2O/H_2SO_4 exceeds unity. The same conclusion follows, for benzene[7] and toluene[8], from a comparison of their two-phase nitrations with those of nitrobenzene[5] and dinitrotoluene[6]. Chemical and physical evidence (especially Raman spectra[4]) shows that no substantial concentrations of nitronium ion can exist in such media. The nitrating agent may be the $H_2NO_3^+$ ion[9], or, perhaps more probably, the NO_2^+ ion, present in very small concentration.

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NITRATION IN SULPHURIC ACID. PART VIII. KINETICS OF NITRATION OF THE TRIMETHYLPHENYLAMMONIUM ION

BY
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AND
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626. *Nitration in Sulphuric Acid. Part VIII.* Kinetics of Nitration of the Trimethylphenylammonium Ion.*

By T. G. BONNER, FREDA BOWYER, and GWYN WILLIAMS.

The rates of nitration of the trimethylphenylammonium ion (put in as nitrate or methosulphate) have been measured in 100—82% sulphuric acid solutions. The velocity coefficient for nitration has a maximum value in 90·4% sulphuric acid; and, in a given medium, it varies with initial concentration in a qualitatively predictable manner.

The variation of the nitration velocity coefficient in 90—82% sulphuric acid can be correlated with the carbinol acidity function J_0 or directly with results for the extent of ionisation of 4 : 4′ : 4″-trinitrotriphenylcarbinol in the same medium range. The correlation suggests that diminution in the extent of ionisation of nitric acid to nitronium ion is the major factor which causes a 200-fold diminution of the nitration velocity coefficient in this medium range.

THE nitration of 2 : 4-dinitrotoluene to 2 : 4 : 6-trinitrotoluene at 60—120° in sulphuric acid–water media (Bennett, Brand, D. M. James, Saunders, and Williams, Part IV, *J.*, 1947, 474) is accompanied by oxidation processes which convert about 40% of the initial nitric acid into nitrous acid at 90°, though without using more than about 3% of the 2 : 4-dinitrotoluene. As shown in Part IV, the nitration reaction can be separated analytically from the simultaneous oxidation, of which the relative extent decreases with falling temperature. Although 2 : 4-dinitrotoluene itself would be nitrated inconveniently slowly at temperatures at which oxidation would be negligible, other compounds can be nitrated at 25° without the complication of a simultaneous oxidation reaction. Detailed experiments have been made with nitrobenzene, *p*-chloronitrobenzene, and the trimethylphenylammonium ion (Bonner, M. E. James, Lowen, and Williams, *Nature*, 1949, **163**, 955). All three compounds are nitrated at an accessible speed at 25° without detectable formation of nitrous acid. The nitration of the trimethylphenylammonium ion has two special features: (*a*) nitration by the nitronium ion is a reaction between two positively charged ions; this circumstance may possibly be expected to give rise to special features in the nitration kinetics; (*b*) the formation of a conjugate acid of the aromatic substance, through proton uptake by the substituent group, is excluded. With some compounds the formation of a conjugate acid may complicate the reaction kinetics in strongly acid media (cf., *e.g.*, Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277), though, in the light of recent measurements of basic strengths of aromatic nitro-compounds in sulphuric acid media (Brand, *J.*, 1950, 997; Gillespie, *ibid.*, p. 2542), it seems unlikely that formation of the actual conjugate acid can affect the nitration results in 99—85% sulphuric acid, for those nitro-compounds which are nitrated *at measurable speeds* in this medium range, since the extent of their ionisation becomes very small in media containing less than 99% sulphuric acid. However, the results for the nitration of 2 : 4-dinitrotoluene in oleum media (Part IV, *loc. cit.*) require correction for salt formation by the aromatic compound.

The nitration of the trimethylphenylammonium ion has been carried out by using, as starting materials, both trimethylphenylammonium nitrate (the reagents then being automatically present in equivalent concentrations, unless additional nitric acid is added) and (in order to vary initial reagent concentrations independently of one another) trimethylphenylammonium methosulphate in combination with nitric acid. The progress of reaction was followed by analysis for residual nitric acid concentration as a function of time.

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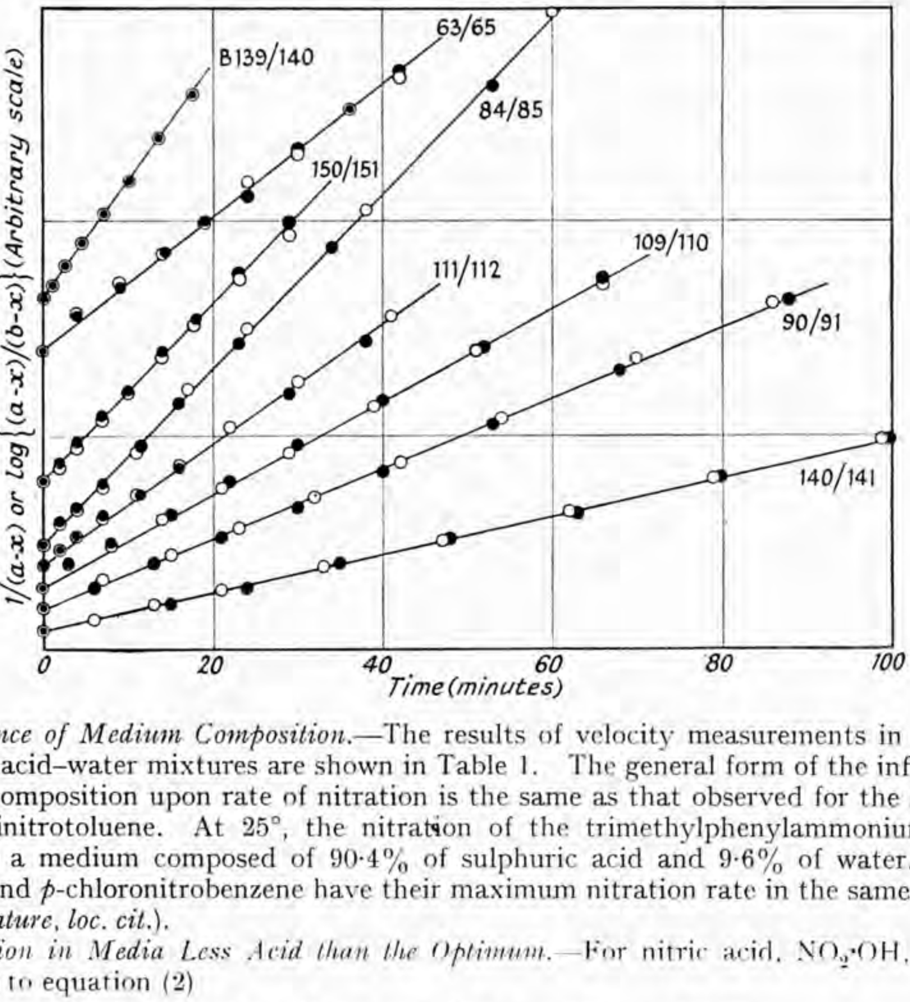
* Part VII, *J.*, 1950, 3318.

The trimethylphenylammonium ion is well known to be nitrated (by concentrated nitric acid at 100°) exclusively in the *m*-position (Vorländer and Siebert, *Ber.*, 1919, **52**, 283). The present work shows that, for given initial reactant concentrations in a specified medium, the rate of nitration (in sulphuric acid at 16—35°) is given by the equation

$$-\mathrm{d}[\mathrm{HNO_3}]/\mathrm{d}t = k_2[\mathrm{NMe_3Ph^+}][\mathrm{HNO_3}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $[\mathrm{HNO_3}]$ represents the stoicheiometric total concentration of nitric acid. The validity of equation (1) is demonstrated in Fig. 1, which shows linear graphs of $1/[\mathrm{HNO_3}]$ plotted against time for reactions in which trimethylphenylammonium nitrate was present alone, and linear graphs of $\log\{[\mathrm{HNO_3}]/[\mathrm{NMe_3Ph^+}]\}$ for reaction mixtures containing unequal reagent concentrations. The results in Fig. 1 are for different initial conditions, which may be read from the tables; and they also show the reproducibility of duplicate experiments.

FIG. 1. *Course of individual nitrations.*



Influence of Medium Composition.—The results of velocity measurements in different sulphuric acid–water mixtures are shown in Table 1. The general form of the influence of medium composition upon rate of nitration is the same as that observed for the nitration of 2 : 4-dinitrotoluene. At 25°, the nitration of the trimethylphenylammonium ion is fastest in a medium composed of 90·4% of sulphuric acid and 9·6% of water. Nitrobenzene and *p*-chloronitrobenzene have their maximum nitration rate in the same medium at 25° (*Nature, loc. cit.*).

Nitration in Media Less Acid than the Optimum.—For nitric acid, $\mathrm{NO_2{\cdot}OH}$, ionising according to equation (2)

$$\mathrm{NO_2{\cdot}OH + 2H_2SO_4 \rightleftharpoons NO_2^+ + OH_3^+ + 2HSO_4^-} \quad . \quad . \quad . \quad (2)$$

and for a triarylcarbinol indicator, R·OH, ionising according to a similar equation (cf., *e.g.*, Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644), we may write (Lowen, Murray, and Williams, Part VII, *loc. cit.*) :

$$\mathrm{p}K_{\mathrm{NO_2\cdot OH}} - \mathrm{p}K_{\mathrm{R\cdot OH}} = \log\frac{[\mathrm{NO_2^+}]}{[\mathrm{NO_2{\cdot}OH}]} - \log\frac{[\mathrm{R^+}]}{[\mathrm{R{\cdot}OH}]} + \log\left\{\frac{f_{\mathrm{NO_2^+}}}{f_{\mathrm{NO_2\cdot OH}}}\cdot\frac{f_{\mathrm{R\cdot OH}}}{f_{\mathrm{R^+}}}\right\} \quad . \quad (3)$$

in which the K's are thermodynamic equilibrium constants for equilibria of type (2).

If the logarithmic term in activity coefficients in (3) is zero for the medium range considered (see Part VII, *loc. cit.*), then

$$[NO_2^+]/[NO_2{\cdot}OH] = b[R^+]/[R{\cdot}OH] = bR \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which b is independent of medium composition, and $R = [R^+]/[R{\cdot}OH]$.

An acidity function, J_0, for ionisation of type (2), may be defined by equation (5) * (see Part VII, *loc. cit.*) :

$$J_0 = -pK_{NO_2{\cdot}OH} - \log\,([NO_2^+]/[NO_2{\cdot}OH]) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or by the equivalent definition $J_0 = H_0 + \log a_{H_2O}$ (Gold and Hawes, *J.*, 1951, 2102), where H_0 is Hammett's acidity function.

Then, if the rate or nitration of an aromatic compound is given experimentally by equation (1), and theoretically by equation (6), equations (7) hold; and, from (5) and

$$-d[HNO_3]/dt = k_2^\circ[NO_2^+][ArH] \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

(7), equation (8) should represent the variation of the experimental velocity coefficient, k_2, with medium composition.

$$k_2 = k_2^\circ[NO_2^+]/[HNO_3] = k_2^\circ[NO_2^+]/\{[NO_2^+] + [NO_2{\cdot}OH]\} \quad . \quad . \quad (7)$$

$$\log k_2 = \log k_2^\circ - pK_{NO_2{\cdot}OH} - J_0 - \log\{1 + [NO_2^+]/[NO_2{\cdot}OH]\} \quad . \quad . \quad (8)$$

For media in which $[NO_2{\cdot}OH] \gg [NO_2^+]$, equation (8) reduces to equation (9) :

$$\log k_2 = \log k_2^\circ - pK_{NO_2{\cdot}OH} - J_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Provided that k_2° of equation (6) does not itself vary with medium, equation (9) predicts that $\log k_2$ should be connected with J_0 by a straight line of negative unit gradient.

By this test, equation (9) has been verified in Part VII (*loc. cit.*) for the nitration of the

TABLE 1. *Influence of medium composition upon rate of nitration at 25°*

(Initial concentration of $NMe_3Ph^+\}NO_3^- = 0{\cdot}0252 \pm 0{\cdot}0002$M.)

Medium : H_2SO_4, wt. %	Expt. no.	k_2, min.$^{-1}$	k_2, mean	R *	$(1 + 0{\cdot}56R)k_2/R$
100	24	0·51	0·51		
	23	0·50			
99·6	149	0·531	0·53		
	148	0·534			
99·5	123	0·555	0·56		
	124	0·555			
98·8	68	0·64	0·64		
98·3	88	0·70	0·71		
	89	0·71			
97·5	91	0·81	0·82		
	90	0·82			
96·6	38	0·93	0·94		
	56	0·95			
95·6	118	1·11	1·12		
	120	1·13			
94·7	117	1·27	1·30		
	119	1·32			
93·8	69	1·46	1·46		
91·9	70	1·86	1·88		
	73	1·90			
91·4	77	1·92	1·94		
	80	1·96			
91·0	94	2·01	2·03		
	95	2·05			
90·8	82	2·03	2·03		
	83	2·03			
90·6	92	2·07	2·07		
	93	2·07			
90·3	84	2·06	2·06		
	85	2·06			
90·1	101	2·05	2·05	2·63	1·93
	102	2·05			
89·4	86	1·91	1·92	1·78	2·17
	87	1·92			
88·4	100	1·59	1·60	1·00	2·44
	99	1·60			
88·3	103	1·44	1·44	0·871	2·46
	104	1·44			
87·9	72	1·27	1·27	0·646	2·68
87·5	143	0·98	0·99	0·501	2·52
	142	0·99			
86·5	140	0·444	0·446	0·219	2·29
	141	0·448			
86·0	74	0·343	0·343	0·148	2·50
85·9	162	0·286	0·287	0·132	2·33
	163	0·287			
84·7	B110	0·106	0·106	0·0575	1·90
82·0	B111	0·0101	0·0103	(0·0078) †	(1·33) †
	B112	0·0104			

* For trinitrotriphenylcarbinol.

† In 82·0% sulphuric acid the indicator $(p\text{-}X{\cdot}C_6H_4)_3C{\cdot}OH$ ($X = NO_2$) is only 0·78% ionised and the colorimetric measurement of its ionisation is liable to error. Calculated from the J_0 function and results for the indicator with $X = NMe_3^+$ (Murray and Williams, *loc. cit.*), $R = 0{\cdot}0071$ and $(1 + 0{\cdot}56R)k_2/R = 1{\cdot}46$.

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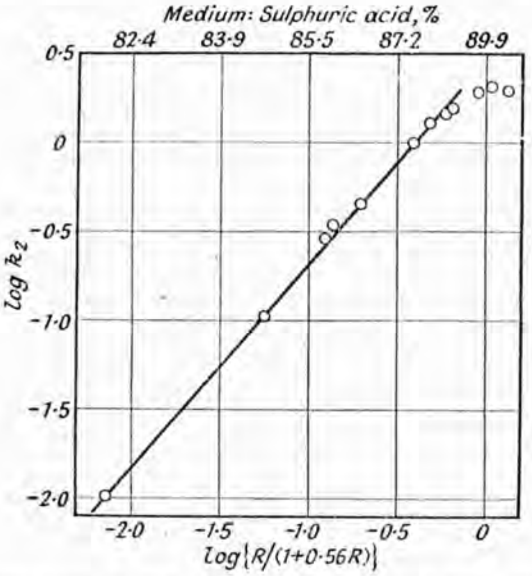
* $K_{NO_2{\cdot}OH}$ is here defined in terms of the ratio $a_{NO_2^+}/a_{NO_2{\cdot}OH}$ and not of its reciprocal (see Gold and Hawes, *loc. cit.*).

trimethyl-*p*-tolylammonium ion in 76—82% sulphuric acid, whereby the hypothesis of nitration by the NO_2^+ ion has been shown to be preferable to that of a nitrating agent (*e.g.*, $H_2NO_3^+$) formed from nitric acid by simple proton uptake (cf. Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871). In more acid media, the condition $[NO_2{\cdot}OH] \gg [NO_2^+]$ no longer holds, equation (9) is invalid, and equation (8) must be used.

Since the medium range 82—90% sulphuric acid for nitration of the trimethylphenylammonium ion falls within the medium range of variable ionisation of a single indicator, namely 4 : 4′ : 4″-trinitrotriphenylcarbinol (Westheimer and Kharasch, *loc. cit.*; Murray and Williams, *J.*, 1950, 3322; see fifth column of Table 1), it is convenient, instead of (8), to use (10), derived from (7) and (4):

$$\log k_2 = \log k_2^\circ + \log b + \log\{R/(1 + bR)\} \quad . \quad . \quad . \quad . \quad (10)$$

FIG. 2.



It has been shown previously (Bonner and Williams, *Chem. and Ind.*, 1951, 820) that, for the medium range 86—89·5% sulphuric acid, the results of Table 1 satisfy the equation derived from (1), (6), and (4):

$$1/R = k_2^\circ b/k_2 - b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

with the constants $b = 0{\cdot}56$, $k_2^\circ = 4{\cdot}3$ (whence the degree of ionisation of nitric acid to the nitronium ion can be estimated). With this value of b, $\log k_2$ is plotted against $\log\{R/(1 + bR)\}$ in Fig 2. The straight line drawn has a gradient of 1·1, which may be compared with the unit gradient demanded by equation (10) if b and k_2°, defined by (4) and (6) respectively, remain sensibly constant over the medium range considered. From Fig. 2, the linear relation appears to hold, within experimental error, for the medium range 82·0—88·4% sulphuric acid, covering a 150-fold variation in k_2 of equation (1). In only slightly more acid media k_2 approaches its maximum value. The linear relation between $\log k_2$ and J_0, predicted by equation (9) when ionisation of nitric acid is small, fails in media more acid than 86% sulphuric acid (Part VII, *loc. cit.*). Otherwise expressed, constancy of b and k_2° in equation (10) requires that the ratio $(1 + bR)k_2/R$ should be independent of medium. Col. 6 of Table 1 shows how far this expectation is realised for 90—82% sulphuric acid media, in which k_2 changes 200-fold. This more sensitive test indicates that the linear log–log plot in Fig. 2 conceals a small curvature. From carbinol-indicator measurements (Part VII), b is probably constant to within 0·2 log unit over the range 80—85% sulphuric acid. From Fig. 2 and Table 1, it may be provisionally inferred, without excluding the possibility of a change in k_2° by a small multiple, that diminution of the degree of ionisation of nitric acid to the nitronium ion is the major factor which reduces k_2 by 200-fold in the medium range 90—82% sulphuric acid.

Nitration in Media More Acid than the Optimum.—The variation in k_2 over the medium range 100—90% sulphuric acid cannot at present be treated quantitatively (cf. Hughes, Ingold, and Reed, *J.*, 1950, 2400). The absence of an isotope effect in aromatic nitration (Melander, *Nature*, 1949, **163**, 499; *Arkiv Kemi*, 1950, **2**, 211), recently confirmed (unpublished experiments) under the conditions of kinetic experiments for nitrobenzene and deuteronitrobenzene, is evidence against the hypothesis of basic catalysis by bisulphate ion (Part IV, *loc. cit.*).

Influence of Reagent Concentrations.—Increase of initial concentration of either reagent causes increase of anion concentration in the system. From the observed influence of water upon the nitration rate (Table 1), it may therefore be expected that rise of initial reagent concentration should increase or decrease k_2 in media more acid or less acid respectively than the optimum. Table 2 shows that these expectations are realised qualitatively. The effects are barely accessible to experiments with trimethylphenylammonium nitrate, because initial heat effects (see Experimental section) forbid any substantial increase of initial concentration; but they are seen clearly in experiments with the methosulphate. Quantitative aspects will be considered in later papers, together with results for other compounds. In media more aqueous than the optimum for nitration, the addition of various substances to the medium produces an apparent lowering of the (colorimetric) extent of ionisation of a triarylcarbinol indicator and thus (if the effect is real) should affect the extent of ionisation of nitric acid to nitronium ion. The effects of added substances upon the apparent ionisation of an indicator can be correlated with their effects upon speed of nitration (unpublished experiments).

TABLE 2. *Variation of initial reactant concentrations at 25°.*

Medium: H_2SO_4, %	Expt. no.	Initial concn. (M) of: NMe_3Ph^+	Initial concn. (M) of: HNO_3	k_2, min.$^{-1}$
100 *	B182	0·0502	0·0301	0·483
	B183	0·0502	0·0301	0·482
	B184	0·300	0·0300	0·728
	B185	0·300	0·0302	0·725
	B186	0·500	0·0300	0·843
	B187	0·500	0·0302	0·873
	B214	2·457	0·0299	0·712
97·4 *	B137	0·0495	0·0298	0·835
	B138	0·0500	0·0303	0·822
	B139	0·1003	0·0305	0·915
	B140	0·1000	0·0305	0·911
	B141	0·200	0·0304	1·00
	B142	0·200	0·0301	1·01
	B143	0·300	0·0303	1·06
	B144	0·300	0·0302	1·08
	B145	0·401	0·0306	1·19
	B146	0·401	0·0304	1·22
96·6 †	38	0·0251	0·0251	0·93
	56	0·0251	0·0251	0·95
	60	0·0253	0·0503	0·99
	64	0·0254	0·0755	0·98
	63	0·0255	0·1004	0·95
	65	0·0251	0·1003	0·95
	58	0·0504	0·0504	1·00
	34	0·0501	0·0501	1·00
88·3 †	103	0·0252	0·0252	1·44
	104	0·0253	0·0253	1·44
	113	0·0252	0·0485	1·42
	114	0·0250	0·0484	1·45
	111	0·0504	0·0504	1·41
	112	0·0504	0·0504	1·39
88·2 *	B170	0·0504	0·0312	1·33
	B180	0·0503	0·0310	1·36
	B168	0·302	0·0312	0·518
	B169	0·302	0·0312	0·510
86·7 *	B162	0·0499	0·0301	0·414
	B164	0·0503	0·0302	0·410
	B163	0·0998	0·0302	0·298

* Expts. with trimethylphenylammonium methosulphate.
† Expts. with trimethylphenylammonium nitrate.

The effects of adding potassium hydrogen sulphate to reaction mixtures resemble (qualitatively at least) those of change of initial concentration of the aromatic salt.

Influence of Temperature.—Results at different temperatures are shown in Table 3. Over the small temperature range of 20°, the graph of log k_2, plotted against $1/T$, is linear for 87·5% sulphuric acid medium and corresponds to $k_2 = 1{\cdot}05 \times 10^8 \exp.-13{,}390/\boldsymbol{R}T$ litre mole^{-1} sec.$^{-1}$. The results for 99·6% sulphuric acid medium correspond roughly to the equation $k_2 = 1{\cdot}4 \times 10^9 \exp.-15{,}300/\boldsymbol{R}T$ litre mole^{-1} sec.$^{-1}$; but the graph of log k_2 against $1/T$ shows a distinct curvature, giving a maximum range for E of 14·9—16·3 kcal. In 100% sulphuric acid E appears to range from 14·7 ± 0·6 to 16·8 ± 0·6 kcal. at 15—35°.

TABLE 3. *Variation of temperature.*

Medium: H_2SO_4, %	Temp.	Expt. no.	Initial concn. (M) of: NMe_3Ph^+	HNO_3	k_2, min.$^{-1}$	Medium: H_2SO_4, %	Temp.	Expt. no.	Initial concn. (M) of: NMe_3Ph^+	HNO_3	k_2, min.$^{-1}$
100 *	15°	B250	0·0501	0·0300	0·209	99·6 †	15·92°	154	0·0252	0·0252	0·225
	25	B251	0·0500	0·0300	0·557		15·92	155	0·0252	0·0252	0·227
	35	B249	0·0503	0·0298	1·25		19·97	158	0·0253	0·0253	0·346
							19·97	159	0·0252	0·0252	0·344
87·5 †	15·92°	156	0·0254	0·0254	0·479		24·96	Mean from Table 1			0·533
	15·92	157	0·0252	0·0252	0·481		29·96	160	0·0254	0·0254	0·821
	24·96	Mean from Table 1			0·985		29·96	161	0·0252	0·0252	0·821
	35·00	150	0·0254	0·0254	2·01		35·00	152	0·0252	0·0252	1·21
	35·00	151	0·0252	0·0252	2·05		35·00	153	0·0252	0·0252	1·21

* Expts. with trimethylphenylammonium methosulphate.
† Expts. with trimethylphenylammonium nitrate.

EXPERIMENTAL

Materials.—Trimethylphenylammonium iodide (made in 96% yield from methyl iodide and dimethylaniline, m. p. after recrystallisation from absolute alcohol 216—218°, decomp.) was converted into the nitrate by the action of aqueous silver nitrate, excess of silver being removed with hydrogen sulphide. The nitrate, obtained by evaporation to dryness, was recrystallised from a solution in the minimum quantity of hot absolute alcohol to which was then added about twelve times the volume of hot dry acetone. The nitrate separated on cooling; m. p. 119—119·5° (Found: C, 54·2; H, 7·1; N, 14·0. Calc. for $C_9H_{14}O_3N_2$: C, 54·5; H, 7·1; N, 14·1%). Vorländer and Siebert (*Ber.*, 1919, **52**, 283) give m. p. 110—115° for the nitrate recrystallised from alcohol–ether.

Trimethylphenylammonium methosulphate was made from dimethylaniline and dimethyl sulphate in dry benzene; it separated out as it was formed, and was recrystallised from a small amount of absolute alcohol. Crystallisation could be accelerated, if desired, by addition of a large volume of dry acetone. It had m. p. 121° (Found: C, 49·1, 49·0; H, 7·2, 7·1; N, 5·5, 5·5; S, 12·8, 12·6. Calc. for $C_{10}H_{17}O_4NS$: C, 48·6; H, 6·9; N, 5·7; S, 13·0%).

Pure nitric acid and other inorganic materials were obtained as described in Part IV (*loc. cit.*).

Nitration Media.—Sulphuric acid–water mixtures were prepared by adding water or redistilled oleum to 98% sulphuric acid. Corresponding media containing nitric acid were obtained by addition of anhydrous nitric acid (freshly distilled from sulphuric acid). Analysis was by alkali titration coupled with ferrous sulphate titration of nitric acid. For example, a medium was found to contain 96·45, 96·56, 96·60, 96·58, mean 96·55%, of sulphuric acid, giving the mol. ratio $H_2O/H_2SO_4 = 0·195$. The corresponding nitric acid solution contained total acid 0·01962, 0·01959, 0·01959, 0·01958 equiv./g., and nitric acid 4153, 4145, 4137 × 10^{-7} mole/g., giving mol. ratio $H_2O/H_2SO_4 = 0·193$.

Alkali was standardised against 1N-hydrochloric acid, itself standardised gravimetrically or referred to standard potassium iodate or sodium carbonate.

100% Sulphuric acid was prepared by adjusting 98% sulphuric acid to maximum freezing point by the addition of sulphur trioxide.

Velocity Measurements.—Temperature was controlled to ±0·02° and measured on an N.P.L. calibrated thermometer. Most of the velocity measurements were made at 25° (more exactly 24·96°). Solutions were made up to known volumes at thermostat temperature and combined in such a way that the weight of each component of the reaction mixture (including weight of solvent) was always known. The reaction vessel was a three-necked flask carrying a thermometer and a mercury-sealed electric stirrer. Before transference to this vessel, the reagents were pre-mixed in a flask with standard socket neck by addition of the second component from a container with standard cone neck.

When trimethylphenylammonium nitrate was used, 0·245—0·250 g. of the solid salt was added to 50 ml. of medium in the pre-mixing flask, thus starting the nitration. When required, nitric acid was incorporated in the medium to give a higher initial concentration than that provided by the salt alone. With trimethylphenylammonium methosulphate, either 25 ml. of nitric solution were added to 25 ml. of salt solution, or, later, a small volume of more concentrated nitric acid solution was added to 50 ml. of medium containing the aromatic salt and, sometimes, an added inorganic salt or other compound when the effects of these upon nitration rate were to be investigated.

The starting time of the reaction was always taken as the instant at which the reagents came together. Pre-mixing and transfer to the reaction vessel (with stirrer already in operation) required 40—50 seconds with the nitrate and 10—15 seconds with the methosulphate.

The temperature rose by 0·4—0·7° when the solid nitrate salt was added to sulphuric acid; and the temperature of the reaction mixture was observed at one-minute intervals. Normally, the temperature of the reaction mixture came to within 0·05° of that of the thermostat in about 5 minutes and to within 0·02° in about 8 minutes. The total time of observation for a reaction varied from 20 to 240 minutes, being frequently of the order 100 minutes. From the known activation energies, the errors in the velocity coefficients caused by the initial temperature fluctuations were calculated to be not more than 1%. Thermal disturbances were minimised by working with only 0·025M-reagents; and initial errors of all kinds were eliminated as far as possible by evaluating velocity coefficients graphically. Initial temperature rise in the reaction mixture was always much less when it was prepared from the solution of the methosulphate salt.

Analysis of Reaction Mixtures.—5-Ml. samples were extracted at intervals in pipettes calibrated to deliver the reaction media employed with a standard delivery time, including drainage, of 25 sec. (*e.g.*, a pipette delivered 4·92 ± 0·02 ml. for 87·8—100% sulphuric acid). The samples were run into 30 ml. of ice-cold concentrated sulphuric acid, and their nitric acid content was determined by titration against M/20-ferrous sulphate solution in 40% sulphuric acid (preserved under nitrogen), Treadwell and Vontobel's potentiometric method (*Helv. Chim. Acta*, 1937, **20**, 573; cf. Part IV) being used. The titration was carried out under nitrogen, with mechanical stirring. The ferrous sulphate solution was run in from a 10-ml. micro-burette, and the end-point of the titration was marked by a sharp increase of potential of 200—300 mv for the addition of 0·02—0·03 ml. of reagent, provided that the sulphuric acid content at the end of the titration lay between 80 and 95%. This was ensured by adjustment, when necessary. Standardisation of a ferrous sulphate solution against (*a*) potassium nitrate dissolved in 96% sulphuric acid, (*b*) aqueous potassium nitrate, and (*c*) potassium permanganate, gave its concentration as (*a*) 0·0504, (*b*) 0·0508, (*c*) 0·0505N.

Some preliminary experiments were made on the reverse method of running nitrate into excess of standard ferrous sulphate, and observing the potentiometric end-point. The following was a test of the reverse titration: 5-ml. portions of approximately M/5-ferrous sulphate solution in 40% sulphuric acid were run into 40 ml. of concentrated sulphuric acid and titrated by running in M/10-potassium nitrate solution (in 40% sulphuric acid) from the burette to the end-point, which was marked by a drop in potential of about 150 mv, not quite so sharply defined as in the commoner forward titration. Volumes required were: 4·71, 4·70, 4·65, 4·66, 4·76, 4·63, 4·65, 4·68, mean 4·68 ml. From these results, 1 ml. of the potassium nitrate solution was equivalent to 1·07 ml. of ferrous sulphate solution, which may be compared with 1·06 ml. obtained by the forward titration. The reverse titration was not used for velocity measurements.

Absence of Nitrous Acid in Reaction Products.—2-Ml. samples of reaction mixture containing initially 0·025M-trimethylphenylammonium nitrate were run into 10 ml. of approx. N/20-chloramine-T solution, diluted to 100 ml.; and the solutions were titrated, by use of potassium iodide and sodium thiosulphate, with the following results:

(i) Medium: 87·5% sulphuric acid.

Time (min.)	14	23	34	45	60	78
Titre (ml.)	11·71	11·79	11·79	11·76	11·70	11·68

(ii) Medium: 99·6% sulphuric acid.

Time (min.)	15	41	70	92	110
Titre (ml.)	11·76	11·71	11·71	11·75	11·72

The blank titration for 10 ml. of chloramine-T solution after addition of 2 ml. of sulphuric acid, containing no aromatic nitrate, was 11·70 ml. Evidently, no nitrous acid is formed in the reaction.

Results.—Unless otherwise stated, times are given in minutes. One experiment is given in full below.

Expt. 91. Temp. 25·0°. Initial concn. of nitrate salt = 0·0254M. Medium: 97·5% H_2SO_4.

Time, min.	0	6	13	21	30	40	53	68	88
Concn. of HNO_3, M	0·0254	0·0223	0·0199	0·0177	0·0158	0·0139	0·0122	0·01055	0·0091
Change, %	—	12·2	21·8	30·4	37·8	45·1	52·0	58·5	64·5
k_2	—	0·91	0·84	0·82	0·80	0·81	0·81	0·82	0·81

k_2 from linear plot (Fig. 1) = 0·81.

The reproducibility of the velocity measurements may be judged from Fig. 1.

The investigation of this compound was originally suggested by Dr. G. M. Bennett, C.B., F.R.S. We wish to acknowledge that most of the experimental work was done (in 1946—1948) while one of us (T. G. B.) held a Further Education Grant from the Ministry of Education. We thank Imperial Chemical Industries Limited for financial help.

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27.

NITRATION IN SULPHURIC ACID.

PART IX. THE RATES OF NITRATION OF NITROBENZENE AND PENTADEUTERO-NITROBENZENE

BY

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FREDA BOWYER,
AND
GWYN WILLIAMS

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540. *Nitration in Sulphuric Acid. Part IX.* The Rates of Nitration of Nitrobenzene and Pentadeuteronitrobenzene.*

By T. G. BONNER, FREDA BOWYER, and GWYN WILLIAMS.

Within the limits of experimental error, the rates of nitration of nitrobenzene in 97·4% and in 86·7% sulphuric acid are identical with the rates of nitration of pentadeuteronitrobenzene in the same media. These results confirm Melander's demonstration (*Arkiv Kemi*, 1950, 2, 211) that breakage of the C–H bond is not part of the rate-determining step in aromatic nitration, and extend it to more highly acid nitrating conditions.

MELANDER has shown (*Nature*, 1949, **163**, 599; *Arkiv Kemi*, 1950, **2**, 211) that the radioactive intensities in the products of nitration of benzene, toluene, bromobenzene, and naphthalene, each containing one appropriately situated nuclear tritium atom, are consistent only with the supposition that nitration at C–T and C–H bonds takes place at approximately the same speed. Melander derived minimum values for the velocity coeffient ratios k_T/k_H for all stages of the nitrations and found them to lie between 0·74 and 0·85. It follows that the breakage of the C–H bond does not form part of the rate-determining step in aromatic nitration under the conditions of these experiments.

This conclusive result applies, in the first instance, to experimental conditions nearer to those of preparative nitration, with relatively high proportions of nitric acid and aromatic compound to sulphuric acid, and with moderately aqueous nitrating mixtures, than to the conditions of the kinetic nitration experiments in homogeneous systems initiated by Martinsen (*Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605). In Melander's experiments, naphthalene was nitrated with a nitric acid–water mixture; but mixtures of nitric acid (*d* 1·40—1·42) and sulphuric acid (96—96·6%) were used for the other three compounds, and reaction was continued to the dinitration stage. Calculation from the quantities used gives typical reaction mixtures as approximately: benzene 0·0055, HNO_3 0·043, H_2SO_4 0·099, H_2O 0·085 mole, molar ratio $H_2O/H_2SO_4 = 0{\cdot}86$; and toluene 0·0046, HNO_3 0·053, H_2SO_4 0·124, H_2O 0·104 mole, molar ratio $H_2O/H_2SO_4 = 0{\cdot}84$. In these nitrations, only the conversion of nitrobenzene into *m*-dinitrobenzene requires a sulphuric acid–water mixture acid enough to convert a considerable proportion of nitric acid into nitronium ion (Hetherington and Masson, *J.*, 1933, 105; Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955; Williams and Lowen, *J.*, 1950, 3312). The molar ratio H_2O/H_2SO_4 in the acid employed corresponds to a nitration medium considerably more aqueous than the medium ($H_2O/H_2SO_4 \sim 0{\cdot}58$) giving maximum rate in the homogeneous nitration of nitrobenzene (Bonner *et al.*, *loc. cit.*). Oleum was used in the nitrating acid for bromobenzene but here also the molar ratio H_2O/H_2SO_4 was not less than 0·79.

Nitrating acids with these relatively high water (and nitric acid) contents must contain considerable concentrations of the basic species bisulphate ion; and the conditions of nitration are different from those prevailing in kinetic nitration experiments in homogeneous solution in concentrated sulphuric acid (Part IV, *J.*, 1947, 474; Part VIII, *loc. cit.*). For example, the reaction mixture in 97·4% sulphuric acid (see Table) has the composition: nitrobenzene 0·0075, HNO_3 0·0017, H_2SO_4 0·909, H_2O 0·132 mole, molar ratio $H_2O/H_2SO_4 = 0{\cdot}145$. It is in the most acid conditions, if anywhere, that the separation of the proton might have kinetic significance in nitration.

In order to put it beyond doubt that Melander's demonstration, that there is no hydrogen isotope effect in nitration, applies also to highly acid conditions, we have compared directly the rates of nitration of nitrobenzene and pentadeuteronitrobenzene, with small reagent concentrations, in homogeneous solution. In the media employed the rates of nitration are given by the equation $-d[HNO_3]/dt = k_2[ArNO_2][HNO_3]$, since $\log\{[ArNO_2]/[HNO_3]\}$ is linear with time (see Figure). The final results for velocity coefficients are given in the Table. The observed identity of nitration rate for nitrobenzene and pentadeuteronitrobenzene, in both media, is not likely to have been simulated

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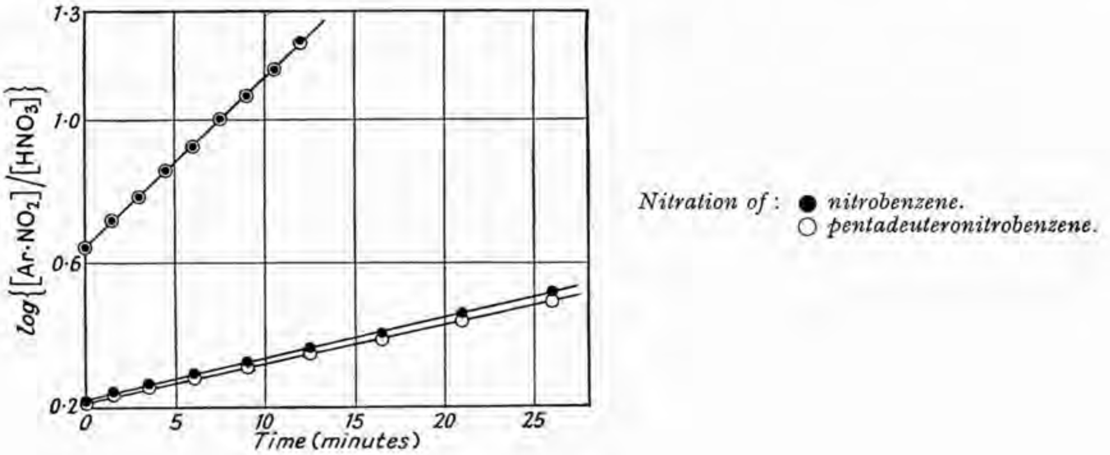
* Part VIII, *J.*, 1952, 3274.

through isotope exchange between aromatic compound and nitrating acid; because (*a*) it could only be due *either* to genuine identity of nitration rate at C–H and C–D bonds *or* to complete transfer of deuterium from aromatic ring to nitrating acid before measurements were started; (*b*) rapid deuterium exchange between a nitro-aromatic compound and sulphuric acid is improbable (cf. Ingold, Raisin, and Wilson, *J.*, 1936, 915, 1637); and (*c*) we have found that pentadeuteronitrobenzene does not change its density after exposure to 97·3% sulphuric acid, at 20°, for a longer time than that required for the nitration experiments (see Experimental section).



Rates of nitration at 25° (k_2 in l. mole^{-1} min.$^{-1}$; concentrations in terms of M).

Medium	Expt.	Nitrobenzene			Expt.	Deuteronitrobenzene		
H_2SO_4, %	No.	[C_6H_5·NO_2]	[HNO_3]	k_2	No.	[C_6D_5·NO_2]	[HNO_3]	k_2
97·4	130	0·1498	0·03402	0·941	129	0·1498	0·03442	0·938
	132	0·1498	0·03419	0·954	131	0·1498	0·03397	0·942
86·7	133	0·05015	0·03040	1·34	135	0·04963	0·03056	1·29
	134	0·05023	0·03205	1·33	136	0·05017	0·02998	1·27

Earlier results, with a less exactly characterised specimen of pentadeuteronitrobenzene, pointed to the same general conclusion as the results in the Table. With k_H and k_D referring, respectively, to replacement of protium and deuterium atoms, the results were: in 97·9% sulphuric acid (0·025M-Ar·NO_2), $k_H = 0·74$; $k_D = 0·67, 0·69$. In 97·6% sulphuric acid (0·15M-Ar·NO_2), $k_H = 0·87, 0·89$; $k_D = 0·82, 0·84$.

We are indebted to Dr. J. C. D. Brand, of the University of Glasgow, for the results of measurements of nitration velocity (made by following the change in extinction coefficient, Brand and Paton, *J.*, 1952, 281) for the same sample of pentadeuteronitrobenzene in 10% oleum (102·25% H_2SO_4). With excess of nitric acid (0·108 molal) and 9 × 10^{-5} molal concentration of aromatic compound, the first-order nitration velocity coefficients were: for C_6H_5·NO_2, $k_1 = 0·0344, 0·0341$; for C_6D_5·NO_2, $k_1 = 0·0320, 0·0323$. In this medium, the greater part (75—80%) of the aromatic compound exists as its (cation) conjugate acid. It is not certain that the extent of cation formation is the same for the protium and deuterium compounds.

If the whole of the difference between the zero-point energies of a C–H and of a C–D bond (*ca.* 2 kcal./mole) were to influence nitration rates, then the ratio k_D/k_H could be as low as 0·035. It is clear, even in the most acid media, that the fission of the C–H bond does not help to determine rate of nitration (cf. Melander, *loc. cit.*). The hypothesis of bisulphate-ion catalysis (Part IV, *loc. cit.*) cannot be sustained.

EXPERIMENTAL

Preparation of Pentadeuteronitrobenzene.—Hexadeuterobenzene was prepared by the method of Ingold, Raisin, and Wilson (*loc. cit.*; Best and Wilson, *J.*, 1946, 239). 10 ml. of benzene (B.D.H. "for molecular weight determinations"; distilled from phosphoric oxide; d_{25}^{25} 0·8760) were shaken for 5 days with 60 g. of deuterosulphuric acid, containing 51 moles % of D_2SO_4 and

49 moles % of D_2O, made by distilling sulphur trioxide (80 g.) into 35 ml. of Norsk Hydro Heavy Water, containing 99·75 atoms % of D, standardising the product by titration with 0·1N-sodium hydroxide, and final adjustment to 83·8% (w/w) D_2SO_4 by distilling in a further 11·4 g. of sulphur trioxide. After this first shaking, the benzene was distilled away and shaken a second time for 5 days with a fresh portion (60 g.) of the same acid. It was then distilled (*a*) on to dry barium oxide, (*b*) after several hours, on to phosphoric oxide, and (*c*) after 3 hr., into a clean receiver. At this stage the benzene had d_{25}^{25} 0·09421, corresponding to a content 92·0 atoms % of D. It was then shaken a third time for 5 days, but this time with 60 g. of 83·8% deuterosulphuric acid prepared from heavy water containing 99·95 atoms % of D. It was then treated with barium oxide and phosphoric oxide as before. It now had d_{25}^{25} 0·9456 corresponding to content 99·3 atoms % of D (Weldon and Wilson, *J.*, 1946, 235); the yield was 5·7 g.

All the benzene distillations referred to were conducted in all-glass apparatus, with oil-pump vacuum, and with appropriate heating baths and refrigerants. In the preparation of deuterosulphuric acid (cf. Best and Wilson, *loc. cit.*), it was found satisfactory to distil sulphur trioxide slowly (without vacuum) from a vessel attached by a ground joint, through a capillary, into two flasks in series, cooled by ice–water, one empty and one containing deuterium oxide, protected from the atmosphere, through a capillary, by a sulphuric acid trap. Sulphur trioxide was driven from the first flask into the heavy water after sealing off the first capillary; and the apparatus was isolated by sealing off the second.

Nitration of Hexadeuterobenzene.—Preliminary experiments with ordinary benzene showed the nitration procedure described by Masson (*Nature*, 1931, **128**, 726) to be the most profitable in yield, though a slightly more aqueous nitrating acid was found to be advantageous in excluding all dinitration. To minimise the (small) risk of isotope exchange during nitration, the nitrating acid was made up with deuterosulphuric acid. The composition was D_2SO_4 (18·4 g.), H_2O (3·14 g.), anhydrous HNO_3 (5·29 g.). Into this were run in, during 70 min., 5·7 g. of hexadeuterobenzene through a capillary, the temperature being kept at 45°, and the reaction flask being shaken throughout. Shaking, still at 45°, was continued for a further 230 min. The temperature was raised to 60° at the end of the reaction, after which the reaction mixture was poured into water, and the product was separated, washed with sodium carbonate solution and then with water, dried with phosphoric oxide and distilled. The yield was 7·7 g. (88·9%). After two distillations a middle fraction (5·5 g.; b. p. 64—65°/5 mm., 215—217°/711 mm.) of very faintly yellow *pentadeuteronitrobenzene* was collected (Found: N, 11·1. $C_6D_5O_2N$ requires N, 10·9%). It had d_{25}^{25} 1·2533 and n_D^{20} 1·5504.

Deuterium Content.—We are very much indebted to Dr. R. I. Reed of the University of Glasgow for a mass-spectrographic examination of the water formed by combustion of our product. The result showed its deuterium content to be $>$99·5 atoms %.

Nitrobenzene.—"AnalaR" material was dried and distilled and purified by fractional crystallisation to constant m. p. 5·82°.

Velocity Measurements.—The rate of nitration was followed by measuring the residual nitric acid concentration at known time intervals. The methods of experiment and of analysis of reaction mixtures and media were as described in Part VIII (Bonner, Bowyer, and Williams, *loc. cit.*).

Test for Deuterium Exchange during Nitration.—A specimen of pentadeuteronitrobenzene (2·3 g.) was dissolved in 97·3% sulphuric acid (5 ml.) and kept at 20° for 1·75 hr. It was then recovered by dilution with 16 ml. of water, repeated extraction with ether, repeated washing with water, drying, and distillation under reduced pressure. The material had d 1·2520 and 1·2518, respectively, before and after exposure to sulphuric acid. Since ordinary nitrobenzene has d^{25} 1·198, deuterium exchange with sulphuric acid during a nitration experiment (requiring $<$30 min.) is evidently inappreciable.

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28.

AROMATIC ARYLALKYLATION. PART I. THE TRIPHENYLMETHYLATION OF *o*-CRESOL IN SULPHURIC ACID–ACETIC ACID

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D.Sc. 1960

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560. *Aromatic Arylalkylation. Part I. The Triphenylmethylation of* o-*Cresol in Sulphuric Acid–Acetic Acid.*

By T. G. Bonner, J. M. Clayton, and (the late) Gwyn Williams.

The reaction between triphenylmethanol and *o*-cresol to form 4-hydroxy-3-methylphenyltriphenylmethane in sulphuric–acetic acid has been studied. Rates of reaction and the extent of ionisation of the alcohol over a wide range of media indicate reaction through the electrophilic attack by the Ph_3C^+ ion: $Ph_3C^+ + C_6H_4Me{\cdot}OH \longrightarrow Ph_3C{\cdot}C_6H_3Me{\cdot}OH + H^+$. The constants of the Arrhenius equation have been evaluated.

The nature of the coloured compound which is immediately formed on mixing of the reactants is discussed.

Studies of absorption spectra, conductivity, freezing-point depression, and salt formation have shown that triphenylmethanol is readily converted into the triphenylmethyl ion in strong acids.[1] The possibility arises that in such media this ion might be an effective electrophilic substituting reagent and this appears to be the case in the reaction between triphenylmethanol and phenols in sulphuric–acetic acid (1 : 6 v/v) first reported by Baeyer and Villiger.[2] They found that phenol formed *p*-hydroxyphenyltriphenylmethane, and anisole formed *p*-methoxyphenyltriphenylmethane. Baeyer[3] also found that tetra-arylmethanes were obtained, with hydrogen chloride, from solutions of triphenylmethyl chloride in various phenols, heat sometimes being needed for reaction; if potassium phenoxide was used substitution in the nucleus did not occur and a triphenylmethylphenyl ether was formed, but it was later shown by Gomberg and Kamm[4] that in the presence of acid the sole product was *p*-hydroxyphenyltriphenylmethane. These workers also found that the action of sulphuric acid in the Baeyer–Villiger reaction was purely catalytic and that it could be reduced to a very small concentration or replaced by hydrochloric acid.

Boyd and Hardy[5] studied the reaction of many phenols with triphenylmethanol in acetic acid containing 10—20% of sulphuric acid. The phenols fell into three groups, (i) those giving a tetraphenylmethane derivative, (ii) those reducing triphenylmethanol to triphenylmethane, and (iii) those which did not react. Phenols of groups (i) and (ii) produced a deep brown colour when added to the yellow solution of triphenylmethanol in the sulphuric–acetic acid, and Hardy[5] proposed that for these the first step was 1 : 4 addition of the ions of triphenylmethyl hydrogen sulphate followed by breakdown of the resulting quinonoid complex to a hydroxyphenyltriphenylmethane (group i) or triphenyl methane (group ii).

Hart and Cassis[6] recently found reaction of triphenylmethyl chloride and phenol in dilute *o*-dichlorobenzene solution to be autocatalytic, the hydrochloric acid liberated acting as a catalyst. They concluded that the acid facilitated the ionisation of the chloride to the triphenylmethyl ion and represented the reaction as direct triphenylmethylation of the aromatic nucleus by the ion. Since there could be little doubt that the same ion is present in a solution of triphenylmethanol in sulphuric–acetic acid and that the extent of its formation varies with the acidity, it was decided to find whether the rate of triphenylmethylation in this medium could be directly correlated with the degree of ionisation of the alcohol.

EXPERIMENTAL

Initial Experiments.—The limited solubility of the tetraphenylmethane product from phenol in the media employed led to the choice of *o*-cresol for the kinetic work. This reaction is known [7] to give 4-hydroxy-3-methylphenyltriphenylmethane. At higher acidities, it was found that some interaction occurred between the medium and *o*-cresol. Quantitative bromination of the product, based on Francis and Hill's method,[8] showed that a mono-substituted derivative had been formed, probably 4-hydroxy-3-methylbenzenesulphonic acid. To limit this and extend the range of sulphuric–acetic media, all media were prepared with a water content of 5% w/w. Provided the initial concentrations of the reactants were not greater than 0·1M, no precipitation of the tetraphenylmethane product occurred. The reported reversibility [5] of the reaction was found to be negligible in media containing 5% of water, the extent of breakdown of the product in an anhydrous media containing 30% of sulphuric acid being only 3·4% after 5 hr. at 55°.

Media and Reagents.—Acetic acid was purified by Orton and Bradfield's method; [9] no sample was obtained by this method with a m. p. lower than 16·5°. B.D.H. "AnalaR" sulphuric acid was used as supplied. B.D.H. *o*-cresol was distilled three times at atmospheric pressure before use (b. p. 195°); triphenylmethanol was recrystallised from alcohol (m. p. 160—162°). Media for kinetic experiments were made up by weight and all figures quoted are for % by wt. The water content was maintained in the range 4·9—5·1%.

Triphenylcarbonium-ion Spectrum.—The spectrum of this ion is well-known.[1, 10] In sulphuric–acetic acid it has the usual broad double-peaked band with maxima at 4080 and 4320 Å ($\varepsilon_{max.}$ *ca.* 35,000). Where there is complete ionisation the extinction coefficient at the maxima changes by only 2% between 18° and 55°. At 4320 Å, the extinction coefficients of *o*-cresol (ε 0·26) and of 4-hydroxy-3-methylphenyltriphenylmethane (ε 0·4) are negligible.

Solutions containing triphenylmethanol were analysed with a Hilger Spekker photoelectric absorptiometer, having a mercury-lamp light source and a filter to transmit a narrow band at *ca.* 4350 Å. Samples (1 ml.) of the mixture were always diluted between 625 and 5000 times with a stock solution containing 1 : 3 sulphuric–acetic acid. Complete ionisation of the triphenylmethanol occurred in this solution, in agreement with Gold and Hawes's observation [10] that ionisation is complete in the anhydrous mixture, 16 : 84 sulphuric–acetic acid. The composition of the stock solution was not critical as the same analytical results were obtained, within 1—2%, when the sulphuric acid content was varied over the range 20—30%.

A sample removed from the diluted solution for measurement in the absorptiometer gave a lower reading if the solution had been kept for some time after shaking than if it had been removed immediately. This suggested that moisture had been absorbed at the surface of the solution in the stoppered flask. The error was avoided by pouring away the first few ml. of solution before transference to the absorption cell.

Kinetic Measurements.—These were carried out at 25° and at 55°. The solutions of triphenylmethanol and *o*-cresol were made up separately in the particular medium at the given temperatures. Triphenylmethanol sometimes dissolved rather slowly and had to be heated to 80—100°. High temperatures and prolonged heating were avoided as a slow reaction then occurred. An appropriate sample, usually 20 ml., of the triphenylmethanol solution was pipetted into a 100 ml. flask, and the flask stoppered and returned to the thermostat. To start the reaction the required volume of the *o*-cresol solution was run in from a pipette, zero time corresponding to the end of the free flow of the solution. Six 1 ml. samples were removed at suitable times. In each case the reaction was stopped by running the solution into 20—40 ml. of the 1 : 3 sulphuric–acetic acid stock solution, and the resulting solution made up to 25 ml. or 50 ml. 1 ml. of this solution was diluted 25—100 times and then measured in the absorptiometer, 1 cm. cells and a control of the stock diluent solution being used. Two separate samples of each solution were measured and three readings were taken on each sample. The corresponding value of the triphenylmethanol concentration was read off from the previously prepared standard curve. Rates were measured over the range of media containing from 5% to 40% of H_2SO_4. Excellent second-order rate constants were obtained below 25% sulphuric acid (Fig. 1). The rate of reaction was unchanged when the glass surface was increased by means of glass balls.

Interaction of the Medium with o-*Cresol.*—Reaction of sulphuric acid in the medium with *o*-cresol in the absence of the triphenylmethanol was followed by the bromination method.[8]

Aliquot parts of the solution, at appropriate intervals, were run into dilute sulphuric acid and treated with a slight excess of standard bromate–bromide solution, and the unconsumed bromine estimated by addition of potassium iodide and titration of the iodine liberated with sodium thiosulphate solution. Analyses of standard *o*-cresol solutions by this method were correct within 1%.

Ionisation of Triphenylmethanol in Sulphuric–Acetic Acid Media.—The extent of ionisation of triphenylmethanol was obtained by plotting the ultraviolet absorption spectrum for each mixture over the range 3600—4600 Å with a Hilger "Uvispek" Spectrophotometer. The "specific colour intensity," S, at a given wavelength is defined as $(\log I_0/I)/(\text{concn. of } Ph_3C{\cdot}OH)$. The % ionisation in any particular medium is obtained from the ratio of the specific colour intensity at a selected wavelength to that at the same wavelength in a medium containing 3 : 7 sulphuric–acetic acid in which triphenylmethanol is completely ionised. Values obtained at the two maxima (at 4080 and 4320 Å) gave identical % ionisation. During measurements the absorption cells were kept in a constant-temperature jacket (±1°). Measurements were carried out at 25° and at 55° over the range 5—22% of sulphuric acid.

FIG. 1.

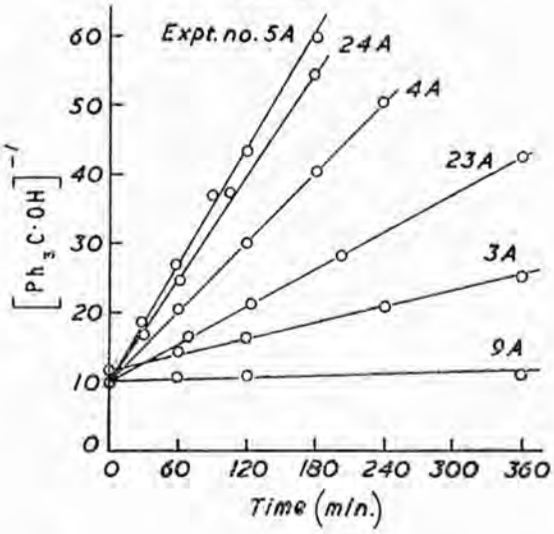
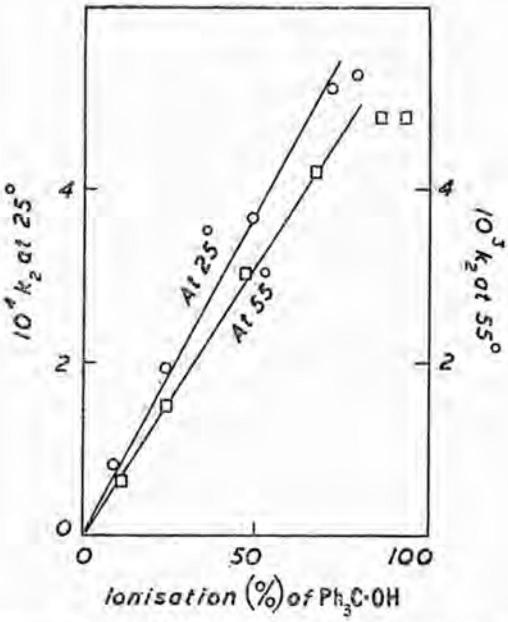


FIG. 2.



Preparation of 3 : 5-*Dideutero-*o*-cresol.*—Deuteration of *o*-toluidine to 3 : 5-dideutero-*o*-toluidine was carried out by repeated treatment of the amine hydrochloride with heavy water at 100°, as in the method used for aniline.[11] Dideuterocresol was obtained from the product by diazotisation and separated by steam-distillation. We are greatly indebted to Dr. D. H. Whiffen of the University of Birmingham for infrared analyses of samples of the deuterocresol which indicated its purity and the rapidity of its exchange reaction in sulphuric–acetic acid.

RESULTS AND DISCUSSION

Kinetics of Triphenylmethylation of o*-Cresol.*—The reaction of triphenylmethanol with *o*-cresol was followed over a range of media containing 0—40% w/w of sulphuric acid in acetic acid, all media containing 5% of water. Over the range 0—22·5% sulphuric acid, the kinetic results fitted the equation :

$$-d[Ph_3C{\cdot}OH]/dt = k_2[Ph_3C{\cdot}OH][o\text{-cresol}] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the reaction always being followed up to 70—90% conversion of the triphenylmethanol. The results for 55° and 25° are shown in Tables 1 and 3. The rate equation is obeyed for a ten-fold change in the initial concentration of either reactant as shown in Table 2. In media containing 25% or more of sulphuric acid the rate equation applies only to the initial stages, a strong deceleration setting in. Triphenylmethanol was stable in media containing up to 40% of sulphuric acid but interaction of the medium with *o*-cresol was marked in media containing more than 25% of sulphuric acid. The attack on the *o*-cresol was followed by a parallel investigation of its rate of disappearance in each medium in the absence of triphenylmethanol. Comparison with the rate of triphenylmethylation was made by calculation of the time of half-change for both reactions, the results of which are shown in Table 1. It can be seen that this side reaction is negligible in media containing less than 25% of sulphuric acid.

TABLE 1. *Variation of k_2 with medium composition for the triphenylmethylation of* o-*cresol at* 55°.

Initial [$Ph_3C{\cdot}OH$] = [*o*-cresol] = 0·1M.

Expt. no.	Medium (% by wt.)			$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)	$t_{\frac{1}{2}}$ for triphenylmethylation (min.)	$t_{\frac{1}{2}}$ for attack of medium on cresol (min.)
	H_2SO_4	H_2O	AcOH			
8*A*	0·0	5·1	95·0	0	—	—
8*B*	0·0	5·1	95·0	0	—	—
9*A*	4·9	5·2	89·9	0·521	3400	—
9*B*	4·9	5·2	89·9	0·516	3400	—
3*A*	10·0	5·1	84·9	6·47	275	—
3*B*	10·0	5·1	84·9	6·53	275	—
23*A*	12·4	5·0	82·7	15·1	112	—
23*B*	12·4	5·0	82·7	15·2	112	—
4*A*	15·0	5·1	80·0	29·5	60	>1500
4*B*	15·0	5·1	80·0	30·1	60	>1500
24*A*	17·2	4·9	77·9	41·8	40	—
24*B*	17·2	4·9	77·9	41·1	40	—
5*A*	20·1	5·1	74·9	47·6	36	1056
5*B*	20·1	5·1	74·9	48·6	36	1056
11*A*	22·4	5·3	72·4	48·3	35	—
11*B*	22·4	5·3	72·4	48·1	35	—
6*A*	25·0	5·1	70·0	46·4	36	496
6*B*	25·0	5·1	70·0	46·6	36	496
7*B*	29·7	5·1	65·3	35·6	42	271
7*B*	29·7	5·1	65·3	36·4	45	271
10*A*	34·5	5·0	60·5	25·0	120	123
10*B*	34·5	5·0	60·5	23·6	130	123
12*A*	39·8	5·2	55·0	17·2	180	68
12*B*	39·8	5·2	55·0	17·2	180	68

In media containing more than 25% of H_2SO_4 only the results for the initial 20% reaction could be considered for the calculation of k_2. The reaction in 39·8% H_2SO_4 appeared to stop at about 62% conversion.

TABLE 2. *Effect on k_2 of change of initial concentrations of the reactants.*

Temp. 55°. 21% H_2SO_4, 5·2% H_2O, 73·8% AcOH.

Expt. no.	Initial concn. (g. mole l.$^{-1}$)		$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)	Expt. no.	Initial concn. (g. mole l.$^{-1}$)		$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)
	$Ph_3C{\cdot}OH$	$C_6H_4Me{\cdot}OH$			$Ph_3C{\cdot}OH$	$C_6H_4Me{\cdot}OH$	
13*A*	0·0807	0·0795	48·6	15*B*	0·0202	0·0793	47·8
13*B*	0·0807	0·0798	47·2	16*A*	0·0803	0·2006	47·8
14*B*	0·0799	0·0197	47·2	16*B*	0·0802	0·2006	46·9
14*C*	0·0793	0·0191	47·2	17*A*	0·2002	0·0304	47·8
15*A*	0·0200	0·0815	48·3	17*B*	0·2002	0·0301	47·2

TABLE 3. *Variation of k_2 with medium composition at* 25°.

Initial [$Ph_3C{\cdot}OH$] = 0·025M, [*o*-cresol] = 0·1M.

Expt. no.	Medium (% by wt.)			$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)	Expt. no.	Medium (% by wt.)			$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)
	H_2SO_4	H_2O	AcOH			H_2SO_4	H_2O	AcOH	
25*A*	21·0	5·2	73·9	5·33	26*B*	17·2	4·9	77·9	3·66
25*B*	21·0	5·2	73·9	5·33	28	14·7	5·0	80·3	1·93
27	19·6	5·1	75·3	5·17	29	12·4	5·0	82·7	0·81
26*A*	17·2	4·9	77·9	3·66	30	0·0	5·1	95·0	0·00

Correlation of Rate Constant and the Ionisation of Triphenylmethanol.—No reaction was observed in a medium which did not contain sulphuric acid, indicating complete lack of reactivity. If the reaction is bimolecular between the triphenylmethyl ion and *o*-cresol the rate of reaction will be given by :

$$\text{Rate} = k_0[Ph_3C^+][o\text{-cresol}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_0, the theoretical rate constant, is independent of the medium. It follows from (1) and (2) that

$$k_2 = k_0[Ph_3C^+]/[Ph_3C{\cdot}OH] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

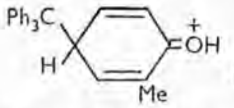
Some values of the % ionisation of triphenylmethanol were directly determined for media in which k_2 had been measured; where they were not directly obtained, the values were read from a plot of the ionisation results given in Table 4 against composition of the medium. The test of equation (3) at 25° and at 55° is shown in Fig. 2. A straight-line relation between k_2 and % ionisation is evident at both temperatures up to 70% ionisation. The failure of the rate constant to continue to rise with increasing formation of the triphenylmethyl ion above this point corresponds to the more strongly acid media containing 20—25% of sulphuric acid. Ionisation of triphenylmethanol is virtually complete in 25% sulphuric acid and its variation with medium strength is normal. The lack of correlation in this range appears therefore to be associated with the *o*-cresol, but it cannot be attributed to chemical attack of the medium on the *o*-cresol as the results in Table 1 show that this is negligible in media having less than 25% of sulphuric acid. A significant fact is that in both the 20% and the 22·4% sulphuric acid the rate equation is followed normally over 80—90% of the triphenylmethylation, as in media of lower acidity, whereas in media above 25% sulphuric acid the rate equation is only followed for about 20% of the reaction. The explanation may be appreciable formation of the conjugate acid of *o*-cresol in the range 20—25% sulphuric acid. The cation $CH_3{\cdot}C_6H_4{\cdot}OH_2^+$ would probably not react with the triphenylmethyl ion, and consequently the experimental rate constant k_2 would be reduced in direct proportion to the extent of formation of this ion.

TABLE 4. *Ionisation of triphenylmethanol in sulphuric–acetic acid.*

$[Ph_3C{\cdot}OH] \sim 10^{-5}$M.

Medium (% by wt.)			Ionisation (%)		Medium (% by wt.)			Ionisation (%)	
H_2SO_4	H_2O	AcOH	at 55°	at 25°	H_2SO_4	H_2O	AcOH	at 55°	at 25°
5·0	5·0	90·0	0·718	0·117	17·2	4·9	77·9	66·9	49·5
9·9	5·0	85·1	9·02	2·41	19·6	5·1	75·3	83·6	71·4
12·4	5·0	82·7	23·2	9·07	22·2	5·0	72·7	92·2	85·0
14·7	5·0	80·3	44·9	23·9					

(I)



(II)

Formation of the Coloured Intermediate.—The immediate development of a deep brown colour on the addition of certain phenols, including *o*-cresol, to a solution of triphenylmethanol in sulphuric–acetic acid was discussed by Hardy.[5] Since the colour change appeared only with those phenols which either yield tetraphenylmethane derivatives or reduce the alcohol to triphenylmethane and not for completely unreactive phenols, Hardy suggested that it indicated the formation of a quinonoid intermediate which for *o*-cresol would be (I), this later losing a molecule of sulphuric acid to give 4-hydroxy-3-methylphenyltriphenylmethane. Baeyer [3] had previously observed that triphenylmethyl chloride gave an intense brown colour in phenol, *m*-cresol, and *p*-cresol, a less intense colour in *o*-cresol, but none in guaiacol, thymol, trichlorophenol, or some other deactivated phenols unless stannic chloride was added. All solutions in which a colour was obtained gave off hydrogen chloride when kept or heated. As the above reactions can now be regarded as taking place through electrophilic attack by the triphenylmethyl ion formed from either the alcohol or the chloride, a more correct representation of the intermediate would be (II). However it is unlikely that structure (II) would be the deep brown intermediate since if the triphenylmethyl ion formed a sp^3-hybridised bond with a carbon atom of the ring as shown, with the predominating resonance structure of the product having the positive charge on the oxygen atom, the electrons should be less mobile. Further, this structure is similar to the usual representation of the transition complex for electrophilic aromatic substitution which is momentarily formed by the relatively small fraction of molecules of high energy content and would be expected to lose a proton to form the product or break down to the reactant molecules almost instantaneously. The fact that the intense brown colour changes on dilution into the yellow colour of the triphenylmethyl ion strongly suggests that it is a π-bonded molecular complex between the triphenylmethyl ion and *o*-cresol. This complex could proceed through (II) and proton-elimination to the product. A study of this complex and others similarly formed is being undertaken.

An attempt was made to discover whether there was a hydrogen isotope effect in the reaction by studying the triphenylation of 3 : 5-dideutero-2-cresol under the same conditions. This however could not be achieved as the deuterocresol compound exchanged its deuterium atoms for hydrogen very rapidly in the acid media used.

The Constants of the Arrhenius Equation.—The true rate constants for the triphenylation reaction at 25° and 55° represented by k_0 in equation (3), evaluated from the slopes of Fig. 2, are $7{\cdot}35 \times 10^{-4}$ and $6{\cdot}16 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$ respectively which lead to the Arrhenius equation $k = 1{\cdot}04 \times 10^{7} \exp(-13{,}480/\boldsymbol{R}T)$ (l. mole^{-1} sec.$^{-1}$). The low value of the energy of activation (13·480 kcal. mole^{-1}) is in accordance with the reactive character expected of the triphenylmethyl ion, while the steric limitations imposed by the attachment of three phenyl groups to the central carbon atom would be expected to reduce the non-exponential term appreciably from the theoretical value of *ca.* 10^{11}.

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341. *The Effect of the Salt* Ph_3CSnCl_5 *on the Stannic Chloride-catalysed Polymerisation of Styrene.*

By T. G. Bonner, J. M. Clayton, and (the late) Gwyn Williams.

Investigation of the polymerisation of styrene by stannic chloride in carbon tetrachloride with conditions and concentrations similar to those previously employed[1] has shown that in the presence of a trace of the (triphenylmethyl)tin pentachloride, Ph_3CSnCl_5, the polymerisation is retarded for some hours, though the reaction later occurs at approximately the same rate as for untreated reaction mixture and with formation of a similar product. The salt Ph_3CSnCl_5 is extremely sparingly soluble in carbon tetrachloride and is precipitated as golden-yellow crystals when solutions of triphenylmethyl chloride and stannic chloride in this solvent are mixed. No absorption at 4350 Å characteristic of the Ph_3C^+ ion was apparent in the carbon tetrachloride solution, although in ethylene dichloride, in which this salt is very soluble, there was a marked absorption at this wavelength corresponding to *ca.* 10% ionisation when the concentration of salt was *ca.* 10^{-4}M. In the presence of the solid salt a slow polymerisation at a constant rate is maintained throughout the reaction in carbon tetrachloride, which indicates initiation at the solid surface only, presumably by the Ph_3C^+ ions. When the amount of triphenylmethyl chloride added to the reaction mixture was in excess of that required to remove all of the stannic chloride present as Ph_3CSnCl_5 no polymerisation occurred although the solid salt precipitated was allowed to remain in contact with the styrene solution. This suggests that styrene reacts only through a monomer–catalyst complex.[2]

In a mixed solvent containing 70% of ethylene dichloride, and in pure ethylene dichloride the pentachloride can be employed in concentrations of the same order as that of the stannic chloride (*ca.* 0·015M). Polymerisation is much faster than in pure carbon tetrachloride and monomer begins to disappear rapidly as soon as the reactants are mixed, both when stannic chloride is present alone and when it is in excess over the pentachloride; when the latter only was added to the styrene solution, a slow reaction preceded the rapid reaction in both solvents. The weight of polymer recovered from the pure ethylene dichloride solutions by precipitation with methyl alcohol exceeded the amount of monomer consumed and indicated incorporation of the triphenylmethyl group in the polymer. In both retardations, the colour of the solution due to the Ph_3C^+ ion (orange in the mixed solvent, red in pure ethylene dichloride) faded gradually during the slow stage.

It has been shown previously[3] that triphenylmethyl chloride initiates polymerisation of alkyl vinyl ethers in strongly ionising solvents, while its retarding effect has been reported in the polymerisation of styrene by sulphuric acid in ethylene dichloride.[4] The present work confirms this dual function of triphenylmethyl chloride in the form of its stannic chloride salt but further investigation is needed particularly on the molecular-weight range of the polymeric product to establish to what extent it acts as a chain-breaker as well as a co-catalyst.[4]

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BORON TRICHLORIDE AS A DEGRADATIVE REAGENT FOR CARBOHYDRATES AND THEIR DERIVATIVES

By S. Allen, T. G. Bonner, E. J. Bourne and N. M. Saville

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In a study of the interaction of Lewis acids with cyclic acetals and ketals of hexitols it has been found that boron trichloride[1] is a valuable reagent for degrading these derivatives to the parent hexitols. In addition, it is effective in demethylation and deacylation of sugar derivatives and in degrading those polysaccharide derivatives which can be brought into solution with this reagent. Demethylation and deacylation usually do not proceed quite to completion in a single treatment but the main product from aldose derivatives is always the parent sugar and the method provides a simple and convenient means of identifying the latter, e.g. 2:3:4:6-tetra-*O*-methyl-glucose, 2:3:6-tri-*O*-methyl-glucose, methyl cellulose, cellulose acetate and amylopectin acetate each give glucose as the main product. Acetals and ketals always regenerate the original sugar or hexitol in high yield.

The possibility of stereochemical changes occurring in the sugar derivatives during reaction is under investigation but results to date indicate that glucose, mannose, galactose and arabinose are essentially unaffected. Fructose and sorbose, however, appear to be almost completely converted to a derivative, which has a much higher R_p value (solvent, butanol: ethanol: water=4:1:5) than either of these ketoses. The disaccharides, lactose, maltose, and sucrose are attacked to only a very slight extent by boron trichloride, probably due to their low solubility in the reagent but in these cases, boron tribromide[2] has been successfully employed to produce the constituent hexoses. From sucrose, only the glucose constituent has been identified, the fructose portion apparently undergoing further reaction, as referred to above.

The experimental procedure is based on that first reported by Gerrard.[1] Redistilled boron trichloride (0·3–0·5 g.) is introduced into a small tube which is sealed off and weighed; the tube is then cooled to −70° prior to opening. About 10 mgm. of the sugar derivative is added to 1–2 c.c. of dry dichloromethane and the contents of the sealed tube added. In some experiments, the dichloromethane was omitted and excess boron trichloride used. The mixture is kept at −70° for 30 minutes, allowed to attain room temperature and then to evaporate overnight under anhydrous conditions before working up. Any remaining solvent and boron trichloride are drawn off under vacuum and about 5 c.c. of aqueous methanol is added to decompose the residue. The methanol is removed under vacuum at room temperature and the solid product investigated by paper chromatography and ionophoresis. An alternative method of treating the residue after removal of the dichloromethane and excess boron trichloride is to shake with an aqueous suspension of silver carbonate.

Larger quantities have been treated in this way, giving products which can be isolated, purified and identified, e.g. mannitol can be obtained in 63% yield from 1:3–2:5–4:6-tri-*O*-methylene-D-mannitol by following the above procedure.

A detailed examination of selected reactions is now being made.

Received March 21, 1958

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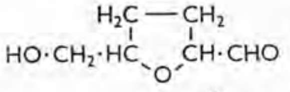
160. *The Iodine-catalysed Conversion of Sucrose into 5-Hydroxymethylfurfuraldehyde.*

By T. G. Bonner, E. J. Bourne, and M. Ruszkiewicz.

Sucrose in dry dimethylformamide containing small amounts of iodine is converted at 100° in comparatively high yield into 5-hydroxymethylfurfuraldehyde (I). The degradation is confined to the fructose unit, and the glucose portion appears to remain unaffected. In the absence of iodine, formation of the aldehyde is negligible.

A mechanism for the reaction is proposed, based on the function of iodine as a catalyst in the dehydration of hydroxy-compounds.

The conversion of pentoses into furfuraldehyde and of hexoses into 5-hydroxymethylfurfuraldehyde (I) by loss of three moles of water per mole of the carbohydrate is normally regarded as an acid-catalysed process.[1] While concentrated mineral acid is used preparatively for the treatment of pentoses, heating with 0·3% oxalic acid at 120° is sufficient to convert either fructose or sucrose into the aldehyde.[2] An investigation [3] of the optimum conditions for the reaction of sucrose established that the formation of the aldehyde originated entirely in the fructose portion of the molecule, the glucose being recovered quantitatively; the maximum yield of aldehyde was 54% (based on the fructose content only). A slightly lower yield (22%, based on the sucrose used) was later obtained,[4] together with humin material, by heating sucrose under pressure in an atmosphere of hydrogen between 130° and 170°, where almost complete fission of the sucrose was found to precede formation of the aldehyde; although no acid was added in this treatment, a pH of 2—3 developed during the heating; this was attributed to the formation of acetol and was regarded as an essential step in the degradation of the fructose.


(I)

Attempts to utilise glucose also as a source of 5-hydroxymethylfurfuraldehyde have been carried out by pre-treatment with potassium or calcium hydroxide followed by heating with oxalic acid,[3] by heating an aqueous solution with and without hydrochloric acid,[5] by reaction with glycine compounds,[6] and by the action of heat on aqueous solutions for several hours.[7,8] The yield from this source is considerably less than from fructose.

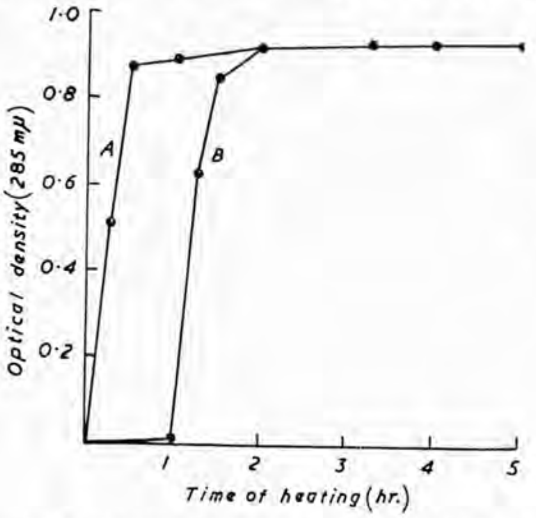
During an investigation of iodine-catalysed condensation of sucrose with carbonyl and other compounds in dimethylformamide, a fast-moving product was found on the chromatograms which by comparison of R_F values in different solvents and by its ultraviolet absorption indicated the presence of 5-hydroxymethylfurfuraldehyde. Further investigation established that a high yield of this was obtained by heating sucrose alone with catalytic quantities of iodine in dry dimethylformamide for 1 hr. Sufficient pure material was separated by paper chromatography to afford its semicarbazone and 2,4-dinitrophenylhydrazone of correct melting points and oxidation with silver oxide gave 5-hydroxymethylfuroic acid. The yield from sucrose by this method was substantially higher than by previous methods and as in the sucrose–oxalic reaction the product appeared to originate solely from the fructose part of the molecule.

Experimental

Materials.—Dimethylformamide was dried over magnesium sulphate and distilled before use. Sucrose and iodine were the AnalaR and resublimed grade respectively.

Identification of 5-Hydroxymethylfurfuraldehyde (I).—Sucrose (14 g.) was heated, with stirring, with dimethyl formamide (50 ml.) and a small crystal of iodine on a boiling-water bath, moisture being excluded. Samples were examined at intervals by paper chromatography with butanol–ethanol–water (4 : 1 : 5 v/v) as solvent. After 30 min. only a trace of unchanged sucrose remained, the main constituents being glucose (R_F 0·18), fructose (R_F 0·16), and 5-hydroxymethylfurfuraldehyde (R_F 0·75). The last spot gave a positive reaction with sprays of *p*-anisidine hydrochloride, urea phosphate, urea hydrochloride, anthrone–phosphoric acid, and diphenylamine–aniline–phosphoric acid, most of which are recognised as reagents for hexoses by virtue of their ability to convert the latter into furfuraldehyde derivatives.[1] After a further hour at 100°, sucrose and fructose had disappeared, only glucose and the aldehyde remaining, with traces of three substances with R_F values intermediate between those of fructose and the aldehyde, and a little oligosaccharide. Heating for a further 3 hr. produced no further change in the pattern of the chromatograms or increase in the amounts of the products. During the experiment, the iodine colour rapidly faded and additional iodine was introduced when the solution appeared colourless. In the absence of iodine, sucrose remained unchanged in dimethylformamide at 100° for 1·5 hr. The need for anhydrous conditions was shown when after an aqueous solution had been heated for 2 hr. at 100°, no sucrose remained, the main products being fructose and glucose together with a little oligosaccharide and a trace of aldehyde; further heating did not modify this result.

The aldehyde was identified by comparison with specimens provided by Drs. O. Theander and H. A. Bouveng, and by Dr. J. D. Garber. The same R_F values were found with the following solvents: butanol–ethanol–water (4 : 1 : 5 v/v); propanol–ethyl acetate–water (7 : 1 : 2, v/v); butanol–acetic acid–water (4 : 1 : 5, v/v); ethyl acetate–acetic acid–water (9 : 2 : 2 v/v); and butanol–benzene–pyridine–water (5 : 1 : 3 : 2, v/v), and the behaviour on electrophoresis in borate [9] buffer was similar. The samples gave identical positive reactions on chromatograms with the spray reagents noted above and with silver nitrate–sodium hydroxide, α-naphthol–phosphoric acid and phloroglucinol–trichloroacetic acid. Identical reactions were also obtained with the orcinol–trichloroacetic acid and 2,4-dinitrophenylhydrazine–hydrochloric acid reagents used [10] in the detection of 5-hydroxymethylfurfuraldehyde.



A, Iodine added at zero time. B, Iodine added after 1 *hour's heating.*

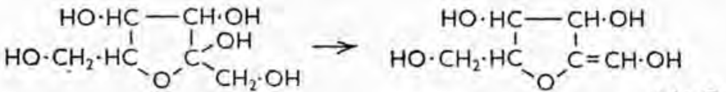
Sufficient material for the preparation of derivatives was obtained by heating sucrose (20 g.) in dimethylformamide (20 ml.) with iodine for 1·5 hr. with stirring. After cooling, water (20 ml.) was added and the solution extracted with ether (3 × 200 ml.). The concentrated ether extract was chromatographed on thick paper (Whatman No. 3) with butanol–ethanol–water; the appropriate section of the paper was pulped and extracted with ether (Soxhlet). This gave the aldehyde which was converted into the semicarbazone,[11,12] m. p. 194—195° (Found: C, 46·2; H, 5·2; N, 23·2. Calc. for $C_7H_9O_3N_3$: C, 45·9; H, 4·9; N, 23·0%), 5-hydroxymethylfuroic acid (by silver oxide in dilute aqueous sodium hydroxide [12]), m. p. 165—166° (Found: C, 50·7; H, 4·2. Calc. for $C_6H_6O_4$: C, 50·7; H, 4·3%), and the 2,4-dinitrophenylhydrazone,[13] m. p. 200—201° (Found: C, 47·1; H, 3·5; N, 18·0. Calc. for $C_{12}H_{10}O_6N_4$: C, 47·1; H, 3·3; N, 18·3%). In the last case the mother-liquor yielded a second crystalline specimen, m. p. 215° (Found: C, 47·1; H, 3·7; N, 18·2%), behaviour previously attributed to geometrical isomerism.[7,13]

In comparative experiments sucrose (4 g.) and fructose (2 g.) were separately dissolved in dimethylformamide (25 ml.) containing catalytic quantities of iodine. On prolonged shaking at room temperature, chemical change became apparent only after two days, the sucrose solution showing the presence of glucose and fructose and of two faster-moving constituents with R_F values intermediate between those of fructose and the aldehyde; the last two constituents were also present in the fructose solution. The glucose solution showed no observable change. There was no evidence for the aldehyde in any of the solutions but further examination of the two fast-moving constituents in the sucrose and fructose solutions may help to establish its precursors. After a further 4 days at room temperature the similar degradation of sucrose and fructose had proceeded further, and in both cases oligosaccharides were also present. Glucose continued to show no change.

Quantitative Determination by Ultraviolet Absorption Spectra.—Paper chromatograms of the sucrose–iodine solutions in dimethylformamide indicated a high yield of aldehyde after 1 hr. at 100°. An attempt was made to determine the yield by mixing the final solution with powdered cellulose, applying the dry mixture to a cellulose column, eluting this with butanol–ethanol–water, analysing the separate 50 ml. fractions by means of anthrone [14] or by the absorption [5] at 285 mμ, and then pooling the appropriate fractions and evaporating them to dryness. This procedure was not satisfactory because of loss of product by " tailing " on the column during elution and by volatilisation during concentration of the eluates. Since the aldehyde can be determined *in situ* [7,15] the conditions for the optimum yield were readily obtained by heating sucrose (1 g.) in dry dimethylformamide (37 ml.), with a crystal of iodine, removing 1 ml. of the mixture at various times, diluting it to 1 l. with water, and measuring the optical density at 285 mμ with a Hilger Uvispek spectrophotometer. The small amounts of iodine and dimethylformamide present had a negligible absorption at this wavelength. The yield of aldehyde after 1 hr. at 100°, calculated from a value of $\varepsilon = 16{,}500$ [5] at 285 mμ, was 71% (based on the fructose portion) and this did not increase on continued heating, as indicated in the Figure.

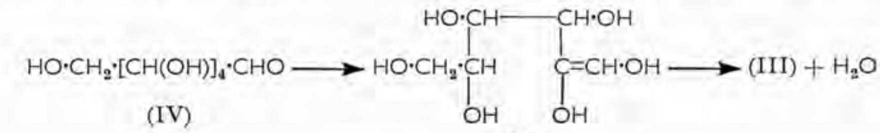
DISCUSSION

The mechanism of elimination of three molecules of water from a pentose or hexose to form the furan ring has not yet been clearly established. Haworth and Jones [3] suggested a sequence for the dehydration of fructose starting with the furanose structure (II) from which the loss of the first molecule of water gives the intermediate (III). They noted that a similar intermediate could in theory be obtained from glucose (IV) *via* the 1,2-enediol tautomer (V).



(II) (III)

Haworth *et al.*[16] had similarly interpreted the conversion of tetramethylfructofuranose (by dilute hydrochloric acid at 80° or warm acetic anhydride and sodium acetate) into 5-methoxymethylfurfuraldehyde (VII) with elimination of three mols. of methanol. This aldehyde was later [17] obtained by the action of acid on tetramethyl-1,2-glucoseen (VI), this reaction providing the only intermediate which has been isolated in reactions of this

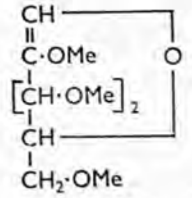


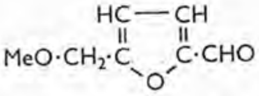
(IV) (V)

type, although the facts adduced to assign to the intermediate the structure of a 3,4-unsaturated osone were not decisive.

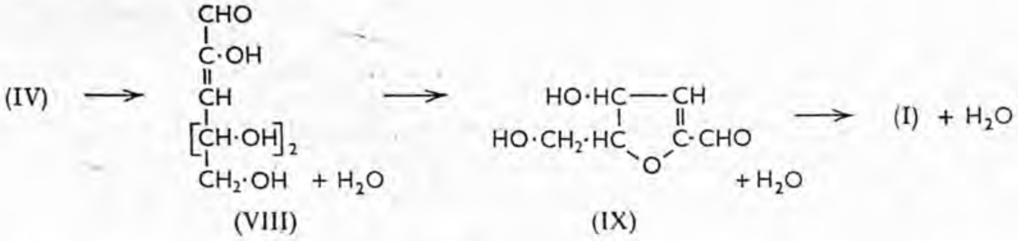
Later studies [5,8] on the ultraviolet absorption of acid solutions of glucose undergoing conversion into the aldehyde by heat revealed the development of strong absorption at 228 mμ before that of absorption at 285 mμ due to the aldehyde. As αβ-unsaturated aldehydes absorb strongly at 230 mμ, the initial appearance of the band at 228 mμ was attributed to the elimination of a molecule of water at $C_{(2)}$ and $C_{(3)}$ in glucose reacting in its open-chain form; an intermediate (VIII) resulted which is structurally suitable for elimination of two further molecules of water through (IX) to the aldehyde (I).

In the present work the existence of an intermediate (VIII) in the reaction could not be tested because of the strong absorption of dimethylformamide at 228 mμ.[18] However, for degradation of fructose or sucrose the dehydration is unlikely to involve this compound


(VI)


(VII)

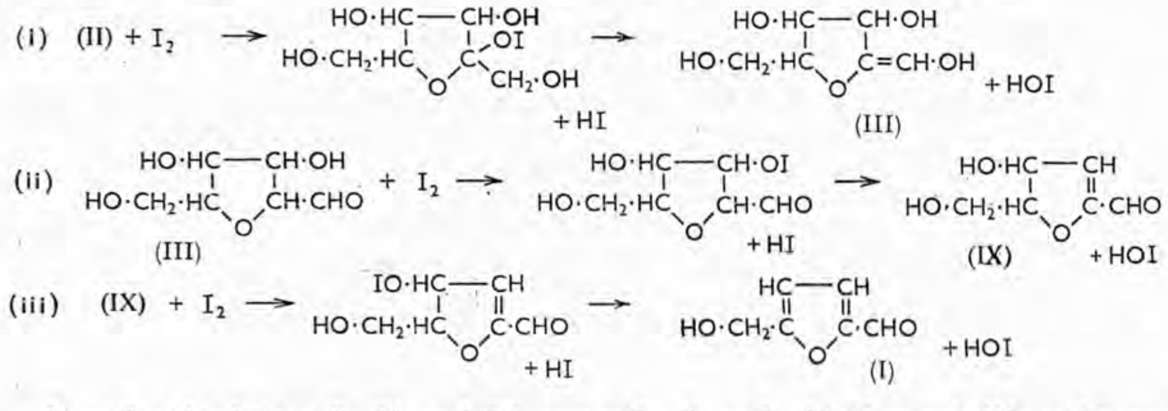
since the furan ring is already present. A more likely intermediate is (III) since it is the enolic form of chitose, which is readily converted into 5-hydroxymethylfurfuraldehyde by hot 0·3% aqueous oxalic acid.[19]



The formation of an intermediate (III) from fructose and its successive dehydration to compounds (IX) and (I) by iodine can be readily envisaged in terms of the interpretation of catalysis by iodine suggested by Hibbert.[20] The familiar dehydration of hydroxy-compounds by iodine was represented:

$$>CH{-}C(OH)< + I_2 \longrightarrow >CH{-}C(OI)< + HI$$
$$>CH{-}C(OI)< \longrightarrow >C{=}C< + HOI$$
$$HI + HOI \longrightarrow I_2 + H_2O$$

For stepwise dehydration of fructose a scheme such as (i)—(iii) would apply.



In each pair of steps (i), (ii), and (iii), one molecule each of hydrogen iodide and hypoiodous acid are eliminated which by interaction can regenerate the catalyst with loss of a molecule of water. The sequence outlined follows naturally from the fact that the order of reactivity of iodine with hydroxyl groups is tertiary > secondary > primary [20] and that once compound (III) is formed, the introduction of an olefinic bond between $C_{(2)}$ and $C_{(3)}$ will be assisted by the α-aldehyde group. A similar recurrent formation of iodine from hydrogen iodide and alkyl iodide intermediates has been proposed in the iodine-catalysed decomposition of acetaldehyde at high temperatures.[21]

It is evident that the same catalyst could achieve this sequence of reactions with glucose under conditions of appreciable isomerisation to the open-chain form, provided that the latter readily undergoes iodine-catalysed dehydration to the intermediate (VIII). However, it is possible that a sequence of dehydration steps such as (i)—(iii) can be initiated only at a tertiary carbon atom in a pre-formed furanoside structure.

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587. *Ring Scission of Cyclic Acetals. Part I. The Formation of a Linear Polyester from* 1,3:2,4:5,6-*Tri*-O-*methylene*-D-*glucitol, Adipic Acid, and Trifluoroacetic Anhydride.*

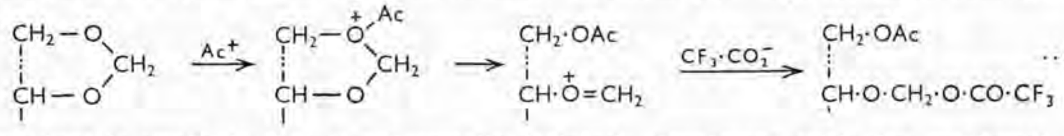
By T. G. BONNER, E. J. BOURNE, and N. M. SAVILLE.

A new synthesis of linear polyesters from a cyclic acetal and a dicarboxylic acid is based on conversion of the latter by trifluoroacetic anhydride into a powerful acylating species having two active centres; the acetal must have two rings susceptible to scission by acylating reagents. Mild hydrolysis of the product, to remove trifluoroacetoxymethyl groups, leaves a polyester with free hydroxyl groups along the chain. The method has been employed with 1,3:2,4:5,6-tri-*O*-methylene-D-glucitol and adipic acid.

TRIFLUOROACETIC ANHYDRIDE converts simple carboxylic acids into powerful acylating agents,[1] which originate in the unsymmetrical anhydride known to be extensively formed in an equimolar mixture of the two reactants: [2]

$$R{\cdot}CO_2H + (CF_3{\cdot}CO)_2O \rightleftharpoons R{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3 + CF_3{\cdot}CO_2H \quad . \; . \; . \; . \; . \; . \quad (1)$$

Cyclic acetals of sugars [3] and hexitols [4] undergo ring scission with acylating agents, and in the acetolysis of hexitol diacetals and triacetals a notable feature is the marked difference in lability of the acetal rings; *e.g.*, the 2,4-*O*-methylenedioxy-ring is left intact [4] after acetolysis of 1,3:2,4:5,6-tri-*O*-methylene-D-glucitol, and the 2,5-*O*-methylenedioxy-ring in the reaction of 1,3:2,5:4,6-tri-*O*-methylene-D-mannitol; in both cases the other two rings open, to give *O*-acetyl groups at the primary carbon atoms and *O*-acetoxymethyl groups at the secondary carbon atoms. The same selectivity is shown towards tri-*O*-methyleneglucitol by an equimolar mixture of acetic acid and trifluoroacetic anhydride [5] in 4—5-fold molar excess over the acetal; with this reagent the attack on labile rings (*i.e.*, the 1,3- and 5,6-rings) is represented as in reactions (2). The bistrifluoroacetoxymethyl product is unstable and is not usually isolated; treatment with dry methanol readily converts it into 1,6-di-*O*-acetyl-2,4-*O*-methylene-D-glucitol. The ease of removal of the trifluoroacetoxymethyl groups by hydrolysis under conditions which do not affect the acetyl groups is a unique feature that makes this method superior to degradation by acetolysis, since the product of the latter is not readily susceptible to selective hydrolysis.



......(2)

The synthesis of a linear polyester from a cyclic acetal and a mixed anhydride of trifluoroacetic acid and a dibasic carboxylic acid depends on the presence of not more than two reactive acetal rings in the acetal. Since of the simple trialkylidenedioxy-derivatives of glucitol only the tri-*O*-methylene derivative contains a ring (2,4) completely resistant to acylating reagents, the investigation of polyester formation was begun with this derivative. The opening of the two labile rings (1,3- and 5,6-) with an adipic acid–trifluoroacetic anhydride reagent should produce a linear polymer, which after mild hydrolysis should contain two free hydroxyl groups per repeating unit of the chain. There is the possibility of an intramolecular reaction if the reactive acylating chain formed by the opening of one acetal ring attacked the other ring in the same acetal molecule; but since the cyclic derivative so formed would have to contain at least ten atoms, the occurrence of this reaction is unlikely in the general case and is highly improbable with tri-*O*-methyleneglucitol. A cyclic acetal with more than two labile rings would lead to branching in the polyester chain and the formation of a cross-linked product.

Free alcohol groups in the polyester are desirable because of the higher absorption of water which is possible through hydrogen-bonding and because of the possibility of high dye-uptake. At some inconvenience these groups can be obtained in polymer molecules by the use, before polymerisation, of blocking agents which are subsequently removed, but by the trifluoroacetic anhydride method the hydroxy-polyester is obtained directly.

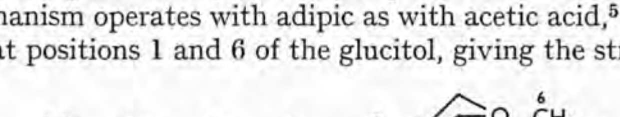
To test the method with 1,3:2,4:5,6-tri-*O*-methylene-D-glucitol and adipic acid equimolar quantities of the two reactants were dissolved in an excess of trifluoroacetic anhydride and left at room temperature for some hours. Volatile constituents were then removed under reduced pressure and the residue treated with aqueous sodium hydrogen carbonate. If the alkaline mixture was left for only a few hours before separating the insoluble product formed, it was found that the latter subsequently decomposed in the presence of atmospheric moisture liberating formaldehyde, thus showing that hydrolysis of the trifluoroacetoxymethyl groups was incomplete. Trifluoroacetic acid would also result from attack by atmospheric moisture, and might catalyse hydrolysis of the adipate ester groupings. This difficulty was overcome by continuing the alkali treatment for a few days, whereafter the insoluble polyester was stable to moisture. The polyester product was a colourless, brittle solid melting at 130—150° to a viscous liquid which could be drawn into brittle threads. The solid became swollen in some solvents and dissolved completely in pyridine. As expected, alkaline hydrolysis yielded adipic acid and crystalline 2,4-*O*-methylene-D-glucitol: the only other carbohydrate constituent detected by chromatography was a trace of glucitol.

A linear polymer made up of alternate 2,4-*O*-methylene-D-glucitol and adipic acid units linked through ester groups was therefore indicated.

The infrared absorption spectrum showed strong absorption by alcoholic hydroxyl groups at 3450 and 1075 cm.$^{-1}$ and by aliphatic carboxylate ester groups at 1726 cm.$^{-1}$ and in the region 1250 and 1180 cm.$^{-1}$ No absorption characteristic of fluorinated esters was detected. A weak band at 2770 cm.$^{-1}$ and a band at 1030 cm.$^{-1}$ indicated a cyclic ether. A medium band at 1565 cm.$^{-1}$ suggested the presence of the carboxylate ion which is also known to give rise to absorption at 1375 cm.$^{-1}$. When the polymer was boiled with N-hydrochloric acid for one minute and then dried at 90° the band at 1565 cm.$^{-1}$ disappeared. No change in intensity was evident in the 1375 cm.$^{-1}$ region but this may be due to the high level of absorption in this range. If it is assumed that the absorption coefficients of the carboxylate ester and carboxylate ion group are the same, the ratio of the optical densities of the two groups indicates that there are ten ester to one carboxylate ion group. This result does not permit calculation of the average chain length of the molecules, however, since individual chains may have two, one, or no carboxylic end groups.

Viscosities of solutions of the polymer in pyridine were measured at different concentrations and the intrinsic viscosity, $[\eta]$, was evaluated.[6] This is related to the average molecular weight, M, by the empirical expression $[\eta] = KM + K_0$, where the constants K and K_0 are calculated from the viscosity of a similar type of polymer of known molecular weight in the same solvent and at the same temperature. No values are available for a polyester in pyridine; using data for polydecamethyleneglycol adipates in chlorobenzene [7] at 25° leads to a weight-average molecular weight of *ca.* 4900, corresponding to an average of 16 2,4-*O*-methylene-D-glucitol adipate residues per chain.

If the same mechanism operates with adipic as with acetic acid,[5] the ester groups in the polymer should be at positions 1 and 6 of the glucitol, giving the structure (I):



(I)

The polymer has a softening point of 88°. Its molecular weight appears to be too low to provide a useful basis for a synthetic fibre but the method of synthesis does not preclude the formation of products of higher molecular weight.

EXPERIMENTAL

Reaction of Adipic Acid–Trifluoroacetic Anhydride with 1,3:2,4:5,6-*Tri*-O-*methylene*-D-*glucitol.*—Trifluoroacetic anhydride[1] (7·6 ml., 6·0 mol.) was added to the acetal (2·0 g.) and adipic acid (1·34 g., 1 mol.); the solids dissolved rapidly with evolution of heat to give a viscous coloured solution. After 3 hr. at room temperature, the volatile constituents were removed at 40° under reduced pressure. Anhydrous carbon tetrachloride was added and the solution evaporated to remove remaining traces of volatile matter; this process was repeated twice and gave a viscous transparent residue (6·46 g.). 10% Aqueous sodium hydrogen carbonate (75 ml.) was added and the mixture left at room temperature for 72 hr. The insoluble residue was filtered off, washed with water, and dried in a vacuum-desiccator. The resulting colourless brittle solid (2·13 g.) softened to a viscous liquid over the range 110—120°. A second specimen, obtained by the same method, melted over the range 130—150°. The melt could be drawn into threads which became brittle on cooling. The solid swelled and then dissolved completely in pyridine; it also swelled in chloroform and benzene but did not dissolve completely in either. It did not dissolve or swell in water. The products of alkaline hydrolysis were obtained by refluxing the solid (0·49 g.) with 0·1N-sodium hydroxide (30 ml.) for 30 min. The solution was cooled, acid was added to give pH 8, the mixture was evaporated to dryness, and the solid residue extracted with boiling pyridine (soluble component, A). The insoluble residue was dissolved in water, and acid was added to give pH 4. After evaporation to dryness, the residue was again extracted with pyridine to give a soluble component, B. The extract containing A was evaporated to give a brown solid, an ethanol extract of which was shown by chromatography to contain 2,4-*O*-methylene-D-glucitol and a trace of glucitol; the former (0·1 g., 33%) was obtained from the ethanol extract and had m. p. and mixed m. p. 161—162°, $[\alpha]_D^{18}$ $-11{\cdot}7°$ (*c* 0·64 in H_2O). The extract containing B yielded a brown solid, soluble in water. The aqueous solution was brought to pH 9 and evaporated to dryness. Examination of the residue by paper chromatography showed the presence of adipic acid; the residue was converted into its *S*-benzylisothiouronium derivative (0·15 g., corresponding to a 52% yield of adipic acid from the polymer), m. p. and mixed m. p. 160°. Analysis of the polyester gave C, 47·6, and H, 6·7%.

Viscosity and density determinations were carried out on solutions of the polymer in pyridine which were first filtered and analysed by titration with standard alkali. Viscosities were measured at 25·4° with an Ostwald viscometer[6] which had been calibrated with water. The viscosities of the pyridine solutions are recorded in the Table as specific viscosities, η_{sp}, and relative viscosities, η_r, where $\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_r - 1$; η is the viscosity of the solution in poises, and η_0 that of pure pyridine; *t* is the time of flow in seconds, *c* the concentration in g. of polymer per 100 ml. of pyridine solution, and ρ the density of the solution in g./ml.

Viscosities of polymer solutions in pyridine at 25°.

	c	*t*	ρ	$10^2\eta$	η_{sp}	η_r
Water	—	225·4	0·9969	8·824	—	—
Pyridine	—	229·6	0·9782	8·818	—	—
Soln. A	0·8405	262·3	0·9812	10·15	0·1510	1·1510
,, B	0·4946	248·4	0·9806	9·564	0·08457	1·0846
,, C	0·1602	235·1	0·9801	9·050	0·02630	1·0263

The intrinsic viscosity $[\eta]$ of the polymer was determined by plotting η_{sp}/c against *c* and measuring the intercept which the linear plot makes with the η_{sp}/c axis. The value obtained was 0·165. Using the data for polydecamethyleneglycol adipates in chlorobenzene at 25° (see above) gives $K = 2{\cdot}12 \times 10^{-5}$, $K_0 = 0{\cdot}06$, from which, with $[\eta] = 0{\cdot}165$, the calculated value of *M* is *ca.* 4900.

Infrared Spectra.—These were determined at the research laboratories of British Nylon Spinners Ltd., Pontypool, Mon., where *X*-ray examination, moisture uptake, and softening points were also recorded. The authors are indebted to Dr. W. A. W. Cummings for arranging this work and for interpretations of the spectral results which were obtained on a Perkin–Elmer spectrometer with a sodium chloride prism. The sample was heated to 100° between sodium chloride plates and these were pressed together to give a film.

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D.Sc. 1960

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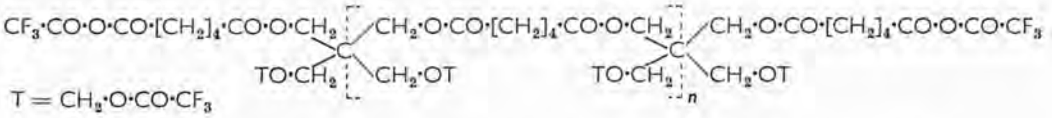
588. *Ring Scission of Cyclic Acetals. Part II.*[1] *The Reactions of Di-*O*-methylenepentaerythritol with Carboxylic Acids and Trifluoroacetic Anhydride.*

By T. G. BONNER, E. J. BOURNE, and N. M. SAVILLE.

The reaction of adipic acid and trifluoroacetic anhydride with di-*O*-methylenepentaerythritol appears to give a cross-linked polyester and not the expected linear product. The interpretation of this result is based on a study of the reaction using a monocarboxylic acid in place of adipic acid which shows that (i) partially esterified pentaerythritols tend to disproportionate in solutions of pH 9, and (ii) the trifluoroacetoxymethyl group is labile to an acylating reagent when linked to the oxygen atom of a primary alcohol group.

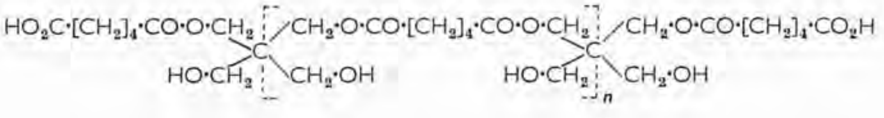
WHEN a linear polyester was obtained from tri-*O*-methylene-D-glucitol by the action of trifluoroacetic anhydride and adipic acid,[1] the analogous reaction was studied with di-*O*-methylenepentaerythritol, which was expected to give products (A) and, after hydrolysis, (B).

(A)



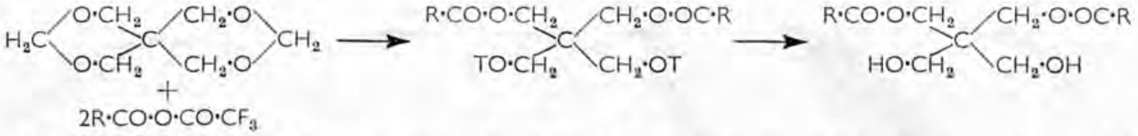
T = $CH_2{\cdot}O{\cdot}CO{\cdot}CF_3$

(B)

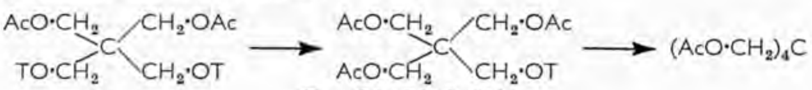


Equimolar quantities of di-*O*-methylenepentaerythritol and adipic acid were dissolved in an excess of trifluoroacetic anhydride and left at room temperature for three hours. Evaporation of volatile constituents and treatment with aqueous sodium hydrogen carbonate solution, as before, gave a colourless, rubber-like solid which did not dissolve completely in any common organic solvent. It did not melt but charring began at *ca.* 300°. These properties were different from those of the linear polyester obtained from 1,3:2,4:5,6-tri-*O*-methylene-D-glucitol and suggested a cross-linked polymer. Alkaline hydrolysis of the polymer gave, as predicted, pentaerythritol and adipic acid in good yield. Viscosity measurements were not possible in absence of a suitable solvent; pyridine which had been in contact with the material was unchanged in viscosity. It was realised that the apparent branching of the polymer chain could be due to dipentaerythritol known to be present in technical pentaerythritol.[2] This would form di-*O*-methylenedipentaerythritol containing two free hydroxy-groups which would be readily acylated to give a product having four active acylating centres. Purification of pentaerythritol by the standard procedure [2] produced a sample of higher m. p., but its di-*O*-methylene derivative had the same m. p. as that from technical pentaerythritol, and reaction with adipic acid and trifluoroacetic anhydride gave a similar colourless, rubber-like product. It seemed that the bismethylenedioxy-derivative had been effectively purified.

Two explanations for the formation of a cross-linked polyester were considered: (i) that the acylating agent displaces trifluoroacetoxymethyl residues which thus do not serve as efficient blocking groups, and (ii) that a third or even a fourth adipate ester constituent is introduced into some of the pentaerythritol units in the chain during removal by mild hydrolysis of the trifluoroacetoxymethyl groups. To examine these possibilities simpler systems were first investigated, with a monocarboxylic acid in place of adipic acid.



With benzoic acid–trifluoroacetic anhydride the product should be the known, crystalline di-*O*-benzoylpentaerythritol.[3] It was, however, an oil, alkaline hydrolysis of which gave pentaerythritol and benzoic acid. Reaction with acetic acid and trifluoroacetic anhydride followed by the usual hydrolysis gave an oil which was shown by chromatography to contain at least two esters. The preparation of the known compound, di-*O*-acetylpentaerythritol, was then carried out for a study of its stability to alkali and its R_F values. This preparation was revealing: mono-*O*-isopropylidenepentaerythritol is converted into its diacetate by acetic anhydride and sodium acetate, and the isopropylidene group is then hydrolysed by N/20-hydrochloric acid, the excess of acid being finally removed with silver carbonate.[3] Chromatography showed that isopropylidenepentaerythritol diacetate contained only a trace of the tetra-acetate, but that the hydrolysis product contained three esters in addition to the tetra-acetate and some pentaerythritol, but no unchanged isopropylidene derivative. When the tetra-acetate was removed from the product, no more appeared to be generated on storage; when samples were then treated with aqueous solutions of pH <8 and the chloroform-soluble products examined by chromatography, no tetra-acetate was detected, but after treatment at pH 9—10 evidence of its presence was obtained, indicating that alkali-catalysed disproportionation of diacetate to tetra-acetate had probably occurred. Intramolecular acyl migrations in partially esterified polyols are known to be catalysed by traces of alkali;[4] while intramolecular migration in a pentaerythritol ester would not yield a different ester, intermolecular migrations could do so. The reaction of di-*O*-methylenepentaerythritol with acetic acid and trifluoroacetic anhydride was therefore repeated with the hydrolysis carried out in an aqueous solution buffered at pH 7; at this pH trifluoroacetoxymethyl groups should be removed[5] without disproportionation of diacetate. The chloroform-soluble material, however, again contained a mixture of three esters including the tetra-acetate, and the R_F values indicated the presence of the di- and tri-esters. Since our experiments indicate that these are not formed during hydrolysis at pH 7, they were presumably formed during acylation of the acetal, by displacement of trifluoroacetoxymethyl by acetyl groups after initial ring opening:



$T = CF_3{\cdot}CO{\cdot}O{\cdot}CH_2$

No such reaction occurs with tri-*O*-methylene-D-glucitol; but there the trifluoroacetoxymethyl groups are linked to oxygen atoms from secondary alcohol groups while in the pentaerythritol derivatives they are linked to oxygen atoms from primary alcohol groups. The preference of an acetylating agent for attack at a primary position is already established in the acetolysis of 1,3:2,5:4,6-tri-*O*-methylene-D-mannitol,[6] which gives 3,4-di-*O*-acetoxymethyl-1,6-di-*O*-acetyl-2,5-*O*-methylene-D-mannitol, and in the reaction of tri-*O*-methylene-D-glucitol with trifluoroacetic anhydride–carboxylic acid mixtures. It appears therefore that when trifluoroacetic anhydride and adipic acid are used, displacement of trifluoroacetoxymethyl groups in the initial linear polymer will lead to further reactive centres and thus to cross-linking.

We next studied some benzylidene and isopropylidene derivatives. Tri-*O*-benzylidene- and di-*O*-isopropylidene-D-mannitol are converted by acetic acid and trifluoroacetic anhydride into mannitol hexa-acetate;[7] the product from di-*O*-benzylidenepentaerythritol contained the tetra-acetate and smaller amounts of three other esters. Hydrolysis with dilute hydrochloric acid liberated benzaldehyde, suggesting that one ester was probably di-*O*-acetyl-*O*-benzylidenepentaerythritol. This compound was prepared by acetylation of mono-*O*-benzylidenepentaerythritol and had the same R_F value as one of the three esters just mentioned. Di-*O*-benzylidenepentaerythritol was also treated with trifluoroacetic anhydride and excess of acetic acid. This reagent opens methylene rings, as in acetolysis, with the formation of one acetate and one acetoxymethyl group per ring opened.[7] The product was similar to that obtained in the previous experiment but contained mostly the tetra-acetate and the di-*O*-acetyl-*O*-benzylidene derivative. Mono-*O*-benzylidenepentaerythritol under the same conditions gave a similar mixture of esters. Thus, one acetal ring in the dibenzylidene compound is readily opened but the other acetal ring is more resistant, which is unusual since under comparable conditions no products containing intact benzylidene rings have been detected with the corresponding benzylidene hexitols. Examination of Catalin models provides an explanation. There is no steric hindrance to the approach of a reagent (unless very bulky) to any of the four ring-oxygen atoms of di-*O*-benzylidenepentaerythritol, but when the first benzylidene ring is opened the acetoxymethyl groups introduced can hinder the approach of the mixed anhydride to the unopened ring. The same situation can arise in mono-*O*-benzylidenepentaerythritol since the free alcohol groups are almost certainly more rapidly attacked than the acetal ring.[7]

With equimolar proportions of acetic acid and trifluoroacetic anhydride mono-*O*-isopropylidenepentaerythritol gave a small yield of the tetra-acetate which was doubled when excess of acetic acid was used. Only traces of other esters could be detected and di-*O*-acetyl-*O*-isopropylidenepentaerythritol was not obtained. This behaviour is similar to that of isopropylidenehexitols which give low yields of the hexitol hexa-acetate under the same conditions.

EXPERIMENTAL

Detection of Products by Paper Chromatography.—The two solvents mainly employed were (*a*) water-saturated butan-1-ol, prepared by shaking the two liquids together for a few hours, cooling to 0°, and removing the organic layer, and (*b*) light petroleum (b. p. 60—80°) saturated with dimethyl sulphoxide,[8] the stationary phase in the paper being the sulphoxide. With the latter solvent the paper is dipped in a 20% solution of the sulphoxide in benzene, pressed between absorbent paper, and dried for 1 min. at 60°; this treatment is repeated and the paper placed between glass plates to prevent absorption of water. After elution of a reaction product with the light petroleum solvent the paper is dried at 120° for 20 min. before being sprayed. Both solvents (*a*) and (*b*) were used with Whatman No. 1 paper. The most satisfactory spray for esters of pentaerythritol is the hydroxylamine reagent [9] [a freshly prepared 1 : 1 v/v mixture of methanolic hydroxylamine hydrochloride (6·95 g./100 ml.) and potassium hydroxide (6·17 g./100 ml.)]. After spraying, the paper is dried at a temperature and for a time depending on the reactivity of the ester, *e.g.*, pentaerythritol tetra-acetate is detected only by heating to 110° for 10 min. The paper is finally sprayed with a 1 : 1 v/v mixture of aqueous ferric chloride and aqueous 0·5N-hydrochloric acid. Acetates and lactones appear as purple spots on a yellow background, but benzoates are not detected. The 2,4-dinitrophenylhydrazine spray [10] was used to detect benzylidene and isopropylidene derivatives.

Reaction of Trifluoroacetic Anhydride–Adipic Acid with Di-O-methylenepentaerythritol.—The acetal (0·5 g.) and adipic acid (0·46 g., 1 mol.) were treated with trifluoroacetic anhydride (2·6 ml., 6·3 mol.) and left for 3 hr. at room temperature. The volatile constituents were removed at 40° under reduced pressure, carbon tetrachloride was added, and the solution again evaporated. This was repeated twice to give a colourless glass. Aqueous sodium hydrogen carbonate was added and after 4 days the insoluble residue was filtered off, washed with water, and dried. The rubber-like solid obtained (0·54 g.) did not melt but darkened at 300° (Found: C, 52·9; H, 7·5%).

The product (0·13 g.) was hydrolysed with boiling 0·1N-sodium hydroxide, and the mixture evaporated to dryness. Extraction of the residue with boiling pyridine gave a soluble product, *A*, which after concentration of the pyridine solution was acetylated with sodium acetate and acetic anhydride, to give tetra-*O*-acetylpentaerythritol (0·08 g., 50%), m. p. 78—79°, mixed

m. p. 79—80°. The residue from the pyridine extraction was dissolved in water, and the solution was acidified and evaporated to dryness. The residue was extracted with methanol and the solution shown to contain adipic acid [*S*-benzylisothiouronium salt (0·06 g., 68%), m. p. and mixed m. p. 161—162°].

Di-O-*acetylpentaerythritol*.—(i) Mono-*O*-isopropylidenepentaerythritol was prepared by stirring together for 15 min. at room temperature pentaerythritol (10 g.), hydrochloric acid (*d* 1·18; 5·0 ml.), water (53 ml.), and acetone (202 ml.) and then refluxing the whole for 30 min. After 24 hr. at room temperature, the solution was treated with aqueous 25% sodium hydroxide to obtain a pH of 8 and then concentrated under reduced pressure, first at 50° and then at 70° (sublimation of the product occurs at higher temperatures). The dry residue was ground and extracted (Soxhlet), first with light petroleum (b. p. 40—60°) for 6 hr., then with ether for 12 hr. The ether yielded colourless crystals (3·6 g., 28%), m. p. 126·5—127·5° (Rapoport[11] gave m. p. 126—127° for isopropylidenepentaerythritol) (Found: C, 54·4; H, 9·3. Calc. for $C_8H_{16}O_4$: C, 54·5; H, 9·2%).

(ii) Di-*O*-acetyl-*O*-isopropylidenepentaerythritol was obtained by refluxing the ketal (0·83 g.), sodium acetate (0·83 g., 2·1 mol.), and acetic anhydride (3·75 ml., 8·6 mol.) in chloroform (16·6 ml.) for 1 hr. and leaving the mixture overnight at room temperature. The solution was filtered and evaporated, and the residue extracted with light petroleum (b. p. 60—80°); concentration of the extract gave the diacetate (0·94 g., 77%), m. p. 45—46° (Orthner and Freyss[3] gave m. p. 48—49°) (Found: C, 55·5; H, 7·7. Calc. for $C_{12}H_{20}O_6$: C, 55·4; H, 7·7%).

(iii) "Di-*O*-acetylpentaerythritol" was obtained by shaking the ketal diacetate (0·7 g.) with 0·05N-hydrochloric acid for 15 min.; after 1 hr. silver carbonate was added; the pH did not rise above 4. The mixture was filtered, concentrated under reduced pressure, and treated with hydrogen sulphide. As no silver sulphide separated, the black solution was shaken with charcoal and filtered, then concentrated and freeze-dried. From the residue ether removed a colourless oil (0·51 g.) from which a solid later separated. Chromatography with solvent (*a*) and the hydroxylamine spray reagent revealed constituents with R_F 0·67 and 0·81—0·89 (tetra-*O*-acetylpentaerythritol, R_F 0·94). With solvent (*b*) some of the product remained on the base line; in addition, there was one constituent with R_F 0·27 (tetra-*O*-acetylpentaerythritol, 0·27). The tetra-acetate was separated from the product by elution on Whatman No. 3 paper with solvent (*b*). The base line was cut away and eluted with chloroform. The chloroform solution was concentrated to give an oil on which chromatograms were run after different time intervals; no disproportionation to tetra-acetate was detected in the oil itself. The oil was left in contact with aqueous solutions of different pH values (see below) for several hours, the mixtures were extracted with chloroform, and chromatograms run on the extracts, examination for tetra-acetate gave the following results: with 0·05N-hydrochloric acid or 1% sodium hydrogen carbonate (pH 7—8), none; with 10% sodium hydrogen carbonate (pH 9), a trace; with a sodium hydrogen carbonate–carbonate (pH 10), an appreciable amount.

Reactions of Trifluoroacetic Anhydride–Acetic Acid.—(i) *With di*-O-*methylenepentaerythritol*. A mixture of acetic acid (0·22 ml., 6·0 mol.), trifluoroacetic anhydride (0·55 ml., 6·3 mol.) and the acetal (0·10 g.) formed a homogeneous solution which was left at room temperature for 3 hr. Volatile constituents were removed to give an oil (0·31 g.) which was shaken for 2 hr. with an aqueous solution (80 ml.) buffered at pH 7 (phosphate) and then left at room temperature overnight. Chloroform-extraction yielded an oil *A* (0·04 g.); the aqueous layer was freeze-dried and the residue extracted with chloroform to give an oil *B* (0·09 g.); finally, the residue was extracted with pyridine to give a solution *C*. Chromatograms with solvent (*a*) showed that these three fractions contained constituents with R_F values: *A*, 0·79 and 0·87; *B*, 0·64 and 0·79; *C*, 0·64 and 0·76. With this solvent pentaerytritol has R_F 0·45 and its tetra-acetate has R_F 0·94; with solvent (*b*), the tetra-acetate was detected in the oil *A*. The products therefore appear to be mono-, di-, tri-, and tetra-acetate.

(ii) *With di*-O-*benzylidenepentaerythritol*. A mixture of acetic acid (0·37 ml., 20 mol.), trifluoroacetic anhydride (0·9 ml., 20 mol.), and the acetal (0·1 g.) formed a red solution. After 24 hr. at room temperature the volatile constituents were removed to give a dark oil (0·20 g.). This was hydrolysed as in (i), and extracted with chloroform to yield a yellow oil (0·13 g.), chromatography of which with solvent (*a*) revealed tetra-*O*-acetylpentaerythritol, and with solvent (*b*) three other products of R_F 0, 0·68, and 0·84. As one of these appeared to be *di*-O-*acetyl*-O-*benzylidenepentaerythritol* this ester was prepared by acetylation of mono-*O*-benzylidenepentaerythritol (0·10 g.) with sodium acetate and acetic anhydride (procedure as above). It was a colourless oil which on chromatography with solvent (*b*) gave two compounds with R_F values of 0·05 (possibly the monoacetate) and 0·66 (cf. 0·68 above). Separation on a cellulose column (length 21 cm., diameter 1·5 cm.) with solvent (*b*) gave an oil (0·1 g.), chromatographically pure and corresponding to the diacetate (Found: C, 62·2; H, 7·1. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5%).

(iii) *With mono-*O*-isopropylidenepentaerythritol.* Acetic acid (0·37 ml., 20 mol.), trifluoroacetic anhydride (1·0 ml., 20 mol.), and the ketal (0·06 g.) gave a yellow solution which became red in 26 hr. This was treated as in (ii), to yield an oil (0·14 g.) which partly crystallised; with solvent (*b*) chromatographic examination revealed tetra-*O*-acetylpentaerythritol and a product with R_F 0. Crystallisation from light petroleum (b. p. 60—80°) gave the tetra-acetate (0·014 g., 14%), m. p. 78—79°, mixed m. p. 79·5—80°.

Reactions of Trifluoroacetic Anhydride and Excess of Acetic Acid.—(i) *With di-*O*-benzylidenepentaerythritol.* Acetic acid (1·90 ml., 100 mol.), trifluoroacetic anhydride (0·45 ml., 10 mol.), and the acetal (0·1 g.) formed a colourless solution which became yellow in 24 hr. Treatment with the aqueous buffer (pH 7) as above and chloroform-extraction yielded an oil (0·14 g.). With solvent (*b*) the chromatogram showed compounds with R_F 0, 0·51, 0·71, and 0·82 (tetra-*O*-acetylpentaerythritol, R_F 0·51; di-*O*-acetyl-*O*-benzylidenepentaerythritol, 0·71). A similar chromatogram was obtained with mono-*O*-benzylidenepentaerythritol after the same treatment.

(ii) *With mono-*O*-isopropylidenepentaerythritol.* Acetic acid (1·90 ml., 100 mol.), trifluoroacetic anhydride (0·5 ml., 11 mol.), and the ketal (0·06 g.) gave a yellow solution, from which after 17 hr. a colourless oil (0·14 g.) was obtained. The chromatogram showed compounds with R_F 0, 0·49 (tetra-*O*-acetylpentaerythritol, R_F 0·49), and 0·78 (very faint). A light petroleum (b. p. 60—80°) extract of the oil yielded crystals of tetra-*O*-acetylpentaerythritol (0·026 g., 25%), m. p. and mixed m. p. 75—77°.

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591. *Dealkylation and Deacylation of Carbohydrate Derivatives with Boron Trichloride and Boron Tribromide.*

By T. G. Bonner, E. J. Bourne, and S. McNally.

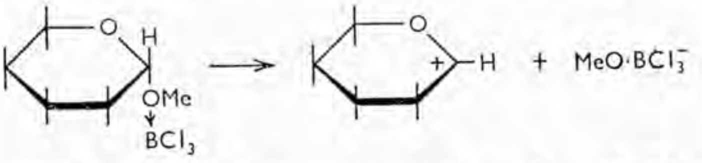
The use of boron trichloride and boron tribromide is described for the deacylation and demethylation of mono-, di-, and poly-saccharide derivatives, the last two types being converted into the monosaccharide constituents.

All the monosaccharides investigated are stable to the reagent, except fructose and sorbose which are both degraded to 5-hydroxymethylfurfuraldehyde.

The oxygen atoms of ethers, esters, and many other derivatives of carbohydrates provide sites for co-ordination with electron-deficient molecules such as Lewis acids. Since some diversity of co-ordinating power can arise in a molecule through variation in polar character and steric environment of these basic oxygen centres there are clearly possibilities for effecting particular reactions at selected sites. Some initial studies with aluminium chloride were only partially successful because this reagent is difficult to separate from the products of reaction. Boron trichloride does not have this disadvantage and has proved to be a versatile reagent in carbohydrate chemistry, as has already been reported briefly.[1] Although it is a gas at room temperature (b. p. 12°), boron trichloride is strongly reactive at temperatures well below its boiling point and can easily be handled in a medium such as a mixture of solid carbon dioxide and acetone (*ca.* −80°).[2] One of its valuable uses is for removal of *O*-methyl groups from methylated sugars which provides a rapid and convenient method of identifying the monosaccharide units in a methylated polysaccharide, or in the methylated monosaccharides derived therefrom. The polysaccharide requires only partial methylation, sufficient to effect dissolution in the reagent, and partial acetylation is equally effective. A survey of this method of converting carbohydrate derivatives into the monosaccharide units present has been carried out for over 60 compounds and forms the main subject of this paper. Cyclic *O*-methylenedioxy-, *O*-ethylidenedioxy-, and *O*-benzylidenedioxy-derivatives of hexitols also react with boron trichloride, giving the unsubstituted hexitol as the main product; the mechanism of this ring opening is the subject of a separate report.[3]

All the monosaccharides so far investigated are unchanged by prolonged contact with boron trichloride, except fructose which, whether free or part of a higher saccharide, is always substantially converted into 5-hydroxymethylfurfuraldehyde; only traces of fructose itself survive.

The formation of oligosaccharides in some reactions indicated that boron trichloride can initiate syntheses in some cases; *e.g.*, with methyl α-D-glucoside co-ordination at the glycosidic oxygen could lead to the formation of a glucosyl cation, the hemiacetal character of a glucoside providing resonance stabilisation through the ring oxygen atom adjacent to $C_{(1)}$. The ionic complex may undergo conversion into glucosyl chloride and methoxyboron dichloride but under suitable conditions either form should behave as a glucosylating agent. This possibility has been investigated by removing the excess of boron trichloride from the product of its reaction with methyl α-D-glucoside and adding an excess of a suitable substrate. The expected products have been obtained with benzene, phenols,



and glucose, the last forming a number of disaccharides. This synthetic use of boron trichloride is being investigated further.

Reactions with boron trichloride are conveniently carried out in dichloromethane

Substance	Principal product	Other products *
Methylated sugars		
2,3,5-Tri-*O*-methyl-L-arabinose	Arabinose	Oligosaccharides, 2·7 † ‡, 3·8 † ‡
2,4-Di-*O*-methyl-L-arabinose	Arabinose	1·4 † ‡
Me 2,3,4-tri-*O*-methyl-α-L-fucoside	Fucose	0·9 † (R_F)
2-*O*-Methyl-L-fucose	Fucose	Oligosaccharides, 2-*O*-methylfucose †
2,3,4,6-Tetra-*O*-methyl-D-galactose and 3,4-di-*O*-methyl-L-rhamnose	Galactose, rhamnose	0·88 † (R_F)
2,3,4,6-Tetra-*O*-methyl-D-glucose	Glucose	Mono-, di-, and tri-*O*-methylglucoses
2,3,6-Tri-*O*-methyl-D-glucose	Glucose	Mono- and di-*O*-methylglucoses, 0·77 † (R_G)
Me 2,3-di-*O*-methyl-α-D-glucoside	Glucose	Mono-*O*-methylglucoses †
3-*O*-Methyl-D-glucose	Glucose	3-*O*-Methyl-D-glucose †
2,3,4,6-Tetra-*O*-methyl-D-mannose	Mannose	0·37, 0·52, 0·61 †, 0·74, 0·93 (R_G) ‡
3,4-Di-*O*-methyl-D-mannose monohydrate	Mannose	0·40, 0·56 (R_G) ‡
Di-*O*-methylsucroses	Glucose, 5-hydroxymethylfurfuraldehyde	Fructose,† di-*O*-methylsucroses †
3-*O*-Methyl-D-xylose	Xylose	—
Methylated amylopectin	Glucose	Mono- and di-*O*-methylglucoses
Methylated cellulose	Glucose	Mono- and di-*O*-methylglucoses
Glycosides		
Me β-D-arabinoside	Arabinose	Me β-D-arabinoside †
Me α-D-fructofuranoside	Fructose, 5-hydroxymethylfurfuraldehyde	—
Me α-D-galactoside	Galactose	—
Me β-D-galactoside	Galactose	—
Me α-D-glucoside	Glucose	Oligosaccharides †
Me β-D-glucoside	Glucose	—
Ph α-D-glucoside	Glucose, phenol	—
Ph β-D-glucoside	Glucose, phenol	—
Quinol β-D-glucoside (arbutin)	Glucose, quinol	—
o-Hydroxymethylphenyl β-D-glucoside (salicin)	Glucose, saligenin	—
Me α-D-mannoside	Mannose	Oligosaccharides †
Me α-L-rhamnoside	Rhamnose	—
Me β-D-riboside	Ribose	—
Me α-D-xylofuranoside	Xylose	—
Acetals and ketals		
4,6-*O*-Benzylidene-D-glucose	Glucose	—
Me 4,6-*O*-benzylidene-α-D-glucoside	Glucose	—
1,2:5,6-Di-*O*-isopropylidene-D-glucose	Glucose	—
1,2-*O*-Isopropylidene-D-glucose	Glucose	—
2,3:4,5-Di-*O*-isopropylidene-D-fructose	5-Hydroxymethylfurfuraldehyde	Fructose †
Acetylated sugars		
Octa-*O*-acetylgentiobiose	Glucose	Gentiobiose, 1·15, 1·5
Penta-*O*-acetyl-β-D-glucose	Glucose	2·7, 5·0 †
Octa-*O*-acetylsucrose	Glucose, 5-hydroxymethylfurfuraldehyde	2·4 †
Acetylated amylopectin	Glucose	Oligosaccharides, 1·9, 2·2
Acetylated cellulose	Glucose	Oligosaccharides, 1·9, 2·2
Anhydro-sugars		
1,6-Anhydro-β-D-galactopyranose	Galactose	Oligosaccharides
1,6-Anhydro-α-D-galactofuranose	Galactose	Oligosaccharides
1,6-Anhydro-β-D-glucopyranose	Glucose	Oligosaccharides
1,6-Anhydro-β-D-gulopyranose	Gulose	Oligosaccharides
1,6-Anhydro-β-D-mannopyranose	Mannose	Oligosaccharides
Me 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannoside	2·3,2·5 (R_{mannose})	4·7 † (R_{mannose})
Me 2,3-anhydro-β-L-riboside	0·7, 1·7 (R_{ribose})	

TABLE. (*Continued.*)

Substance	Principal product	Other products *
Monosaccharides		
L-Arabinose	Arabinose	Oligosaccharide †, 2·4 † (R_{glucose})
D-Galactose	Galactose	
D-Glucose	Glucose	
D-Lyxose	Lyxose	
D-Mannose	Mannose	
L-Rhamnose	Rhamnose	
D-Xylose	Xylose	
D-Fructose	5-Hydroxymethylfurfuraldehyde	0·90 † (R_F)
L-Sorbose	5-Hydroxymethylfurfuraldehyde	Sorbose
Disaccharides		
Lactose	Galactose, glucose	Lactose
Maltose	Glucose	Maltose
Melibiose	Galactose, glucose	Melibiose †, 1·6 † (R_{glucose})
Sucrose	Glucose, 5-hydroxymethylfurfuraldehyde	Sucrose †
Turanose	Glucose, 5-hydroxymethylfurfuraldehyde	Fructose †
Miscellaneous		
Raffinose	Galactose, glucose, 5-hydroxymethylfurfuraldehyde	Fructose †
Inulin	5-Hydroxymethylfurfuraldehyde	
Nitrocellulose	Glucose	0·38, 2·1, 3·6 †
Me 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-glucoside	Glucose	Mono- and di-*O*-methylglucoses, 0·70 † (R_G)
Me 4,6-*O*-benzylidene-2-*O*-*p*-toluene sulphonyl-α-D-glucoside	5·7 (R_{glucose})	Glucose †

* Unless otherwise stated, unidentified products are indicated by R_x values in butanol–ethanol–water (4 : 1 : 5), where x refers to the principal product in each case. R_G indicates that 2,3,4,6-tetra-*O*-methyl-D-glucose is the reference compound.

† Traces only present. ‡ Probably partially methylated products. [a] Solvent propan-1-ol–ethyl acetate–water (7 : 1 : 2).

which is inert and easily removed. Few solvents are suitable since the reagent co-ordinates readily with any electronegative centre in the solvent molecule and even if there is no subsequent decomposition the complex formed is usually non-volatile. The only other solvents which appear to have found use are n-pentane [2] and tetrahydropyran.[4] Reaction of a substrate with boron trichloride requires a homogeneous environment. This is sometimes achieved without the addition of a solvent, dissolution gradually occurring in the boron trichloride as the temperature rises from *ca.* −80° to room temperature. Where dissolution did not occur, boron tribromide (b. p. 92°) often provided an alternative. Disaccharides, in particular, which were recovered unchanged from prolonged contact with boron trichloride underwent partial dissolution in boron tribromide with the expected scission at the glycosidic linkage. Boron tribromide was also more effective in the reaction with tri-*O*- and tetra-*O*-methyl-D-glucose, almost complete demethylation being effected in a single treatment in both cases, in contrast to the formation of some partly methylated derivatives in the reaction with boron trichloride.

In the general procedure, the reactants and solvent were mixed at *ca.* −80°, allowed to attain room temperature, and left overnight. After removal of excess of boron trichloride and dichloromethane, and treatment of the residue with methanol or silver carbonate, the product was isolated and examined by paper chromatography in several different solvents; where desirable, separation by ionophoresis in a borate buffer was also used. The results reported in detail in the Table are based on a qualitative examination only of 1—10 mg. amounts of substrate.

Methylated monosaccharides form the monosaccharide as the chief product (see Table), and frequently any other formed is only present in traces. Highly methylated sugars that are not completely demethylated in a single treatment with boron trichloride give the expected partially methylated derivatives which in some cases were identified chromatographically; when authentic compounds were not available for comparison, the R_F values of the products clearly indicated this type of derivative. In the case of the monomethyl product from 2,3,4,6-tetra-*O*-methyl-D-glucose, elution from the paper on which it was separated and examination of the eluted product by ionophoresis established that no selective demethylation had occurred. The M_G values of 0·21 and 0·81 (with values of 0·26 and 0·82 in a duplicate determination) indicate the presence of either or both 2- (M_G 0·23) and 4-*O*-methylglucose (M_G 0·24), and of either or both the 3- (M_G 0·82) and 6-*O*-methylglucose (M_G 0·82).[5] The two methylated polysaccharides gave mainly glucose as expected, with some mono- and di-*O*-methylglucose. Di-*O*-methylsucrose is converted into glucose and 5-hydroxymethylfurfuraldehyde; the latter showed the same chromatographic behaviour as the product obtained on a preparative scale directly from the same treatment of fructose. The structure of this product was established by comparison of its ultraviolet absorption spectrum with that of an authentic specimen and by conversion by mild oxidation into 5-hydroxymethyl-2-furoic acid. Stoicheiometrically, the reaction involves loss of three molecules of water from fructose. Mechanisms have been proposed for this dehydration when brought about by acids[6] and by iodine in dry dimethylformamide.[7] In the latter reaction, the presence of the furanoside ring and of the attached hydroxy- and hydroxymethyl groups at the tertiary carbon atom at position 2 provide a plausible route for the progressive elimination of three molecules of water. A similar scheme for the interaction with boron trichloride could be formulated based on the formation of a carbonium ion at $C_{(2)}$ similar to that of the glucosyl ion (above), followed by elimination of a proton at $C_{(1)}$ to give an aldehyde group; the aldehyde group would assist the elimination of the second and third molecules of water from positions 2,3 and 4,5 by resonance stabilisation through conjugation with the olefinic bonds so formed, as in the iodine reaction.

Glycosides, acetals, and ketals are converted almost exclusively into the parent sugar (accompanied on chromatograms by the corresponding aglycone in the case of the phenyl glucosides), except when a fructose unit is present. Acetylated sugars behave similarly, but small amounts of subsidiary products are formed which appear to be incompletely deacetylated derivatives; oligosaccharides appear in addition with cellulose and amylopectin acetates. Nitrocellulose also gives glucose as the main product, with smaller amounts of other derivatives. The behaviour of 1,6-anhydro-sugars contrasts with that of 2,3-anhydro-compounds. The former react normally with boron trichloride, but neither of the 2,3-anhydro-sugars examined gave detectable quantities of the parent sugar, the chief products in both cases having R_F values well removed from the expected values. Chloro-sugars may be formed with these substrates and this possibility is being examined. No evidence has been obtained that any monosaccharide formed as the principal product in the reaction of boron trichloride with its derivatives itself undergoes detectable degradation with this reagent under the experimental conditions reported in the Table. The effect of boron tribromide was examined when no dissolution in boron trichloride was apparent, but no differences in the type of reactivity of the two reagents were observed. D-Fructose forms 5-hydroxymethylfurfuraldehyde with both reagents; this product is also obtained by the action of boron tribromide on L-sorbose, which is not soluble in boron trichloride.

The disaccharides investigated, together with raffinose, did not dissolve in or react with boron trichloride, but reaction occurred with boron tribromide in all cases, with fission into the expected monosaccharide units; as expected, 5-hydroxymethylfurfuraldehyde appears in the products from sucrose, turanose, and raffinose with only traces of fructose. This was the only product from inulin which, in contrast to the other three substrates, reacts with boron trichloride.

One type of sugar derivative which is being investigated further is that containing the toluene-*p*-sulphonyl group. Only a trace of glucose was obtained from methyl 4,6-*O*-benzylidene-2-*O*-toluene-*p*-sulphonyl-α-D-glucoside, the main product having a high R_F value. Unless there is some particular effect exerted by the toluene-*p*-sulphonyl group, the α-methyl and benzylidene groups should be completely removed by the reagent; the product might then be the monotoluene-*p*-sulphonyl ester. If this is the case, it should be possible to demethylate methylated toluene-*p*-sulphonic esters of sugars with retention of the ester group.

EXPERIMENTAL

Materials.—Commercial methanol was used without purification.

Boron trichloride was handled as described elsewhere.[3] Boron tribromide (b. p. 92°) was distilled before use. Dichloromethane was washed with 5% aqueous sodium carbonate and water, dried ($CaCl_2$), and distilled, the fraction boiling at 39·5—41° being collected.

Paper Chromatography and Paper Ionophoresis.—Paper chromatography was carried out on Whatman No. 1 filter paper, with the following solvents (the organic phase being used where two phases form): (1) butan-1-ol–ethanol–water (4 : 1 : 5); (2) propan-1-ol–ethyl acetate–water (7 : 1 : 2); (3) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3), (4) ethyl acetate–acetic acid–water (9 : 2 : 2); (5) butan-1-ol–acetic acid–water (4 : 1 : 5). The sprays most commonly used to detect the sugars and their derivatives were: (1) silver nitrate and ethanolic sodium hydroxide; (2) *p*-anisidine hydrochloride; (3) aniline hydrogen phthalate; (4) urea hydrochloride; (5) diphenylamine, aniline, and phosphoric acid; (6) 2,4-dinitrophenylhydrazine and hydrochloric acid; (7) α-naphthol and phosphoric acid; (8) phloroglucinol and trichloroacetic acid; (9) potassium periodatocuprate.[8]

Paper ionophoresis was carried out on Whatman No. 3 paper in borate buffer (0·2M) at pH 10·0.

Interaction of Sugar Derivatives and Boron Trichloride.—The sugar derivative (1—10 mg.) was dissolved or suspended in dry dichloromethane (1—2 ml.) and cooled in acetone–solid carbon dioxide. Boron trichloride (1—2 g.), cooled to −80°, was then added. The mixture was kept at −80° for 30 min., then allowed to warm to room temperature and kept for 16 hr. under anhydrous conditions. Substances which were insoluble in dichloromethane initially frequently became soluble as the mixture attained room temperature. Any solvent or boron trichloride remaining was removed under diminished pressure at room temperature. The glassy residue was treated by adding either (*a*) methanol (3 × 3 ml.) and evaporating to dryness under diminished pressure after each addition or (*b*) an aqueous suspension of silver carbonate to neutralise the solution, filtering from the insoluble silver salts, and freeze-drying the aqueous filtrate. The residue in either case was dissolved in a small amount of methanol or water and examined by paper chromatography and paper ionophoresis.

Interaction of D-*Fructose and Boron Trichloride.*—Boron trichloride (10 g.) was added to a suspension of D-fructose (1·6 g.) in dichloromethane at −80°. After 30 min. at −80° and 16 hr. at room temperature excess of boron trichloride and of dichloromethane was removed and the product treated by the silver carbonate method. On examination by paper chromatography (with solvents 1, 2, 3, and 5) and by paper ionophoresis, the principal product could not be distinguished from authentic 5-hydroxymethylfurfuraldehyde. This product was purified by chromatography on several sheets of thick paper (Whatman No. 3) in solvent 1. The papers were viewed under ultraviolet light, which rendered 5-hydroxymethylfurfuraldehyde visible. The appropriate sections were cut into thin strips and extracted with ether (Soxhlet). Concentration of the extract gave a syrup (0·4 g.) which was shown to be pure 5-hydroxymethylfurfuraldehyde by chromatography and by oxidation with silver oxide (1 g.) and sodium hydroxide (1·6 g.) in water to 5-hydroxymethyl-2-furoic acid (0·37 g.), m. p. and mixed m. p. 165°. A solution of the sample in water had the same ultraviolet absorption spectrum as a pure sample of 5-hydroxymethylfurfuraldehyde.[9]

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