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DENITRATION OF NITROGUANIDINES

A thesis submitted by Joyce Colquhoun Lockhart in
candidature for the degree of Doctor of Philosophy
of the University of London.

June, 1957.

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Abstract.

The reversible denitration of several nitroguanidines in sulphuric acid media above 67%, in perchloric acid of 59-72% strength and in sulphuric acid-acetic acid media of 49-85% strength, has been investigated.

The state of the nitroguanidine molecule in strong acid and the condition of the acid molecules themselves have been discussed.

The equilibrium position between the nitroguanidine and corresponding guanidine has been established in all the media used and a correlation of equilibrium position with activity of water in the medium, deduced by Simkins and Williams, has been applied in suitable cases.

The rate of denitration over the measurable range has been obtained for several compounds in sulphuric acid-water mixtures, for one in sulphuric acid-acetic acid mixtures and for two in perchloric acid-water mixtures. The rate of guanidine nitration was also measured in sulphuric acid-acetic acid. Rates in perchloric acid are directly proportional to the Hammett acidity function h_0 . In sulphuric acid this relation does not hold but a relation with h_0 together with the activities of certain solvent species does apply.

The ultra-violet absorption spectra of the nitroguanidines in dilute acid were measured for use in the analysis of reactions. These, together with further spectral data, were used to furnish pKa values for several of the compounds.

Certain acidity functions were also investigated, including the H_+ function in sulphuric acid-water and perchloric acid-water mixtures, and the H_0 function in the higher ranges of perchloric acid.

Acknowledgements.

The author wishes to acknowledge her indebtedness to the late Professor Gwyn Williams, who suggested the topic of this thesis, and to Dr. T.G. Bonner for his unfailing advice and encouragement throughout the greater part of the work.

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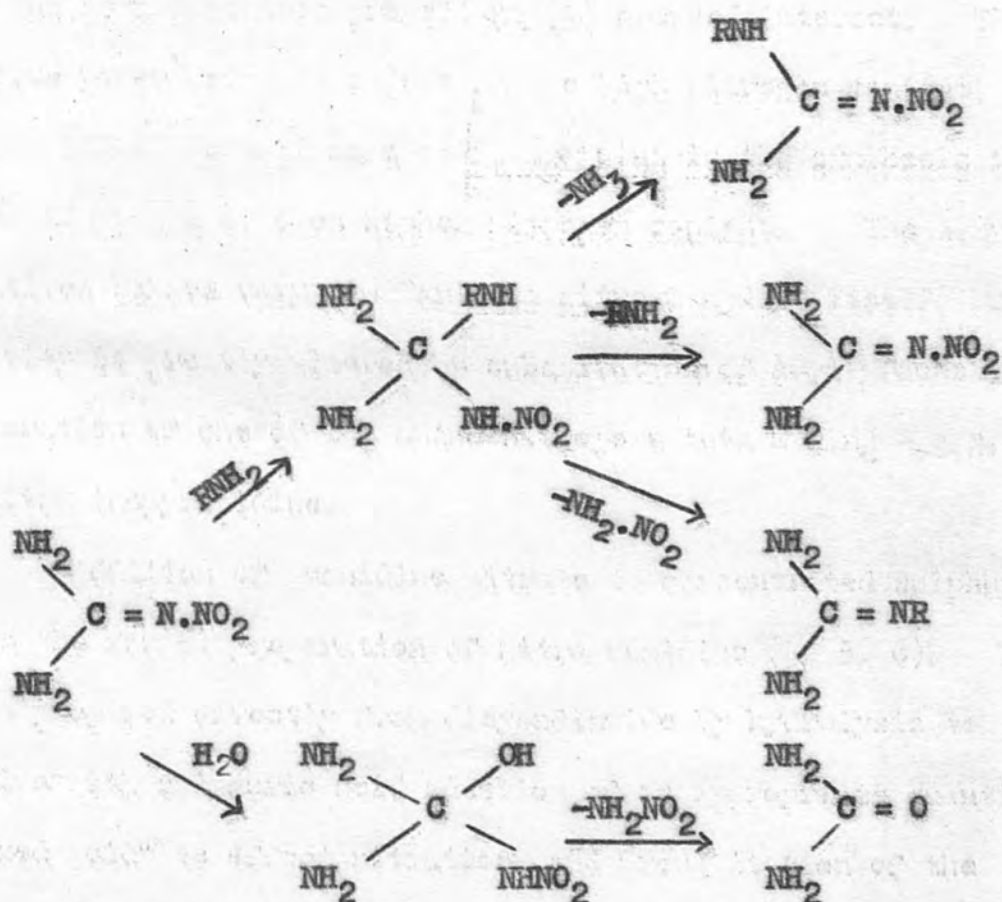
Section I. Introduction.

A. Nitroguanidines.

The product obtained by Jousselin (1) from the reaction between fuming nitric acid containing nitrous oxide, and guanidine nitrate thought at first to be nitroseguanidine, was identified as nitroguanidine by both Pellizzari (2) and Thiele (3). The chemistry of the compound received little attention until the use of nitroguanidine as a flashless propellant (4) aroused interest. The explosive power being dependent on the high nitrogen content, nitroguanidine was used as a starting-point in the synthesis of related compounds of even higher nitrogen content. The alkyl derivatives behave very similarly to nitroguanidine itself, but reactivity is greatly altered by substitution of aryl groups or incorporation of one of the amino-nitrogens into a ring - e.g. as in 2-nitraminopyrimidine.

Addition of guanidine nitrate to concentrated sulphuric acid is the normal preparation of nitroguanidine (4, 5, 6). It may be prepared directly from dicyandiamide by hydrolysis to guanidine with sulphuric acid addition of an appropriate quantity of "mixed acid" to effect nitration, and precipitation of the nitroguanidine by dilution with water. Mono- and N:N-di-alkyl-guanidine (7) and aminodiazacycloalkanes may be nitrated in this way, but arylguanidines undergo nitration in the ring and hydrolysis of the guanidine grouping. N:N'-dialkyl-N''-nitroguanidines cannot be isolated from such a reaction (7, 8).

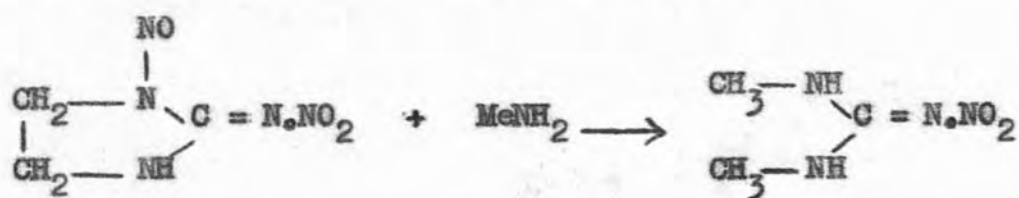
Amines will react with nitroguanidine (9), nitrothioureas (10), and N-methyl-N-nitroso-N'-nitroguanidine (9) to provide substituted nitroguanidines. Arylamines are too weak to react with nitroguanidine but can be used with the two other reagents. Alkyl- or aryl-guanidines and ureas are also formed. An addition-elimination reaction has been postulated by McKay (4) which will explain satisfactorily all the products. The scheme represents a possible



set of reactions.

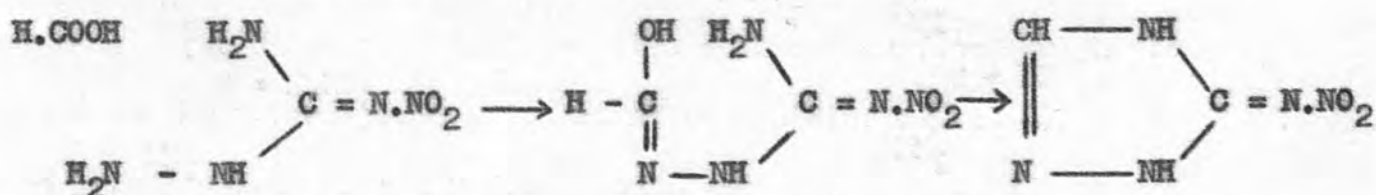
The alkyl nitroguanidine formed in this reaction might conceivably react with a further molecule of amine to give a

dialkylnitroguanidine. Normally, dialkylureas are obtained, but N:N'-dimethyl-N''-nitroguanidine has actually been obtained as a side product in the reaction of methylamine with nitroguanidine, in very low yield (11). These dialkyl compounds are rather elusive (8,12) but have been obtained (also in very low yields) by McKay (13) as a subsidiary product in the reaction of amines with 1-nitroso-2-nitrimino-1:3-diazacyclopentane. The dimethyl, diethyl and dibenzyl compounds are reported (13, 14, 15).

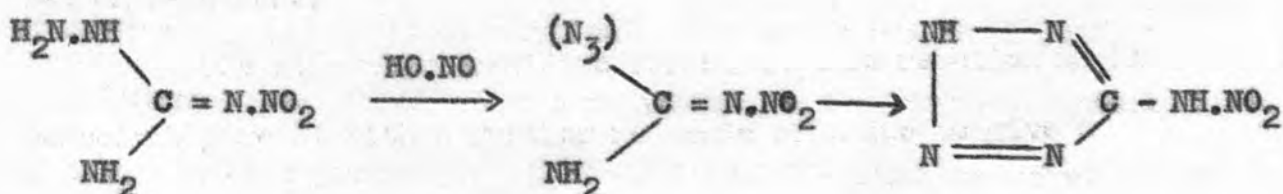


Several new routes to the dimethyl compound were unsuccessfully attempted in this work.

Triazoles may be obtained by condensing aminonitroguanidine with acids, e.g. formic, and cyclising the product (16).



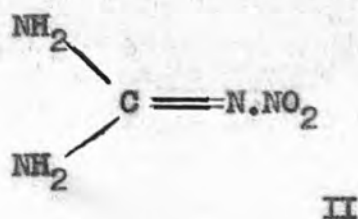
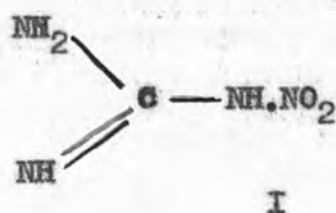
Nitramine tetrazoles can also be synthesized from aminonitroguanidine by reaction with nitrous acid. Nitroguanylazide is an intermediate (17, 18).



Although N:N'-dialkyl-N''-nitroguanidines are not preparable by nitration, it is possible to prepare N-alkyl-N':N''-dinitroguanidines by nitration (19), best in acetic anhydride. The cyclic 1-nitro-2-nitrimino-1:3-diazacyclopentane and its 4-methyl analogue have been prepared by nitration in acetic anhydride, but with the corresponding six- and seven-membered rings, the nitrimino group hydrolysed resulting in a cyclic nitrourea (8, 20). The reason for the specificity is not obvious.

The nitroguanidines are usually white, crystalline solids of high melting point. A recent X-ray analysis of nitroguanidine gives the C - N bond-lengths as 1.34 - 1.35 Å (21). Previous studies on guanidinium iodide give a C - N bond length of 1.18 Å (22, 23) and for methylguanidinium nitrate a C - N bond length of 1.33 Å is reported (24). Normal C - N bond lengths are C - N 1.48 Å, C=N 1.28 Å, C≡N 1.14 Å, so the special nature of the guanidinium ion is evident.

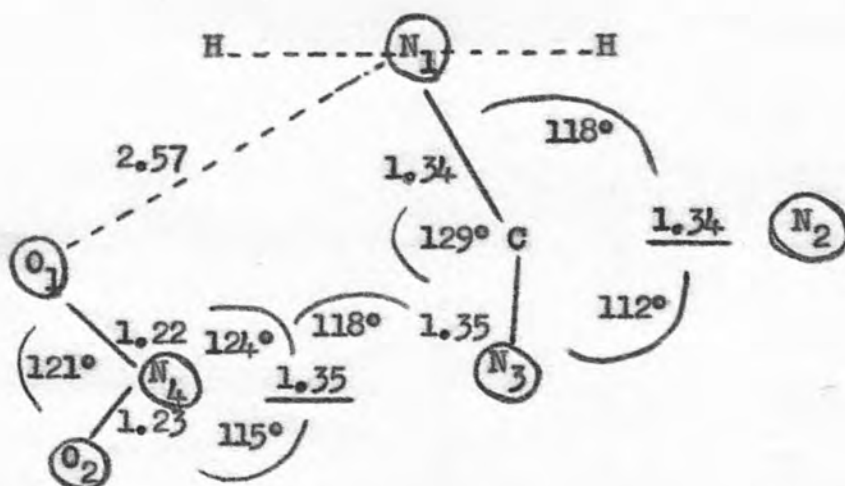
There are two possible conventional formulae for nitroguanidine. Thiele originally proposed the unsymmetrical form (I), (25), but no proofs of the structure were offered until recently when there was a controversy over the nitrimino (II) and nitramine (I) forms. Wright's evidence for the nitrimino structure was based on the absence of nitramine group reactions (12). Nitroguanidine and 2-nitrimino-1:3-



diazacyclopentane did not react with diazomethane and acetyl chloride. The 1-nitro derivative of the pentane did not react with diazomethane but did with acetyl chloride, which suggests some labile tautomerism in the compound. Kumler and Sah argued from their dipole moment and ultraviolet absorption spectrum measurements that nitroguanidine, aminonitroguanidine and 2-nitrimino-1:3-diazacyclopentane are resonance hybrids with the main contribution from the nitrimino form (26).

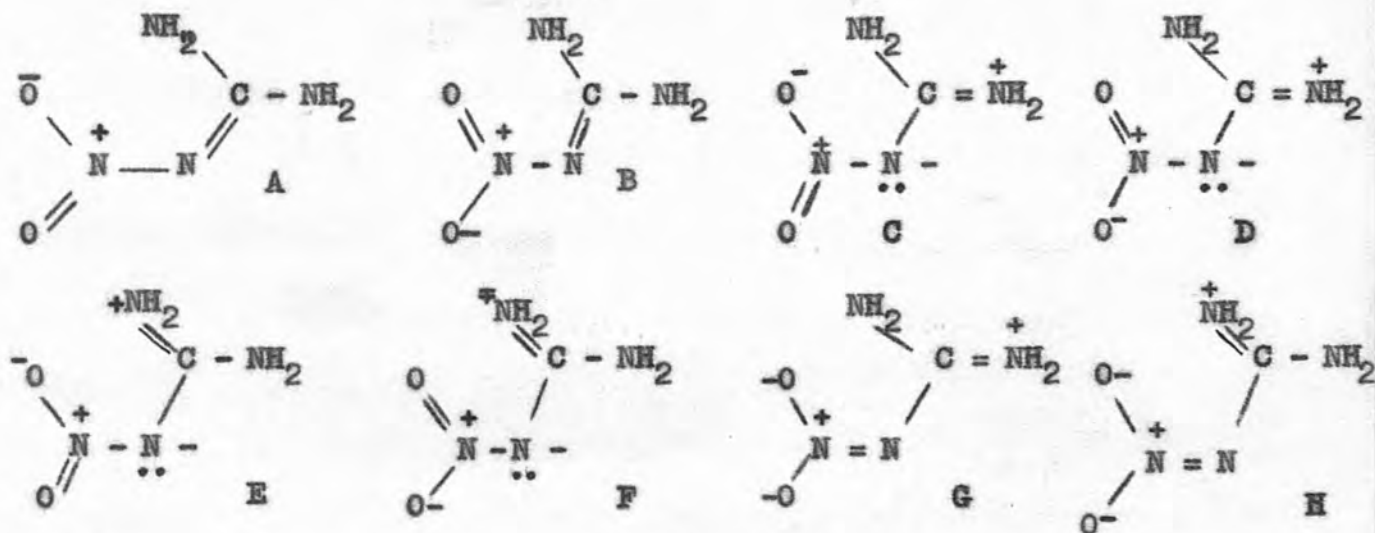
McKay, Picard and Brunet regarded the structure as a nitramine one on the basis of spectral measurements (27).

Bryden, Burkardt, Hughes and Donohue on the strength of their X-ray studies of nitroguanidine disagreed with all of these proposals (21).



The distances observed in this work are given above along with bond angles. The molecule was found to be nearly planar, the greatest deviation from the plane being 0.03 Å for N₂ and O₁. The strain

in the molecule is relieved by the unusually large bond angles N_3CN_1 and $O_1N_4N_3$ rather than by reduction of planarity or enlargement of the CN_3N_4 angle which is normal (118°). The C - N bond lengths are almost equal so that the bond order of all three must also be the same. The authors wrote down eight possible resonance structures:-



To these they gave arbitrary weights in the complete representation of the structure. Allowing for 15% each of A and B and 10% each of G and H and dividing the remaining 50% between C, D, E and F, they managed to calculate bond lengths in reasonable agreement with the measured values. The authors suggest that nitroguanidine is not a nitrimino compound (A, B) nor yet a nitramine compound (G,H) and that C,D, E and F do contribute to the actual resonance structure.

In strongly acid media however, nitroguanidines are mainly present in the mono-protonated form, and as it is the structure of this

ion which is important in the present investigation, this was studied by means of ultra-violet absorption spectra.

Nitroguanidine is very insoluble in water and organic solvents but is more soluble in acids because of its weakly basic character. Solubility varies widely amongst the substituted compounds. For instance, 2-nitrimine-1,3-diazocyclohexane is insoluble in ethanol but the N:N'-dimethyl-N''-nitroguanidine is exceedingly soluble. Most alkylnitroguanidines are soluble in water and alcohol but not in other solvents.

The ultra-violet absorption spectra of a large number of nitroguanidines have been investigated (26-33). A peak at approximately 2600-2700 Å is observed and its position and height are modified by substituent groups on the amine nitrogens.

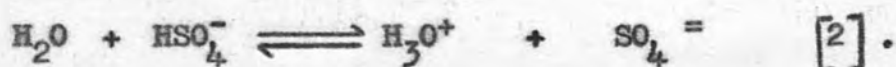
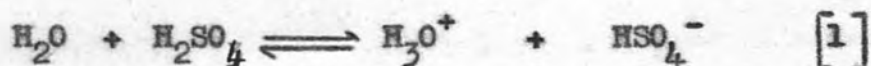
The basic properties of nitroguanidine were observed by Thiele who prepared the nitrate by cooling a solution of nitroguanidine in nitric acid. The nitrate is very readily hydrolysed to nitroguanidine. The pKa of the nitroguanidine conjugate acid has been calculated as -0.55 (32) and that of the N-methyl-N'-nitroguanidine conjugate acid is -0.86 (11).

Nitroguanidine forms a silver salt (25) and the spectrum in alkaline solution is different from that in neutral solution (27,29), indicating an acidic function. The pKa of nitroguanidine obtained by titration with alkali (26) and by ultra-violet absorption determination of ionisation (32) are reported.

The reactions of nitroguanidine in acid solution will be dealt with in the denitration section.

B. Constitution and Acidity of Media Used.

Absolute sulphuric acid has a high dielectric constant [evaluated as 101 at 25°C. and 122 at 8°C. by Gillespie and Cole (34) and as 110 at 20°C. Brand, James and Rutherford (35)] and a low ionic strength. The apparent ideality of electrolyte solutions in sulphuric acid has been attributed to the low ionic strengths available. Addition of water increases the ionic strength probably because of the reactions:-



The following table lists the species which have been reported present in the binary system $\text{H}_2\text{O} - \text{H}_2\text{SO}_4$ at various compositions.

Table I.

Mole ratio $\text{H}_2\text{O} : \text{H}_2\text{SO}_4$	Less than 1	1	More than 1
% H_2SO_4 w/w	100 - 84.5	84.5	84.5 and below
<u>Species present</u>	$\text{H}_2\text{SO}_4, \text{H}_3\text{O}^+, \text{HSO}_4^-$	$\text{H}_3\text{O}^+, \text{HSO}_4^-$, (H_2SO_4)	$\text{H}_3\text{O}^+, \text{HSO}_4^-, \text{SO}_4^{=}$, H_2SO_4 .

References:- (36-49).

Much of the evidence for these species is conflicting, particularly interpretation of Raman spectra. Woodward and Horner (39) claim that

molecular sulphuric acid persists as low as the equimolar mixture, but that bisulphate ion only reaches a maximum concentration at 40% H_2SO_4 . Sulphate ion begins to appear at 65% H_2SO_4 but is not appreciable above 40% H_2SO_4 . These results are not self-consistent but seem to indicate that [1] is never complete. Bell and Jeppeson (42) interpret their data similarly, excepting that they say molecular sulphuric acid persists as low as 30% H_2SO_4 , that the maximum intensity of bisulphate is at 60% H_2SO_4 and that sulphate appears at 70% H_2SO_4 .

Rao (44) attempted a quantitative estimation of the species observed in his Raman Spectra data, and his results were recalculated by Young and Grinstead (48). They estimated only 15% completion of [1] in the equimolar mixture.

The most recent work on Raman Spectra of sulphuric acid-water mixtures by Millen and Vaal (45) states that the monohydrate shows bands corresponding only to bisulphate ion, no molecular sulphuric acid or hydroxonium ion bands being discernible, and the interpretation is an ionic structure $[H_3O^+][HSO_4^-]$. Similarly for the dihydrate, where only sulphate bands were observed the structure $[H_3O^+]_2[SO_4^{=}]$ is proposed. This is in agreement with previous work on nuclear magnetic resonance spectra (49).

Gillespie deduced from cryoscopic work that water was incompletely ionised in 99.8% sulphuric acid and in fact estimated a basic dissociation constant but this is open to doubt. Vapour pressure measurements indicate that only 6% of the total water is

present as such in the dihydrate. However this need have no significance as the water need not be involved either in equilibrium [1] or [2] but may be involved in some hydrogen-bonded structure.

Less evidence is available on the perchloric acid-water system but some suggestions on the constitution of the equimolar mixture, $H_2O-HClO_4$, M.Pt. $45^\circ C.$, have been made. Millen and Vaal (45) made some Raman Spectra measurements on the mixture and obtained lines corresponding to the perchlorate ion, but no lines corresponding to molecular acid or hydroxonium ion. Mullhaupt and Hornig (50) obtained apart from the perchlorate lines, two very diffuse bands which may correspond to hydroxonium ion. Taylor and Vidale (51) have actually assigned certain bands obtained in their Raman Spectra of the 1:1 $HClO_4-H_2O$ mixture, to the hydroxonium ion. The constitution $[H_3O^+][ClO_4^-]$ is thus likely for the monohydrate. Proton magnetic resonance studies (52) (53) and infra-red work confirm this (54).

No evidence is available about acetic acid-sulphuric acid, except that acetic acid, present in small amount, is completely ionised in 100% sulphuric acid (37).

The H_0 Function.

Acidity in dilute aqueous solutions is normally discussed in terms of pH where $pH = -\log (H^+)$. The term (H^+) , meaning activity of hydrogen ion, can be neither rigorously defined nor rigorously measured. In solutions where $(H^+) > 1$, pH becomes negative.

A method was developed by Hammett and Deyrup (55) for measuring the acidity of such acid solutions in terms of their ability to donate protons to neutral bases. They defined the function H_0 such that

$$H_0 = -\log (H^+) \cdot f_B / f_{BH^+} \dots \dots \dots [3]$$

and f_B / f_{BH^+} has the same value for all neutral bases in the same medium. This function will equal pH in dilute solution provided that the standard state to which the activities refer is very dilute aqueous solution.

$$\text{For any base B, } pK_a^{BH^+} = -\log (H^+)(B)/(BH^+) = H_0 - \log [B]/[BH^+] \dots \dots [4]$$

where () denote activity and [] concentration of the species within the brackets.

$$\text{For any base C, } pK_a^{CH^+} = H_0 - \log [C]/[CH^+] \dots \dots \dots [5]$$

$$pK_a^{CH^+} - pK_a^{BH^+} = \log [B]/[BH^+] - \log [C]/[CH^+] = \text{const.} \dots \dots [6]$$

There should then be a constant difference between $\log [B]/[BH^+]$ and $\log [C]/[CH^+]$ over any range of media. Hammett and Deyrup measured ionisation ratios colorimetrically for a series of weak bases and showed that the log ionisation ratio plotted against acid concentration gave a series of parallel curves (see Fig. 1) so that $\log [B]/[BH^+] - \log [C]/[CH^+]$ was reasonably constant and the fundamental assumption of constancy of f_B / f_{BH^+} justified. Choosing as their first and strongest base an amine of known pK_a and ensuring that the ranges of ionisation of the other bases overlapped Hammett and Deyrup were able to derive H_0 stepwise for various acids, including $H_2SO_4-H_2O$ 0-100% and $HClO_4-H_2O$ 0-60%.

A method of determining $[B]/[BH^+]$ spectrophotometrically was developed by Flexser, Hammett and Dingwall (56), extending the possibilities for new indicators and increasing the accuracy of measurements. H_0 has since been evaluated for many other acids, including sulphuric acid-acetic acid mixtures (57) up to 50% w/w. The function H_0 for 50-70% $HClO_4$ was required for interpretation of denitration kinetics and has accordingly been measured.

An indication of the species present in $H_2SO_4 - H_2O$ mixtures of high H_2SO_4 content is obtained from the work of Brand (58) and of Deno and Taft (59), who calculated values of H_0 down to 77% H_2SO_4 , in reasonable agreement with Hammett's measured values, using certain assumptions. Brand has shown that

$$H_0 \text{ calcd.} = -8.36 + \log X_{H_2SO_4} / X_{H_2O} \dots\dots\dots [7]$$

(where X denotes stoichiometric concentration and 8.36 is an arbitrary constant) applies with precision above 88% H_2SO_4 if reaction.... [1] is assumed to lie completely to the right. Deno and Taft were able to extend the application^{of} [7] on assumption of a mole fraction equilibrium constant $K = 50$ for reaction [1] between 83 and 89% H_2SO_4 . The use of equation [8]

$$H_0 = 6.66 + \log X_{H_2O} / X_{H_3O^+} \dots\dots\dots [8]$$

alternatively to [7] is possible as low as 83% H_2SO_4 but a correction must then be applied for the rapidly changing value of f_{H_2O} which is constant above 84% H_2SO_4 (59).

$$H_0 = -6.66 + \log \frac{X_{H_2O}}{X_{H_3O^+}} + 1.67 + \log f_{H_2O} \dots\dots [9]$$

This equation will evaluate H_0 correctly as low as 77% H_2SO_4 . These data may be taken as evidence for the complete ionisation of water as low as 88% H_2SO_4 to give oxonium ion and bisulphate ion, and considerable ionisation to form bisulphate or bisulphate and sulphate ions in acids as low as 77% H_2SO_4 , and are in agreement with the more recent Raman Spectra evidence on the structure of such acids.

The calculation of H_0 values for sulphuric acid-acetic acid mixtures of high sulphuric acid content is equally feasible but no measured values are yet available for comparison. Such data might throw light on the entities present in sulphuric acid-acetic acid mixtures.

The numerical value of H_0 for certain acids does not vary greatly over a temperature range of 20-80°C., according to the measurements of some Russian workers (60). Between 0 and 30% H_2SO_4 , values at 80°C. are more acid than those at 20°C. by at most 0.15 unit, and from 30-50% values between 20°C. and 80°C. are identical. Above 50% H_2SO_4 , acidity at 20°C. becomes increasingly greater than at 80°C. until at 100% H_2SO_4 the respective values are -10.65 and -9.90. Temkin et al. have calculated H_0 by the method of Brand (58) and of Deno and Taft (59) in agreement with their results at 20°C., but the results at higher temperatures are less amenable. This

they ascribe to a displacement of [1] and [2] further to the left at higher temperatures. An arbitrary allowance could be made for this in the calculation. It thus seems likely that there is more water present in highly acid solutions at higher temperatures.

The other acids studied in this paper were aqueous hydrochloric acid up to 6M, and aqueous phosphoric acid up to 100% at 20°, 40°, 60° and 80°C. and the phosphorus pentoxide-water system 72-81% w/w at 4°, 20° and 40°C. The hydrochloric acid solutions are slightly more acid at 80°C. than 20°C. over the whole range measured. Temperature does not affect phosphoric acid solutions of less than 20% strength, but above that value the solutions become more acid at lower temperatures, there being nearly a unit difference between the values at 20° and 80°C. for 100% H_3PO_4 . H_0 for the phosphorus pentoxide-water system reaches a maximum at 79.7% w/w pentoxide at all temperatures and is more acid at 4° than at 40°C. throughout the range measured.

These temperature variations presumably reflect changes in the degree of ionisation of solvent species as seems to be the case in aqueous sulphuric acid.

The H_0 function is useful in kinetic studies for deciding between mechanisms in acid catalysis, and it is also useful for determining pK_a s of very weak bases.

In the original paper on H_0 (55), Hammett and Deyrup

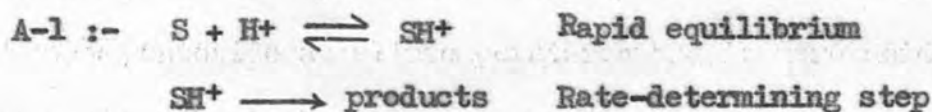
discussed several reactions whose rates obeyed the relation

$$\log k + H_o = \text{const.} \quad \dots\dots\dots [10]$$

or $k/h_o = \text{const.} \quad \dots\dots\dots [11]$

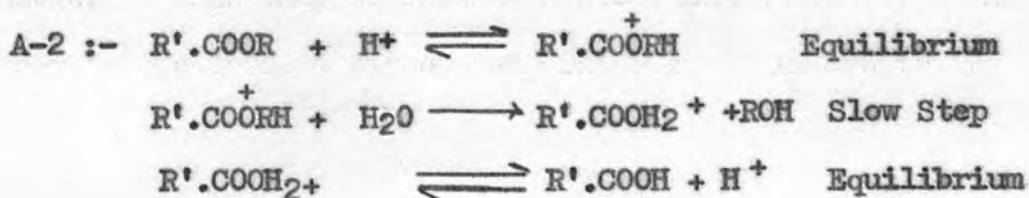
where k is the rate of any reaction and $h_o = -\text{antilog } H_o$. This, Hammett claimed, was to be expected if the velocity was proportional to the concentration of ion formed by protonation to a slight extent of the substrate. The equation may be modified to cover more extensive ionisation of the substrate, the reaction rate becoming constant at complete ionisation .

Zucker and Hammett (61) later proposed that while for a reaction proceeding by uptake of a single proton to form the transition state (an

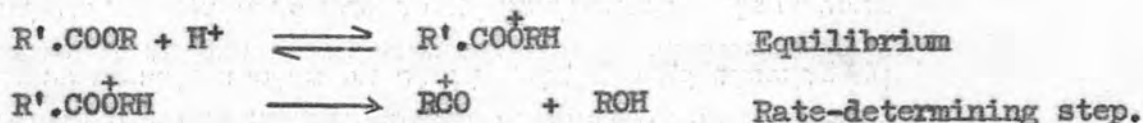


A-1 reaction) the rate should parallel h_o , reactions in which a water-molecule is involved in the transition state (an A-2 reaction) should parallel $C_{OH_3^+}$ (stoichiometric acid concentration).

Long and others (62) have recently attempted to verify this hypothesis by applying it to reactions whose mechanisms had been previously ascertained by other methods. For instance in the hydrolysis of simple esters such as methyl acetate, methyl benzoate, the mechanism is generally supposed to be A-2 (63).

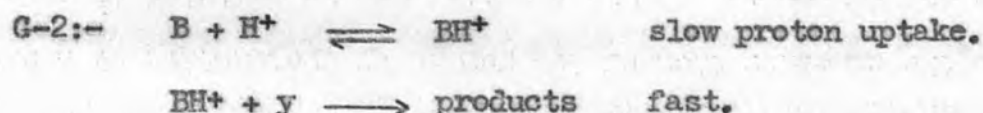


But for such an ester as methyl mesitoate, the presence of electron-releasing groups would cause the reaction to proceed through ionisation to acylium ion (A-1). (64).



Application of the Zucker-Hammett hypothesis to these two situations would lead one to expect a relation with $C_{OH_3^+}$ for the rate of methyl acetate hydrolysis and with h_0 for mesitoate hydrolysis. The experimental results bear this out (65, 66).

Long has collected data of this type for many other acid-catalysed reactions and has interpreted them in the light of the Zucker-Hammett hypothesis. The general conclusion is that an A-1 mechanism normally can be correlated with h_0 and an A-2 with $C_{OH_3^+}$. However the fact that the rate of a reaction parallels h_0 is not necessarily evidence for an A-1 reaction because other mechanisms such as G-2 can lead to the same result.



To distinguish amongst possible mechanisms, a reaction should be performed in acid solutions for which H_0 has been measured and at high enough concentrations of acid to permit the divergence between $C_{OH_3^+}$ and h_0 to become obvious (above 1.5M for nitric, perchloric acids etc.) Many reactions in dilute acid solutions have been interpreted in this way, e.g. hydrolysis of esters, epoxides, acetals,

anhydrides and inversion of sugars. The rate in each case parallels $\log k$ or $C_{OH_3^+}$, this relation being taken as diagnostic.

For an exact relation between $\log k$ and $\log k$, a plot of $\log k$ against $\log k$ will be unity. In dilute acid solutions this very seldom happens and slopes ranging from -0.7 to -1.5 have been used as evidence for the A-1 mechanism. Slopes also vary for the same reaction from acid to acid. There is much less data available for concentrated acid solutions. It has been suggested that a constancy of $\log k + \log k$ summations above 90% H_2SO_4 may be a direct result of the ideality of the medium and have no significance as regards elucidation of mechanism, apart from implication of general acid catalysis.

There have been several explanations of the non-unity of slopes of $\log k$ versus $\log k$, the most interesting being that of Long and McIntyre (67). Thermodynamically, the relation $\log k + \log k = \text{constant}$ [10] should be written

$$\log k + \log k + \log \frac{f_B \cdot f_{T^+}}{f_{BH^+} \cdot f_R} = \text{const.} \quad \dots [12]$$

where f denotes activity coefficient of subscript, B is any Hammett base, R is the substrate in the reaction and T^+ is the positively charged transition state of the substrate. Consequently, if the activity coefficient term is not constant, deviation in [10] should be observed. The relation [10] assumes that the ratio of activity coefficients of the reactant and its transition state will vary in the same way with changing medium as that of the Hammett base used for the

determination of H_0 in the same range of media and its protonated form. This assumption may be queried on the grounds that activity coefficients of non-electrolytes are very specifically affected by ionic strength, polarity and size of non-electrolyte molecule. (Established by Long and McDevitt (68) and Paul (69)). Moreover, the slope of $\log k$ versus H_0 for the hydrolysis of methylol was improved by a semi-quantitative survey of the variation of activity coefficients of reactant and of indicator molecule (Long and McIntyre, loc. cit.). The bases used by Hammett in constructing his scale were all aromatic and polar molecules, with the ionising groups $-\text{NH}_2 \longrightarrow -\overset{+}{\text{N}}\text{H}_3$, $=\text{O} \longrightarrow =\overset{+}{\text{O}}\text{H}$, and $-\text{N}=\text{N}- \longrightarrow -\text{N}=\overset{+}{\text{N}}\text{H}-$. The group $-\text{NO}_2 \longrightarrow -\overset{+}{\text{N}}\text{O}_2\text{H}$ has also been used (Brand, 58).

Bell and Brown have suggested that $\log k$ might depend on H_0 and to a small extent on $[H_0]^2$, but no theoretical justification has been offered (70).

The hydrogen isotope exchange reaction studied by Gold, Satchell (71) and others gives rise to slopes ranging from -0.9 to -1.5 and Gold has suggested the non-unity sometimes occurs because the reaction was studied over a wide range of acidity (4 H_0 units) whereas reactions are normally studied over 1 or 2 unit ranges. Slopes were much nearer unity in any small range studied.

In concentrated sulphuric acid ($> 84\%$) the constancy of activity coefficients has been postulated by Deno and Taft following on their elegant H_0 calculation. Above 84% acid activity coefficient

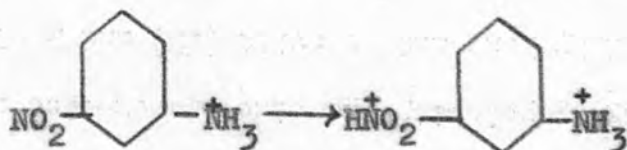
ratios should then necessarily be constant, thus all reactions which follow H_0 should give unit slopes. This is not always the case. For instance in the cyclisation of anils (72, 73, 74) slopes ranging from -0.92 to -1.18 have been obtained. The possibility of some factor other than activity coefficients causing non-unit slopes is thus supported.

The H_+ Function.

The acidity function H_+ governing the ionisation of a protonated base CH^+ to the form CH_2^{++} may be defined as

$$H_+ = - \log (H^+) \frac{f_{CH^+}}{f_{CH_2^{++}}} \text{ where } () \text{ and } f \text{ have the usual significance.}$$

It has been suggested by Coryell and Fix (76) that H_0 and H_+ are the same function or differ by a constant. Brand, Horning and Thornley (77) have estimated the difference between H_0 and H_+ in 100% H_2SO_4 to be ~ -0.28 which they decided was negligible. In their construction of an H_0 scale for oleum, the same authors used the *m*-nitroanilinium ion as an indicator and the plot of



$\log (\text{base/ion})$ for this indicator paralleled those for the neutral indicators used. Thus

$$\log \left[\frac{[B]}{[BH^+]} \right] - \log \left[\frac{[CH^+]}{[CH_2^{++}]} \right] = \text{constant}$$

and so the difference between H_+ and H_0 must be constant in this medium.

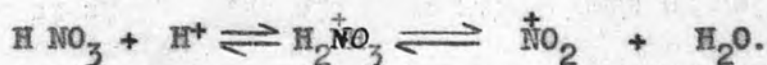
Lewis and Bigeleisen (78) also extended the H_0 scale for sulphuric acid into oleum using fluorescein indicators which strictly measured H_{3+} but their scale does not coincide with that of Brand, Horning and Thornley.

An acidity function G based on substituted thiazine indicators taking up variously from one to three protons was measured by Michaelis and Granick (79) for sulphuric acids up to 11M. This function plotted against molarity of acid gave a straight line of slope 0.57 as opposed to 0.52 for H_0 . Rogers, Campbell and Maatman (80) used the G function and the H_0 function in the calculation of the second ionisation constants for amino-azobenzenes and obtained a difference in absolute but not in relative values.

No firm decision on the parallelism of H_0 and H^+ was possible on this evidence and the H^+ function was more fully investigated in this work.

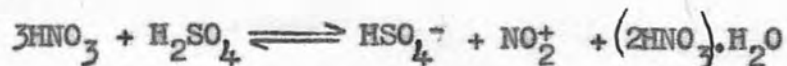
C. State of Nitric Acid in Media Used and the J_0 Acidity Function.

A wealth of evidence is available to show that nitric acid in small quantities in solution in sulphuric acid of greater than 84.5% behaves as a secondary base, ionising according to the reaction



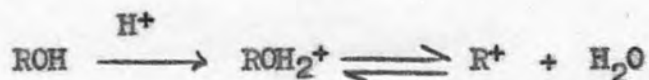
Indeed, a $pK_{NO_2.OH}$ value for nitric acid has been evaluated. (Bonner and Williams, 75). The evidence for nitric acid ionisation has been

reviewed by Gillespie and Millen (81). The nitronium ion thus produced is the effective agent of nitration in these media. However below 84.5% acid, where NO_2^+ is not present in amounts detectable by usual methods, no other entity is capable of nitration at the rates found and so the nitronium ion was assumed to be formed in very small amounts. When the amount of nitric acid in solution is very large Feneant and Chedin (82) claim that the reaction:



becomes increasingly important.

The relation of the rate of aromatic nitration to the ionisation of 4-4'-4''-trinitrotriphenylcarbinol by Westheimer and Kharasch (83) was the beginning of the concept of a new kind of acidity function. Triaryl carbinols do not ionise as simple bases in strong acid but as shown (84,85),

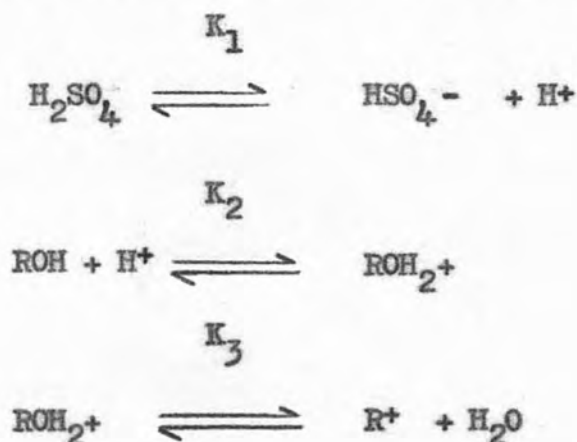


which is analogous to the ionisation of nitric acid (75).

Williams and Murray (86) measured the ionisation of a series of triarylcarbinol indicators and established the constancy of $[\text{R}^+] / [\text{ROH}] - [\text{S}^+] / [\text{SOH}]$ thus giving validity to the J_o function for which a more complete set of data was published by Williams and Bevan (88). Meanwhile a method of calculating J_o

from other experimental data was proposed by Gold and Hawes (87).

They considered triarylcarbinol ionisation in three steps



where K_1 , K_2 , and K_3 are the equilibrium constants of these steps, and called the over-all equilibrium constant K . Then,

$$\begin{aligned}
 K &= K_1 \cdot K_2 \cdot K_3 \\
 &= (\text{R}^+)(\text{HSO}_4^-)(\text{H}_2\text{O})/(\text{ROH})(\text{H}_2\text{SO}_4)
 \end{aligned}$$

Now $h_0 = -\log (\text{H}^+) f_B/f_{\text{BH}^+}$

$$= -\log_{10} h_0$$

$$\therefore h_0 = (\text{H}^+) f_B/f_{\text{BH}^+}$$

$$(\text{HSO}_4^-)/(\text{H}_2\text{SO}_4) = K_1 \cdot f_{\text{ROH}}/h_0 \cdot f_{\text{ROH}_2^+} = K_1/(\text{H}^+)$$

$$\therefore K = (\text{R}^+)(\text{H}_2\text{O}) K_1 \cdot f_{\text{ROH}}/(\text{ROH})h_0 \cdot f_{\text{ROH}_2^+}$$

If K_{ROH} is a measure of the "secondary" basicity of ROH, then

$$K_{\text{ROH}} = K/K_1$$

$$= K_2 \cdot K_3$$

$$= [\text{R}^+] (\text{H}_2\text{O}) f_{\text{R}^+} / [\text{ROH}] h_0 f_{\text{ROH}_2^+}$$

By analogy with Hammett's suggestion that $(f_{\text{AH}^+} \cdot f_B/f_{\text{BH}^+} f_A)$ will be unity in all solvents, Gold and Hawes then assumed $f_{\text{R}^+}/f_{\text{ROH}_2^+}$ to

be unity. Rearranging the last expression and taking logs,

$$H_o + \log H_2O = -pK_{ROH} + \log \left[\frac{ROH}{R^+} \right] + \log \frac{f_{ROH_2^+}}{f_{R^+}} \dots [12]$$

cf. $H_o = -pK_B + \log \left[\frac{B}{BH^+} \right].$

Gold and Hawes then defined J_o , such that,

$$J_o = H_o + \log (H_2O) \dots [13]$$

$$+ -pK_{ROH} + \log \left[\frac{ROH}{R} \right] \dots [14]$$

Knowing H_o and $\log (H_2O)$ for sulphuric acid-water mixtures they obtained J_o using equation [13]. We will call Gold and Hawes' function J_o' and the function obtained from indicator measurements of Williams and Bevan (88) J_o .

Published values of J_o and J_o' are not in accord with each other and a synthesis was put forward by Deno et al (89, 90), who suggested that $J_o - J_o' = \log (f_{ROH} \cdot f_{BH^+}) / (f_B \cdot f_{R^+})$. They themselves measured the ionisation of many carbinol indicators over almost a complete range of sulphuric acid-water mixtures and called the related function C_o .

According to Williams and co-workers

$$J_o = pK_{ROH} + \log \left[\frac{ROH}{R^+} \right] \dots [15]$$

Gold and Hawes' definition was

$$J_o' = H_o + \log (H_2O) \dots [13]$$

and Deno et al proposed

$$C_o = pK_{R^+} - \log \left[\frac{R^+}{ROH} \right] \dots [16]$$

where $K_{R^+} = (ROH)(H^+) / (R^+)(H_2O)$

$\therefore Co = -\log (ROH)(H^+) / (R^+)(H_2O) - \log [R^+] / [ROH]$
 $= -\log (H^+) + \log (H_2O) + \log f_{R^+} / f_{ROH}$

Now $Ho = -\log (H^+) f_B / f_{BH^+}$

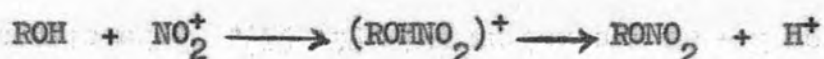
$\therefore Co = Ho + \log(H_2O) + \log f_{R^+} \cdot f_B / f_{ROH} \cdot f_{BH^+}$

$\therefore Co - Jo' = \log f_{R^+} \cdot f_B / f_{ROH} \cdot f_{BH^+} \dots\dots\dots [17]$

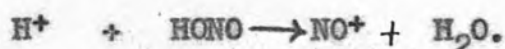
Co and Jo should be identical.

Above 83% H_2SO_4 activity coefficient ratio in [17] should be constant and so (Co or Jo) - Jo' should also be constant, but this is not the case. Nowhere do the three functions agree exactly. In Fig. 2, Jo and Jo' are plotted against Co. Unit slopes should be obtained if the functions are all varying in the same way with acid concentration but Fig. 2 demonstrates the lack of agreement. That the two measured sets of results disagree suggests that the function may not be a valid one. Notwithstanding both sets of authors claim a relation between nitration rates and their functions, of the type $\log k + Jo = \text{constant}$ (91, 92, 93). The slopes of lines obtained by plotting $\log k$ against Jo are seldom unity. The tremendous difference in size and electron distribution between the triarylcarbinol and nitric acid molecules may cause a great variation in activity coefficients and so imperfect relations with Jo must be expected. Such relationships do lend credence to the belief that the nitronium ion is still the effective nitrating agent in acids as weak as 50% H_2SO_4 .

The most satisfying evidence for the existence of the nitronium ion in dilute acid solution comes from the work of Frizel and Bonner (94) on nitric acid esterification in 50-60% perchloric acid. The reaction is essentially a nitration



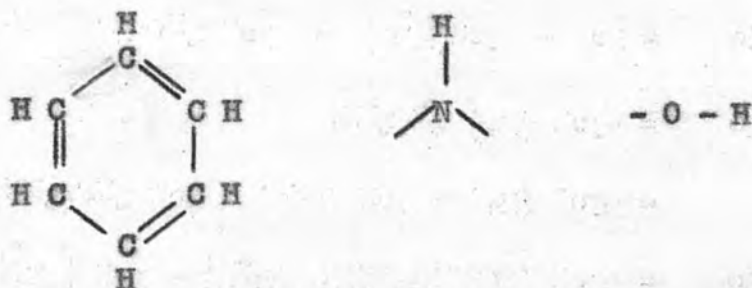
The rate of the reaction was found to parallel exactly the ionisation of nitrous acid in the same range of perchloric acid (as measured by Singer and Vamplew, 95) and to bear a less precise relation to the ionisation over the same range of a triarylcannabinol indicator (94). Nitrous acid ionises in the same way as nitric acid



These results imply that the use of Jo as measured by triarylcannabinols for nitration reactions may be superceded.

D. Nitration and Denitration.

Direct nitration has been effected at C, N and O in the following groupings.



Reaction may occur in media ranging from organic solvents to oleums according to the reactivity of the compound to be nitrated. The

X - NO₂ link can be broken under the nitration conditions when X is -N or -O but only a few cases of direct denitration are known where X is -C= and these are special cases involving steric hindrance. In general aromatic nitration is irreversible.

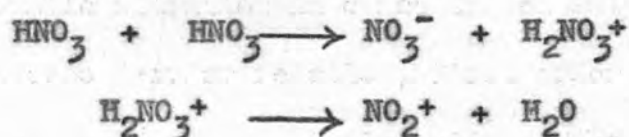
Nitration in Strong Acids.

Aromatic Nitration.

Aromatic nitration in concentrated sulphuric acid is found to be a second-order reaction, first order with respect to the aromatic compound and to nitric acid. The nitrating agent has been conclusively shown to be the nitronium ion for acids above 84.5% w/w, and for oleums (81). In the more aqueous media from 75-85%, Williams and others have concluded that nitration still proceeds exclusively through the nitronium ion because of the parallelism obtained between nitration rates and ionisation of triarylcbinol indicators (91, 92), a conclusion reached also by Deno and Stein (93). This conclusion is discussed more critically in the previous section C.

The rate of aromatic nitration increases to a maximum in sulphuric acid of ~ 90% and then decreases as the acid concentration rises to 100% (81). While there is no accepted explanation of this phenomenon, there is a suggestion that solvation of the substrate may be a contributory factor (96). The initial increase of rate with decreasing water content is ascribed to increasing ionisation to nitronium ion.

In a mixture of equal amounts of nitric acid and nitromethane (97) or acetic acid (96), zero order kinetics for nitration of various reactive aromatic compounds were obtained showing that the rate-determining stage must involve some ionisation of nitric acid itself. The only slow reaction that nitric acid can undergo is a heterolytic fission with possible formation of the nitronium ion in a fast second step.



With less reactive compounds, nitration is of first order with respect to the aromatic compound for constant initial nitric acid concentration. In this case nitration is so slow that an equilibrium concentration of the nitrating agent is set up and the rate-determining step becomes the attack of the nitrating agent (96).

O-Nitration. Formation of nitrate esters.

Nitrate esters are commonly made by alcohol esterification in mixed acid (98). Nitric acid alone or mixed with acetic anhydride has also been employed. Nitronium ion is the effective nitrating agent in the formation of isooamyl nitrate from isooamyl alcohol in aqueous perchloric acid (94).

N-Nitration.

Secondary amides may be directly nitrated in strong acids

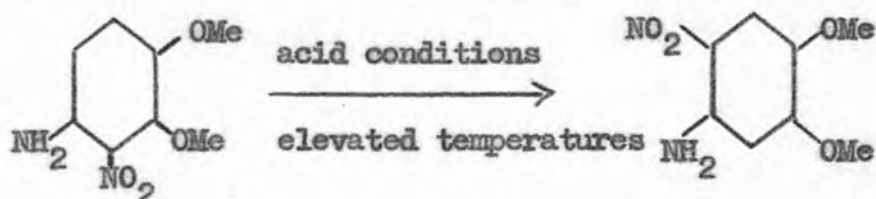
such as nitric and its mixtures with sulphuric acid. A few primary nitramides may be prepared in this way, but are probably susceptible to decomposition. Primary aliphatic nitramines also decompose under nitration conditions. Secondary aliphatic amines may be satisfactorily nitrated by use of a catalyst. The weakest of them may react without a catalyst. Aromatic amines (generally weakly basic) may be nitrated in acetic acid or anhydride (99).

Guanidines and others do not come into any of these categories. They are reversibly nitrated in sulphuric acid (100, 101). The nitration of guanidine and of N-methylguanidine has been found to be of second order (102, 11). The amount of nitroguanidine formed was found to reach a maximum in 88% H_2SO_4 for both of these compounds. The rates were too fast to be measured in that region but it seems likely that the eventual decrease in % nitration is caused by a decrease in nitration rate accompanied by continuing increase of denitration rate. Simkins and Williams found a parallel between the rate of nitration of guanidine and the ionisation of triarylcarbinols which Hardy also found for the N-methyl guanidine case. A nitronium ion mechanism was thus proposed for these nitrations. Data on the nitration of several other guanidines in various solvents have been obtained in the present work.

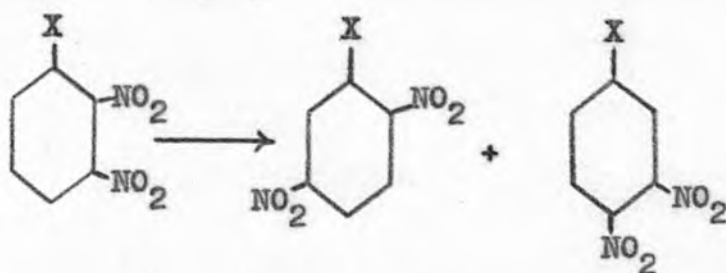
Denitration in Strong Acids.

C-Denitration.

Frisch, Silvermann and Bogart, (103) were unable to obtain a quinoline when they subjected 3-nitro-4-aminoveratrole to the conditions of the Skraup reaction. The starting material rearranged under those conditions and in a mixture of phosphoric and acetic acids to 5-nitro-4-aminoveratrole.



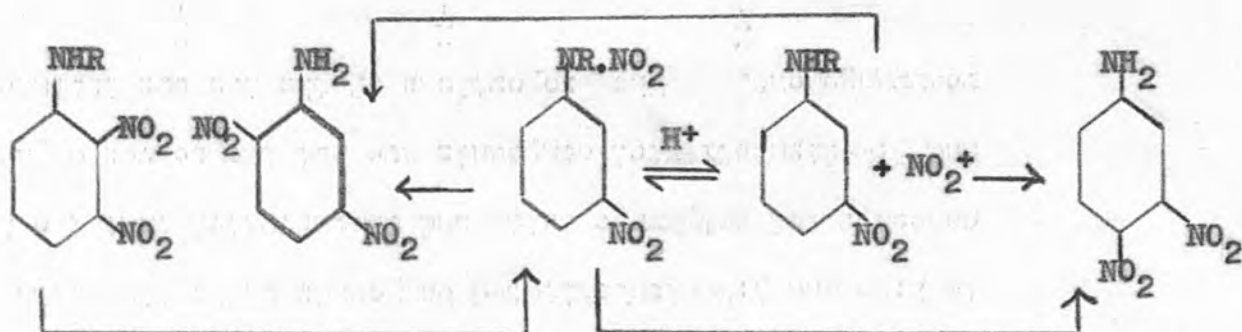
More recently, Pausacker and Scroggie (104) noted a similar migration of nitro-groups in sterically hindered molecules. They investigated the rearrangement of 2:3-dinitroacetanilide, 2:3-dinitroaniline, and 2:3-dinitrophenol to 2:5- and 3:4-disubstituted compounds on heating with concentrated sulphuric acid, and demonstrated that the 2:5- and 3:4-disubstituted compounds are not themselves capable of rearrangement. The proportions of the isomers isolated were



dependent on time of reaction and concentration of reactants.



A mechanism was proposed for the first two reactions involving conversion of the 2:3-dinitro compound to a 3:N-dinitro compound which then rearranges to give the various products.

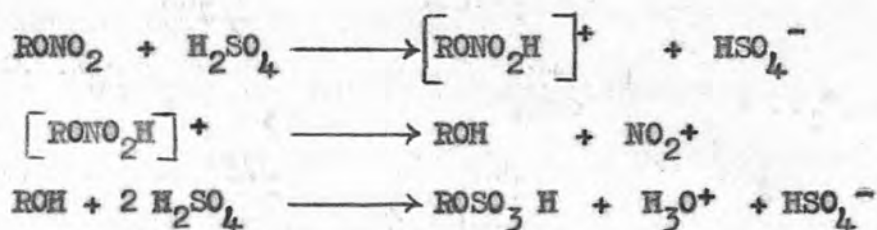


Gore (105) disagreed with the last suggestion of a reversal of the phenylnitramine rearrangement on the grounds that a similar mechanism would be necessary for the 2:3-dinitrophenol, an unlikely situation. Again, the nitration and denitration of phenylnitramine occur at very different rates while this mechanism requires similar speeds. Gore then suggested an acid-catalysed denitration as a more attractive mechanism.

Another instance of such a denitration was examined by Gore. The initial denitration of 9-nitroanthracene on treatment with acid was not followed by nitration in a different aromatic position. No free anthracene was obtained however, but only a 20% yield of anthraquinone. He concluded that a nitro group on an aromatic ring is hydrolysable when its position is activated and sterically hindered, and when sufficiently acidic solvent conditions avail.

O-Denitration. Nitrate Ester Hydrolysis.

Cryoscopic data are available on solutions of ethyl and isoamyl nitrates in concentrated sulphuric acid which point to a complex ionisation to give nitronium ion and sulphate esters.



Van't Hoff i-factors are given as 4.95 for ethyl nitrate (Kuhn, 106) and greater than 4 for amyl nitrate (Oddo and Scandola, 107). The ultra-violet absorption spectrum of ethyl nitrate in concentrated sulphuric acid is almost identical with that of nitric acid (106) indicating more or less complete denitration.

N-Denitration.

In the Bamberger-Orton Conversion - NHX substituents on aromatic rings rearrange with substitution of the -X group in the ring. X may be NO₂⁻, Cl⁻ etc. Rearrangement of primary and secondary aryl nitramines has been investigated kinetically by Hughes and Jones (108). The nitramine in acid solution rearranged to a nuclear nitrated amine. A reactive aromatic compound such as p-xylene was added to the reaction mixture in the hope of isolating the nitrating entity but no transfer was obtained with p-nitrophenylmethyl-nitramine. The rearrangement of 2:4-dinitrophenylmethyl-nitramine, which is a slow process, did however release enough

nitronium ion to nitrate a foreign aromatic nucleus but insufficient to account for the speed of rearrangement, so that a predominantly intramolecular process characterises the reaction.

A further proof of intramolecular character was offered by Brownstein, Bunton and Hughes (109). They studied the rearrangement of phenyl nitramine in 74% H_2SO_4 containing N^{15} introduced as KNO_3 . The determination of N^{15} in the resulting o- and p-nitroanilines was sufficiently precise to detect even a 1% occurrence of intermolecular mechanism, but isotopic contents were normal.

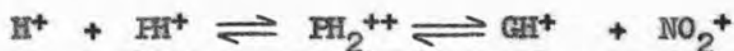
Although aromatic nitramines cannot act as nitrating agents in strongly acid solution, many aliphatic nitramines do. The extent of denitration of such compounds has been measured by Holstead and Lamberton (100) by adding the nitro compound to sulphuric acid containing acetanilide and weighing the quantity of p-nitroacetanilide precipitated on dilution of the acid. Potassium nitrate was used as a control. The compounds examined were divided into three groups according to their behaviour. The first group contained the primary and secondary nitramides, the nitroguanidines and the N-nitrosulphonamides which all furnished nitric acid, the sulphonamides only in small amount. The second group, the simple secondary nitramines did not denitrate (with one exception) although they eventually decomposed. The

exception, dicyclohexylnitramine, gave a mixture of nitric acid and nitrous acid, cyclohexylamine and cyclohexanone. Primary aliphatic nitramines decompose even in dilute acid solution. The third group consisted of linear and cyclic derivatives of methylene diamine of which only cyclonite denitrated, but it also decomposed somewhat. The other members of the group showed remarkable stability to concentrated acid.

The nitrations of urethane, N-methylurethane, urea, hexahydro-1:3-dinitro-1:3:5-triazine (110) guanidine (101) and N-methylguanidine (11) have been shown to be reversible in sulphuric acid, the position of equilibrium depending on the strength of acid used. The amount of nitration reaches a maximum for the last four compounds at 88% H_2SO_4 . For urethane and N-methyl urethane, the amount of nitration shows an inflexion from 83-88% and a continued increase above that.

Nitroguanidine and nitrourethane also denitrate in perchloric acid and selenic acid, but nitration in acetic anhydride is irreversible. (111).

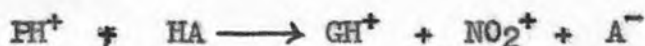
Simkins and Williams made a study of the kinetics of denitration of nitroguanidine in concentrated sulphuric acid and found a first-order reaction and an increase of rate with acid concentration over the range 72-83% H_2SO_4 . They suggested the mechanism.



where P is a neutral nitroguanidine molecule and G is a neutral guanidine

molecule. If the second proton uptake occurred to a very small extent and the breakdown of the transition state was the rate-determining step, then the rate should be related to the acidity function H_+ by the equation $\log k + H_+ = \text{const.}$ No figures for H_+ were available and a plot of $\log k$ against H_0 had a slope of -1.42 , giving no definite conclusion.

In a more detailed study of denitration, using N-methyl-N'-nitroguanidine, Hardy (11) obtained a similar slope (-1.5) of $\log k$ against H_0 , assuming H_+ and H_0 to be similar functions of medium composition. This in itself did not preclude breakdown of FH_2^{++} as the rate-determining step, for if the second ionisation occurs to any extent (5% even) the $\log k + H_0$ relation will not hold. Hardy measured the spectrum of N-methyl-N'-nitroguanidine in various acids and concluded that the first ionisation (to nitroguanidinium ion) is complete in 30% H_2SO_4 and that no further ionisation occurs up to the region in which her kinetic results were obtained. Thus she supposed the breakdown of FH_2^{++} could not be the rate-determining step. She then considered a bimolecular process,



where HA is any acidic species present, and deduced the following relations.

If H_3O^+ is the effective acid, then $\log k_1 - \log (\text{H}_2\text{O}) = \text{constant.}$

If H_2SO_4 is the effective acid, then $\log k_1 - \log (\text{H}_2\text{SO}_4) + H_0 = \text{constant.}$

Her results did not fit either of these relationships but it is interesting to note that the summation $\log k_1 - \log (H_2O) - \log (H_2SO_4) + H_0$ did in fact remain constant. The results of Simkins on nitroguanidine, subjected to this treatment, likewise give a constant summation, although the precision is less. (See Table VIII). However, denitration of nitroguanidine never occurred to more than 20% and the concentrations used probably affected the acidity of the medium. Further kinetic data on the denitration of nitroguanidines form a large portion of this thesis.

Section II. Experimental Work.

A. Materials.

100% Sulphuric Acid.

Sulphur trioxide was distilled from a strong commercial oleum into "Analar" sulphuric acid (98%) in an all-glass apparatus until a strong oleum was obtained. This colourless oleum was distilled into a known weight of "Analar" sulphuric acid to make a weak oleum ($\sim 10\% \text{H}_2\text{SO}_4$). This oleum was standardised by titrating weighed amounts with N NaOH solution using Screened Methyl Orange as indicator. The value obtained was used as a rough guide to the amount of water required to convert the oleum to 100% sulphuric acid. Successive amounts of water were added from a micro-burette until the acid of maximum F.Pt. was obtained.

Sulphuric Acid Media.

Media used in kinetic and acidity function measurements were prepared by dilution of the Analar acid with distilled water and analysed by titration with N NaOH solution referred through N HCl to potassium iodate as standard. Sufficient sulphuric acid to give a 25 ml. titration of N NaOH was weighed from a weight-pipette into a clean conical flask and diluted with distilled water to 25 ml. volume. The solution was titrated with N NaOH to a gray end-point with 2 drops of Screened Methyl Orange.

Typical Analysis:-

85.09%, 85.17%, 85.11%, 85.07%. Average value 85.1% w/w H_2SO_4

Perchloric Acid Media.

Media used in kinetic and acidity function work were prepared

by dilution of Hopkin and Williams' Analar 72% acid with water and analysed in the same way as the sulphuric acid media.

Typical Analysis:-

72.29%, 72.23%, 72.23%, 72.18%. Average value 72.2% w/w HClO_4 .

Sulphuric Acid - Acetic Acid Media.

The amounts of 100% sulphuric acid and 100% acetic acid (Analar material of M.pt. $> 16.2^\circ\text{C}.$) required for a particular medium were calculated. The sulphuric acid was carefully weighed into a Quickfit conical flask of the required size and the acetic acid was weighed into this. No successful method of analysis has been reported for such media.

Storage of strong acid media.

Media were stored in Winchesters with polythene or ground glass stoppers and did not deteriorate appreciably over a period of eighteen months.

N Sodium Hydroxide Solution.

B.D.H. N solution was used and standardised against N HCl referred to potassium iodate as standard.

Typical Titres.

25 ml. 0.9977N HCl required	24.96	} ml. NaOH
	24.96	
	24.96	
	24.96	

∴ NaOH solution was 0.9993 N.

N Hydrochloric Acid Solution.

B.D.H. N solution was used and standardised against potassium iodate solution using sodium thiosulphate and starch.

Typical Tires.

25 ml. 0.1563 N KIO_3 required	39.17)	} ml. HCl
	39.16)	
	39.17)	
	39.17)	

. . HCl solution was 0.09977 N.

Potassium Iodate.

The Analar salt was ground in a porcelain mortar and dried at 120°C. before use.

Potassium Chromate.

The Analar salt (> 99.0% pure) was recrystallised five times from 0.005 N KOH solution, washed once with water and dried for 24 hours at 120°C. The crystals were finely ground and dried at 120°C. for a further 24 hours. The spectrum of this material was examined and a further recrystallisation and drying produced no change in the spectrum (112).

Absolute Ethanol.

Sodium was very carefully added to an ice-cooled flask containing 99.5% ethanol (7g/litre) and 27.5 g. ethyl phthalate per litre added to the cooled solution which was refluxed for several hours using adequate precautions to exclude moisture, and then distilled. The first and last quarters of the distillate were rejected.

Nitroguanidine.

Nitroguanidine was obtained from nitration of guanidine (113)

56 g. of commercial guanidine nitrate was slowly stirred at $< 20^{\circ}\text{C}$. into an ice-cooled beaker containing 80 ml. 98% sulphuric acid. The mixture was stirred overnight at room temperature and poured into 600 ml. of clean, cracked ice and water. The precipitated nitroguanidine was recrystallised from water and dried in air. Further re-crystallisation was not attempted as the material had an extinction coefficient as high as reported data (E_{max} . 14,000 at λ 2640 $\overset{\circ}{\text{A}}$). Yield = 70% (3).

Methylnitroguanidine.

Methylnitroguanidine was prepared by reaction of methylamine hydrochloride on an alkaline solution of nitroguanidine (9).

10.5 g. nitroguanidine was stirred into a solution of 12 g. potassium hydroxide in 30 ml. water. The temperature was raised to 40°C . and 13.5 g. methylamine hydrochloride was stirred into the solution. The temperature was slowly raised to 60°C . and maintained at $59-61^{\circ}\text{C}$. for thirty minutes. The clear solution, cooled in ice, deposited a heavy white precipitate of methylnitroguanidine contaminated with potassium chloride. This precipitate was filtered and washed with 6 x 5 ml. ice-cold water and crystallised from water till chloride-free. It was then crystallised from ethanol to a constant spectrum. (E_{max} . = 14,040 at λ 2670-75 $\overset{\circ}{\text{A}}$ at 25°C .) m.p. 161° (11).

N:N'-Dimethyl-N''-nitroguanidine.

Several methods of preparing this compound were tried but the only successful preparation, resulting in a very small yield was a modification of the preceding preparation (11). The mother liquor from the methylnitroguanidine precipitate was heated at 60°C. for a further thirty minutes and after several days in a refrigerator deposited long fine needles of N:N'-dimethyl-N''-nitroguanidine m.p. 167°C. These were recrystallised from water until they were chloride-free. The results of ten preparations combined gave 0.5 g. material, m.p. 171-172° (11).

N-Methyl-N-nitroso-N'-nitroguanidine.

A nitroso group was introduced to methylnitroguanidine by reaction with sodium nitrite in nitric acid (9).

A solution of 10 g. methylnitroguanidine in 30 ml. concentrated nitric acid was diluted with water to 100 ml. Into this was stirred over a period of fifteen minutes a solution of 12.2 g. sodium nitrite in 20 ml. water, the temperature being maintained below 5°C., and yellow crystals with a pinkish reflex began to deposit. Stirring was continued at 5° for eighteen minutes. The golden material was filtered off, washed acid-free with ice-water and recrystallised from ethanol. Yield = 9 g. The substance detonates at the melting-point.

N:N-Dimethyl-Dimethyl-N'-nitroguanidine.

Dimethylamine reacts with N-methyl-N-nitroso-N'-nitroguanidine with substitution of dimethylamino- for the N-methyl-N-

nitroso-amino-group (9).

10 ml. of a 30% alcoholic solution of dimethylamine was carefully stirred into a well cooled and stirred solution of 9 g. N-methyl-N-nitroso-N'-nitroguanidine in 10 ml. of 50% v/v aqueous ethanol. After half-an-hour effervescence ceased and the white precipitate crystallised from water gave 5 g. of NN-dimethyl-N'-nitroguanidine. This was further recrystallised from water (x 10) and from 95% ethanol (x 3) to a constant spectrum. ($E_{max.} = 11,440$ at $2720\overset{\circ}{\text{A}}$) m.p. 195°C .

2-Nitrimino-1:3-diazacyclopentane.

The preparation was identical to that for methylnitroguanidine (9) except 13.3 g. of ethylene diamine dihydrochloride was used instead of methylamine hydrochloride. The compound was crystallised from water (x 6) and 95% ethanol (x 3) to a constant spectrum ($E_{max.} = 16160$ at $2655\overset{\circ}{\text{A}}$) m.p. $220-221^{\circ}\text{C}$.

4-Methyl-2-nitrimino-1:3-diazacyclopentane.

The method was again that used for methylnitroguanidine (9) and employed 15 g. propylene diamine dihydrochloride. The compound was recrystallised from water and ethanol to a constant spectrum ($E_{max.} = 17100$ at $2660\overset{\circ}{\text{A}}$) m.p. 170°C .

2-Nitrimino-1:3-diazacyclohexane.

The compound was prepared and purified analogously to the last two using 15 g. trimethylenediamine dihydrochloride. ($E_{max.} = 15450$ at $2680\overset{\circ}{\text{A}}$) m.p.

The crude yield of the last three compounds could be obtained in a more pure condition from a reaction described by McKay (4).

The free diamine was added in equimolar quantity to a suspension of nitroguanidine (14.1 g.) in 30 ml. water containing 1.5 g. ammonium chloride. The solution was gently heated to 60°C. (with tremendous effervescence of ammonia) and maintained at 59-61°C. for thirty minutes. Precipitation began before the temperature reached 60°C. and the mixture became too thick to stir mechanically. The material was less contaminated with chloride than before and required less purification.

Nitraminoguanidine.

The procedure of Phillips and Williams involving reaction of nitroguanidine with hydrazine was used (114).

Hydrazine sulphate (32.5 g.) was placed in a 2 litre conical flask with 200 ml. ^{water} and 500 ml. N ammonium hydroxide. Nitroguanidine (26 g.) was added to the solution and dissolved on heating to 60°C. The temperature was kept at 50-60°C. for one hour during which nitrous oxide was evolved and the solution went orange. The liquor was evaporated to one third volume and cooled. The white crystals thus precipitated were filtered and air-dried. Yield = 12 g. The pinkish tinge of the material was removed by boiling it in water with charcoal, filtering hot and allowing it to crystallise.

Fermamide nitroguanidine.

Nitroaminoguanidine (5 g.) was heated with 15 g. of 90% formic acid at 85-90°C. for one and a half hours. The ice-cooled solution deposited white crystals which were filtered, and well-washed to remove formic acid and recrystallised from water. M.p. 191°C. (16).

5-Nitroamino-1:2:4-triazole.

Fermamide nitroguanidine undergoes an internal condensation to form the triazole (16).

Fermamide nitroguanidine (5 g.) and anhydrous sodium carbonate (3.25 g.) were mixed with 44 ml. water and heated on a steam-bath for twenty-five minutes. The mixture was ice-cooled and faintly acidified to litmus with concentrated hydrochloric acid when a fine white precipitate appeared. This mixture was allowed to stand in a refrigerator overnight, filtered and washed with ice-water. It was re-crystallised from water and air-dried. This material may not be kept dry and so spectra are not of highest accuracy.

Guanidine Nitrate.

A commercial specimen was recrystallised from water after filtering the hot solution through a sinter. It was then crystallised 6 times from water containing 10% alcohol. m.p. 215°C.

4:6-Dimethyl-2-aminopyrimidine.

This was prepared by condensation of guanidine and acetylacetone (115, 116). 4.5 g. Guanidine carbonate and 5.2 g.

acetylacetone were refluxed together. No visible change took place for nearly an hour, then a vigorous effervescence took place and the solid dissolved. After two hours the solution was cooled, filtered and the precipitate washed with acetone. The sparkling white crystals were recrystallised twice from acetone. Yield = 2 g., m.p. 154.2 °C.

2:4-Dinitroaniline.

A commercial specimen (5 g.) was recrystallised by boiling with charcoal (2 g.) in 100 ml. alcohol for 30 minutes, filtering hot and boiling again with added water (20 ml.) before cooling. Three further boilings with charcoal and three recrystallisations from 5:1 ethanol:water provided material of a constant spectrum $\left\{ \begin{array}{l} \epsilon = 12,300 \text{ at } 3480\text{\AA} \text{ in } 40\% \text{ perchloric acid;} \\ \text{of } E_{\text{max.}} = 12,800 \text{ at } 3480\text{\AA} \text{ in dilute sulphuric acid (117).} \end{array} \right\}$
m.p. 181°C.

4-Dimethylaminoazobenzene.

Addition of dimethylaniline to benzene diazonium chloride solution afforded the desired product. (118, 119).

Aniline (12.8 g.) and crushed ice (150 g.) were hand-stirred in a 600 ml. beaker during the addition of 41 ml. concentrated hydrochloric acid, the temperature being maintained below 50°C. by external cooling. Sodium nitrite solution (10 g. in 20 ml. water) was added slowly at < 5°C. When a permanent test for nitrite (with starch-iodide paper) was obtained the reaction was judged complete.

Mechanical stirring was commenced when all the ice in the beaker had melted (120).

The method of Clark and Korner for addition of dimethylaniline to the diazonium salt was followed (121).

Dimethylaniline (24.6 g.) was poured into the diazonium salt solution which was stirred a further hour at 5°C. 14.5 ml. of a previously prepared solution of 19.7 g. sodium acetate in 35 ml. water was added and the mixture stirred at <7°C. overnight. The rest of the sodium acetate solution was added and stirring continued for one hour, then the temperature was allowed to rise to 20°C. during the course of a day. 6 ml. of a 40% caustic soda solution was added and the mixture was filtered after standing overnight. The tarry material was washed with acetic acid until the washings were pale pink. The tar was suspended in methanol and refluxed for several hours. Dark brown crystals resulted. Soxhlet extraction of the crystals with n-propanol produced no improvement in the colour, but a bright golden-orange sample was obtained by five crystallisations after boiling with its own weight of charcoal in n-propanol. m.p. 117°C. This material was recrystallised to a constant spectrum, of $E_{\text{max.}} = 28,900$ at 4050\AA (cf. 119) in absolute ethanol.

4-Nitro-1:2-phenylene diamine.

The ortho nitro group of 2:4-dinitroaniline was preferentially reduced by polysulphide yielding the desired compound according to the method of Kehrmann (122).

Crystalline sodium sulphide (16 g.) was dissolved in 50 ml. water and powdered sulphur (4.2 g.) was added. Gentle heating caused complete solution of the sulphur. Finely powdered 2:4-dinitro aniline (10.9 g.) was suspended in 400 ml. water and the water was allowed to boil gently. The disulphide solution was added over fifteen minutes, a deep red colour appearing instantly. Gentle boiling was continued for thirty minutes, then 50 ml. water was added and the whole was boiled vigorously for five minutes before being filtered hot. Fine red needles came out on the filter and in the filtrate. The filtrate was cooled in ice and the red crystals, m.p. 197°C., filtered off. These were dissolved in alcohol-water and the solution was filtered hot to remove sulphur. This is the ortho diamine. The para diamine, which is also formed, remained in the filtrate. The ortho diamine was recrystallised to a constant spectrum after several boilings in water with charcoal. It was dried at 110°C. m.p. 205°C. Spectrum in sulphuric acid $E_{\max.} = 8,700$ at $24,750\overset{\circ}{\text{A}}$.

4-Aminoacetophenone.

A commercial specimen (pale yellow) was boiled in water with half its weight of charcoal for fifteen minutes, the solution was filtered hot and allowed to crystallise. The filtered crystals were dried at 80°C. Eight repetitions of this provided colourless material m.p. 106.4°C. Further crystallisations produced no change in the spectrum of $E_{\max.} = 16,400$ at $3100\text{-}3120\overset{\circ}{\text{A}}$ in water (cf. 123, 124).

2:4-Dinitronaphthylamine.

Acetyl naphthylamine was nitrated on the 2:4 positions and the acetyl group was hydrolysed off (125).

1-Naphthylamine (40 g.) was dissolved in the minimum amount of ether. An equivalent weight of acetyl chloride was slowly added to the carefully cooled solution. After the reaction had subsided an equal volume of water was added and the precipitated acetnaphthalide recrystallised from aqueous ethanol. The recrystallised material was dissolved in glacial acetic acid (2 ml./g.) and nitrated with a mixture of equal volumes of nitric and acetic acids (1 ml./g.) The nitrating mixture was added at a temperature of $\sim 70^{\circ}\text{C}$. and the temperature was then raised to 96°C . until the dinitro compound began to separate. On cooling a reddish-brown crop of crystals was obtained and recrystallised from acetic acid. 20 g. of this material was suspended in a cold solution of 200 ml. sulphuric acid and 30 ml. water and heated at 70°C . for fifteen minutes. After external cooling the mixture was poured on to 400 g. crushed ice and a dirty brown mud was obtained. Chromatography of the material on potassium carbonate was attempted but no separation of impurity was effected with any of the solvents used. Eventually the material was purified by dissolution in excess alcohol and boiling for thirty minutes with twice its own weight of charcoal. The ethanol was filtered hot partially evaporated and allowed to precipitate the solid. This was repeated twice and the material after several

crystallisations from alcohol had a constant spectrum of E_{max} . 10,600 at 3960\AA in dilute perchloric acid.

B. Velocity Measurements.

Temperature Control.

Reaction vessels were kept in a thermostat maintained at a thermometer temperature of 25°C . within $\pm 0.05^{\circ}\text{C}$. by a toluene-mercury regulator. The thermometer was calibrated by comparison with an N.P.L. standard thermometer and the actual temperature of the bath was found to be 24.93°C .

Technique of a typical run.

A 25 ml. portion of the acid to be used was weighed into a 50 ml. Quickfit conical flask which was then immersed in the thermostat for thirty minutes to acquire temperature equilibrium. The required quantity of the nitroguanidine in use was weighed in a small weighing bottle on an Oertling Semi-micro balance, accurate to ± 0.00002 g., and ejected on to the surface of the acid. Reaction time was measured from this moment. The flask was stoppered and vigorously shaken till the solid was entirely in solution. Solution time was from 1-2 minutes in $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ < 1 min. in $\text{HClO}_4 - \text{H}_2\text{O}$ and took upto 5 mins. in $\text{H}_2\text{SO}_4 - \text{HOAc}$ mixtures. Eight 2 ml. samples were removed by pipette at suitable time-intervals, the reaction was stopped by running the contents of the pipette into 100 ml. ice-cold water in a 250 ml. volumetric

flask which was instantly stoppered and shaken and these aqueous solutions were later made up to 250 ml. and analysed for nitroguanidine by an absorptiometric method. (11). Times were measured on a stop-clock which lost only 30 secs. in 24 hours. Further samples were then removed at appropriate intervals to determine the point of equilibrium.

Calibration of Pipettes.

The pipettes used were calibrated in terms of the weight of acid delivered on emptying and draining for 30 seconds for every medium used. As the sulphuric-water and sulphuric-acetic mixtures used were rather viscous, pipettes used for these media had the tips ground to permit rapid emptying.

Typical Calibrations.

Weights of 85.1% H_2SO_4 - H_2O delivered at 25°C.

3.4263 g. 3.4307 g. 3.4269 g. 3.4356 g. 3.4164 g. 3.4442 g.

Average weight delivered = 3.430 g.

Weights of 67.0% $HClO_4$ delivered at 25°C.

3.2009 g. 3.2009 g. 3.2105 g. 3.2076 g.

Average weight delivered = 3.205 g.

Weights of 64.4% H_2SO_4 in HOAc delivered at 25°C.

2.9439 g., 2.9477 g. 2.9542 g.

Average weight delivered = 2.946 g.

Method of Analysis.

The convenient ultraviolet absorption of nitroguanidines in a region in which neither guanidine nor nitric acid absorb appreciably provides a simple method of analysis. The spectra of nitroguanidines between 2100 and 3000 $\overset{\circ}{\text{A}}$ have been measured in water, alcohol and other solvents (26-33), and they show a characteristic absorption band with a peak of $E_{\text{max.}} \sim 10,000 - 20,000$ at 2600-2700 $\overset{\circ}{\text{A}}$ with a smaller peak at 2100-2200 $\overset{\circ}{\text{A}}$ of $E_{\text{max.}} \sim 5000$. An investigation of the absorption spectra of all the compounds used in water and dilute acid was undertaken and the results together with comparable previous measurements are given in Table III.

The spectra were measured on a Hilger Uvispek, the cell-jacket of which was controlled at a temperature of $25 \pm 1^{\circ}\text{C}$. by the continuous pumping through it of water from a thermostat. The peaks in acid solutions of $< 0.15\text{N}$ strength were found to be similar to those in water solution but above that acid strength the maximum extinction value began to drop. Solutions for analysis were thus diluted to an appropriate acid strength below 0.15N. Solutions obeyed Beer's Law to within 0.5% within the most accurate optical density range of the instrument ($D = 0.2 - 1.0$) where density, $D = \log I_0/I$, I_0 = intensity of light transmitted from the solvent and I is that transmitted by the solution in question.

Table III

<u>Compound</u>	<u>Solvent</u>	<u>E_{max.}</u>	<u>λ_{max.}</u>	<u>Reference</u>
Nitroguanidine	water	14.100	2650	31
	0.2N H ₂ SO ₄	14.100	2640	
N-Methyl-N'-nitroguanidine	ethanol	15600	2690	27
	0-0.16N H ₂ SO ₄	14.040	2670	11
	0-0.16N HClO ₄	14.030	2670	
N-Cyclohexyl-N'-nitroguanidine	ethanol	15500	2710	27
	0-0.1N H ₂ SO ₄			
2-Nitrimino-1:3-diazacyclopentane	ethanol	16600	2670	27
	0-0.2NH ₂ SO ₄	16160	2655	
	0-0.2N HClO ₄	16160	2655	
4-Methyl-2-nitrimino-1:3-diazacyclopentane	ethanol	17700	2655	27
	0-0.2N H ₂ SO ₄	17140	2660	
2-Nitrimino-1:3-diazacyclohexane	ethanol	17400	2710	27
	0-0.2N H ₂ SO ₄	15450	2680	
	0-0.2N HClO ₄	15450	2680	
N:N-Dimethyl N'-nitroguanidine	0-0.2N H ₂ SO ₄	11350	2710	
5-Nitramino-1:2:4-triazole	0-0.2N H ₂ SO ₄	12400	2820	

Test of Accuracy of Method.

A known weight of the compound was introduced into a known weight of 50% H₂SO₄ contained in a 50 ml. conical flask immersed in a thermostat at 25°C. Samples were removed with a 2 ml. pipette as in a normal run and run into distilled water in 250 ml. volumetric

flasks. The absorption of the solutions obtained was investigated on a Uvispek spectrophotometer and found to agree with that calculated to within 0.5%.

Example:-

2-Nitrimino-1;3-diazacyclopentane,		Optical density at 2655 ^o Å.	
Observed		Calculated	100 Obs./Dcalc.
.479	} Average .481	.483	99.6%
.483			
.479			

The absorption of guanidine (126) alkylguanidines (11) and that of 2-aminotetrahydropyrimidine (127) is negligible at 2600-2700^oÅ. The absorption of 2-amine-1;3-diazacyclopentane nitrate (p. 56) was investigated and found to be negligible also. The nitrate ion has an extinction of $\epsilon = 2$ in this region and from previous considerations (11), may be neglected so long as denitration is less than 95% complete.

C. Measurement of Ionisation Ratios.

The spectrophotometric method developed by Flexser, Hammett and Dingwall was used (56). If ϵ is the extinction coefficient at a particular wavelength of any solution containing a partially ionised indicator base and ϵ_{BH^+} and ϵ_B those of the ion and the base at the same wavelength then the ratio of ion to base in the solution may be computed from the equation $[BH^+] / [B] = (\epsilon_{BH^+} - \epsilon) / (\epsilon - \epsilon_B)$

Absorption measurements were carried out on a Hilger Uvispek, the cell-jacket being thermostatically maintained at 25°C. (see p. 50). The spectra of indicator solutions at various stages of ionisation were measured from 2100Å to the limit of measurable absorption and plotted as ϵ versus wavelength. From such a graph, suitable wavelengths for evaluating the ratio $\frac{[BH^+]}{[B]}$ were found. A specimen graph for the ionisation of 4-nitro-1:2-phenylene diamine is shown. (Fig. 15). The wavelengths chosen were 3300 - 4000 Å at intervals of 100 Å. At other wavelengths insufficient divergence of the curves for the ionised and unionised forms would limit severely the accuracy of $\frac{[BH^+]}{[B]}$ values. An arithmetic mean of $\frac{[BH^+]}{[B]}$ values for any particular acid was taken over all the calculated values.

Determination of Extinction Coefficients.

A solution of the compound in 25 ml. of acid solution was made. An appropriate amount of this solution was weighed out and diluted with a further 25 ml. of acid. Concentrations were designed to produce an optical density of 0.2 - 1.0 on the Uvispek. Solutions were inserted by pipette into the closed cells used. The cell was rinsed with solution several times then filled and stoppered. The outside of the cell was rinsed with distilled water and carefully wiped dry with filter paper, and the optical density of the solution measured at various wavelengths. The spectrum of the compound was

worked out as follows from these data.

Spectrum of 4-Nitro-1:2-phenylenediamine in 72.2%

Perchloric Acid.

1st weight of weighing bottle + compound = 6.16792 g.

2nd " " " " " = 6.16277

∴ weight of compound used = 0.00515

Solution I.

weight of flask + compound = 69.4828 g.

" " " " + acid = 111.0196

∴ weight of acid used = 41.5368

∴ Concentration of Solution I = $0.00515/41.54 \times 153$ m/g. soln.

Solution II.

weight of flask = 53.6576 g.

" " " + Solution I = 56.9581

" " " " + acid = 99.4216

∴ Concentration of Solution II = $\frac{.00515 \times 1000 \times 3.301 \times 1.708}{41.54 \times 153 \times 45.76}$ m/l
= 9974×10^{-5} m/l.

Densities were obtained from the International Critical Tables.

Solution II

λ	D	log D	log ϵ	ϵ
2100	.683	1.8344	3.8355	6850
2200	.335	1.5250	3.5261	3360
2300	.531	1.7251	3.7262	5320
2400	.759	1.8802	3.8813	7608
2450	.786	1.8954	3.8965	7880
2475	.791	1.8982	3.8993	7930
2500	.774	1.8887	3.8898	7760
2600	.578	1.7619	3.7630	5800
2700	.329	1.5172	3.5183	3300
2800	.184	1.2648	3.2659	1850
2900	.102	1.0086	3.0097	1020
3000	.047	2.6721	2.6732	500

Solution I

3000	.960	1.9823	2.8142	690
3100	.551	1.7412	2.6001	400
3200	.210	1.3222	2.1811	150
3300	.193	1.2856	2.1445	140
3500	.122	1.0864	1.9453	90

D. Recovery of Denitration Products.

Each nitro guanidine (0.01 m) was accurately weighed out and dissolved in a solution of 0.01 m. acetanilide in 10 ml. 96% sulphuric acid kept in a thermostat at 25°C. After solution the mixture was kept at 25°C. for twenty minutes and then poured into 75 ml. of cracked ice and water. The precipitated p-nitroacetanilide was recovered and recrystallised from 25 ml. alcohol. The alcoholic filtrate was evaporated to 5 ml. and a second crop obtained. The quantities of p-nitroacetanilide formed were thus ascertained.

In the case of 2-imino-1:3-diazocyclopentane the base was recovered as nitrate.

The ice-water filtrates were neutralised to Congo Red paper with barium hydroxide. The barium sulphate was recovered by filtration and the filtrate was evaporated with 2 ml. concentrated nitric acid to a bulk of 4 ml. and allowed to cool. A mass of elongated dirty brown needles m.p. 104°C. was obtained. On recrystallisation from ethanol (x 10) the crystals were still straw-coloured and had m.p. 112-113°C.

The compound was identified as 2-amino-1:3-diazacyclopentene nitrate by conversion to its known carbonate and picrate (128).

A hot solution of the compound in the least volume of alcohol was added to a hot concentrated alcoholic solution of picric acid, and the picrate instantly precipitated m.p. 219-220°C. (lit. 218-220°C.) (128).

A solution of the compound in alcohol was treated with solid carbon dioxide and a white precipitate was slowly formed, m.p. 134°C. (lit. 135-137°C.) (128).

Section III. Results and Discussion.

A. The Nature of the Reaction.

When nitroguanidine is dissolved in a concentrated solution of a strong acid, its concentration falls to a constant value with time. The concentration of nitric acid meanwhile rises from zero to a constant value. The reaction has been shown to be an equilibrium between nitroguanidine on the one hand and guanidine and nitric acid on the other (100, 101, 102).

Holstead and Lambertson demonstrated that when acetanilide was dissolved in 95% H_2SO_4 prior to addition of nitroguanidine, transfer of the nitro-group to acetanilide occurred. By isolating and weighing the p-nitroacetanilide formed they were able to show that nitroguanidine was as efficient a nitrating agent as potassium nitrate (100).

When 2-nitrimino-1:3-diazacyclohexane, 2-nitrimino-1:3-diazacyclopentane, 4-methyl-2-nitrimino-1:3-diazacyclopentane and N:N-dimethyl-N'-nitroguanidine were dissolved in 95.6% H_2SO_4 , the concentration of nitroguanidine, as determined by spectrophotometric analysis of samples diluted to 0.2N H_2SO_4 , fell to a constant value. Acetanilide was dissolved in the acid before addition of the nitroguanidine and the quantities of p-nitroacetanilide obtained on dilution of the acid are shown in Table IV.

Table IV.

<u>Compound.</u>	<u>% of theoretical p-nitro-acetanilide obtained.</u>
Potassium nitrate (control)	72)
Nitroguanidine	73) from Ref.(100).
2-Nitrimine-1:3-diazacyclopentane	72
4-Methyl-2-nitrimine-1:3-diazacyclopentane.	72.5
2-Nitrimine-1:3-diazacyclohexane	71
N:N-Dimethyl-N'-nitroguanidine	71

The quantity of nitric acid liberated was thus in all cases equivalent to that obtained from potassium nitrate and amounted to complete denitration. These data confirm that denitration analogous to that of nitroguanidine occurs for all the compounds in Table IV.

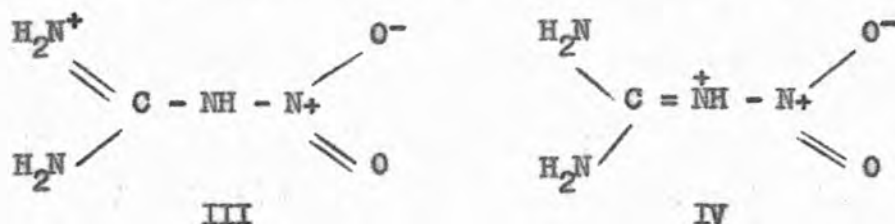
B. Structure of Nitroguanidines in Acid Solution.

The nitroguanidine molecule is probably a resonance hybrid with appreciable contributions from forms with a nitrimine group present. When the compound is dissolved in water, the ultra-violet absorption spectrum shows a band with maximum extinction at $2640\overset{\circ}{\text{A}}$ of 14,000 (26-33) and the beginning of another band at $2100\overset{\circ}{\text{A}}$. The spectrum of nitramide $\text{NH}_2\cdot\text{NO}_2$ shows a broad band at $2260\overset{\circ}{\text{A}}$ with a peak of 5900 (29). A nitramine structure for nitroguanidine implies no conjugation between the nitramide and guanidine residues and so the spectrum would be similar to that of nitramide plus that of guanidine (transparent in this region). The large wavelength

shift and increase in maximum found are therefore not consistent with the nitramine structure. The spectrum could result either from a nitrimine structure or a resonance hybrid with a major contribution from the nitrimine form. See Fig. 3.

Similar spectra are observed for most nitroguanidines except those with aryl substituents. Spectra of N,N-dimethyl-N'-nitroguanidine and 5-nitramine-1:2:4-triazole used in this work were not previously recorded and are noted in Fig. 4 and Table V. All the spectral data in this Table were measured in this work as previous recorded results were by various authors and in various solvents. In acid solutions the peak at $\sim 2700\overset{\circ}{\text{A}}$ has a lower extinction value for all compounds studied and a new peak appears at $\sim 2250\overset{\circ}{\text{A}}$. In 40-50% H_2SO_4 the peak at $\sim 2250\overset{\circ}{\text{A}}$ reaches a maximum value of ~ 9000 for all nitroguanidines studied, while the $\sim 2700\overset{\circ}{\text{A}}$ peak disappears. The spectrum of N-methyl-N'-nitroguanidine has been measured up to 79% H_2SO_4 (11) and the results indicate that no further change takes place in structure to that level. Measurements on this compound at higher acidities are impossible because denitration is too rapid. The change in spectrum is consistent with the addition of a proton to the nitroguanidine molecule, and pK_a values for the conjugate acid of several of the compounds are given in Table V. The spectrum of the ion is in each case similar to that of the simple nitramide (29) and methylnitramide (129) molecules, having

a slightly higher extinction maximum at similar wavelengths.



Resonant forms of III are consistent with the nitramine spectrum, but IV is not. Resonant forms of IV will in any case have two adjacent positive charges and on these grounds are unlikely to make much contribution. Nitreguanidines in strongly acid solutions are probably resonance hybrids of a nitramine structure.

Table V.

<u>Compound.</u>	<u>ϵ max.</u> <u>Unionised</u>	<u>$\lambda_{\text{max.}}$</u> <u>Form.</u>	<u>ϵ max.</u> <u>Ionised</u>	<u>$\lambda_{\text{max.}}$</u> <u>Form.</u>	<u>pKa</u>
2-Nitrimine-1:3-diaza-cyclopentane.	16170	2655 (27)	9440	2260	-1.36
4-Methyl-2-nitrimine-1:3-diazacyclopentane.	17140	2660 (27)			
2-Nitrimine-1:3-diaza-cyclohexane.	15450	2680 (27)	9700	2315	-0.71
N:N-Dimethyl-N'-nitro-guanidine.	11350	2710	8010	~2100	-1.20
Nitreguanidine	14000	2640 (26-33)	9940	2250	-0.96(32)
Methylnitreguanidine	14040	2670 (11)	8700	2260	-0.86(11)
5-Nitramine-1:3:4-triazole	12400	2820			
Nitramide	5000	2200 (29)			
Methylnitramide	7000	2300 (129)			

Assuming a second proton is taken up, it could add either to the amino nitrogen or the nitramino group. No simple method of detecting a second ionisation is available. Hardy and Williams (130) have shown from cryoscopic measurements that guanidine, which forms guanidinium ion in dilute acid, does not accept a second proton to any great extent in acids weaker than 99% H_2SO_4 . By analogy, Hardy-Klein has concluded that the weakly basic nitroguanidinium cation is unlikely to form a doubly charged ion below this acid strength. Urea, a base of similar strength to nitroguanidine does however add two protons in concentrated sulphuric acid (131). In any case only a very small fraction of diprotonated form (10^{-6}) need be necessary for a reaction to proceed through this form and such quantities would escape detection by the most sensitive methods.

C. Denitration.

Order of the Reaction.

The rate of approach to equilibrium for 2-nitrimino-1:3-diazacyclopentane, 4-methyl-2-nitrimino-1:3-diazacyclopentane, N:N-dimethyl-N'-nitroguanidine, 2-nitrimino-1:3-diazacyclohexane and 5-nitramino-1:2:4-triazole, has been measured by following the change of nitroguanidine concentration with time in sulphuric acid and also in perchloric acid (for 2-nitrimino-1:3-diazacyclohexane and N-methyl-N'-nitroguanidine) and in sulphuric acid - acetic acid mixtures (for the hexane only).

Simkins and Williams (102) and Hardy-Klein (11) have previously shown that the denitration reaction for nitroguanidine and its methyl-derivative is first order and is opposed by a second order nitration reaction and they employed the rate equation,

$$k_1 = \frac{2.303 x_e}{t (2a - x_e)} \log \frac{a(x_e - x)}{ax_e + x(a - x_e)} \dots\dots\dots [18]$$

(where k_1 is the velocity coefficient of the forward (first order) reaction, a is initial concentration of nitroguanidine, x is the concentration at time t , and $x_e = x$ at equilibrium), to obtain velocity coefficients for the denitration reaction. The quantity $\log \left[\frac{a(x_e - x)}{ax_e + x(a - x_e)} \right]$ when plotted against time gave accurate straight line plots for the five compounds studied in all ranges of sulphuric and perchloric media, up to about 80% completion of the reaction. Typical plots are shown in Figs. 5 and 6. This confirms that denitration is of first order and the back reaction of second order. In sulphuric acid-acetic acid mixtures, the denitration was only followed to about 50% completion as from there on a more rapid secondary decomposition took place. The nature of this decomposition was not investigated but was assumed to be of the type mentioned by Hardy-Klein (11) and Lamberton (132). The latter investigated quantitatively the decomposition of nitroguanidine in sulphuric acid at 55°C. Nitroguanidine is converted into urea, but the final products depend on the concentration of acid because urea can be nitrated to nitrourea which will also decompose forming nitrous oxide, carbon dioxide

and ammonia. Hardy-Klein noted the occurrence of this reaction at 25°C., but its rate was conveniently slow in comparison with the rate of denitration and so was neglected.

Variation of k_1 with Medium.

Values of k_1 obtained using the equation [18] are quoted in Tables VI - VIII.

Table VI. Variation of k_1 at a fixed initial concentration in Sulphuric Acid-Water Mixtures at 25°C.

<u>2-Nitrimino-1:3-diazacyclopentane.</u>			<u>Concn. 0.008 M.</u>		
<u>% H₂SO₄</u>	<u>k_1 (mins.⁻¹)</u>	<u>k_1 (mean)</u>	<u>% H₂SO₄</u>	<u>k_1 (mins.⁻¹)</u>	<u>k_1 (mean)</u>
76.1	0.000292	0.00302	85.1	0.0239	0.0243
	0.000312			0.0247	
78.5	0.00134	0.00133	87.5	0.0738	0.0740
	0.00131			0.0742	
81.2	0.00398	0.00399	89.9	0.1841	0.1911
	0.00399			0.1992	
81.9	0.00595	0.00598	92.6	0.522	0.526
	0.00609			0.529	
83.3	0.01209	0.01207			
	0.01204				

<u>4-Methyl-2-nitrimino-1:3-diazacyclopentane</u>			<u>Concn. 0.01 M.</u>		
<u>% H₂SO₄</u>	<u>k_1 (mins.⁻¹)</u>	<u>k_1 (mean)</u>	<u>% H₂SO₄</u>	<u>k_1 (mins.⁻¹)</u>	<u>k_1 (mean)</u>
76.1	0.000514	0.000514	83.3	0.0138	0.0136
	0.000514			0.0134	
79.2	0.00185	0.00186	85.1	0.0261	0.0260
	0.00186			0.0259	
81.2	0.00510	0.00516	87.5	0.0912	0.0919
	0.00521			0.0925	

4-Methyl-2-nitrimino-1:3-

Concn. 0.01 M.

diazacyclopentane (contd.)

<u>% H₂SO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁ (mean)</u>	<u>% H₂SO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁ (mean)</u>
81.9	0.00582	0.00595			
	0.00608				

2-Nitrimino-1:3-diazacyclohexane.

Concn. 0.01 M.

<u>% H₂SO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁ (mean)</u>	<u>% H₂SO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁ (mean)</u>
68.03	0.000	0.000274	74.8	0.00743	0.00738
	0.000			0.00733	
69.70	0.000	0.000546	76.1	0.0110	0.0118
	0.000			0.0125	
70.5	0.000	0.000834	78.6	0.0358	0.0364
	0.000			0.0373	
72.8	0.00286	0.00284			
	0.00282				

N:N-Dimethyl-N'-nitroguanidine.

Concn. 0.01 M.

<u>% H₂SO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁ (mean)</u>	<u>% H₂SO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁ (mean)</u>
69.7		0.000468	79.2	0.0374	0.0364
				0.0353	
72.8	0.00185	0.00184	81.9	0.121	0.121
	0.00183			0.116	
74.8	0.00432	0.00437		0.127	
	0.00441				

<u>5-Nitramino-1:2:4-triazole.</u>			<u>Concn. 0.01M.</u>		
<u>% H₂SO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁(mean)</u>	<u>% H₂SO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁(mean)</u>
67.0	0.000420	0.000436	74.8	0.01243	0.01243
	0.000452			0.01243	
70.5	0.001130	0.001128	78.6	0.0622	0.0630
	0.001126			0.0638	
71.8	0.00213	0.00209			
	0.00205				

Table VII. Variation of k₁ at a fixed initial concentration in Perchloric Acid - Water Mixtures at 25°C.

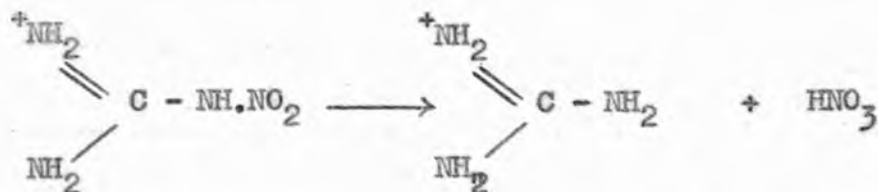
<u>2-Nitrimino-1:3-diazacyclohexane.</u>			<u>Concn. 0.01M.</u>		
<u>% HClO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁(mean)</u>	<u>% HClO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁(mean)</u>
59.6	0.000182	0.000186	64.6	0.00341	0.00346
	0.000189			0.00350	
63.6	0.00169	0.00167	67.0	0.01288	0.01274
	0.00165			0.0126	
<u>N-Methyl-N'-nitroguanidine.</u>			<u>Concn. 0.01M.</u>		
<u>% HClO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁(mean)</u>	<u>% HClO₄</u>	<u>k₁(mins.⁻¹)</u>	<u>k₁(mean)</u>
59.6	0.0000371	0.0000380	69.0	0.0101	0.0102
	0.0000388			0.0102	
64.6	0.000307	0.000316	72.0	0.0632	0.0632
	0.000324			0.0631	
66.4	0.00207	0.00202			
	0.00196				

Table VIII. Variation of k_1 at fixed initial concentration in
Sulphuric Acid - Acetic Acid Mixtures at 25°C.

<u>2-Nitrimino-1:3-diazacyclohexane.</u>		<u>Concn. 0.01 M.</u>
<u>% H₂SO₄ w/w.</u>	<u>k_1</u>	
52.7	0.000736	
55.8	0.000894	
59.1	0.00150	
64.6	0.00207	
65.5	0.00378	
71.1	0.0105	

The values of k_1 increase rapidly with increasing acid concentration (as seen in Fig. 7). Simkins and Williams (102) and Hardy-Klein (11) attempted to explain this effect but without success.

Nitroguanidine probably exists in a nitramino form in acid solutions



and the reaction produces a guanidinium cation and a nitric acid molecule.

A common mechanism for first-order reactions in acid solutions is represented by the scheme



where a base B takes up a proton, the conjugate acid thus formed undergoing decomposition. The Zucker-Hammett hypothesis (61, 62) provides a convenient method of examining a reaction in terms of such a mechanism. The proton-uptake is for convenience supposed to occur to a very small extent, so that $[\text{B}] \gg [\text{BH}^+]$.

The Bronsted equation for the rate of the reaction is
 $\text{rate} = k (\text{BH}^+) / f_{\text{tr}^+}$ where (BH^+) represents activity
 f_{tr^+} the activity coefficient of the transition state.

If k is the equilibrium constant for the proton-uptake, then

$$\text{rate} = k K (\text{B})(\text{H}^+) / f_{\text{tr}^+} .$$

Equating this with the experimental rate, $k_1 [\text{B}]$

$$\begin{aligned} k_1 [\text{B}] &= k K (\text{B})(\text{H}^+) / f_{\text{tr}^+} \\ k_1 &= K (\text{H}^+) f_{\text{B}} / f_{\text{tr}^+} \end{aligned}$$

Now, $\text{H}^+ = h_0 f_{\text{CH}^+} / f_{\text{C}}$ where C is any Hammett base.

$$\therefore k_1 = k.K.h_0.f_{\text{CH}^+}.f_{\text{B}} / f_{\text{tr}^+}.f_{\text{C}}$$

Provided the activity coefficient product $(f_{\text{CH}^+}.f_{\text{B}}) / (f_{\text{tr}^+}.f_{\text{C}})$ remains constant with change in medium, then by taking logs we

obtain the expression

$$\log k_1 + H_0 = \text{constant} \dots \dots \dots [10]$$

(when the ionisation of B is considerable, a new expression is necessary and is similarly derived $\log k_1 + H_0 + \frac{\log [B]}{[BH^+]} = \text{constant}$).

If the relation [10] is obeyed the mechanism of the reaction is assumed to be represented by the scheme above.

Nitroguanidine in 40% H_2SO_4 exists entirely in the form of its conjugate acid, thus the mechanism of its denitration possibly involves uptake of a second proton, followed by breakdown of the molecule. For such a reaction, the analogous expression

$$\log k_1 + H_+ = \text{constant} \dots \dots \dots [19]$$

may be derived, where H_+ is a Hammett acidity function defined as

$$H_+ = -\log (H^+) \cdot \frac{f_{BH^+}}{f_{BH_2^{++}}}$$

Simkins and Williams, and Hardy-Klein also proposed this mechanism but in absence of data for H_+ they used Hammett's H_0 values. The best method of testing [10] is to plot $\log k_1$ against H_0 . Simkins and Williams obtained a slope of -1.42 for this plot of their results and Hardy-Klein -1.5 for hers, but not knowing whether H_0 and H_+ were really parallel, they were unable to make a firm conclusion. The parallelism of H_0 and H_+ in both sulphuric and perchloric acids is demonstrated in Section III, G (). Values of H_0 for sulphuric acid (84) and perchloric acid (84 and Section IIIF) may thus be used in [10] without affecting the constancy. No H_0 values have been published for

the sulphuric acid-acetic acid media under consideration.

Plots of $\log k_1$ against H_0 are shown in Fig. 8. The corresponding slopes are shown in Table IX.

Table IX.

<u>Compound</u>	<u>Acid</u>	<u>Slope</u>
5-Nitramino-1:2:4-triazole	H_2SO_4	- 1.50
2-Nitrimino-1:3-diazacyclo- hexane	H_2SO_4	- 1.44
	$HClO_4$	- 0.94
N:N-Dimethyl-N'-nitro- guanidine	H_2SO_4	- 1.50
N-Methyl-N'-nitroguanidine	H_2SO_4	- 1.50 (11)
	$HClO_4$	- 0.96
Nitroguanidine	H_2SO_4	1.42 (102)
4-Methyl-2-nitrimino-1:3- diazacyclopentane	H_2SO_4	1.40
2-Nitrimino-1:3-diazacyclo- pentane	H_2SO_4	1.40

The slopes in perchloric acid are close to unity indicating the unimolecular mechanism discussed above. However in sulphuric acid the slopes approximate to -1.4 in all cases. Fig. 9 demonstrates the very different slopes obtained for the same compound in the two different acids.

Before dismissing a unimolecular mechanism in sulphuric acid,

it is necessary to consider previous work on the correlation of rates with H_0 . Slopes ranging from -0.7 to -1.5 have been interpreted in favour of this mechanism.

In deriving [10] it was assumed that $(f_{CH^+} \cdot f_B) / (f_{tr^+} \cdot f_C)$ would remain constant with changing medium. In seeking a constancy of [10] we are assuming that this activity coefficient term is invariant, i.e. that f_B / f_{tr^+} and f_C / f_{CH^+} vary in the same way with medium. Hammett and Deyrup (84) established that f_B / f_{BH^+} and f_C / f_{CH^+} vary in the same way with medium to a fair approximation, where B and C are two Hammett bases (see Fig. 1). The f_{tr^+} term is the activity coefficient of a positively charged transition state which is another form of the molecule BH^+ . It is thus feasible that f_{tr^+} should vary in the same way with medium as f_{BH^+} . However, even the constancy of $(f_{CH^+} \cdot f_B) / (f_{BH^+} \cdot f_C)$ may break down where B and C are very different in size and polarity - for these properties affect activity coefficients very specifically. A review by Long and McDevitt (68) summarises such effects, along with salt effects. Paul (69) has actually measured the effect of concentration of various salts on the H_0 function itself at low acidities, establishing specific salting-in and salting-out for various salts. The salt order was similar to that for the variation of activity coefficients of weakly basic non-electrolytes. Salt effects on H_0 might explain slight differences in slope of $\log k$ against H_0 found for the same reaction in different acids, a common phenomenon.

Long and McIntyre (67) found slopes of -1.25, -1.15 and -1.08 for the hydrolysis of methylal in various acids, and obtained a slope of -1.4 for that of ethylal in hydrochloric acid (using the kinetic data of Leiminger and Kilpatrick) (133). They suggested that

$$\log k + H_0 - \log (f_M \cdot f_{BH^+}) / (f_{tr^+} \cdot f_B) = \text{constant} \dots \dots [20]$$

where f_M and f_{tr^+} are the activity coefficients of a methylal molecule and its transition state and f_B and f_{BH^+} those of a Hammett indicator and its conjugate acid respectively. Long and McIntyre also considered the possibility of the terms in [20] being subject to salt effects. The effect of changing salt concentration on f_M , f_B , f_{BH^+} and H_0 , and on k (at constant acid concentration was measured. An estimation of all the terms in [20] was thus made possible. Taking account of these salt effects the slope of $\log k$ v. H_0 for methylal in hydrochloric acid was improved from -1.25 to -1.04.

Gold and Satchell obtained slopes of -1.36 and -1.40 for the rates of deuterium exchange in sulphuric acid of deuterobenzene (134) and p-deutero-toluene (135) respectively, while for o-deutero-p-cresol (136) in hydrochloric acid the slope was -1.42. For many other deuterated compounds and various acids which these authors and others studied, slopes were very close to unity and it seems equally likely that the mechanism suggested (rate-determining reaction of the

conjugate acid of the substrate) for deuterium exchange is possible even in these three cases. Specific salt effects were invoked as an explanation of the non-unit slopes. A complete list of these papers will be found in a paper by Satchell (137).

Gold and Hilton (138) have applied the Zucker-Hammett hypothesis to results for the rate of hydrolysis of acetic anhydride in perchloric, sulphuric and phosphoric acids, obtaining slopes ^{of} -0.7 to -1.3 in plots of $\log k$ v. H_0 . These were interpreted in favour of the formation of acetylium ion from a protonated acetic ⁿ anhydride molecule in the rate-determining step. Various explanations of the deviation were suggested (a) the wide range of H_0 covered (b) temperature effects on H_0 (c) variation of the activity coefficient term in equation [20] (d) specific salt effects e.g. of bisulphate or sulphate ions. Measurements of H_0 at various temperatures have since been published (60) showing that H_0 can in fact vary with temperature. The first two explanations cannot, of course, be applied to the denitration reaction.

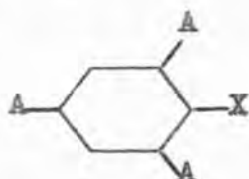
The nitroguanidinium ion is very different in size and polarity from the type of indicator used by Hammett and Deyrup. An explanation, similar to Long and McIntyre's seemed at first likely. But data were on hand to test this. In the calculation of the first pK_a of several nitroguanidines (p. 60), values of $\log \frac{[B]}{[BH^+]}$ were obtained and are shown in Fig. 1 plotted against % H_2SO_4 . Plots of $\log \frac{[B]}{[BH^+]}$ are parallel to those

for the Hammett indicators. Again, the fact of H_+ and H_0 being parallel, means that the activity coefficients of positively charged and neutral indicators vary in the same way with medium. Accordingly, for the positively charged nitroguanidinium ion, activity coefficients should vary in the same way as for a neutral Hammett indicator. A slope of -1.4 for the denitration results in sulphuric acid cannot therefore be regarded as satisfactory evidence for the unimolecular mechanism.

It is obvious from Fig. 9, that in sulphuric acid, rates are increasing at a greater rate than in perchloric acid for a corresponding increase in acidity as measured by H_0 . The reaction rate is satisfactorily correlated with h_0 in perchloric acid, but not in sulphuric acid. This suggests catalysis in sulphuric acid by some species not present in perchloric acid. In the discussion of species present (p.8) it was noted that in perchloric acids in the kinetic region investigated (60-70%) the species present were ClO_4^- , H_3O^+ and H_2O . In sulphuric acid however HSO_4^- , H_3O^+ , SO_4^{2-} , H_2O and H_2SO_4 were all present to some degree throughout most of the kinetic range. Little H_2SO_4 can be present in 67% H_2SO_4 , the lower boundary and no H_2O or SO_4^{2-} is present in 92% H_2SO_4 , the upper boundary.

Schubert and Zahler (139) and Schubert, Donohue and Gardner (140) have attempted to explain decarboxylation of

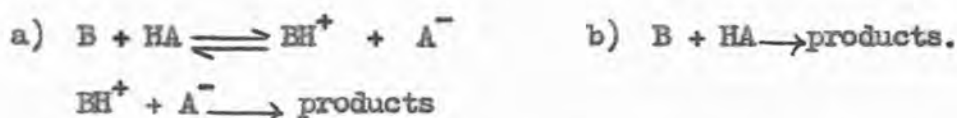
aldehydes and decarboxylation of aromatic acids of the type



(where A is alkyl, X is -CHO
or -COOH)

in sulphuric acid in terms of specific acid catalysis. The rates of these reactions reach a maximum at a particular point, associated with the degree of ionisation of substrate to conjugate acid, and fall off towards 100% H_2SO_4 . Long (141) considers the unimolecular mechanism is the best explanation of variation of rate with medium for these results, although it does not explain the fall off in the highest regions. Schubert and Zahler, however, consider the relation obtained with H_0 (slope -0.87) fortuitous, and consider bimolecular or termolecular reactions with unspecified solvent species to be more suitable. Only qualitative evidence for this is cited and no strict quantitative treatment seems yet possible. Isotopic effects (142) are in accord with a bimolecular reaction. The decrease in rate at highest acid concentrations might be associated with decrease in concentration of some catalytic solvent species. Again, an explanation on the lines suggested by Hughes, Ingold and Reed (96) for the similar fall in rate of aromatic nitration in concentrated acid may be possible.

Hardy-Klein also considered bimolecular mechanisms such as those studied by Schubert and co-workers, and proposed a quantitative treatment.



B is the neutral substrate molecule. Both mechanisms give rise to the same rate equation (11). Hardy-Klein derived the expressions

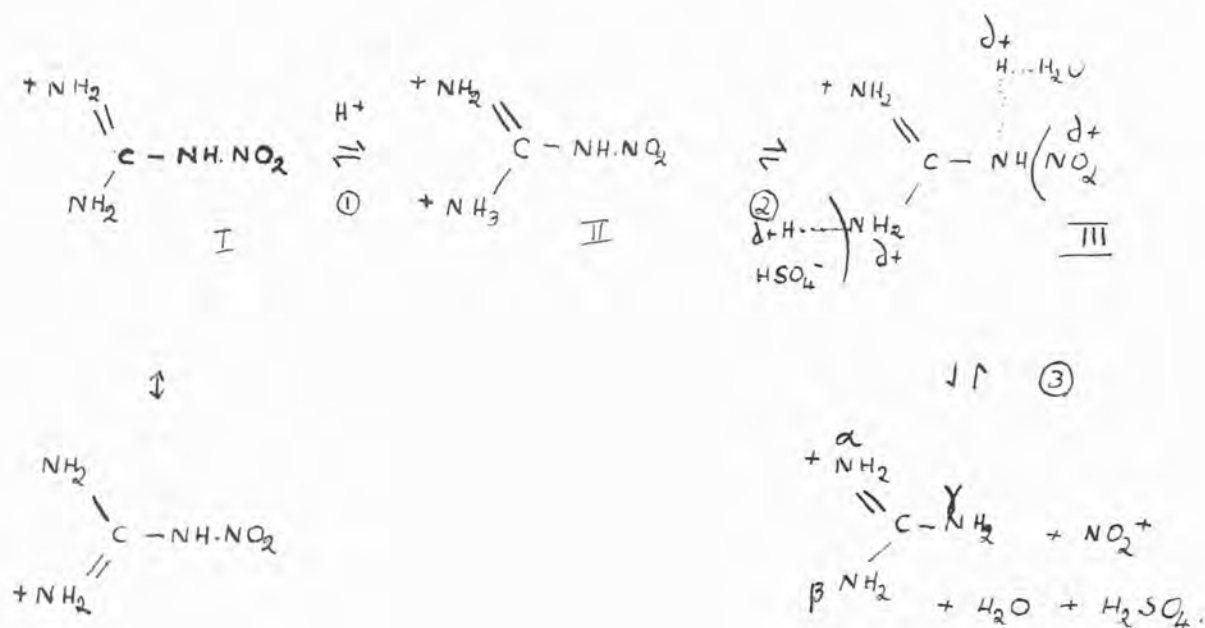
$$\begin{array}{ll} \log k_1 - \log (H_2SO_4) = \text{const.} \dots\dots\dots [21] & \text{for HA} = H_2SO_4 \\ \log k_1 + H_0 - \log (H_2O) = \text{const.} \dots\dots\dots [22] & \text{for HA} = H_3O^+ \end{array}$$

These were tested with experimental values of k_1 , using values of (H_2O) from a paper by Gold and Hawes (87), values of (H_2SO_4) calculated by Abel from other data (143, 144) and Hammett and Deyrup's values of H_0 (55). Neither of the two expressions

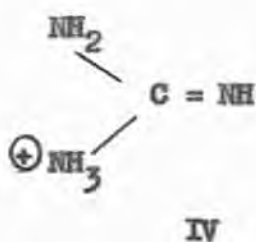
fitted the results as will be seen in Table X. A third expression [23] was incorrectly derived but fortunately the results were found to fit this expression.

$$\log k_1 + H_0 - \log (H_2SO_4) - \log (H_2O) = \text{constant} \dots\dots\dots [23]$$

No termolecular mechanisms were considered, but expression [23] can in fact be derived for more than one termolecular mechanism.



If the nitroguanidinium ion is depicted as I, imagine a rapid protonation to the form II. Loss of the nitronium ion from II would leave an entity such as IV which would be extremely unstable and would rearrange to the



guanidinium ion. All these steps can be accomplished in sulphuric acid by a scheme such as step ③, involving attack of H_3O^+ on the γ position to release the nitro-group and simultaneous attack of HSO_4^- on the β -position to create the symmetrical guanidinium ion. A transition state for

this reaction might be envisaged as III.

The Bronsted rate equation for the reaction is

$$\begin{aligned} \text{rate} &= k (\text{BH}_2^{++})(\text{HSO}_4^-)(\text{H}_3\text{O}^+) / f_{\text{tr}^+} \\ \text{experimental rate} &= k_1 [\text{BH}^+] \\ &= k (\text{BH}_2^{++})(\text{HSO}_4^-)(\text{H}_3\text{O}^+) / f_{\text{tr}^+} \end{aligned} \quad \left\{ \begin{array}{l} \text{where brackets denote} \\ \text{activities and B is} \\ \text{the neutral nitro-} \\ \text{guanidine molecule.} \end{array} \right.$$

$$\begin{aligned} \text{From step 1 } \text{BH}^+ + \text{H}^+ &\overset{K}{\rightleftharpoons} \text{BH}_2^{++} \\ K_{\text{BH}^+} &= (\text{BH}_2^{++}) / (\text{BH}^+)(\text{H}^+) \end{aligned}$$

Substituting for (BH_2^{++})

$$k_1 [\text{BH}^+] = k K_{\text{BH}^+} (\text{BH}^+)(\text{H}^+) (\text{HSO}_4^-)(\text{H}_3\text{O}^+) / f_{\text{tr}^+}$$

To eliminate (H_3O^+) $\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^- + \text{H}_3\text{O}^+$

$$K_{\text{H}_2\text{O}} = (\text{HSO}_4^-)(\text{H}_3\text{O}^+) / (\text{H}_2\text{O})(\text{H}_2\text{SO}_4)$$

$$k_1 [\text{BH}^+] = k K_{\text{BH}^+} (\text{BH}^+)(\text{H}^+) K_{\text{H}_2\text{O}} (\text{H}_2\text{O})(\text{H}_2\text{SO}_4) / f_{\text{tr}^+}$$

$$k_1 = k K_{\text{BH}^+} (\text{H}^+) (\text{H}_2\text{O})(\text{H}_2\text{SO}_4) K_{\text{H}_2\text{O}} f_{\text{BH}^+} / f_{\text{tr}^+}$$

Now $h_0 = (\text{H}^+) f_{\text{C}} / f_{\text{CH}^+} \dots \dots \dots [3]$ where C is any base.

$$k_1 = k K_{\text{BH}^+} K_{\text{H}_2\text{O}} \cdot h_0 (\text{H}_2\text{O})(\text{H}_2\text{SO}_4) f_{\text{CH}^+} \cdot f_{\text{BH}^+} / f_{\text{tr}^+} \cdot f_{\text{C}}$$

Taking logs of both sides and assuming constancy of the activity coefficient portion.

$$\log k_1 + H_0 - \log (H_2O) - \log (H_2SO_4) = \text{constant} \dots \dots [23]$$

The experimental results fit this expression very well as seen in Table ~~VIII~~ over the range 65-85% H_2SO_4 . $\log k_1$ is plotted against $H_0 - \log (H_2O) - \log (H_2SO_4)$ in Fig. 10. and near-unit slopes are obtained in every case. The results of Hardy-Klein and Simkins and Williams are included for comparison. Above 85% H_2SO_4 the rate begins to increase much more sharply and the reaction may then proceed through another mechanism.

Table X

2-Nitrimino-1;3-diazacyclopentane, Conc. 0.008M at 25°C.

% Acid	76.0	78.5	81.2	81.9	83.3	85.1	87.5	89.9	92.6
$\log k_1$	-3.51	-2.87	-2.39	-2.22	-1.93	-1.63	-1.13	-0.72	-0.28
H_0	-6.33	-6.67	-7.04	-7.12	-7.34	-7.57	-7.91	-8.21	-8.47
$\log(H_2O)$	-1.88	-2.10	-2.38	-2.46	-2.61	-2.79	-3.10	-3.48	-3.95
$\log(H_2SO_4)$	6.96	7.34	7.71	7.79	7.99	8.21	8.50	8.78	9.05
$\log k_1 + H_0 - \log(H_2O)$	-7.96	-7.44	-7.05	-6.88	-6.66	-6.41	-5.94	-5.45	-4.80
$\log k_1 - \log(H_2SO_4)$	-10.47	-10.21	-10.10	-10.01	-9.92	-9.84	-9.63	-9.50	-9.33
$\log k_1 + H_0 - \log(H_2O) - \log(H_2SO_4)$	-14.92	-14.78	-14.76	-14.67	-14.65	-14.62	-14.44	-14.23	-13.85

2-Nitrimino-4-methyl-1:3-diazacyclopentane. Conc. 0.01 M at 25°C.

% Acid	76.0	79.2	81.2	81.9	83.3	85.1	87.5
log k_1	-3.29	-2.73	-2.29	-2.24	-1.87	-1.58	-1.04
Ho	-6.33	-6.76	-7.04	-7.12	-7.34	-7.57	-7.91
log (H ₂ O)	-1.88	-2.18	-2.38	-2.46	-2.61	-2.79	-3.10
log (H ₂ SO ₄)	6.96	7.45	7.71	7.79	7.99	8.21	8.50
log $k_1 + Ho - \log(H_2O)$	-7.74	-7.31	-6.95	-6.90	-6.61	-6.36	-5.85
log $k_1 - \log(H_2SO_4)$	-10.25	-10.18	-10.00	-10.03	-9.86	-9.79	-9.54
log $k_1 + Ho - \log(H_2O) - \log H_2SO_4$	-14.70	-14.76	-14.66	-14.69	-14.60	-14.57	-14.35

Nitroguanidine Conc. 0.2M at 25°C. (Simkins & Williams)

	Concn. 0.1M				Concn. 0.4M.			
% Acid	82.94	79.24	75.47	71.48	79.24	75.47	79.24	75.47
log k_1	-1.56	-2.36	-3.02	-3.74	-2.19	-2.97	-2.38	-3.17
Ho	-7.27	-6.77	-6.27	-5.72				
log (H ₂ O)	-2.32	-2.18	-1.83	-1.39				
log (H ₂ SO ₄)	+7.94	+7.46	+6.88	+6.23				
log $k_1 + Ho - \log(H_2O)$	-6.51	-6.85	-7.46	-8.07	-6.77	-7.41	-6.97	-7.62
log $k_1 - \log(H_2SO_4)$	-9.40	-9.72	-9.90	-9.97	-9.83	-9.92	-9.84	-10.05
log $k_1 + Ho - \log(H_2O) - \log H_2SO_4$	-14.45	-14.31	-14.34	-14.30	-14.24	-14.29	-14.43	-14.49

Table X (contd.)

N-Methyl-N'-nitroguanidine Concn. 0.02M at 25°C. See ref.(11)

N,N-Dimethyl-N'-nitroguanidine. Concn. 0.01M at 25°C.

% Acid	69.7	72.8	74.8	79.2	81.9
log k_1	-3.33	-2.73	-2.36	-1.44	-0.92
Ho	-5.48	-5.92	-6.16	-6.78	-7.12
log (H ₂ O)	-1.34	-1.59	-1.76	-2.18	-2.46
log (H ₂ SO ₄)	5.93	6.43	6.74	7.45	7.79
log $k_1 + Ho - \log(H_2O)$	-7.47	-7.06	-6.76	-6.04	-5.58
log $k_1 - \log(H_2SO_4)$	-9.26	-9.16	-9.10	-8.89	-8.71
log $k_1 + Ho - \log H_2O$ -log(H ₂ SO ₄)	-13.40	-13.49	-13.50	-13.49	-13.37

2-Nitrimino-1:3-diazacyclohexane

Concn. 0.01M at 25°C.

% Acid	68.0	69.7	70.5	72.8	74.8	76.1	78.6
log k_1	-3.56	-3.26	-3.08	-2.56	-2.13	-1.96	-1.45
Ho	-5.21	-5.44	-5.61	-6.92	-6.16	-6.33	-6.67
log (H ₂ O)	-1.22	-1.34	-1.41	-1.59	-1.76	-1.88	-2.12
log (H ₂ SO ₄)	+5.68	5.95	6.08	6.44	6.76	6.98	7.36
log $k_1 + Ho - \log(H_2O)$	-7.55	-7.36	-7.28	-6.89	-6.53	-6.41	-6.00
log $k_1 - \log(H_2SO_4)$	-9.24	-9.21	-9.16	-9.00	-8.89	-8.94	-8.81
log $k_1 + Ho - \log(H_2O) - \log$ (H ₂ SO ₄)	-13.23	-13.31	-13.36	-13.33	-13.29	-13.39	-13.36

<u>5-Nitramino-1:2:4-triazole.</u>		<u>Concn. 0.01 M at 25°C.</u>			
% Acid	67.0	70.5	71.8	74.8	78.6
log k_1	-3.64	-2.95	-2.68	-1.91	-1.20
Ho	-5.16	-5.61	-5.76	-6.16	-6.67
log (H ₂ O)	-1.16	-1.41	-1.50	-1.76	-2.12
log (H ₂ SO ₄)	5.52	6.08	6.28	6.98	7.36
log $k_1 + Ho - \log(H_2O)$	7.64	7.15	6.94	6.31	5.75
log $k_1 - \log(H_2SO_4)$	9.16	9.03	8.96	8.89	8.56
log $k_1 + Ho - \log(H_2O) - \log(H_2SO_4)$	13.16	13.23	13.22	13.29	13.11

Table XI

<u>2-Nitrimino-1:3-diazacyclopentane.</u>		<u>25°C. Concn. 0.008M.</u>		
% Acid	85.1	87.5	89.9	92.6
log k_1	-1.63	-1.13	-0.72	-0.28
log (H ₂ O)	-2.79	-3.10	-3.48	-3.95
log $k_1 + \log(H_2O)$	-4.42	-4.23	-4.20	-4.23

The equation [23] can be derived in other ways.

Termolecular mechanisms between the species H₃O⁺, H₂SO₄ and BH⁺

or between H₂O, H₂SO₄ and BH₂⁺⁺ would give rise to the same expression.

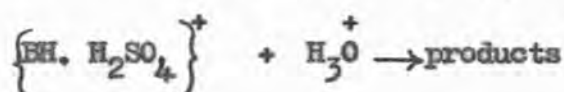
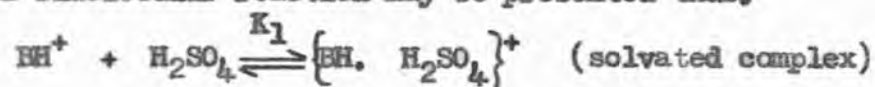
But H₂SO₄ will not be present to any great extent in media below 84.5%

H₂SO₄. Oxonium and bisulphate ions will be present in large quantities

in all the media studied and so the first termolecular mechanism proposed is more plausible.

Hardy-Klein (145) has recently suggested bimolecular and unimolecular reactions of a solvated nitroguanidinium ion which would lead to [23] .

A typical bimolecular reaction may be presented thus.



$$\text{rate} = k(\{\text{BH} \cdot \text{H}_2\text{SO}_4\}^+)(\text{H}_3\text{O}^+)/f_{\text{tr}^{++}}$$

$$\text{For the solvation } K_1 = (\{\text{BH} \cdot \text{H}_2\text{SO}_4\}^+)/(\text{BH}^+)(\text{H}_2\text{SO}_4)$$

$$\therefore \text{rate} = kK_1(\text{BH}^+)(\text{H}_2\text{SO}_4)(\text{H}_3\text{O}^+)/f_{\text{tr}^{++}} = k_1 [\text{BH}^+] \quad (\text{experimental rate})$$

Eliminating (H_3O^+) as before (p. 78)

$$k_1 = kK_1(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})h_0 K_{\text{H}_2\text{O}} \cdot f_{\text{CH}^+} \cdot f_{\text{BH}^+} / f_{\text{C}} \cdot f_{\text{tr}^{++}}$$

$$\therefore \log k_1 = \log (\text{H}_2\text{SO}_4) + \log (\text{H}_2\text{O}) - H_0 + \text{constant.}$$

Other equivalent mechanisms include solvation by H_3O^+ and bimolecular attack by H_2SO_4 , and solvation by H_3O^+ and H_2SO_4 , with unimolecular breakdown of the complex. The most likely solvation mechanism would presumably involve BH_2^{++} and the hydroxonium and bisulphate ions, as these are most prevalent in the media studied.

Above 85% H_2SO_4 , a few results are available for 2-nitrimino-1:3-diazacyclopentane. They do not fit any of the relations derived previously [21], [22] and [23], but the relation $\log k_1 + \log (H_2O) = \text{constant} \dots$ [24] seems to hold. (Table XI). The fact that the rate is increasing much more sharply above 85% H_2SO_4 suggests the participation of a solvent species previously present in very small amount, or the disappearance of some solvent species which previously retarded the reaction or simply rapidly increasing diprotonation. Equation [24] implies retardation by H_2O .

The fact that a sharp rise in rate occurs just above the equimolar mixture of sulphuric acid-water is definitely consistent with the picture of specific catalysis by the solvent species. The range of acid covered was from just over the 2:1 molar ratio of water to sulphuric acid to just under the 1:1 ratio. Nitroguanidines with rates faster or slower than those measured would extend the range and this may clarify the picture.

The constancy found experimentally for [23] is of course dependent on the quantities H_0 , (H_2O) and (H_2SO_4) . The first two are of known reliability. Abel's values of (H_2SO_4) are based on indirect vapour pressure measurements. Activity data from direct vapour pressure measurement of H_2SO_4 vapour would be more valuable.

Variation of k_1 with initial reagent concentration.

Simkins and Williams (102) and Hardy-Klein (11) found that k_1 increased slightly as the initial concentration of nitroguanidine was decreased. This effect has been verified for 2-nitrimino-1:3-diazacyclohexane and N:N-dimethyl-N'-nitroguanidine but for 2-nitrimino-1:3-diazacyclopentane and its 4-methyl analogue, no change in k_1 with reagent concentration was observed. Results are in Table XII.

Table XII.

Variation of Denitration Velocity Coefficients with Initial Reagent Concentration.

<u>Compound</u>	<u>Acid</u>	<u>Concn. (m/l.)</u>	<u>k_1 (mins.⁻¹)</u>
2-Nitrimino-1:3-diazacyclopentane	81.2	0.1	0.00399
"	"	0.044	0.00385
"	"	0.022	0.00400
"	"	0.0098	0.00405
"	"	0.0072	0.00391
"	"	0.0045	0.00384
4-Methyl-2-nitrimino-1:3-diazacyclopentane	87.0	0.0965	0.0451
"	"	0.0082	0.0444
2-nitrimino-1:3-diazacyclohexane	78.6	0.0299	0.0302
"	"	0.01	0.0364
2-nitrimino-1:3-diazacyclohexane	72.8	0.0296	0.00270
"	"	0.01	0.00286

Table XII. (Contd.)

<u>Compound</u>	<u>Acid</u>	<u>Concn. (M/l.)</u>	<u>k_1 (mins.⁻¹)</u>
N:N-dimethyl-N'-nitroguanidine	79.2	0.038	0.0328
"	"	0.009	0.0374
"	72.8	0.041	0.00173
"	"	0.01	0.00184

The variation in k_1 with initial concentration, where it occurs, has been attributed (102, 11) to (1) a simple dilution effect, (2) reduction of the acidity by nitroguanidine present, (3) change in ionic strength. The second and third explanations are feasible on the grounds that salts such as ammonium sulphate (88) have been shown to have a definite effect on the acidity. The fact that the rates for 2-nitrimino-1:3-diaza-cyclopentane and its 4-methyl derivative do not alter noticeably with initial reagent concentration seems to contradict this, as the effect of all nitroguanidines with simple alkyl substituents should be the same. But it should be noted that for the other two compounds at lower acid concentrations (e.g. 72.8%) the rates do not vary nearly so markedly with initial reagent concentration.

On p.89 the % denitration for all compounds in all media studied is given. The pentanes denitrate to at least 80% in most media, and so the back reaction can occur only to 20% and the reaction is almost entirely a first order denitration. For the hexane and the dimethyl compound the amounts of denitration vary much more with medium, and in

the region of greatest denitration, the rates are less affected by concentration. In regions where the back reaction takes place to any extent (say 50%) a definite rate change with initial ~~rate~~ concentration is observed. Thus the unchanged nitroguanidine in a reaction may have an effect on the rate, and the phenomenon for particular compounds may be caused by the state of the equilibrium for the particular medium and concentration.

D. The Nitroguanidine - Guanidine Nitrate Equilibrium.

The extent to which each nitroguanidine was converted to the corresponding guanidine was measured by means of finding the equilibrium concentration of nitroguanidine, for 5-nitramino-1:2:4-triazole, 2-nitrimino-1:3-diazacyclohexane, N,N-dimethyl-N'-nitroguanidine, 2-nitrimino-1:3-diazacyclopentane and 4-methyl-2-nitrimino-1:3-diazacyclopentane in sulphuric acid, up to 100%, for the hexane and N-methyl-N'-nitroguanidine in perchloric acid, and for the hexane and guanidine nitrate in sulphuric acid-acetic acid mixtures. The % conversion is plotted against % acid in Fig. 11 and the data are collected in Tables XIII - XV. The mean value of % conversion quoted is normally an average of at least two experimentally obtained values, except in sulphuric acid-acetic acid mixtures, where all media were made up separately for each individual run, and so no run could be repeated.

From Fig. 11 it is seen that in sulphuric acid-water mixtures the minimum amount of denitration for all compounds occurs in the 85-88% H_2SO_4 region; in sulphuric acid-acetic acid mixtures it is a minimum at 73% H_2SO_4 . No minimum is observed in perchloric acid. The results for the three media appear quite unrelated, but the quantity percentage acid w/w is not necessarily an appropriate function of medium composition. Consider instead the mole ratios of base to acid at which the minima occur. The minima in $H_2SO_4 - H_2O$ are at the mole ratio 0.77 - 0.93 of water to acid, the minimum in sulphuric acid-acetic acid is at 0.62 mole ratio of acetic acid to sulphuric acid, while the mole-ratio is greater than 1 for all perchloric acid media studied. The mole ratio $H_2O:HClO_4$ is less than unity only in acids over 86% strength and possibly this is the reason no minimum is observed in the media studied, although a trend to more nitration occurs at higher acid strengths.

The quantity % denitration gives a measure of the relative rates of the forward and the back reactions. At the lower acid strengths, the rate of nitration is increasing faster than that of denitration, but beyond the minimum the nitration rate does not increase so fast, and probably begins to fall off, while k_1 continues to increase. For 2-nitrimino-1:3-diazacyclopentane, k_1 does in fact increase very sharply beyond the minimum (see Table VIII).

Simkins and Williams expressed the corresponding data for nitroguanidine itself in the form of an equilibrium product K.

Table XIII.

% Denitration in Sulphuric Acid.

2-Nitrimino-1:3-diazacyclohexane

Concn. 0.01M

Temperature 25°C.

<u>% H₂SO₄</u>	<u>% Denitration</u>	<u>log K</u>
68.0	70.0	1.800
69.7	68.0	1.840
72.8	53.1	2.221
74.8	47.4	2.369
76.1	44.6	2.443

<u>% H₂SO₄</u>	<u>% Denitration</u>	<u>log K</u>
78.6	35.6	2.706
81.9	27.2	2.993
85.1	23.1	3.159
87.5	22.0	3.207
94.9	71.6	1.744

NN-Dimethyl-N'-nitroguanidine

Concn. 0.01M

Temperature 25°C.

<u>% H₂SO₄</u>	<u>% Denitration</u>	<u>log K</u>
69.7	96.0	0.510
72.8	94.6	0.790
74.8	89.4	1.107
79.2	77.2	1.583
81.2	68.1	1.838

<u>% H₂SO₄</u>	<u>% Denitration</u>	<u>log K</u>
81.9	66.8	1.871
85.1	47.9	2.356
87.5	43.0	2.509
94.9	93.9	
99.1	96.8	

Table XIII (contd.)

<u>2-Nitrimino-1:3-diazacyclopentane.</u>			<u>Concn. 0.008M Temp. 25°C.</u>		
<u>% H₂SO₄</u>	<u>% Denitration</u>	<u>log K</u>	<u>% H₂SO₄</u>	<u>% Denitration</u>	<u>log K</u>
76.1	84.1	1.4487	87.0	76.9	1.689
78.6	81.5	1.542	87.5	76.6	1.689
81.2	79.7	1.601	89.9	77.3	1.677
81.9	79.3	1.614	92.6	78.7	1.633
83.3	78.7	1.633	94.9	81.7	1.558
85.1	77.9	1.658			

<u>5-Nitramino-1:2:4-triazole.</u>			<u>Concn. 0.01M Temp. 25°C.</u>		
<u>% H₂SO₄</u>	<u>% Denitration</u>	<u>log K</u>	<u>% H₂SO₄</u>	<u>% Denitration</u>	<u>log K</u>
67.0	74.0	1.741	84.1	43.9	2.470
70.5	67.2	1.861	87.5	58.0	2.096
71.8	63.0	1.970	89.5	59.3	2.063
74.8	56.1	2.145	91.2	88.6	1.162
78.6	53.6	2.217	93.8	91.6	1.000
83.4	44.9	2.437			

Table XIV.

% Denitration in Perchloric Acid.

<u>2-Nitrimino-1:3-diazacyclohexane</u>			<u>Concn. 0.01M Temp. 25°C.</u>		
<u>% HClO₄</u>	<u>% Denitration</u>	<u>log K</u>	<u>% HClO₄</u>	<u>% Denitration</u>	<u>log K</u>
59.6	85.9	1.281	64.6	63.1	2.071
63.6	68.6	1.824	67.0	54.0	2.198

<u>N-Methyl-N'-nitroguanidine</u>			<u>Concn. 0.01M Temp. 25°C.</u>		
<u>% HClO₄</u>	<u>% Denitration</u>	<u>log K</u>	<u>% HClO₄</u>	<u>% Denitration</u>	<u>log K</u>
59.6	98.0	0.319	69.0	60.9	2.0231
64.6	85.7	1.289	72.0	48.1	2.351
66.4	76.7	1.598			

Table XV.

% Nitration in Sulphuric Acid-Acetic Acid.

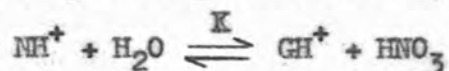
<u>Guanidine Nitrate.</u>		<u>Concn. 0.013M. Temp. 25°C.</u>	
<u>% H₂SO₄</u>	<u>% Nitn.</u>	<u>% H₂SO₄</u>	<u>Mean % Nitn.</u>
49.6	40.4	64.4	82.9
52.7	50.4	66.1	86.5
56.2	61.0	70.1	93.8
58.2	66.9	74.1	95.1
60.3	71.7	76.1	88.7
		80.2	73.1

$$K = [N]_e / [G]_e [HNO_3]_e$$

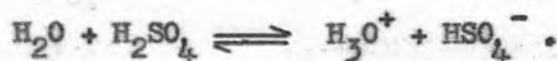
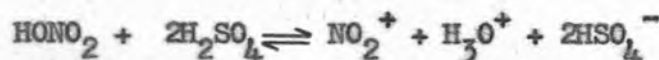
$$= k_1 / k_2$$

where N and G are the neutral nitroguanidine and guanidine molecules respectively and k_1 and k_2 are the velocity constants of denitration and nitration, respectively. K decreases with initial nitroguanidine concentration. The following treatment was applied (11, 101).

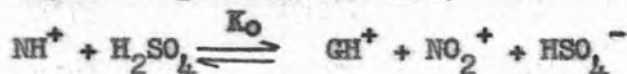
The simplest expression of the denitration is



with the other equilibria also occurring.



Collecting these, the expression becomes,



$$\therefore K_0 = (NH^+)(H_2SO_4) / (GH^+)(NO_2^+)(HSO_4^-)$$

Eliminating (HSO_4^-) and then (H_2SO_4) by means of the other equilibria,

$$K_0 = (NH^+)(H_2O) K_{H_2SO_4} / (GH^+)(HNO_3) K_{HNO_3}$$

$$= [NH^+] (H_2O) K_{H_2SO_4} f_{NH^+} / [GH^+] [HNO_3] K_{HNO_3} \cdot f_{GH^+} \cdot f_{HNO_3}$$

$$\text{but } K = [NH^+] / [GH^+] [HNO_3] \quad (\text{where } [NO_2^+] \ll [HONO_2])$$

$$\therefore \log K_0 = \log K + \log(H_2O) + \log (f_{NH^+} / f_{GH^+} \cdot f_{HNO_3}) + \text{const.} \quad [25]$$

The activity coefficient ratio is symmetrical in charge, and any variation

in it may be attributed mainly to f_{HNO_3} , which could conceivably be constant in this range.

Slopes of $\log K$ against $\log (H_2O)$ for media below the minima were obtained as follows from Fig. 12.

N:N-dimethyl-N'-nitroguanidine	(-1.23)
2-Nitrimino-1:3-diazacyclohexane	(-0.99)
5-Nitramino-1:2:4-triazole	(-0.90)

and indicate that the variation in K is proportional to the variation of activity of water in the medium. The activity coefficient ratio in [25] is then approximately constant.

For 2-nitrimino-1:3-diazacyclopentane and its 4-methyl derivative, slopes were -0.14 and -0.22 respectively. The amount of denitration for these last two compounds is never less than 76% (see Fig. 11) and values of $\log K$ for denitration of more than 90% would be subject to considerable error. Thus only over 11% denitration (a range of 3% H_2SO_4) could the relation [25] hold in any case.

The possibility that the equilibrium for the last two compounds is not in fact a true equilibrium was considered, in view of the fact that nitration on the 4- or 5-position as well as the amino-nitrogen, upsets the equilibrium in sulphuric acid of the similar 2-nitramino-thiazole (14.6). However any such

nitro compound would be revealed in the spectrum of the final product and no trace of it was seen. The kinetic results fit the kinetic equation for a reversible reaction perfectly for both compounds.

In perchloric acid and sulphuric acid-acetic acid mixtures, a similar relation between $\log K$ and $\log (H_2O)$ or $\log (CH_3COOH)$ may be deduced, but no values for the activities are available to test the relation.

The results for guanidine nitration in sulphuric acid-acetic acid media demonstrate that nitration is more complete in the optimum medium than in the corresponding sulphuric acid-water optimum. The maximum amount of nitration in sulphuric acid-water mixtures was 93.5% (101) for 0.2M solutions and in sulphuric acid-acetic acid was 99% for 0.01M solutions. The situation is even more in favour of the acetic acid media than these results imply as the amount of nitration decreases with increasing initial concentration of reagent. However this more effective nitrating power is offset by a decomposition of nitroguanidine other than by denitration (noted in IIIC p. 63).

Beyond the point of maximum nitration (85-88% H_2SO_4) ionisation of nitric acid to nitronium ion becomes too great to permit the use of equation [25]. A modified version making allowance for this ionisation has been used. Hardy-Klein considered the extent of nitric acid ionisation quantitatively in her treatment of the

equilibrium data for N-methyl-N'-nitroguanidine (11) but she did not succeed in explaining the fall of K beyond the maximum. If the nitration rate reaches a maximum about 90% H₂SO₄ (as is the case with aromatic nitration) and the denitration rate continues to increase (as is found for 2-nitrimino-1;3-diazacyclopentane) the picture is qualitatively correct.

E. Nitration.

Velocity constants for the back nitration reaction may be obtained indirectly from the equilibrium products (K) and the denitration velocity constants (k_1), because $K = k_2/k_1$. Values of k_2 calculated from this expression are given in Table XVI. Values of k_2 were also obtained from velocity measurements of the nitration of guanidine in sulphuric acid-acetic acid mixtures and are given in Table XVII.

Table XVI. Nitration in Sulphuric Acid - Water Mixtures.

<u>2-Nitrimino-1;3-diazacyclopentane.</u>		<u>4-Methyl-2-nitrimino-1;3-diazacyclopentane.</u>					
<u>Concn. 0.008M.</u>		<u>Temp. 25°C.</u>		<u>Concn. 0.01M.</u>		<u>Temp. 25°C.</u>	
<u>% H₂SO₄</u>	<u>k₂</u>	<u>% H₂SO₄</u>	<u>k₂</u>	<u>% H₂SO₄</u>	<u>k₂</u>	<u>% H₂SO₄</u>	<u>k₂</u>
76.1	0.00877	85.1	1.106	76.1	0.0107		
78.6	0.0460	87.5	3.69	81.9	0.185		
81.2	0.159	89.9	9.11	83.3	0.451		
81.9	0.248	92.6	2.26	85.1	0.933		
83.3	0.519			87.5	3.418		

Table XVI. (contd.)

<u>2-Nitrimino-1:3-diazacyclo-</u>		<u>N:N-dimethyl-N'-nitro-</u>		<u>5-Nitramino-1:2:4-</u>	
<u>hexane.</u>		<u>guanidine.</u>		<u>triazole.</u>	
<u>Concn. 0.01M</u>	<u>Temp. 25°C.</u>	<u>Concn. 0.01M</u>	<u>Temp. 25°C.</u>	<u>Concn. 0.01M</u>	<u>Temp. 25°C.</u>
<u>% H₂SO₄</u>	<u>k₂</u>	<u>% H₂SO₄</u>	<u>k₂</u>	<u>% H₂SO₄</u>	<u>k₂</u>
69.7	0.0378	69.7	0.00148	67.0	0.0240
72.8	0.462	72.8	0.0115	70.5	0.0813
74.8	1.73	74.8	0.0562	71.8	0.522
76.1	3.48	79.2	0.138	74.8	1.74
78.6	18.6	81.9	0.759	78.6	10.47

Table XVII. Nitration in Sulphuric Acid-Acetic Acid Mixtures.

<u>Guanidine Nitrate.</u>		<u>Concn. 0.013M.</u>		<u>Temp. 25°C.</u>	
<u>% H₂SO₄</u>	<u>k₂</u>	<u>% H₂SO₄</u>	<u>k₂</u>		
49.6	0.264	58.2	2.501		
52.7	0.457	60.3	5.45		
56.2	1.963				

Rates show a sharp increase with acid concentration. The nitrating agent in sulphuric acid over 85% strength has been shown to be the nitronium ion. Although its concentration below this strength is so small as to be undetectable by the usual physical methods, the nitronium ion is still an effective nitrating agent, as the order of

nitration rate increase with acid concentration is similar to that above 85% acids.

If the nitronium ion is the nitrating agent, then a relation between $\log k_2$ and the acidity function J_0 may be derived. If $\log k_2$ from Table XVI is plotted against the various J_0 scales, a rough dependence is observed and the slopes all approximate to unity as seen in Table XVIII and Fig. 14. But in view of the inaccuracy of k_2 values (especially where denitration is extensive) and the uncertainties of all the J_0 scales, no reliable conclusion can be reached concerning the relationship of the rate and the acidity scales.

Table XVIII

<u>Compound.</u>	<u>Slopes of $\log k_2$ against</u>		
	J_0	J_0'	C_0
2-nitrimino-1:3-diazacyclopentane	+0.76		1.0
4-methyl-2-nitrimino-1:3-diazacyclopentane	+0.70		-0.80
5-nitramino-1:2:4-triazole	+0.97	-1.04	-1.3
2-nitrimino-1:3-diazacyclohexane	+0.83		-1.25
N:N-dimethyl-N'-nitroguanidine	+0.94		-1.25
nitroguanidine (102)	+0.95		-1.13

J_0 = data of Bevan and Williams (88)

J_0' = data of Gold and Hawes (87)

C_0 = data of Deno, Schriesheim and Jaruzelski (89, 90).

If the theoretical rate of guanidine nitration is given by

rate = $k (\text{NO}_2^+)(\text{GH}^+) / f^\ddagger$ where G is the neutral guanidine molecule and f^\ddagger is the activity coefficient of the transition state.

and the experimental rate = $k_2 [\text{HNO}_3] [\text{GH}^+]$ where $[\text{HNO}_3]$ is the stoichiometric nitric acid concentration and $[\text{HONO}_2]$ is the concentration of molecular nitric acid.

$$\therefore k_2 [\text{HNO}_3] [\text{GH}^+] = k (\text{NO}_2^+)(\text{GH}^+) / f^\ddagger$$

$$\therefore k_2 = k (\text{NO}_2^+)(\text{GH}^+) / [\text{HNO}_3] [\text{GH}^+] f^\ddagger$$

$$\therefore \log k_2 = \log k + \log [\text{NO}_2^+] / [\text{HNO}_3] + \log f_{\text{NO}_2^+} \cdot f_{\text{GH}^+} / f^\ddagger$$

Now $J_0 = -pK_{\text{ROH}} - \log [R^+] / [\text{ROH}]$ where $K_{\text{ROH}} = (R^+)(\text{H}_2\text{O}) / (\text{ROH})(\text{H}^+)$
 $= -pK_{\text{HONO}_2} - \log [\text{NO}_2^+] / [\text{HONO}_2]$

In media below 84% H_2SO_4 $[\text{HONO}_2] \approx [\text{HNO}_3]$

$$\therefore \log k_2 = \log k - J_0 - pK_{\text{HONO}_2} + \log f_{\text{NO}_2^+} \cdot f_{\text{GH}^+} / f^\ddagger$$

Thus $\log k_2 + J_0$ should be constant in such media provided that the activity coefficient ratio is also constant.

F. Substituent Effects.

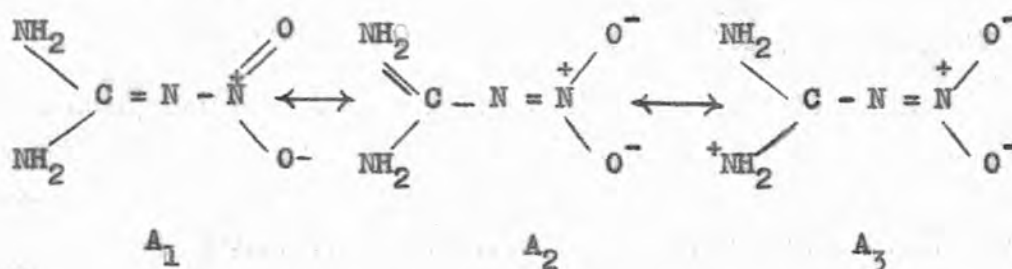
Various properties of the nitroguanidines studied such as ultra-violet absorption spectra, pKa values and the rates of nitration and denitration, vary in a definite manner according to the particular substituents on the nitroguanidine molecule. For instance, 2-nitrimino-1:3-diazacyclopentane and its 4-methyl analogue were the two weakest bases and had the highest values of E_{max}. and the slowest rates of denitration. The various properties (with respect to sulphuric acid) for each compound are collected in Table XIX.

Table XIX.

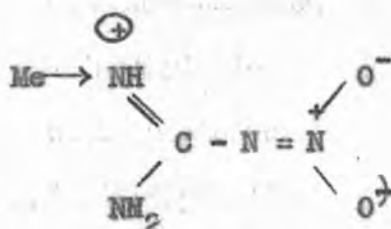
<u>Compound</u>	<u>Rel. Rate of Denitration</u> (mins. ⁻¹)	<u>Rel. Rate of nitration</u> (m.l. ⁻¹)	<u>pKa</u>	<u>E_{max}. λ_{max}.</u> (free base)	<u>E_{max}. λ_{max}.</u> (first ion)	<u>Ref.</u>
5-Nitramino-1:2:4-triazole.	16.6	32.4		12400 2820		
2-Nitrimino-1:3-diazacyclohexane.	8.5	42.7	-0.71	15450 2680	9700 2315	
NN-Dimethyl-N'-nitroguanidine.	6.6	2.0	-1.20	11350 2710	8010 2250	
NN'-Dimethyl-N''-nitroguanidine.	6.3	.465		13200 2675		(11)
N-Methyl-N'-nitroguanidine.	3.8	5.4	-0.86	14040 2670	8700 2260	(11)
Nitroguanidine.	1	1	-0.96	14400 2640	9940 2250	(12)
4-Methyl-2-nitrimino-1:3-diazacyclopentane.	.41	.063		17140 2660		
2-Nitrimino-1:3-diazacyclopentane.	.33	.083	-1.36	16170 2655	9440 2260	

a) Spectra of free bases in dilute acid solution.

Nitroguanidine has an ultra-violet absorption spectrum consisting of a structureless band with a maximum extinction $E_{max.} = 14,400$ at 2640\AA and a smaller band at 2300\AA . Addition of a methyl group causes a slight fall in $E_{max.}$ to $14,040$ and a bathochromic wavelength shift to 2665\AA .



The above three structures probably make the largest contributions to the ground state of the nitroguanidine molecule. From previous considerations (p.59) we supposed that A_1 was the most important factor. A methyl group on one of the amino nitrogens will increase electron availability on that nitrogen

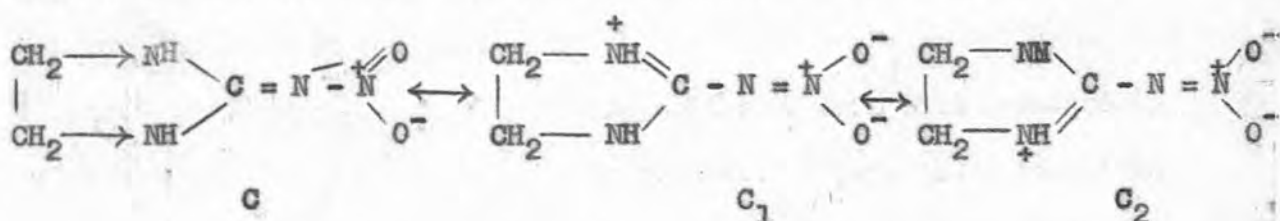


and so the B_2 form will increase in importance. This would result in the diminished $E_{max.}$ from that of nitroguanidine actually observed.

As nitroguanidine is planar (21) the experimental facts can also be explained by a non-planar methyl nitroguanidine molecule. If planarity of the molecule is sterically inhibited by the bulk of the methyl group the conjugation of the molecule would be reduced with the observed consequence in $E_{max.}$ and $\lambda_{max.}$

If a further methyl group is added a further decrease in E_{\max} , and λ_{\max} , is observed. N:N'-Dimethyl-N'-nitroguanidine has an extinction of 13200 at λ_{2675} while in the NN-dimethyl compound with E_{\max} . 11350 at $\lambda_{2710\text{\AA}}$, the effect is even more marked. Operation of the inductive effect or a further deviation from a planar structure could again account for the result. { Unlike benzamide and its N-methyl derivative, NN-dimethylbenzamide cannot have a planar structure because of the interference of the methyl groups. This is apparent in the ultra-violet absorption ^{decrease.} (λ_{247}). }

The five-membered ring compound, 2-nitrimino-1:3-diazacyclopentane has a spectrum with E_{\max} . 16160 at 2655\AA . This compound is necessarily planar. The inductive effect will operate equally on each nitrogen and so the forms C_1 and C_2 will contribute equally to the electron distribution of the molecule.



The 4-methyl analogue, E_{\max} . 17140 at λ_{2660} is not symmetrical but it is necessarily planar.

Introduction of trimethylene however, causes a drop in E_{\max} . to 15450 at $\lambda_{2680\text{\AA}}$ although a spectrum comparable to that of 4-methyl-2-nitrimino-1:3-diazacyclopentane might be expected. Inhibition

of planarity by reason of the steric requirements of the 6-membered ring might produce this result. N-Cyclohexyl-N'-nitroguanidine has ϵ_{max} 14,000 at 2690Å. Here the bulky substituent, itself non-planar, inhibits resonance.

5-Nitramino-1:2:4-triazole, a five-membered ring, has ϵ_{max} 12,400 at 2820Å. The bathochromic shift may be attributed to the third ring nitrogen. The ring must be strained due to the presence of three nitrogens and two double bonds.

b) pKa Values.

Nitroguanidine has a pKa of -0.96 as calculated from the results of de Vries and St. Clair Gantz (31) by the method used in Section II, employing the H_0 data of Hammett and Paul for hydrochloric acid (148). Addition of a methyl group should facilitate proton-uptake due to electron release, and so the pKa should be higher. It is in fact -0.86 for N-methylnitroguanidine (11). In the face of this argument NN-dimethyl-N'-nitroguanidine should be a still stronger base, but it has a pKa of -1.20. The inductive effect has been superceded, possibly by steric hindrance of the dimethylamino group to the incoming hydrogen.

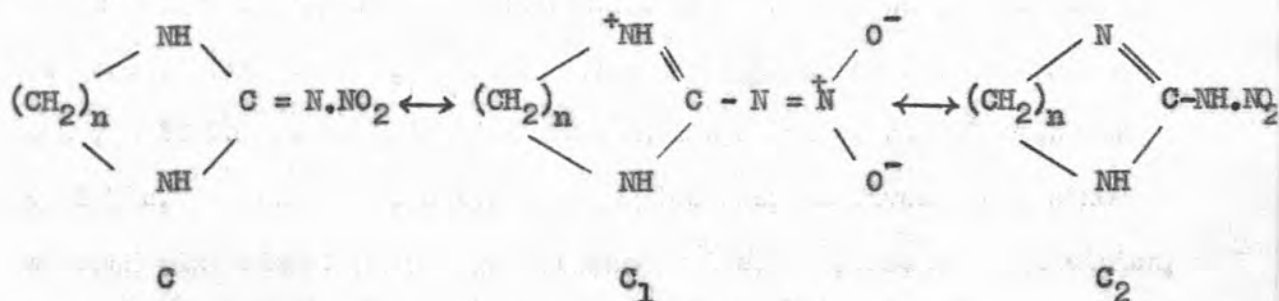
2-Nitrimino-1:3-diazacyclopentane is the weakest base and the corresponding 6-membered ring is the strongest. Brown, Brewster and Schechter (149) have interpreted the chemical behaviour of certain five- and six-membered ring compounds in terms of the stability of endo-

or exo-double bonds connected with the systems. The generalisation which they make is that reactions will proceed in such a way as to favour the formation or retention of an exo-double bond in a five-membered ring and to avoid it in a six-membered ring. The compounds they discussed were simple and substituted hydrocarbons, cyclic esters (for instance, ethylene and trimethylene carbonates), lactones, thiolactones, imides and lactams. In all cases except that of the lactams, literature surveys provided evidence that the five-membered rings with exo-double bonds and the six-membered rings with endo-double bonds were the more stable isomers. Both five- and six-membered lactam rings were stable but no quantitative data on the relative stabilities were available. Brown & Co. cited no examples where a five- and a six-membered ring with 2 nitrogens possessed widely different reactivities.

A specificity of reaction for 2-nitrimino-1,3-diazacyclopentane as opposed to the corresponding six- and seven-membered rings was noted by McKay and Wright (8) and McKay and Manchester (19). The mono-nitro five-membered ring can be denitrated in acetic anhydride, as can its 4-methyl analogue, but the corresponding six- and seven-membered rings are preferentially hydrolysed to cyclic ureas. The planarity of the five-membered ring and consequent resonance stabilisation are suggested to account for this behaviour.

Jones (150) found a hundredfold difference in the rates of alkaline hydrolysis of cyclic nitramines with five- and six-membered rings. Cyclotrimethylene trinitramine decomposed 118 times faster than 1:3-dinitro-1:3-diazacyclopentane. Jones postulated a greater ring strain in the transition state for this latter compound, which would slow the reaction. If Brown's concept applies here the explanation might well involve formation of endo or exo double bonds.

Brown's postulate may be applicable to the case of the pKas we are considering.



C₁ and C₂ each have two equivalent forms.

The structures C, C₁, and C₂ probably represent fairly adequately the actual electron distribution in the cyclic nitroguanidines. From spectral considerations we have concluded that the nitroguanidine molecule has predominantly the electron distribution of C. In this case, the six-membered ring will have an exo double bond. If the resultant protonated molecule can by protonation create resonance structures which avoid an exo double bond, then addition of a proton

to the six-membered ring will occur at a lower acidity than addition to the five-membered ring. Spectral data for the protonated form of cyclic nitroguanidines were previously (pp. 61) interpreted in favour of a molecule with an endo double bond. Thus the relative basicities of the five- and six-membered ring nitroguanidines favour Brown's hypothesis.

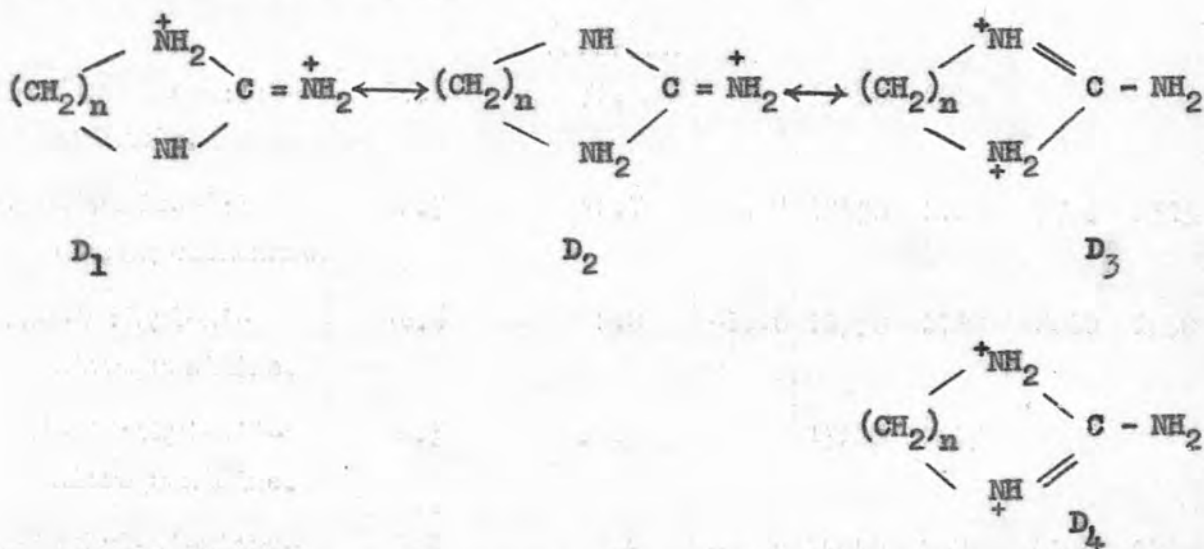
c) Denitration rates.

The order of rate increase for nitroguanidines is the same as that of pKa increase, except for N:N-dimethyl-N'-nitroguanidine. A plot of pKa against the logarithm of the relative rate constant obtained from Table XIX is a straight line. See Fig. (13). If the order of increase of the second pKa for these compounds is the same as for the first pKa, then the observed order of rate increase should be obtained.

The molecules for which the description strained or non-planar was put forward in a) above are those which denitrate most quickly. This suggests a transition state involving great steric strain and so the molecules in the most strained conformation react fastest. The planar molecules, nitroguanidine and the diazacyclopentanes require more energy to reach the strained transition state, and so react more slowly. The denitration rates vary qualitatively in the way that can be predicted from spectral evidence of non-planarity.

d) Nitration rates.

The nitration of 2-nitrimino-1,3-diazacyclohexane is fastest—43 times that of nitroguanidine in 80% acid. The triazole is 25% slower, although its denitration was actually faster than that of the hexane. Methylnitroguanidine has a rate of the expected order but the NN-dimethyl and NN'-dimethyl compounds are much slower. The entrance of the nitronium ion is probably sterically hindered by the presence of the methyl groups. The rates of the two diazapentanes are again similar and even slower than for nitroguanidine. The diazacyclohexane nitrates 500 times faster than the diazacyclopentane. The



aminocycloalkane which undergoes nitration is possibly in some form intermediate between D_1 , D_2 , D_3 , D_4 . The five-membered ring will probably incline more to structures such as D_1 and D_2 , while the six-membered ring will be nearer to D_3 and D_4 according to Brown's

hypothesis. If the nitrating entity is the positively charged nitronium ion, as seems quite probable, then the nitration of the five-membered ring will be retarded by the repulsion between the positive charges at the point of nitration and the nitronium ion.

G. The Ho Function in Perchloric Acid.

The original Ho scale in perchloric acid, measured by Hammett and Deyrup (54) extends only as far as 61% perchloric acid, although perchloric acid is commercially available and readily handled in strengths up to 72%. Hammett and Deyrup found that 4-nitrodiphenylamine and benzalacetophenone, both of which were successfully used in sulphuric acid, decomposed irreversibly in perchloric acid of strength more than 65%, and so they feared to use higher acids in case of explosion.

Various indicators of suitable strength for extending the scale have been prepared - benzalacetophenone, 2:4-dinitrodiphenylamine and 2:4-dinitronaphthylamine. Benzalacetophenone was rejected because it was unstable to ultra-violet light and could not therefore be estimated spectrophotometrically. (This difficulty is also recorded by Thomas and Branch (51). 2:4-Dinitrodiphenylamine formed a rapidly darkening, brown solution in 72% perchloric acid, but the solution in concentrated sulphuric acid was pale yellow as expected

from loss of conjugation of the amino group on protonation (the colour in dilute acid is orange). The material must have undergone decomposition in perchloric acid similar to that observed by Hammett and Deyrup (54) for 4-nitrodiphenylamine. 2:4-Dinitronaphthylamine was found to be perfectly stable in concentrated perchloric acid and its ionisation was investigated. The weakest indicator used by Hammett and Deyrup (54) in the construction of their scale, 2:4-dinitroaniline, received only meagre attention and it has been re-investigated.

The ionisation ratios of these two compounds were obtained by the method on p. 52 and are shown in Table XVIII.

A plot of $\log \frac{[B]}{[BH^+]}$ against % $HClO_4$ for 2:6-dichloro-4-nitroaniline (data of Hammett and Deyrup), 2:4-dinitroaniline and 2:4-dinitronaphthylamine is shown in Fig. 16. From such a graph the difference in pK_a of the indicators may be obtained using Hammett's value of -3.18 for 2:6-dichloro-4-nitroaniline.

$$H_o = pK_a + \log \frac{[B]}{[BH^+]}$$

Values of H_o can be calculated from this equation and are shown in Table XVIII. These values fit smoothly over Hammett and Deyrup's scale. The last two points are probably inaccurate, because the slightest error in extinction coefficient at extreme values of ionisation is greatly magnified in derivation of $\frac{[B]}{[BH^+]}$.

Table XXI.

<u>2:4-Dinitraniline</u> pKa = -4.36			<u>2:4-Dinitronaphthylamine</u> pKa = -6.37.		
<u>% HClO₄</u>	<u>log [B] / [BH⁺]</u>	<u>-Ho</u>	<u>% HClO₄</u>	<u>log [B] / [BH⁺]</u>	<u>-Ho</u>
49.6	1.27	3.09	59.6	1.29	5.09
50.3	0.80	3.56	61.4	0.90	5.47
53.0	0.55	3.81	62.0	0.84	5.53
54.2	0.31	4.05	62.7	0.58	5.79
55.5	0.04	4.32	64.0	0.25	6.12
57.2	-0.28	4.64	65.0	-0.03	6.40
59.5	-0.78	5.14	65.4	-0.05	6.42
62.2	-1.25	5.61	66.4	-0.40	6.77
			67.35	-0.61	6.98
			67.44	-0.69	7.06
			68.3	-0.87	7.24
			70.2	-1.31	7.68
			71.3	-1.70	8.07

Satchell, (137), in an attempt to relate the rate of hydrogen-isotope exchange between deuterated aromatic compounds and perchloric acid, to the acidity of the medium, used values of Ho for perchloric acid extrapolated from Hammett's results beyond the 60% region.

log λ (where λ is the rate of deuterium exchange) plotted against these Ho values for benzene and m-anisole gave rise to slopes of

-1.12 and -0.98. Recalculation of these slopes using the values of H_0 derived in this work gave -1.25 and -0.90. The slope for benzene in sulphuric acid mixtures is -1.36. (134). Satchell's extrapolation appears to have been a straight line continuation of the final portion of Hammett's graph of H_0 against % $HClO_4$, an unwise procedure in view of the non-linearity of H_0 increase with acid concentration.

H. The H_+ Function in Sulphuric and Perchloric Acids.

When Hammett and Deyrup first proposed and measured the acidity function H_0 in sulphuric and perchloric acids, they postulated other functions, for instance H_+ , which would be valid for positively-charged bases becoming doubly charged and defined as

$$H_+ = -\log a_{H^+} \cdot \frac{f_{BH^+}}{f_{BH_2^{++}}} \quad \text{where } BH^+ \xrightleftharpoons{H^+} BH_2^{++},$$

and H_- , valid for negatively charged bases becoming neutral on acceptance of a proton, for which

$$H_- = -\log a_{H^+} \cdot \frac{f_{B^-}}{f_{BH}} \quad \text{where } B^- \xrightleftharpoons{H^+} BH \quad (54).$$

These functions, as Hammett has pointed out, do not necessarily vary with medium in the same fashion as H_0 (54). In glacial acetic acid Hammett gives a value of $H_0 = + 3.5$ while H_- has a high negative value (152). Coryell and Fix however claim that H_0 and H_- become

parallel above 4M sulphuric acid with a constant difference of 0.8 log units (76). These authors assume that H_- , H_0 , H_+ , etc. will be parallel functions of medium composition.

The acidity function G of Michaelis and Granick (79) is based on the ionisation in sulphuric acid up to 11M of several substituted thiazine indicators, taking up variously from one to three protons. The slope of a plot of this function against molarity of sulphuric acid was 0.57 while that of H_0 was 0.52 which the authors considered an excellent agreement in view of the different methods of measurement.

Lewis and Bigeleisen (78) attempted to extend the H_0 scale into sulphuric acid oleum using some H_3^+ indicators of the fluorescein type, but their results are not in agreement with those of Brand (58) whose indicators took up only one proton. Brand, Horning and Thornley actually used an H_+ indicator, the *m*-nitroanilinium cation, in a further extension of the H_0 scale in oleum (77). If $H_+ - H_0$ is zero or constant then from the definitions of the two, $\log [BH^+] / [BH_{2++}] - \log [C] / [CH^+]$ will be constant, where C is an H_0 indicator, and BH^+ is an H_+ indicator. A plot of such quantities against % acid in the results of Brand, Horning and Thornley shows that $\log [BH^+] / [BH_{2++}]$ is parallel to $\log [C] / [CH^+]$. The parallelism of H_+ and H_0 is thus established for oleums. It is not necessarily established for less concentrated acid however. A divergence of H_- from H_0 has

been observed (152) below a certain acid strength. It was therefore necessary to measure H_+ in more dilute media.

The difference between H_+ and H_0 in 100% sulphuric acid has been estimated as -0.28 units (77), but the authors place little reliance on the calculation. The G function, established by Michaelis and Granick for multi-charged bases, is slightly more negative than H_0 (79). Rogers, Campbell and Maatman (80) used G and H_0 to calculate the second ionisation constants of substituted aminoazobenzenes and found a difference in absolute but not in relative values of pK. G, however, was not measured in the same way as H_0 , and it still seemed desirable to measure H_+ by Hammett's method.

The bases 4-nitro-1:2-phenylene diamine and 4-aminoacetophenone were found, on spectral evidence, (see, for example, Fig.15), to undergo two ionisations in suitable acid ranges. (152). The values of $\log \frac{[BH^+]}{[BH_2^{++}]}$ for the second ionisation of these compounds are given in Table XIX. These values are plotted against % H_2SO_4 in Fig. 1, and % $HClO_4$ in Fig. 16, alongside values of $\log \frac{[C]}{[CH^+]}$ taken from the results of Hammett and Deyrup.

The parallelism of H_0 and H_+ is thus established in perchloric and sulphuric acids. The functions as defined must be equal in very dilute acid, and so it seems probable that the two are identical over the whole range of sulphuric and perchloric acids.

Table XXI.

<u>4-Nitro-1:2-phenylene</u>		<u>4-Nitro-1:2-phenylene</u>		<u>4-Nitro-aceto-</u>	
	<u>diamine.</u>		<u>diamine.</u>		<u>phenone.</u>
<u>% HClO₄</u>	<u>log [BH⁺]/[BH₂⁺⁺]</u>	<u>% H₂SO₄</u>	<u>log [BH⁺]/[BH₂⁺⁺]</u>	<u>% H₂SO₄</u>	<u>log [BH⁺]/[BH₂⁺⁺]</u>
29.1	1.30	30.0	1.08	76.0	1.08
39.8	0.49	36.6	0.58	78.5	0.61
41.8	0.34	43.19	0.12	81.9	0.34
43.2	0.26	43.21	0.09	83.3	-0.05
44.5	0.17	46.8	-0.14	87.5	-0.55
46.7	0.01	52.4	-0.70	89.9	-0.81
48.4	-0.17	55.4	-1.01	92.6	-1.06
49.0	-0.30	pKa ^{II} = -2.67		pKa ^{II} = -7.65	
49.9	-0.31				
51.0	-0.48				
53.0	-0.71				
54.9	-0.95				
pKa ^{II} = -2.64					

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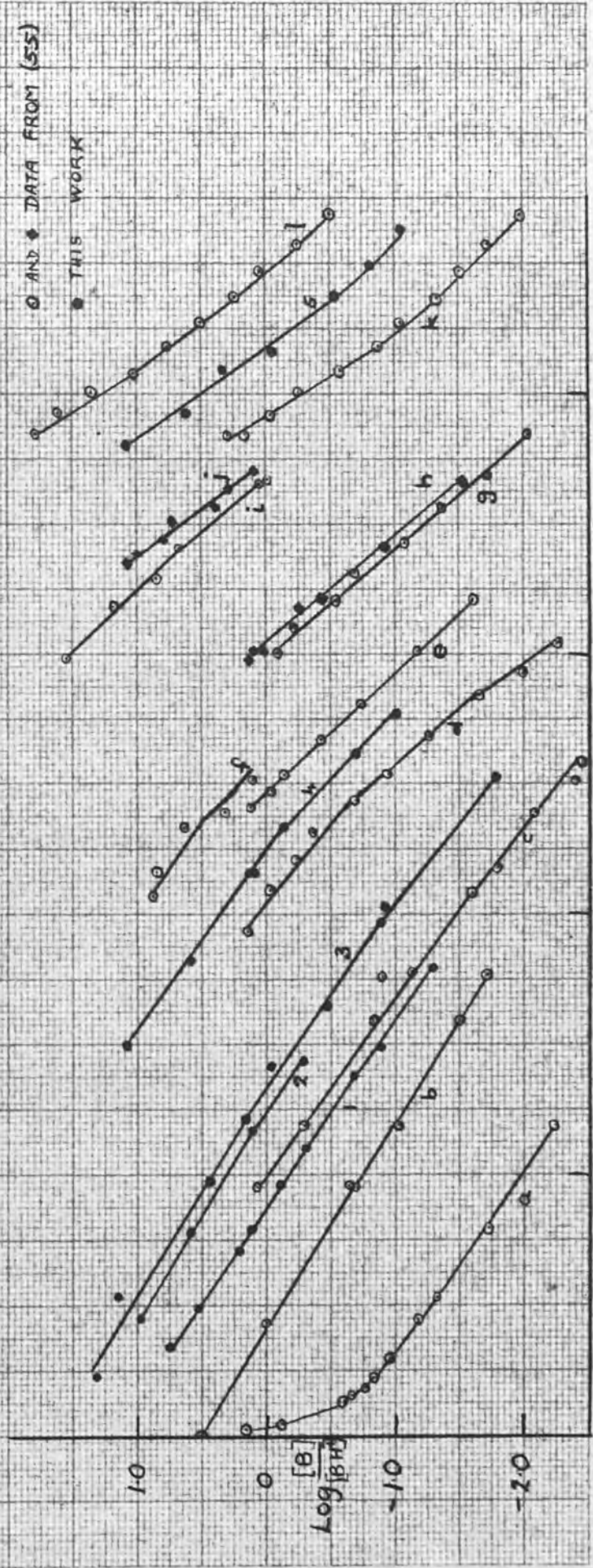
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Fig. 1. IONISATION OF INDICATORS IN SULPHURIC ACID

- | | | | | | |
|---|-----------------------------|---|------------------------------|---|-----------------------------------|
| a | 4-NITROANILINE | g | 2,4-DINITRO-6-METHYLANILINE | 1 | 2-NITRIMINO-1,3-DIAZACYCLOHEXANE |
| b | 2-NITROANILINE | h | 2,4-DINITROANILINE | 2 | N,N-DIMETHYL-N'-NITROGUANIDINE |
| c | 4-CHLORO-2-NITROANILINE | i | β -BENZOYL NAPHTHALENE | 3 | 2-NITRIMINO-1,3-DIAZACYCLOPENTANE |
| d | 4-NITRODIPHENYLAMINE | j | 4-BENZOYLDI PHENYL | 4 | 4-NITRO-2-AMINOANILINE |
| e | 2,4-DICHLORO-6-NITROANILINE | k | 6-BROMO-2,4-DINITROANILINE | 5 | 4-AMINOACETOPHENONE |
| f | 4-NITRAZO BENZENE | l | ANTHRAQUINONE | | |



20 40 60 80
 H_2SO_4

1.0
 0
 -1.0
 -2.0
 $\log \frac{[B]}{[BH^+]}$

Fig. 2.

RELATIONSHIP BETWEEN THE J_0 + C_0 SCALES.

○ J_0 GOLD + HAWES, J.C.S., 1961, 2102.

● J_0 BEVAN + WILLIAMS, CHEM + IND., 1955, 171.

○ C_0 DENO, JARUZELSKI + SCHRIESHEIM, J.A.C.S. 1955, 77 3064

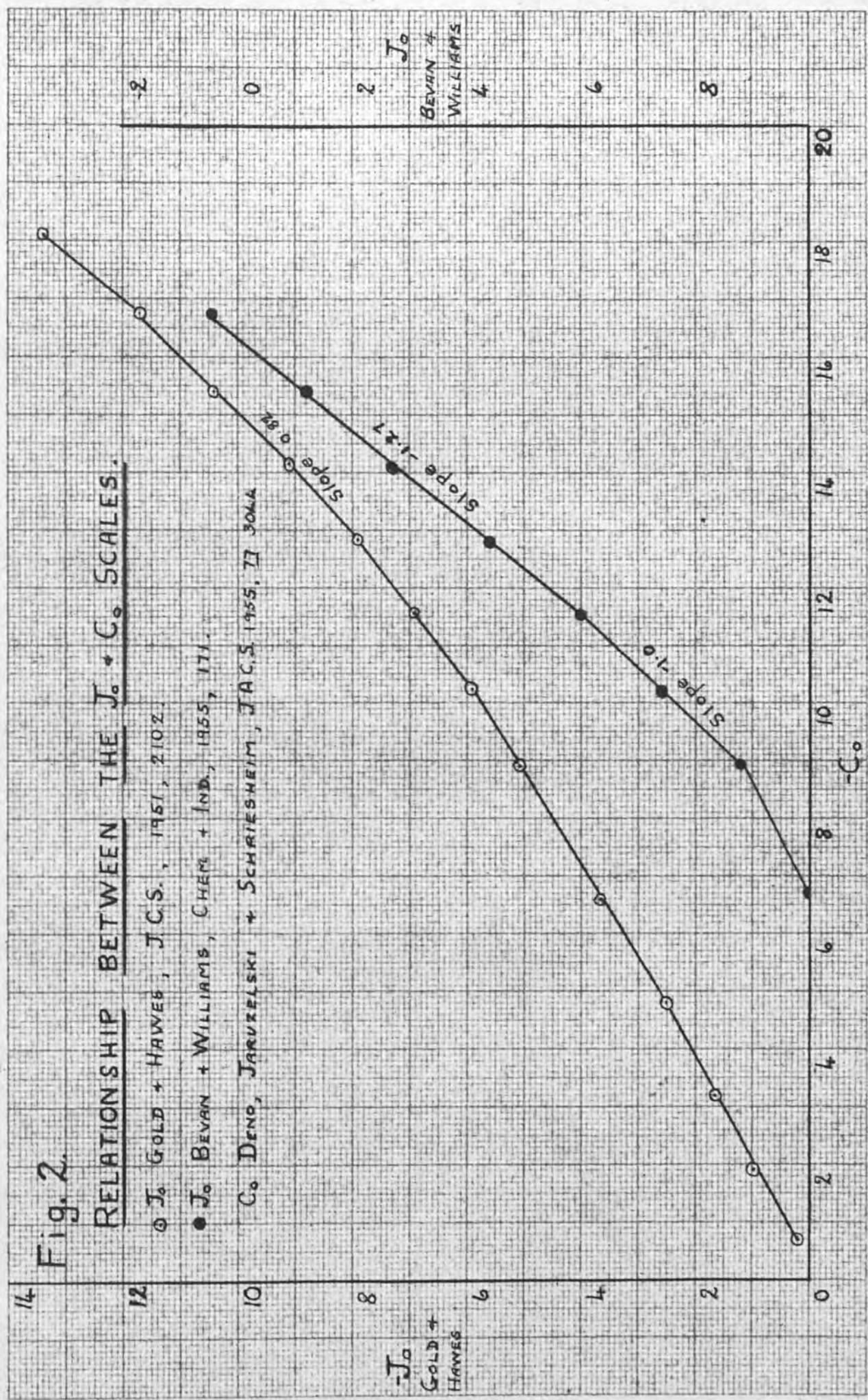


Fig. 3. COMPARISON OF SPECTRA OF NITROGUANIDINES AND NITRAMIDES

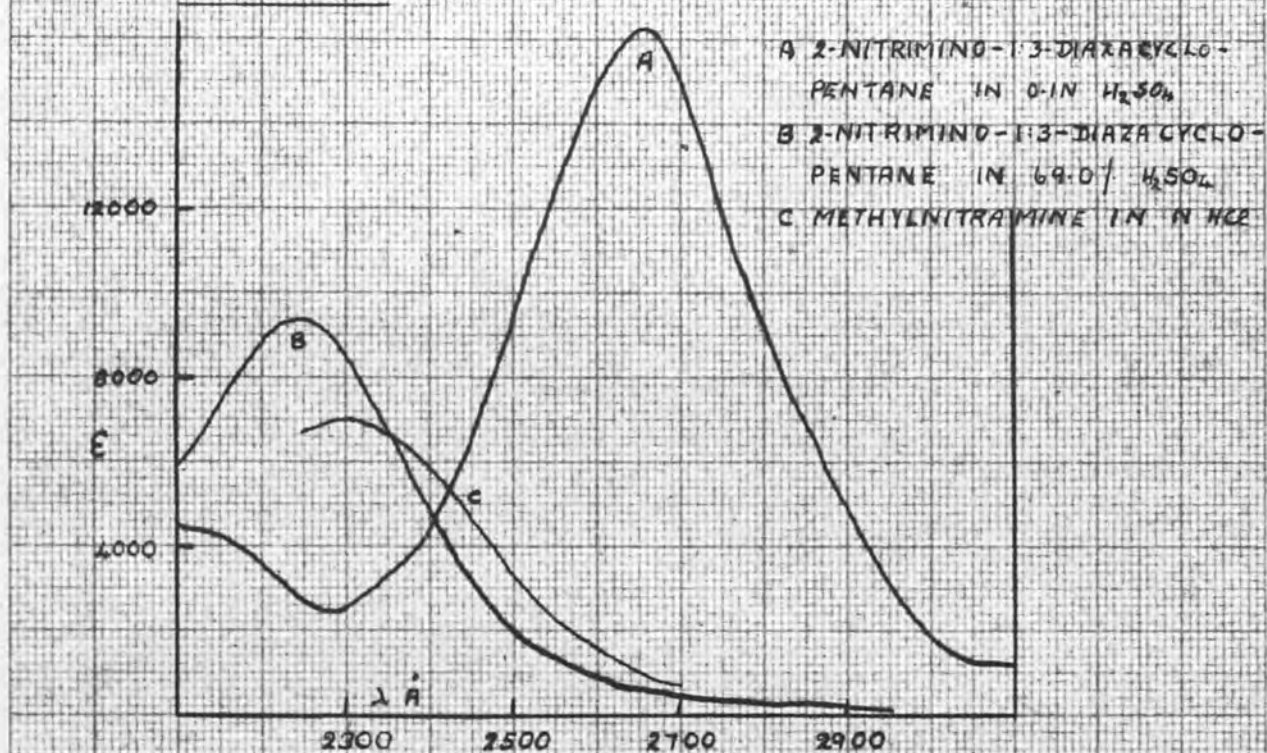


Fig. 4. SPECTRA OF NITROGUANIDINES IN WATER

- | | |
|--|----------------------------------|
| 1. 1-METHYL-2-NITRIMINO-1,3-DIAZACYCLO-PENTANE | 5. N-CYCLOHEXYL-N-NITROGUANIDINE |
| 2. 2-NITRIMINO-1,3-DIAZACYCLO-PENTANE | 6. N,N-DIMETHYL-N-NITROGUANIDINE |
| 3. 2-NITRIMINO-1,3-DIAZACYCLOHEXANE | 7. 5-NITRAMINO-1,2,4-TRIAZOLE |
| 4. NITROGUANIDINE | |

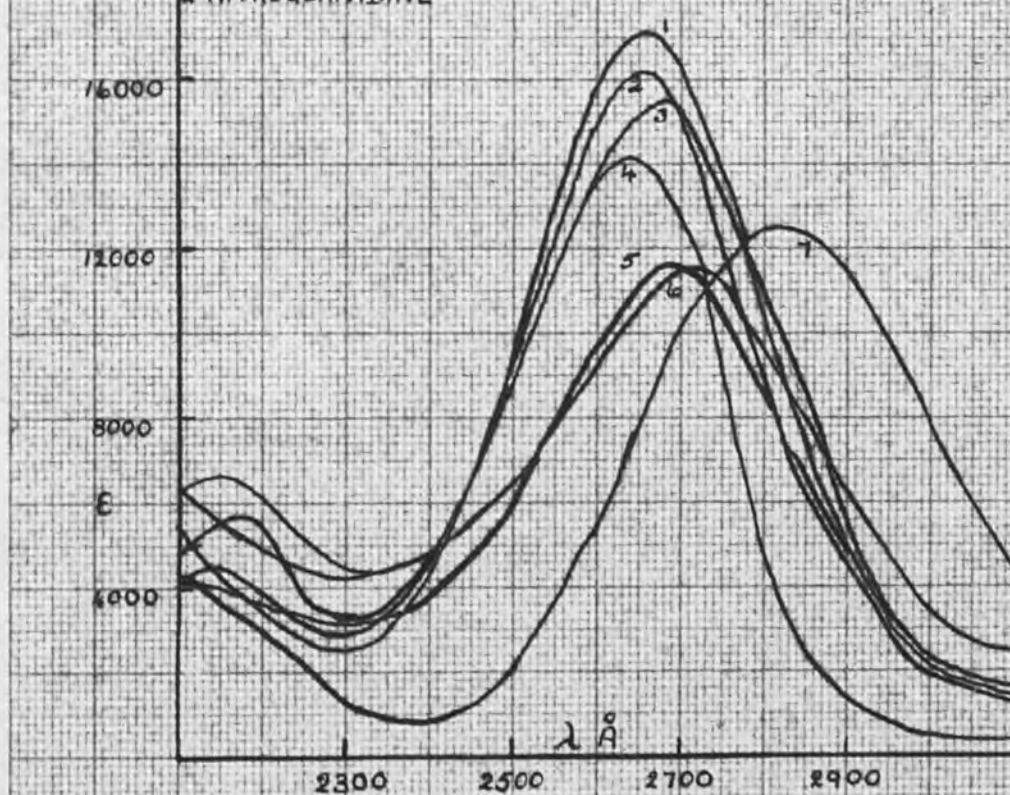


Fig. 5. DENITRATION OF 2-NITRIMINO-1,3-DIAZACYCLOPENTANE IN

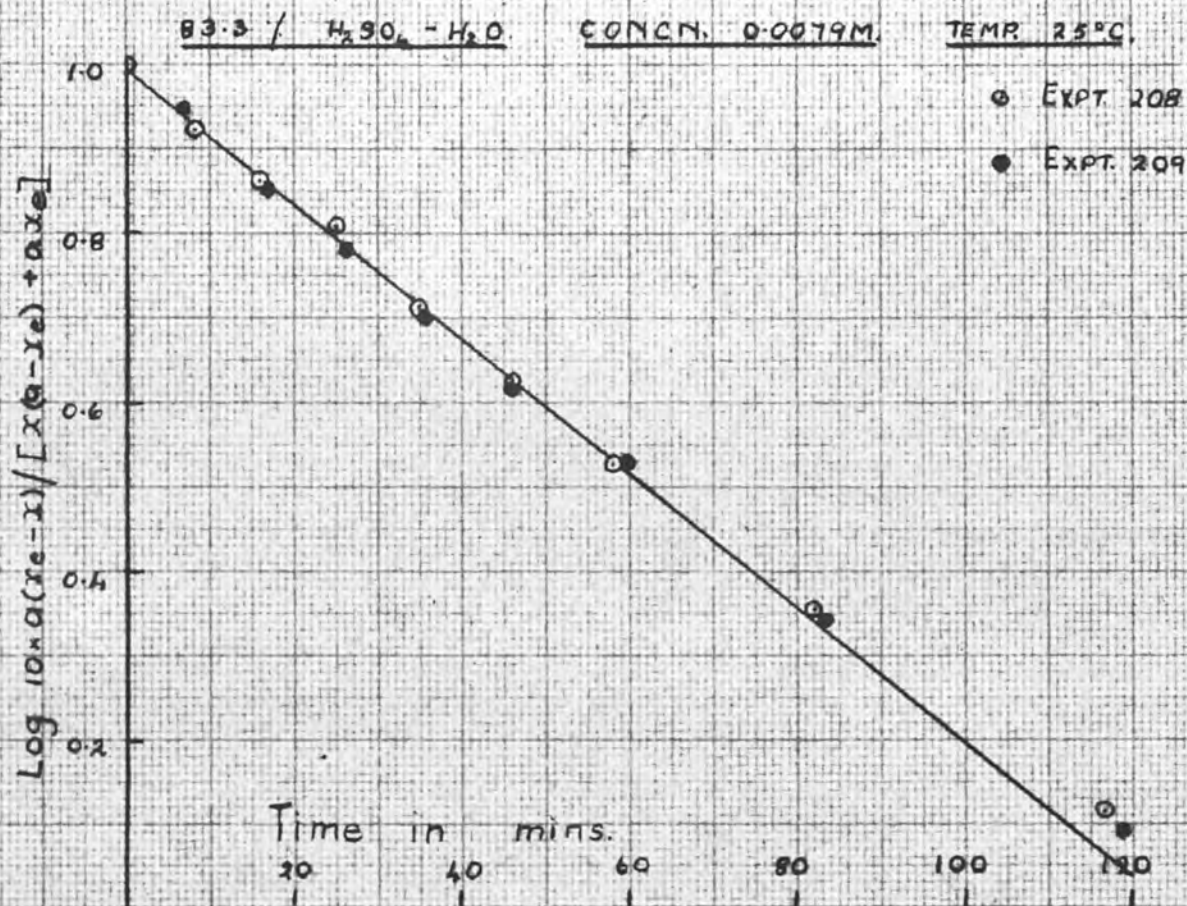


Fig. 6. DENITRATION OF 2-NITRIMINO-1,3-DIAZACYCLOHEXANE IN

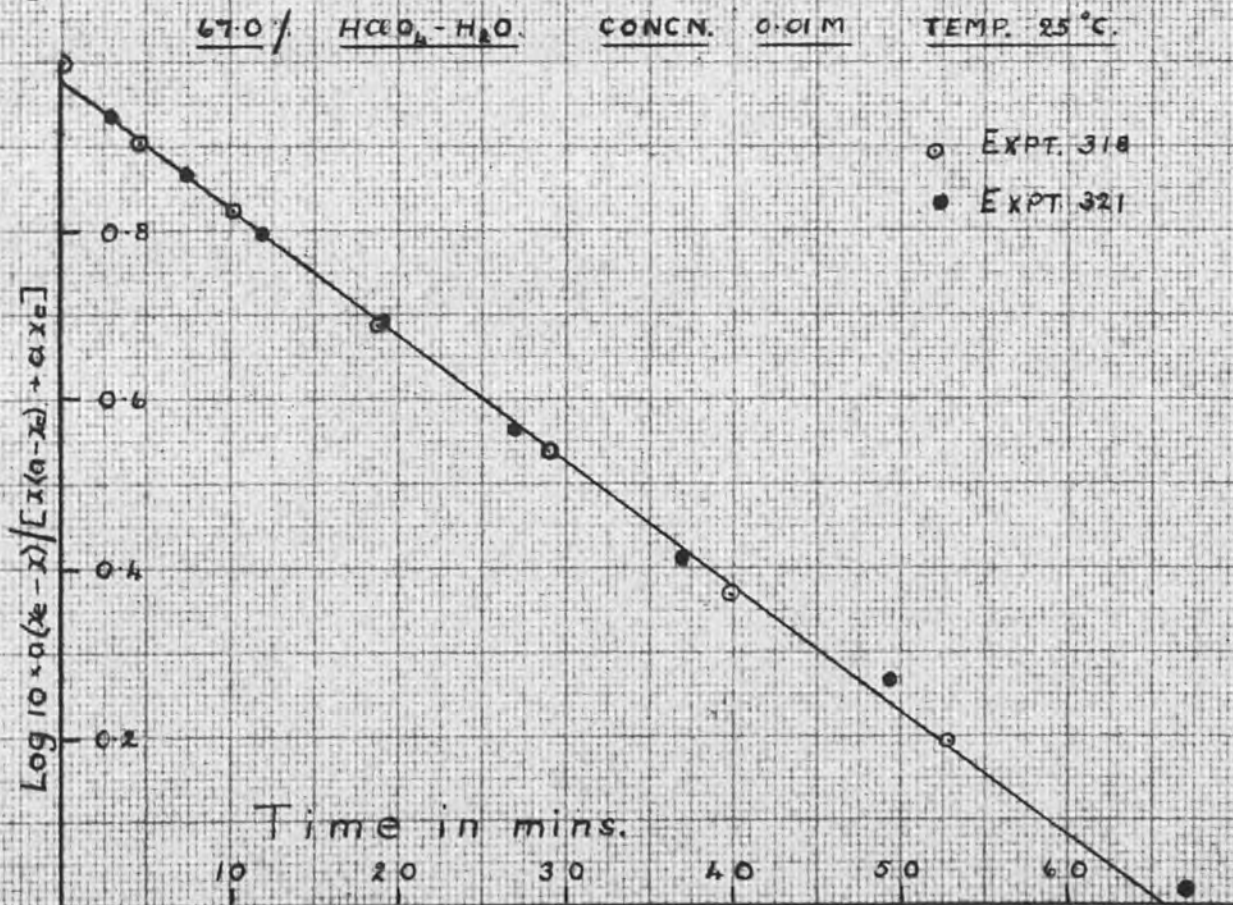


Fig. 7.

VARIATION OF LOG (RATE DENITRATION)
WITH % ACID.

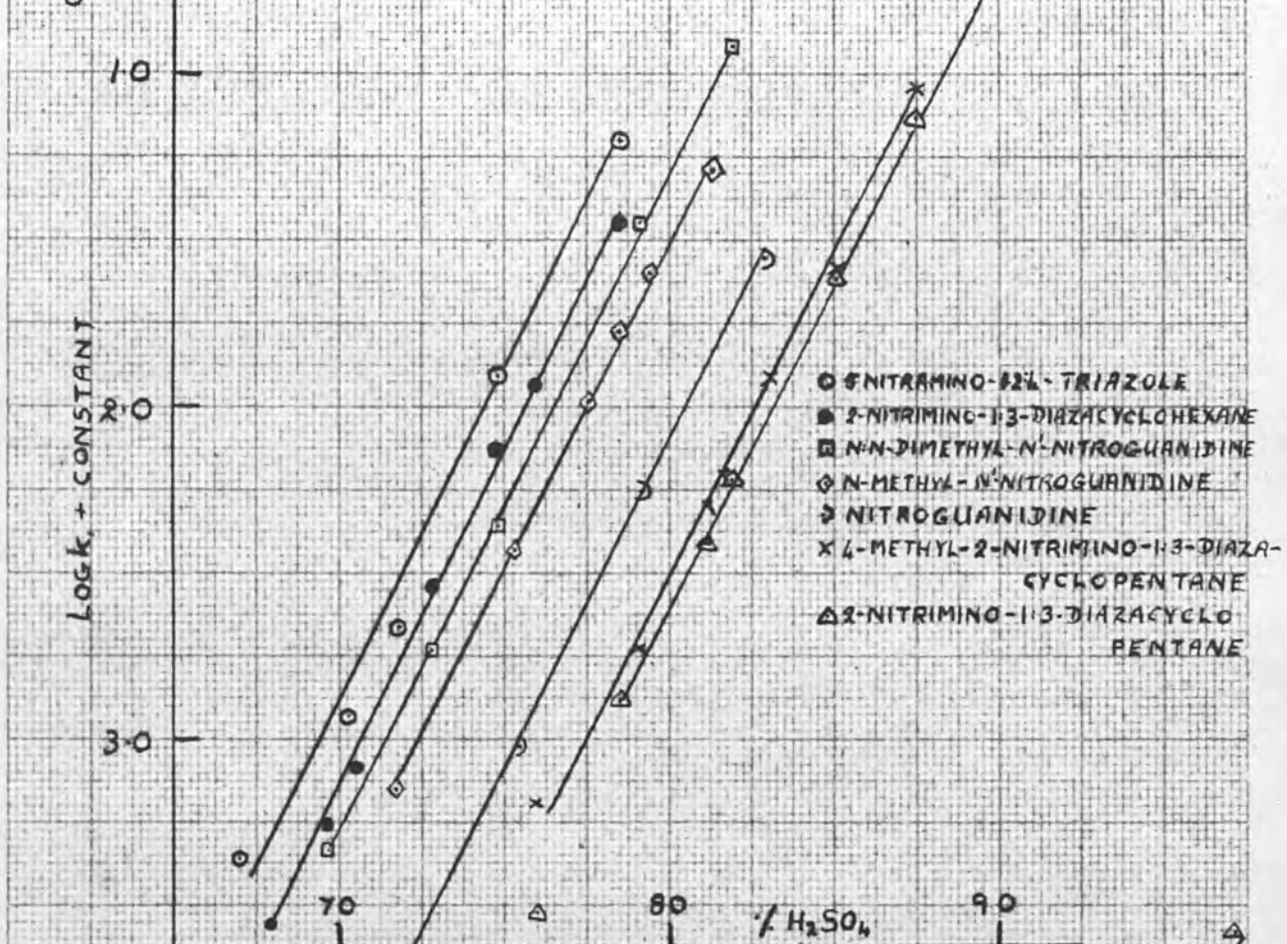


Fig. 8.

VARIATION OF LOG (RATE DENITRATION)
WITH H_0 .

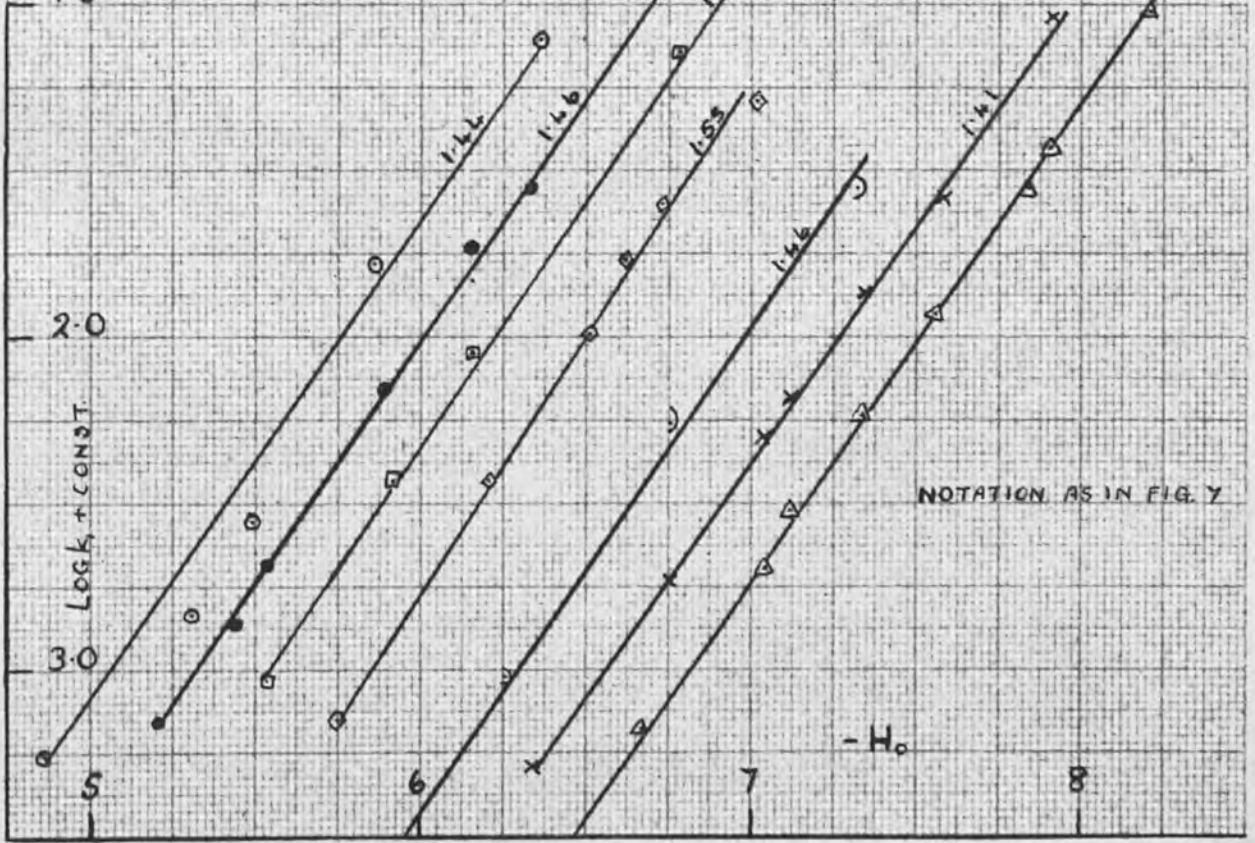


Fig. 9.

DENITRATION OF NITROGUANIDINES IN

H₂SO₄ AND HClO₄

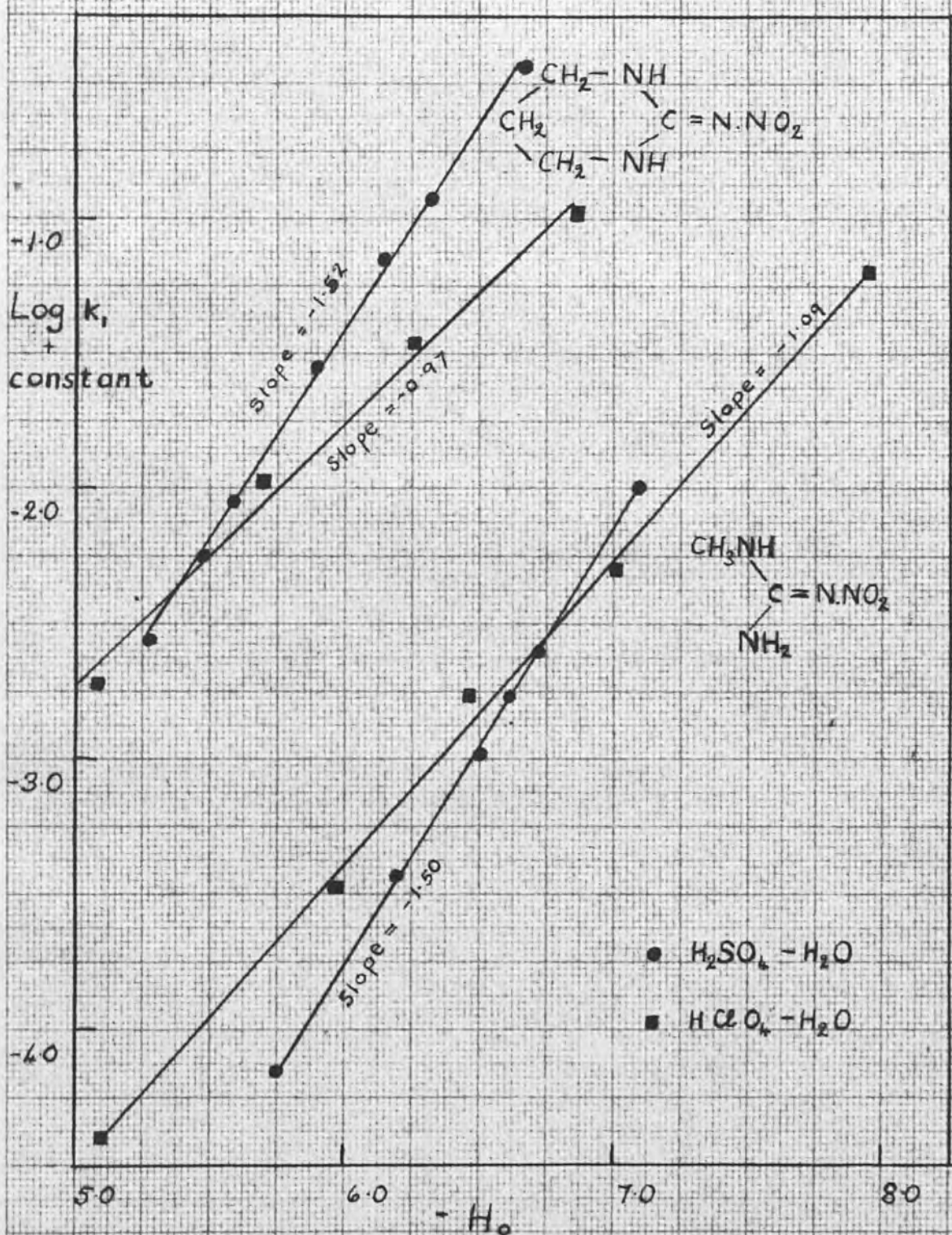
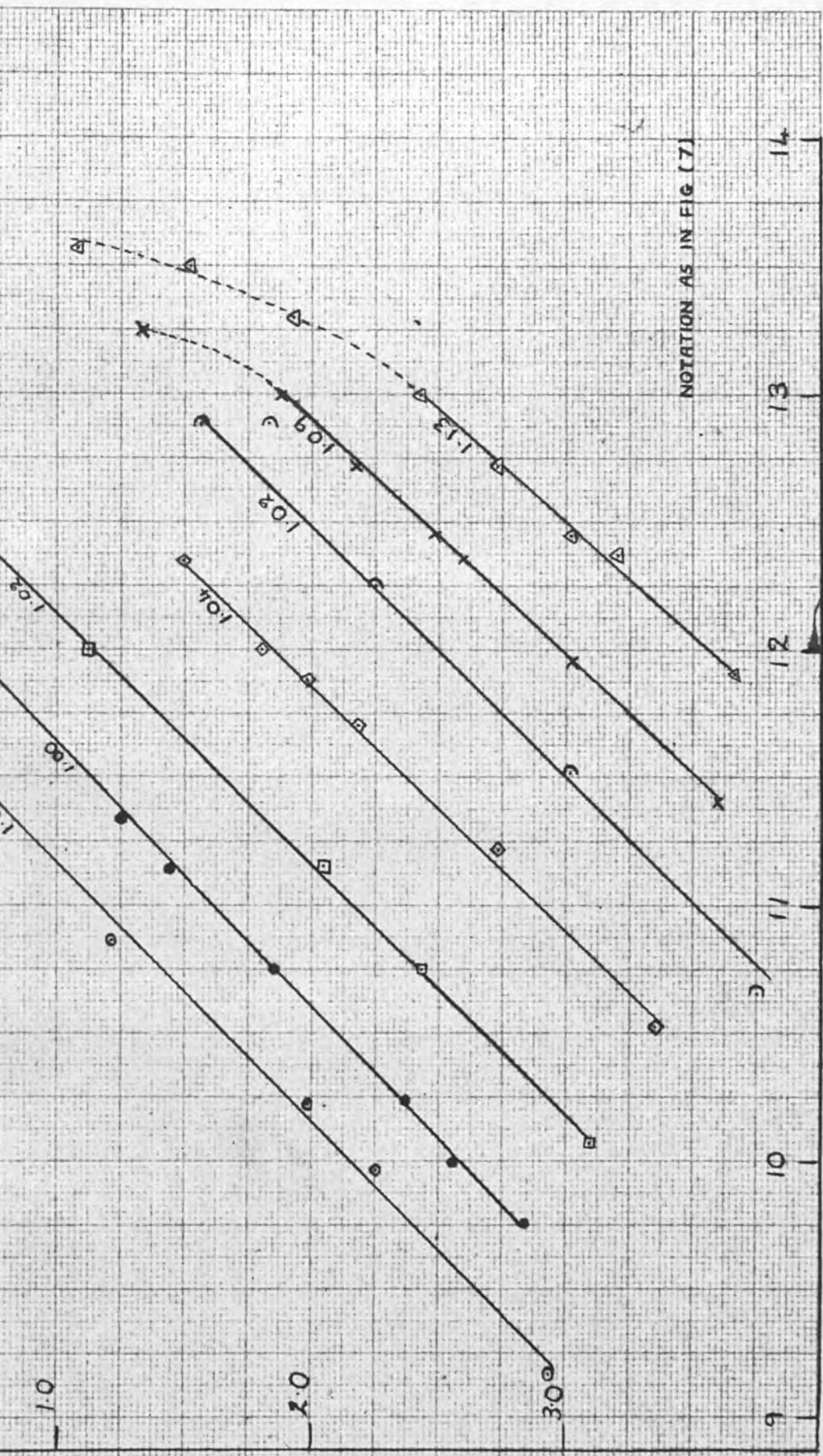


Fig. 10.

VARIATION OF LOG(RATE DENITRATION) WITH A
 FUNCTION OF ACID STRENGTH
 TEST OF EQUATION (23)



$$H_0 - \text{Log}(H_2SO_4) - \text{Log}(H_2O)$$

Fig. 11. EXTENT OF DENITRATION AT EQUILIBRIUM

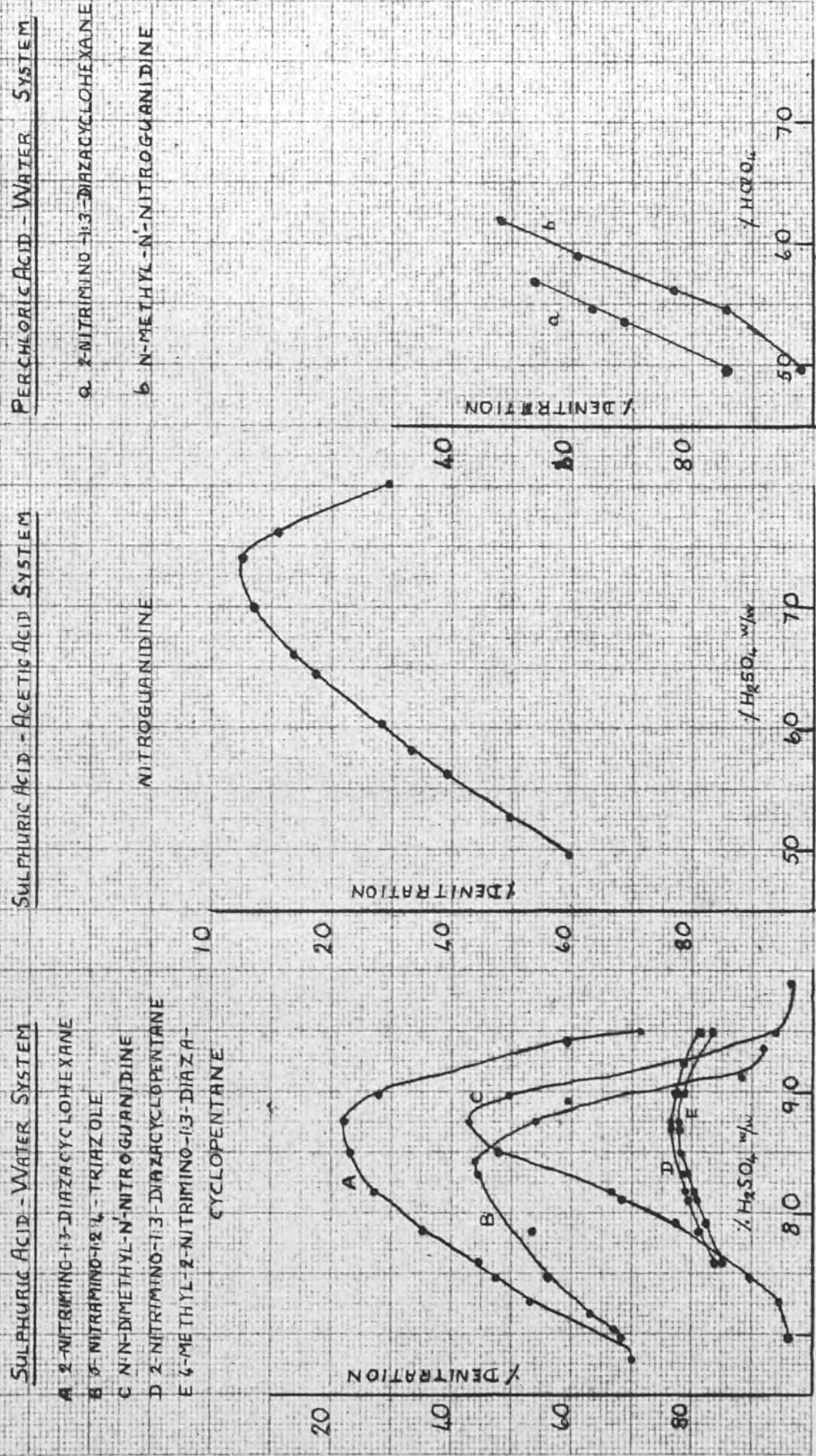


Fig. 13. RELATION BETWEEN pK_a AND RELATIVE RATE CONSTANT FOR PENETRATION OF VARIOUS NITROCHAMIDINES

NOTATION AS IN FIG. 7

- RESULTS FROM REF. (102) EXTRAPOLATED TO 0.01M CONC.
- ◇ RESULTS FROM REF. (11) EXTRAPOLATED TO 0.01M CONC.

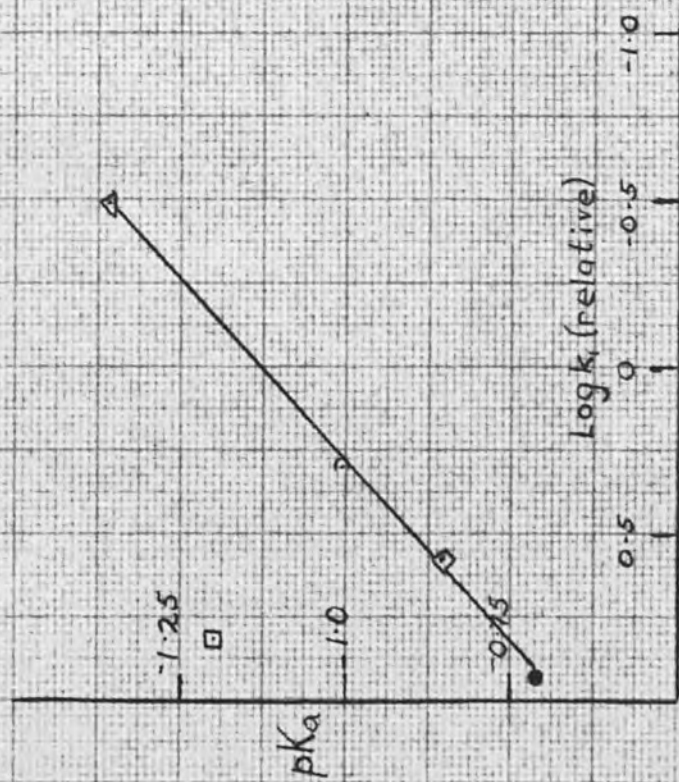


Fig. 12. RELATION BETWEEN EQUILIBRIUM CONSTANT AND ACTIVITY OF WATER (P/P_0) IN THE MEDIUM

NOTATION AS IN FIG. 7

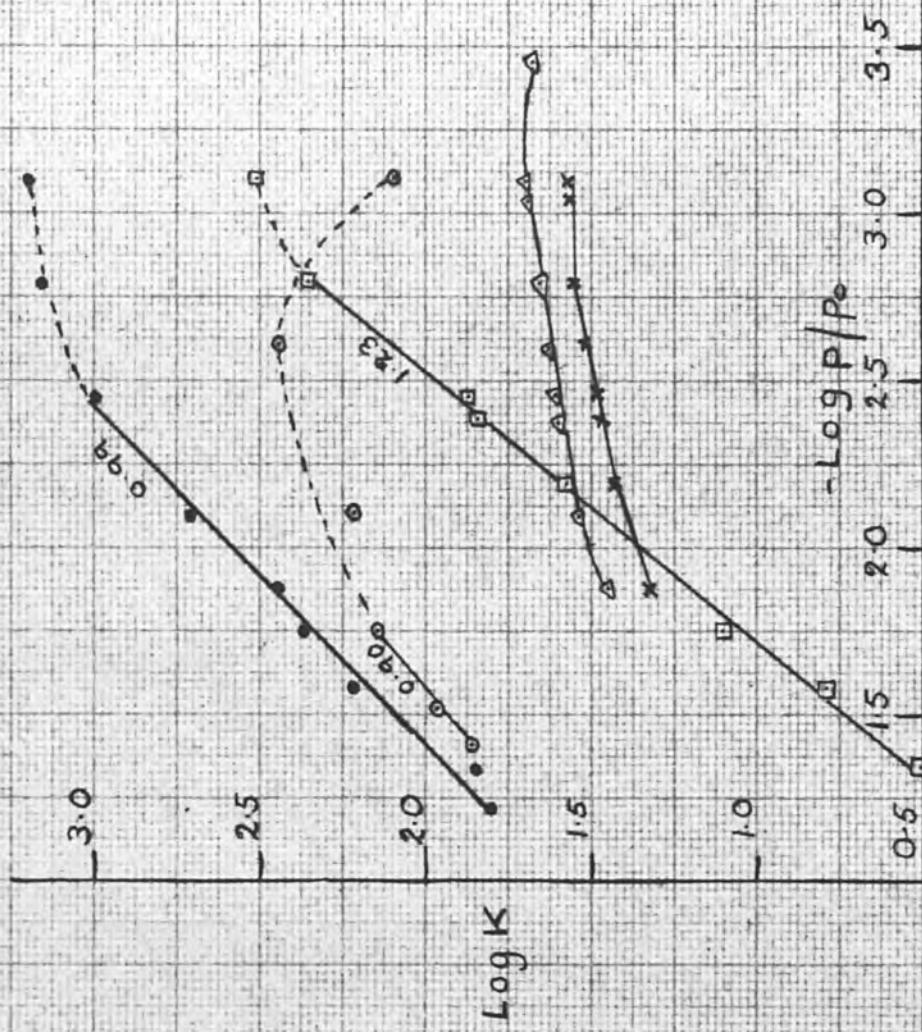


Fig. 14. VARIATION OF LOG (RATE NITRATION) WITH C_0

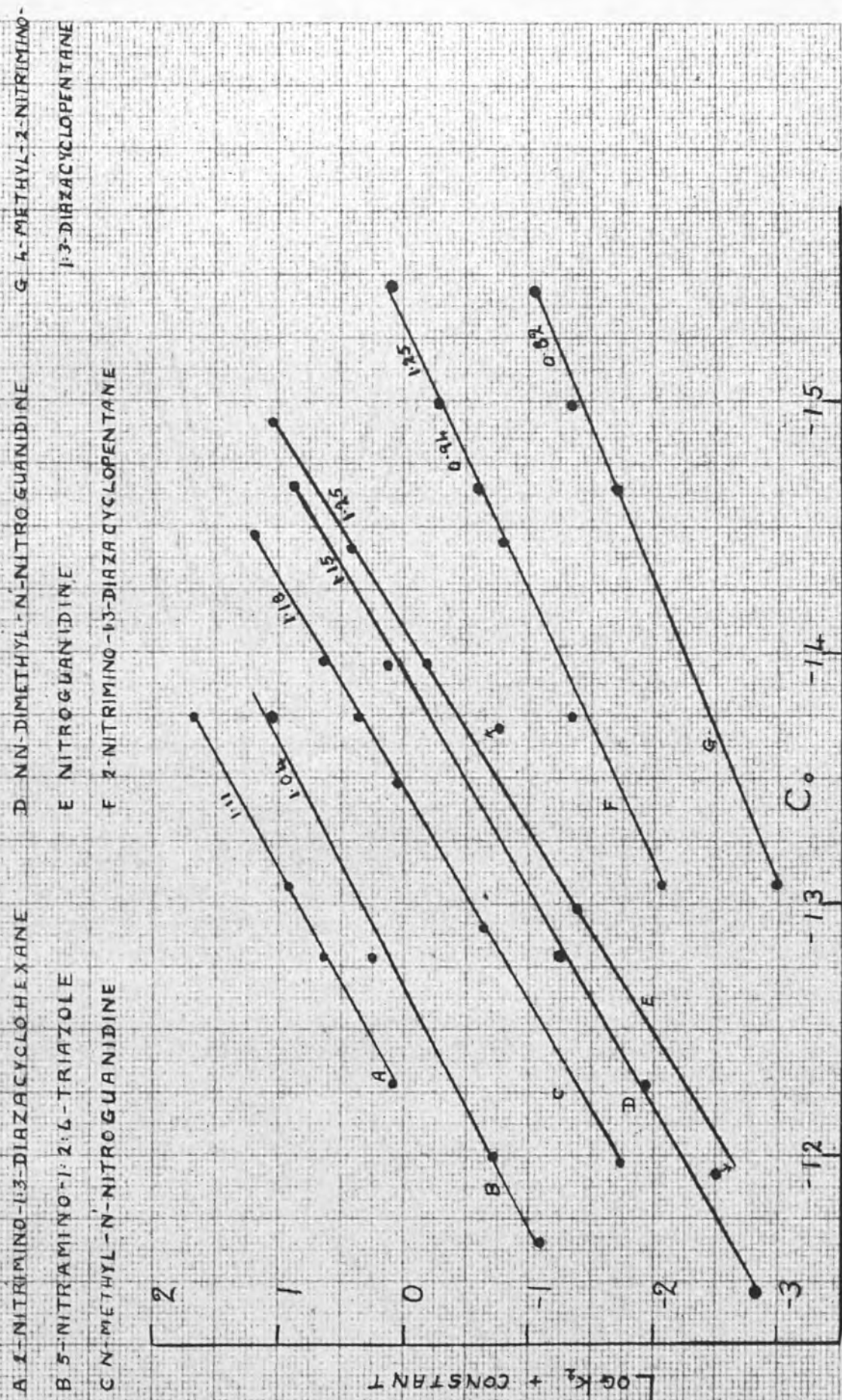


Fig. 15. SPECTRA OF 2-NITRO-2-AMINOANILINE.

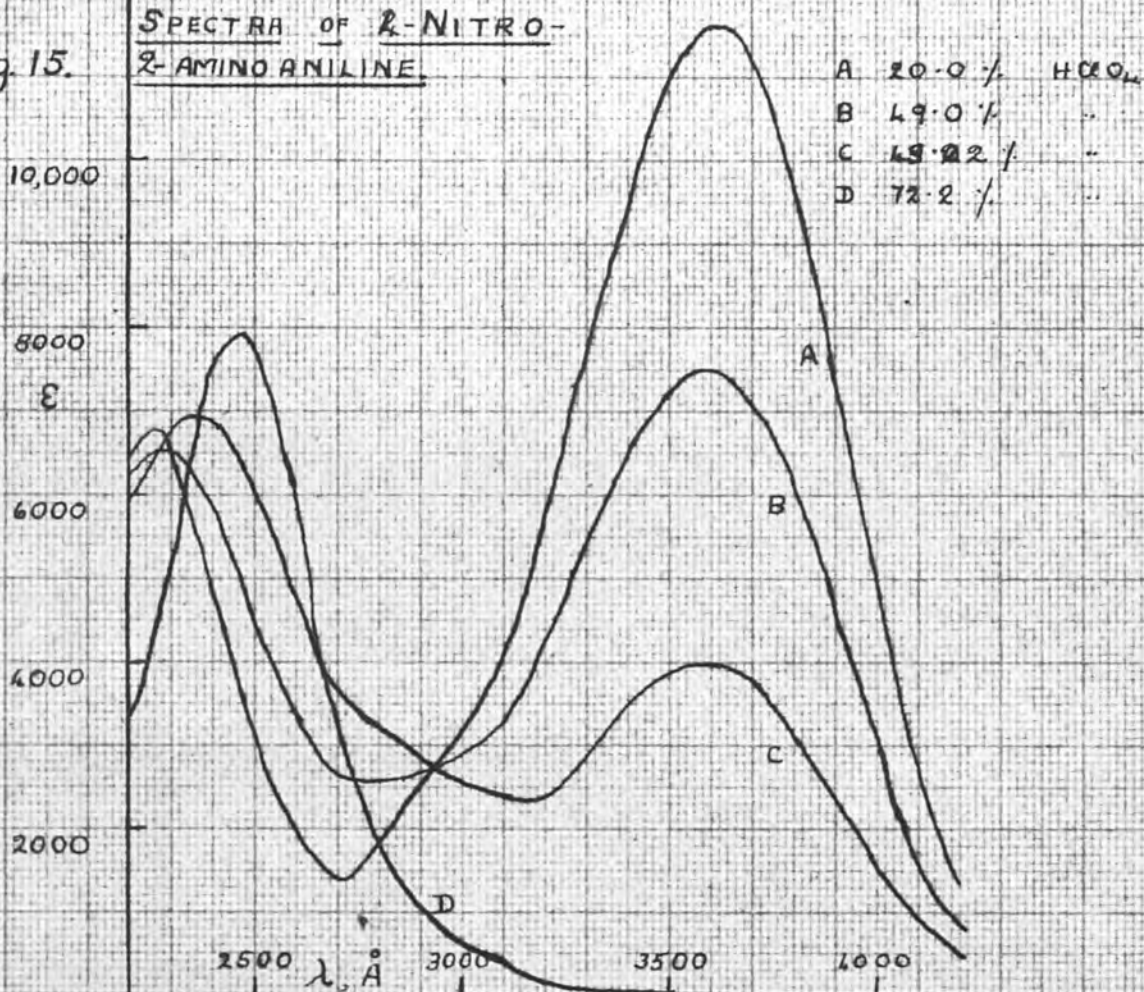


Fig. 16. INDICATOR IONISATION IN PERCHLORIC ACID

- a 2-NITROANILINE
- b 4-CHLORO-2-NITROANILINE
- c 4-NITRO-2-AMINOANILINE
- d 2,4-DICHLORO-6-NITROANILINE
- e 4-NITROAZOBENZENE
- f 2,4-DINITROANILINE
- g 2,4-DINITRONAPHTHYLAMINE

