ESTERIFICATION IN SULPHURIC ACID

BY

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Being a thesis presented to the University of London in candidature for the degree of Doctor of Philosophy in the Faculty of Science.

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ACKNOWLEDGEMENTS

The author wishes to thank Dr. T.G. Bonner for his help and encouragement, the late Professor Gwyn Williams for suggesting the subject of this work, and Dr. T.M. Walters for his continued interest.

ABSTRACT.

The possible nitrating entities for the esterification of alcohols by nitric acid in sulphuric and perchloric acids have been discussed, and the interpretation of nitration mechanisms by correlation with acidity functions considered. The nitric acid esterification of 2:4-dinitrobenzyl alcohol has been investigated over a wide range of sulphuric acid, but the alcohol proved unsuitable for kinetic study. Results have been obtained for the equilibrium formation of the sulphuric and nitric esters of this alcohol in 75% - 85% H_2SO_4.

Kinetic studies have been made on the nitric acid esterification of iso-amyl alcohol in H_2SO_4 at $0^{\circ}C$. and $25^{\circ}C$. The results have been correlated with acidity functions, but a critical survey of the latter has shown that they are not completely reliable guides to reaction mechanisms. Rates of esterification have been obtained in perchloric acid, and considered in relation to the ionisation of nitrous acid to the nitrosonium ion NO^+ in this acid. Correlation of results indicate that the nitronium ion NO_2^+ is the nitric acid esterifying agent in $HClO_4$. Corresponding information on the ionisation of nitrous acid in H_2SO_4 supports the NO_2^+ mechanism in sulphuric acid.

A tri-aryl carbinol indicator has been measured at 7°C. in H_2SO_4 to give some indication of the effect of temperature on the ionisation of such indicators. A tri-aryl carbinol indicator has also been measured in $HClO_4$ at 25°C. as there is at present no existing acidity scale in this acid corresponding to Jo in H_2SO_4.

Equilibrium constants for the nitric acid esterification of iso-amyl alcohol have been obtained in H_2SO_4 and $HClO_4$, and the rate constants for the hydrolysis calculated. A possible mechanism for the hydrolysis involving proton uptake by the nitrate, and the production of NO_2^+ has been suggested.

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III. DISCUSSION OF RESULTS.

The Nitronium Ion.

The nature of solutions of nitric acid in sulphuric acid has been the subject of much investigation and the existence of the nitronium ion in H_2SO_4 concentrations over 80% established. The nature of mixtures of nitric and sulphuric acids and water depends primarily on the molecular proportions of water and sulphuric acid present, for these components form the ionised hydrate $[H_3O^+][HSO_4^-]$. In equimolecular mixtures of water and H_2SO_4, nitric acid is present mainly as NO_2OH, but when H_2SO_4 is in excess, the nitronium ion is formed.

Hantzsch (1) investigated the U.V. spectra of mixtures of HNO_3 and H_2SO_4, and concluded that in excess H_2SO_4 a new species existed; Chedin (2) studied the Raman spectra very comprehensively, and the 1400 cm^{-1} line which he observed has been attributed to the nitronium ion by Bennett (3). Some cryoscopic work was done by Hantzsch (4), but a more accurate repetition of the work by Ingold (5) gave a van't Hoff factor of 3·82, which agrees with the equation

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

Further evidence was obtained from conductivity measurements (Saposchnikof (6), and the isolation of salts $[NO_2^+][HS_2O_7^-]$, $[NO_2^+][ClO_4^-]$, $[NO_2^+]_2[S_2O_{10}^{--}]$ and others (7).

Kinetics of nitration have also been used as evidence for the nitronium ion, but these will be discussed in more detail later.

While there is considerable information concerning nitric acid in higher concentrations of H_2SO_4, there is little evidence of the state in concentrations more aqueous than the mole ratio $H_2O/H_2SO_4 = 1$. Chédin's (8) results gave the approximate values for the limiting acid composition in which the line 1400 cm^{-1} is just observable. This is at about 85% H_2SO_4, and roughly corresponds to the strength of H_2SO_4 at which nitrobenzene is no longer nitrated, according to the results of Hetherington and Masson (9). They stated that the reaction came to a standstill before all the nitrobenzene and nitric acid were used up, unless there was enough H_2SO_4 present to form $H_2SO_4 \cdot H_2O$ with the water initially present plus that chemically formed. It has however been noted by Bonner (41) and Lowen (42) that the reaction does not actually cease in more aqueous acids, but the velocity coefficient approaches zero asymptotically .

The Nitracidium ion.

The possibility of nitration by the nitracidium ion, $H_2NO_3^+$, was considered by Ingold and Hughes (10). They carried out the nitration of sodium toluene w-sulphonate in aqueous H_2SO_4 with concentrations of HNO_3 such that it was largely present as molecules and not almost wholly as nitrate ions. They found that the reaction was first order with respect to the aromatic compound, and that the reaction was accelerated by added $HClO_4$ and H_2SO_4, which showed that a proton uptake was involved, and that the nitric acid molecule itself was not the nitrating agent. The effect of adding small amounts of an acid stronger than HNO_3 is to increase the proton uptake by a form of reaction

$$HNO_3 + HX \rightleftharpoons H_2NO_3^+ + X^-$$

Together with the fact that the reaction was retarded by added nitrate ions, which indicated that NO_3^- was present in a reversible stage, they considered that it pointed to the mechanism $$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

The fact that zero order was not observed, which would be the case if the rate-determining step depended on NO_2^+ formation from $H_2NO_3^+$, and the dubious existence of NO_2^+ in less than 70% H_2SO_4, led them to postulate $H_2NO_3^+$ as the nitrating agent. Further evidence (11) for the formation of $H_2NO_3^+$ was obtained in the nitration of benzene by 3M HNO_3 and toluene by 7M HNO_3 in nitromethane. Acceleration by H_2SO_4 was observed in this solvent, and retardation by added nitrate, the latter effect being particularly significant. The zeroth order nitration was retarded by NO_3^- without losing its zero order character, which showed that the formation of NO_2^+ consists of two stages, since some stage in its production must be irreversible, for the interpretation of zeroth order nitration is that all the NO_2^+ formed is consumed.

Thus for the formation of NO_2^+ in zero order nitration catalysed by H_2SO_4, the following equations apply

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$$
$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$$

while in the absence of a catalysing acid the expression is

$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$
$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$$

This is a definite demonstration of the existence of $H_2NO_3^+$.

Acidity Functions.

Considerable evidence in favour of the nitrating agent being NO_2^+ is obtained by comparison of kinetic results with the acidity functions H_0 and J_0.

The concept of the acidity function as a measure of the acidity of solutions was first introduced by Hammett and Deyrup (12). They considered acidity in terms of a basic indicator, and for the equilibrium in any reaction in which the H^+ ion is added to a neutral molecule they gave a definite formulation in terms of H_0^0, the acidity function.

The strength of any mono-acid base whose ionisation is represented by

$$B + H^+ = BH^+$$

is given by the equation

$$\underline{pK_a^B} = - \log \frac{a_{H^+} \, a_B}{a_{BH^+}}$$

which can be written as

$$pK_a^B = - \log a_{H^+} \frac{f_B}{f_{BH^+}} - \log \frac{C_B}{C_{BH^+}}$$

Hammett defined H_o such that

$$H_o = - \log \frac{a_{H^+} f_B}{f_{BH^+}} .$$

This is independent of the indicator used to measure it to the extent that the fundamental assumption that the ratio $\frac{f_B}{f_{BH^+}}$ is the same for different bases in a given solution is exact. In dilute aqueous solution as reference standard, $\log \frac{f_{H^+} f_B}{f_{BH^+}} = 0$ and H_o becomes equal to pH.

H_o can also be expressed as

$$H_o = pK_a + \log \frac{C_B}{C_{BH^+}}$$

and thus H_o can be determined by indicator measurements of $\frac{C_B}{C_{BH^+}}$ if pK_a is known, and by a series of stepwise colorimetric measurements the H_o scale was obtained.

The value of the H_o scale in connection with reaction velocity lies in the fact that parallelism should occur if the velocity is proportional to the concentration of the ion formed by the addition of H^+ to the neutral molecule, when $H_o + \log k = \text{const.}$

While the acidity function H_o is a criterion of the acidity of a medium relative to a simple Brönsted base, it is of no value for substances ionising in H_2SO_4 according to the equation

$$XOH + 2H_2SO_4 = X^+ + H_3O^+ + 2HSO_4^-$$

This type of ionisation is shown by triaryl carbinols

$$Ar_3COH + 2H_2SO_4 = Ar_3C^+ + H_3O^+ + 2HSO_4^-$$

and these have been used as indicators in measuring a new acidity function J_o.

Gold and Hawes (13) showed that the equilibrium could be split up into 3 steps

$$H_2SO_4 = HSO_4^- + H^+$$

$$ROH + H^+ = ROH_2^+$$

$$ROH_2^+ = R^+ + H_2O.$$

and denoting equilibrium constants by k_1, k_2, k_3 obtained

$$K_1 = k_1\ k_2\ k_3 = \frac{(R^+)\ (HSO_4^-)\ (H_2O)}{(ROH)\ (H_2SO_4)}$$

where the parentheses refer to activities.

By substituting h_o ($H_o = -\log_{10} h_o$) and defining K_{ROH} as the basicity constant

$$K_{ROH} = \frac{[R^+]}{[ROH]}\ \frac{(H_2O)}{h_o}\ \frac{f_{R^+}}{f_{ROH_2^+}}$$

Assuming that $\frac{f_{R^+}}{f_{ROH_2^+}} = 1$ in all solvents, which has later been questioned, by analogy with Hammett's assumption that

$\frac{f_{AH^+}}{f_A}\frac{f_B}{f_{BH^+}}$ = 1, and taking logs

$$H_o + \log (H_2O) = - pK_{ROH} + \log \frac{[ROH]}{[R^+]}$$

Comparing this with

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

Gold and Hawes defined

$$J_o = H_o + \log (H_2O)$$
$$= - pK_{ROH} + \log \frac{[ROH]}{[R^+]} \text{ where } pK_{ROH}$$

is the basicity constant.

Since this work was done, further investigations by Deno have indicated that the assumption that in the equation

$$J_o = pK_{R^+} - \log \frac{[R^+]}{[ROH]} + \log \frac{f_{ROH}\, f_{BH^+}}{f_B\, f_{R^+}}$$

the last term would reduce to zero is not valid, and they defined an acidity function C_o as

$$C_o = pK_{R^+} - \log \frac{[R^+]}{[ROH]} = - \log a_{H^+} + \log a_{H_2O} + \log \frac{f_{R^+}}{f_{ROH}}$$

Thus by subtraction

$$C_o = J_o + \log \frac{f_{R^+}}{f_{ROH_2^+}}$$

The accuracy of these acidity functions will be considered later. However, they have been used by Lowen, Murray and Williams to distinguish between the two possible nitrating entities NO_2^+ and $H_2NO_3^+$ in 75 - 85% H_2SO_4. The two modes of ionisation are

$$HNO_3 + H_2SO_4 = H_2NO_3^+ + HSO_4^- \qquad (1)$$

and $$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (2)$$

For reaction 2, the rate of nitration is given by

$$r = k\left[NO_2^+\right]\left[ArH\right] \qquad (3)$$

and experimentally

$$r = k_2\left[HNO_3\right]\left[ArH\right] \qquad (4)$$

Since results have justified the assumption that

$$\log\frac{[R^+]}{[ROH]} - \log\frac{[S^+]}{[SOH]} = \text{const.}$$

for two indicators, then it is reasonable that

$$\log\frac{[R^+]}{[ROH]} - \log\frac{[NO_2^+]}{[NO_2OH]} = \text{const.} \qquad (5)$$

Equation (3) can be written as

$$r = \frac{k\left[NO_2OH\right]\left[ArH\right]\left[NO_2^+\right]}{\left[NO_2OH\right]}$$

and $$r = \frac{k\left[HNO_3\right]\left[ArH\right]\left[NO_2^+\right]}{\left[NO_2OH\right]} \qquad (6)$$

if the extent of ionisation of the nitric acid is small and $[HNO_3]$ denotes the stoichiometric concentration of total nitric acid.

Equations (4) and (6) give

$$\log k_2 = \log k + \log\frac{[NO_2^+]}{[NO_2OH]} \qquad (7)$$

and this combined with equation (5) gives

$$\log k_2 = \log k + \log\frac{[R^+]}{[ROH]} + D$$

Then if the variation of log k_2 with medium composition is parallel with that of log $\frac{[R+]}{[ROH]}$ the NO_2+ mechanism is indicated. Williams et al showed that this parallelism did exist, and that none occurred between plots of log k_2 and H_o, which would be observed if nitration had been effected by the nitracidium ion.

The work of Deno (16) has covered nitration from 40% H_2SO_4 upwards and the results generally support the NO_2^+ mechanism, though there are discrepancies which will be considered later.

Esterification by Nitric Acid.

All the preceding discussion, although concerned with the nature of HNO_3 in H_2SO_4, has been in connection with aromatic C-nitration. As far as esterification of alcohols by nitric acid is concerned, there is very little evidence for the nature of the esterifying agent. The kinetic measurements carried out by Blackhall and Hughes (17) indicate that esterification by nitric acid in nitromethane is effected by NO_2^+. These authors used the same argument as previously described for aromatic nitration, i.e. that if a compound is sufficiently reactive, zero order kinetics will be observed since the rate will depend only on the rate of formation of the nitronium ion from the nitracidium ion.

They found that the esterification of 0.5 M methyl alcohol by 4M HNO_3, the conversion of N-methyl 2 : 4 : 6 - trinitroaniline into N-methyl-N : 2 : 4 : 6 tetranitroaniline, and the nitration of toluene all proceeded at the same zero order rate. With less reactive aromatic compounds, the kinetics approach first order, and similarly it was found with neo-pentyl alcohol that the reaction is slower, and approximately first order, comparable to the nitration of chlorobenzene. The O-nitration of glycerol and cellulose is indirectly shown to involve attack on oxygen by NO_2^+, but the reaction is complicated by the number of steps involved.

Farmer (18) concluded that nitration of cellulose is brought about by 'pseudo-nitric acid', and attributed the maximum nitration which occurs at about 90% H_2SO_4 to increasing conversion of pseudo-nitric acid to nitronium ion above this concentration.

Chédin (19) claimed that the nitration of cellulose in H_2SO_4 media is represented by the equation

$$ROH + HNO_3 \rightleftharpoons RONO_2 + H_2O$$

for which $$\frac{[RONO_2][H_2O]}{[ROH][HNO_3]} = K \sim 0.55$$

Other investigations have been concerned with finding optimum conditions for the nitration of polyhydric alcohols, e.g. Rinkenbach and Aaronson (20) studied the effect on the nitration of diethylene glycol of varying the H_2O proportion in the HNO_3, H_2SO_4, H_2O mixture, the proportion of HNO_3, and temperature, and obtained a maximum yield of 83% when the relative proportions were 50% HNO_3, 45% H_2SO_4, 5% H_2O at 25°C. Although 3% of the yield remained unaccounted for after recovery from washings, etc., they concluded that the loss was not due to oxidation, as no trace of oxidation products was found. Aubertin (21) nitrated glycol, diethylene glycol, triethylene glycol, and 1·3 butanediol, and obtained yields varying from 55 - 94%. He found that while increase of H_2SO_4 at first increases the yield due to lower solubility, it then decreases due to sulphation, and decreases the stability of the mixed acids: this instability was also noted in work on dinitrodiglycol (22).

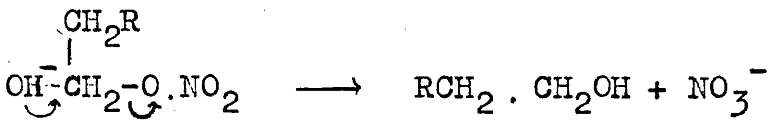
Hydrolysis of Nitrate Esters.

There is considerably more evidence on the hydrolysis of nitrate esters in acid solution (23) (26) (31) in aqueous media (24) (30), and in alkaline media (25) (27); a review of hydrolysis was included in a survey of the chemistry of nitrate esters by Boscham (28).

Baker & Neale (23) have studied the acid hydrolysis of ethyl, iso-propyl, benzyl, methyl-benzyl and tertiary butyl nitrates in aqueous ethanol. They had previously established that in neutral and alkaline media the complex products of hydrolytic decomposition could be explained on the basis of three mechanisms. By comparison with the hydrolysis of carboxylic esters (23) there is a possibility of both nitrate $\geq C \,\vdots\, ONO_2$ and nitrite $\geq C\ O \,\vdots\, NO_2$ fission, and so there might be both substitution and elimination reactions.

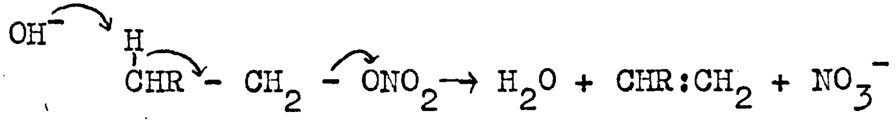
In terms of the bimolecular mechanism these are :-

SN2 Nucleophilic substitution



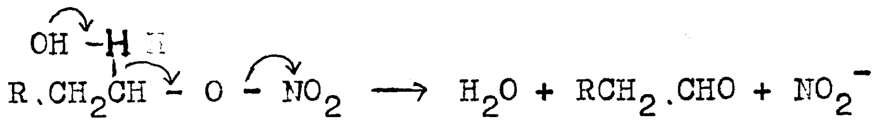
$$OH^- \; \overset{CH_2R}{\overset{|}{CH_2}} - O.NO_2 \longrightarrow RCH_2 . CH_2OH + NO_3^-$$

E2 β - Hydrogen elimination, olefin formation



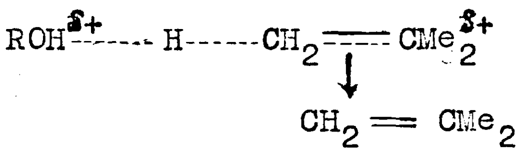
$$OH^- \quad \overset{H}{\overset{|}{CHR}} - CH_2 - ONO_2 \rightarrow H_2O + CHR{:}CH_2 + NO_3^-$$

$E_{co}2$ α Hydrogen elimination, carbonyl formation



$$R.CH_2\overset{\overset{OH\;-H}{|}}{C}H - O - NO_2 \longrightarrow H_2O + RCH_2.CHO + NO_2^-$$

Whereas with alkaline hydrolysis of ethyl nitrate the proportion of E2 and $E_{co}2$ is small but significant, with iso-propyl all 3 mechanisms occur, and with tert-butyl both S2 and E2 are important, in the solvolytic reaction in aqueous alcohol no nitrite or carbonyl formation has been detected. Thus substitution at C_α with the liberation of HNO_3 is the sole reaction except when in a structurally suitable ester undergoing solvolysis by the unimolecular mechanism elimination of a proton from the carbonium ion first produced gives the olefin.



$$ROH^{\delta+} \cdots H \cdots CH_2 \overset{\cdots}{=} CMe_2^{\delta+} \xrightarrow{} CH_2 = CMe_2$$

No evidence of acid catalysis was obtained, and in any one run the first order velocity coefficient remained unchanged, showing no upward drift as the medium became increasingly acid. Moelwyn-Hughes (30) investigated the hydrolysis of methyl nitrate in aqueous solution and found the reaction to be first order, without any detectable catalysis by the nitric acid produced. Farmer (31) studied the hydrolysis of nitroglycerin in 70% H_2SO_4, and found that it hydrolysed progressively to glyceryl dinitrate, glyceryl mono-nitrate and glycerol.

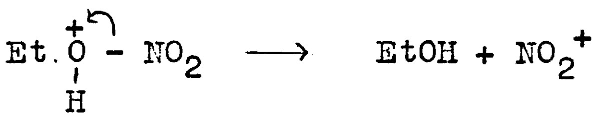
The absence of acid catalysis is in harmony with the general observation (29) that esters of strong acids, unlike carboxylic esters, are not subject to acid-accelerated hydrolysis in aqueous media. The difference between RO.COR and $RONO_2$ probably arises from the much greater loss of resonance stabilisation which would result from proton addition to the nitrate ester.

$$\bar{O} - \overset{+}{\underset{|}{N}} = O \ \& \ O = \overset{+}{\underset{|}{N}} - \bar{O} \rightarrow HO - \overset{+}{\underset{|}{N}} = O$$

In 100% H_2SO_4 proton transfer can occur to organic nitrates with consequent acid-accelerated fission

$$EtO.NO_2 + 3H_2SO_4 \rightarrow EtO.SO_3H + NO_2^+ + 2HSO_4^- + H_3O^+$$

This suggests that proton addition occurs at the alkoxy-oxygen atom to give initial fission.



$$Et.\overset{+}{\underset{\underset{H}{|}}{O}} - NO_2 \longrightarrow EtOH + NO_2^+$$

though the behaviour in 100% H_2SO_4 can be more complicated.

In conc. H_2SO_4 a van't Hoff i factor approaching 5 has been found for ethyl nitrate (26) as indicated by the above equation, and the formation of NO_2^+ indicated by these results probably explains the potency of H_2SO_4 solutions of nitrate esters as nitrating agents. Examples of this are the nitration of toluene in 98% H_2SO_4 (38) by ethyl nitrate and butyl nitrate.

State of Alcohols in H_2SO_4.

There is little evidence of the molecular condition of alcohols in aqueous H_2SO_4 media. Strong mineral acids ionise in alcoholic solvents to form alkyloxonium ions

e.g. $HCl + EtOH \rightleftharpoons EtOH_2^+ + Cl^-$

so a similar ionization is to be expected when alcohols are dissolved in strong mineral acids. In concentrated sulphuric acid alcohols are rapidly converted to alkylsulphuric acids

$$ROH + 2H_2SO_4 \rightleftharpoons RHSO_4 + H_3O^+ + HSO_4^-$$

Triarylmethanols ionise in concentrated acid to give

$$R_3C,OH + 2H_2SO_4 \rightleftharpoons R_3C^+ + H_3O^+ + 2HSO_4^-$$

but in aqueous H_2SO_4 ionization is incomplete, and it is not certain whether the undissociated alcohol exists as the oxonium ion $R_3COH_2^+$ or as unchanged R_3COH.

From work done by Clark (4o) it has been shown that the time taken for the sulphation of alcohols to reach equilibrium is far longer than that required for nitration.

Comparison of HNO_3 and HNO_2.

There is a certain similarity between HNO_3 and HNO_2 in their behaviour in sulphuric and perchloric acids, since they are converted to the nitronium ion NO_2^+ and nitrosonium ion NO^+ respectively. The existence of NO^+ is well established, salts such as nitrosonium perchlorate (32) nitrosyl halides and many others (37) have been isolated and the Raman spectra investigated. The frequency 2320 cm^{-1} is assigned as the fundamental frequency of the NO^+ ion, which is observed in the spectra of nitrosonium hydrogen sulphate.

However, from spectra measurements (34) on mixtures of corresponding composition of HNO_3 and HNO_2 in H_2SO_4, it is concluded that the equilibrium constant for the ionisation of nitrous acid by H_2SO_4,

$$HNO_2 + 2H_2SO_4 = NO^+ + 2HSO_4^- + H_3O^+$$

is much greater than the corresponding ionisation of nitric acid. The larger negative Gibbs free-energy of formation of nitric than of nitrous acid shows that the forward reaction (i.e. formation) will occur more readily since it will be accompanied by a greater decrease in total free energy, and at stable equilibrium the free energy is a minimum. The reverse order of thermodynamic stability of the corresponding cations also contributes to this difference in equilibrium constants. The existence of $H_2NO_2^+$, corresponding to $H_2NO_3^+$ is dubious. The ultraviolet spectrum of HNO_2 in $HClO_4$ (35) has shown that HNO_2 is fully ionised in 60% $HClO_4$, only partially ionised in 48%, and negligibly ionised in 40% $HClO_4$, which corresponds to the strength of Raman lines observed by Angus and Leckie (32). These authors measured the Raman spectra of solutions of nitrosyl perchlorate $NOClO_4$ in perchloric acid, and attributed the strong frequency at 2329 cm^{-1} to the NO^+ group. The intensity was strong in 62% $HClO_4$, weaker in 51%, almost negligible in 45% and absent in 40%. The ultraviolet spectra were measured by adding perchloric acid to sodium nitrite solutions, the concentration of nitrous acid was also measured independently. The decrease in concentration of NO^+ obtained corresponded with the increase in molecular nitrous acid concentration, and there was no indication of a third entity such as $H_2NO_2^+$. The work of Bayliss and Watts (36) on nitrous acid does include the existence of $H_2NO_2^+$, but as this does not contribute to the U.V. spectra the calculations involved are not altogether conclusive, and will be discussed later.

Bunton (37) considered the proposal that the active nitrosating agent in diazotisation was N_2O_3 but that under certain circumstances it could be either $H_2NO_2^+$ or NO^+. Any of these entities could give oxygen exchange between nitrous acid and water by three mechanisms.

1) $H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$

2) $NO^+ + H_2O \rightleftharpoons H_2NO_2^+$

3) $H_2{}^{18}O + H_2NO_2^+ \rightleftharpoons H_2NO^{18}O + H_2O$

By studying the exchange rate, which for reaction 1) was given by $r = k_2 [HNO_2]^2$, and for 2 & 3 by $r \propto [H^+][HNO_2]$ he distinguished between the mechanisms. A solution of $NaNO_2$ between 0•4 and 1 M was used, and to this was added not more than 1/5 the equivalent of $HClO_4$, so that the concentration of molecular nitrous acid was assumed to be given by the $HClO_4$ concentration, after correcting for the initial decomposition of nitrous acid. He found that the exchange rate depended on $[HNO_2]^2$, and concluded that the first mechanism was correct under these conditions, but probably for higher acid concentrations the nitrite ion concentration would be reduced sufficiently for mechanisms (2) and (3) to be effective.

Materials.

Inorganic.

Sulphuric Acid.	98% Analar H_2SO_4 was used for the preparation of media.
Perchloric Acid.	70% Analar $HClO_4$ was used for media.

Potassium iodate, potassium dichromate, potassium nitrate, Analar, dried at 110°C for 1 hr.

Standardisation of H_2SO_4 media.

Media were standardised using KlO_3 as ultimate standard, and N.HCl as intermediate standard. Approximately N.KlO_3 was made up accurately and used to standardise N.sodium thiosulphate, and kept as subsidiary standard. Sodium hydroxide solutions were standardised against HCl using phenolphthalein indicator.

The H_2SO_4 and $HClO_4$ were then standardised against the NaOH. Amounts of the acid were weighed out from a weight pipette into flasks containing about 20 c.c. water each, such that the titration figure was approximately 20 c.c.

The caustic soda solution was also checked by standardisation against potassium hydrogen phthalate, Owing to solubility difficulties, the standard phthalate solution prepared was O.IN, and this necessitated the dilution of the N.NaOH. Standardisation of the HCl by the two methods showed excellent agreement, and estimations of the sulphuric and perchloric acids are given correct to the nearest 0·1%. Stoppers were wiped with filter paper after use thus preventing dilution of the medium by moisture absorbed from the air by exposed H_2SO_4.

Organic Reagents.

Benzene. Analar benzene (B.D.H) was used for absorption spectra measurements.

Hexane. B.D.H. Laboratory reagent, b.p. 60 - 80°C was used.

Iso-amyl alcohol. Light & Co: redistilled at 130°C.

2 : 4 - dinitrobenzyl chloride. Light & Co:

2 : 4 - dinitrobenzyl alcohol. Prepared via acetate from chloride.

Preparation of 2 : 4 - dinitrobenzyl acetate (Method of Friedlander & Cohn, Monatsh 1902.23.546)

225 gm.	2 : 4 - dinitrobenzyl chloride.
90 gm.	Anhydrous sodium acetate.
90 c.c.	Glacial acetic acid.
675 c.c.	Methyl alcohol.

The contents of the flask were refluxed for 6 hrs and filtered hot, the filtrate being left overnight to crystallize. The yellow crystals of acetate were filtered off and the mother liquor refluxed with an added 90 gm. sodium acetate and 90 c.c. glacial acetic acid for 7 hrs. It was filtered hot, and the yellow crystals obtained combined with those previously obtained. They were recrystallised from methyl alcohol with charcoal, m.p. 96°C. Yield 37%.

Preparation of 2:4-dinitrobenzyl alcohol (Friedlander & Cohn).

90 gm. 2:4-dinitrobenzyl acetate.
450 gm. concentrated H_2SO_4.
840 c.c. distilled water.

The water and H_2SO_4 were mixed in a flask, and 2:4-dinitrobenzyl acetate added. The mixture was heated to 120°C, and maintained at that temperature for about 30 mins. The solution was left overnight, when the alcohol separated as pale yellow crystals. On dilution of the filtrate with water, more crystals were obtained, and recrystallization was carried out from water and charcoal. Yield 30%. M.P. 115°C.

Material used for kinetic experiments was further purified by recrystallization from methyl alcohol (with charcoal), and from benzene. Final M.P. 115 - 116°C. The alcohol was stored in a dark bottle as it turns yellow on exposure to light.

Preparation of 2:4-dinitrobenzyl nitrate.

This was first prepared by the action of silver nitrate in acetonitrite on 2:4-dinitrobenzyl bromide, but it was a long process, and the yields were very poor. It was found that very good yields were obtained by the action of anhydrous nitric acid on 2:4-dinitrobenzyl alcohol. 15 gm. of anhydrous HNO_3 were added slowly to 5 gm. 2:4-dinitrobenzyl alcohol, after a few minutes the solution was poured on to ice and water with vigorous stirring. A pale yellow oil separated which solidified on cooling. It was recrystallized from ether and gave M.P. 39.5, yield 4.5 gm.

Preparation of Anhydrous Nitric Acid.

This was prepared by mixing two volumes of Analar 72% HNO_3 with 3 volumes of concentrated H_2SO_4 in a specially designed all-glass distillation unit, and distilling from a steam bath under reduced pressure. The receiver was surrounded by a mixture of solid carbon dioxide and acetone, and the distillate formed a white solid. It could be kept for some time in this state without decomposing, if it was also protected from light.

Nitric acid media were prepared by pouring the 100% HNO_3 directly into a weighed standard flask, reweighing and making up to the mark with sulphuric or perchloric acid at the required temperature.

Analytical Methods.

In the attempt to follow the rate of nitric acid esterification of 2:4-dinitrobenzyl alcohol, several methods were used, and others tried and rejected. This particular alcohol was investigated fairly thoroughly partly because an accurate method for its analysis had been worked out by Clark (40), and information was available on the sulphuric acid esterification; also that in more aqueous media

2:4-dinitrobenzyl alcohol was known to be resistant to oxidation by nitric acid.

Determination of 2:4-dinitrobenzyl alcohol.

The estimation of unchanged alcohol in the reaction mixture was carried out by running a 10 c.c. sample on to a partly frozen mixture of 25 c.c. 0.32N potassium dichromate, and sufficient water to make the resultant solution 6N with respect to acid. The solution was left to stand overnight, and the excess dichromate then titrated against 0.2 M ferrous ammonium sulphate (in 0.8 N H_2SO_4) using sodium diphenylamine sulphonate as indicator, in the presence of phosphoric acid. The ferrous ammonium sulphate was standardised against 0.2 N aqueous $K_2Cr_2O_7$.

The concentration of alcohol is calculated from the expression

$$\mathrm{ROH} = (\mathrm{c.c.Fe.Amm.SO_4} \equiv \mathrm{ROH}) \times \left(\frac{\mathrm{Molarity\ Fe.Amm.SO_4}}{4}\right) \times \frac{1}{V}$$

where Vc.c. is the volume of reaction mixture delivered by the pipette.

The acidity of the dichromate solution and time of oxidation were carefully adjusted so that quantitative oxidation of the alcohol occurred without appreciable hydrolysis of the ester.

When the method was used with nitric acid and 2:4-dinitrobenzyl nitrate present, it was checked to ensure that neither interfered. Under the above conditions, nitric acid does not affect the titration with ferrous ammonium sulphate, and the dichromate mixture to which 2:4-dinitrobenzyl nitrate had been added and left to stand for 25 hrs. gave the same titration reading as the corresponding blank without the nitrate present.

In later experiments the method was combined with another for estimating the nitrate present in the same sample, but the conditions remained almost the same.

Determination of Nitric Acid.

In preliminary experiments, in acids ranging from 79 - 93% H_2SO_4 & 0:IN concentrations of 2:4-dinitrobenzyl alcohol and HNO_3, the alcohol concentration only at equilibrium was measured, and compared with Clark's figures for sulphation alone. It was found that only slightly more alcohol was used up, and it was obvious that very little information could be gained without estimating either HNO_3 or the nitrate ester.

Methods which were tried at various times for their estimation included the use of the nitrometer; nitron; phenol, p-toluene sulphonic acid, α-naphthylamine sulphonic acid and naphthalene α-sulphonic acid to remove the free nitric acid so that the ester could be estimated, but none of these were satisfactory. The method used finally was that of Kolthoff & Sandell (43), which is based on the reduction of nitrate by ferrous ion in strong HCl solution.

$$3\,Fe^{++} + NO_3^- + 4H^+ \longrightarrow 3\,Fe^{+++} + NO + 2H_2O$$

and the amount of nitrate estimated from the ferrous ammonium sulphate used up. Since the reaction mixture contained both HNO_3 and the nitrate ester, it was necessary to remove the latter by extraction with CCl_4 before commencing the estimation. This consisted essentially of adding ferrous ammonium sulphate and HCl to the sample solution in a flask equipped with a dropping funnel and tube leading to sodium bicarbonate solution, and adding some bicarbonate just before stoppering to remove air, since NO is readily oxidised by oxygen. The flask was heated, and ammonium molybdate added after 2 or 3 minutes boiling. The solution turned brown; boiling was continued for a further 10 mins, then the solution cooled, 6N ammonium acetate added, a few c.c. of phosphoric acid, and sodium diphenylamine sulphonate indicator. The solution was then titrated with $K_2Cr_2O_7$, and the titre compared with that of a blank solution. Experiments were carried out to ensure that the presence of 2:4-dinitrobenzyl alcohol and H_2SO_4 did not affect the results.

Results of Combined HNO_3 and Alcohol Estimations.

The experiments ranged from 65 - 93% H_2SO_4 at $0^\circ C$, with alcohol and HNO_3 concentrations at 0.1 M; in lower acid media the alcohol took a considerable time to dissolve. The results showed that under these conditions the nitric acid esterification was too rapid to be measurable, even in 70%

H_2SO_4, while in 65% H_2SO_4 the amount of nitrate formed was negligible. The only advantage of lower concentrations of H_2SO_4 was that the amount of sulphate ester was also very small; acting on this basis, measurements were made of the alcohol only with a large excess (2N) HNO_3 in 65% H_2SO_4, when there was some indication of a measurable rate.

Some experiments were carried out in 75 - 87% H_2SO_4 starting with from 2:4-dinitro-benzyl nitrate, in lower acid media this again took a considerable time to dissolve. There appeared to be less nitrate and more sulphate ester present at equilibrium than that obtained from the forward reaction.

A third group of results were obtained from experiments where a large excess of HNO_3 was used and the nitrate ester only measured by the Treadwell-Vontobel method.

Estimation of Nitrate by Treadwell & Vontobel's Method.

As before the reaction was stopped by running a sample into water, and the ester extracted with CCl_4, which was washed and then evaporated off. The residual oil was dissolved in concentrated H_2SO_4, and transferred to the Treadwell-Vontobel tube. In concentrated H_2SO_4 nitrate ion is rapidly reduced to nitrite by ferrous salts

$$NO_3^- + 2\,Fe^{++} + 2H^+ \rightarrow NO_2^- + 2\,Fe^{+++} + H_2O$$

The solution was kept at 0-5°C, and titrated with ferrous sulphate (in 40% H_2SO_4). The solution was stirred during the titration and a slow stream of CO_2 bubbled through to protect the solution from atmospheric oxidation. The end-point was determined potentiometrically, the electrodes consisting of a 1 cm. square of platinum foil dipping into the nitrate solution, and a platinum spiral coated with lead dioxide dipping into concentrated H_2SO_4. The ferrous sulphate was standardised by electrometric titration with a standard solution of KNO_3 in H_2SO_4.

Under these conditions, a much larger percentage of nitrate ester was formed, but even so there was only one indication of a measurable rate at 55% H_2SO_4, with 4N HNO_3 at $0^{\circ}C$.

Absorption Spectra.

Having found that to obtain a measurable rate very low concentrations of reactants would be necessary, a method was sought involving absorption spectra measurements on the Hilger ultra-violet spectrometer, which would give accurate results with very low concentrations. The original hope of measuring the formation of 2:4-dinitrobenzyl nitrate by its absorption spectrum failed because the difference in the peak between nitrate ester and alcohol was only about 70Å .

A compound was sought which would show a definite change in its absorption spectrum on nitration, among compounds tried were p-toluene sulphonic acid, 2:4-xylenol, 3:4-xylenol and phloroglucinol, but none of these gave satisfactory results. Finally the tri-aryl carbinols were tried, and though these proved to have possibilities for the estimation of small amounts of HNO_3 in H_2SO_4, for this particular problem they could not be used, since in the concentration of H_2SO_4 involved, the nitrate ester decomposed too rapidly.

The conclusion was reached that kinetic measurements for the esterification could not be obtained, but that it would be possible to measure the equilibrium constants for both nitrate and sulphate ester, using a combination of the alcohol estimation previously described, and an absorption method for the nitrate ester.

Measurement of Equilibrium Constants.

The measurements were carried out in the range 75 - 85% H_2SO_4 at 25°C, with alcohol concentrations 0.1 N, and 0.3N HNO_3. The analytical method for the ester was based on the fact that its absorption in benzene could be measured on the Hilger Spekker photometer using the filter H556.

The experimental procedure was as follows; the reaction flask contained 20 c.c. of the HNO_3/H_2SO_4 mixture at 25°C, delivered by a pipette calibrated for each concentration of acid. A weighed amount of the alcohol was added in a Quickfit cap, and the flask well shaken. 2 c.c. samples were removed after suitable intervals of time, usually 4 samples at ½ hourly intervals, and added to an ice-cooled solution of 20 c.c. 0.05 N $K_2Cr_2O_7$ and sufficient water to bring the final solution to 6 N H_2SO_4. A blank solution was also prepared, since the alcohol estimation depended on the difference in titre between the reaction solution and the blank. The 2 c.c. pipette was also calibrated for each strength of acid, and each run duplicated.

The solutions were left to stand overnight, and the next day the dichromate solution was transferred to a separating funnel, to which 10 c.c. benzene were added and shaken. The benzene extracted the 2:4-dinitrobenzyl nitrate; the 2:4-dinitrobenzyl alcohol had been converted to 2:4-dinitrobenzoic acid, which was also extracted. The benzene layer was removed to a small flask and shaken with the $K_2Cr_2O_7$ solution. The latter was then returned to the flasks and the 20 c.c. benzene washed with water, the washings being added to the dichromate solution, which was then ready for titration. This was done by adding 100 c.c. water and 10 c.c. 10% Kl, leaving for a few minutes, and then titrating with 0·1N sodium thiosulphate, using starch indicator, and a micro-burette.

The benzene solution was washed twice with 5 c.c. 0·2 N NaOH, to extract the 2:4-dinitrobenzoic acid, and once more with water, then filtered into a 25 c.c. standard volumetric flask and made up to 25 c.c. with benzene.

The benzene solutions were estimated on the Spekker using filter H556 and 1 cm. cells. The readings were converted into concentrations by reference to a standard graph which had been prepared with 2:4-dinitrobenzyl nitrate. This was done by dissolving 0·1 gm. nitrate in 50 c.c. benzene and diluting with benzene in the ratios 3:6, 5:6, 5:4, 5:3, 10:4 and 12:3.

Equilibrium constants were calculated from the relations

$$K_{B_zNO_3} = \frac{[R.NO_3]}{[HNO_3][ROH]}$$

$$K_{B_zHSO_4} = \frac{[RSO_4]}{[ROH]}$$

A typical set of results obtained is shown in the following tables

In 80·7% H_2SO_4 Concentration HNO_3 = 0·318 N
Concentration alcohol in Run A = 0·100 N
" " " " B = 0·100 N

	1 hr.		2 hr.		3 hr.		4 hr.	
	A	B	A	B	A	B	A	B
Alcohol Estimation								
Thiosulphate Titration	6·05	6·00	6·00	5·98	5·97	5·97	6·03	5·98
Alcohol Conc$^{n.}$	·0400	·0407	·0407	·0401	·0411	·0411	·0403	·0403
Nitrate Estim$^{n.}$								
Spekker Reading	249	246	246	248	252	247	247	251
Nitrate Conc$^{n.}$	·0203	·0201	·0201	·0202	·0205	·0201	·0201	·0204
By subtraction Sulphate Conc$^{n.}$	·0397	·0392	·0392	·0388	·0384	·0388	·0396	·0386
$K_{B_zNO_3}$	1·71	1·66	1·66	1·66	1·68	1·64	1·67	1·67
$K_{B_zHSO_4}$	0·991	0·962	0·962	0·945	0·935	0·945	0·482	0·941

Mean $K_{B_zNO_3}$ = 1·67 Mean $K_{B_zHSO_4}$ = 0·960

Results for range 75 - 85% H_2SO_4.

Conc^n H_2SO_4	K_{BzNO_3}	K_{BzHSO_4}
84·9%	2·87	2·22
82·5	2·08	1·41
80·7	1·67	0·96
78·6	1·23	0·76
76·8	0·95	0·55
74·6	0·71	0·46

Experiments were attempted on the hydrolysis of 2:4-dinitrobenzyl nitrate in this region, but owing to the insolubility of the ester, and speed of hydrolysis, no corresponding results were obtained.

It was then decided to investigate another alcohol, which might possibly give measurable rates in some suitable sulphuric acid range. Ethyl alcohol had been considered by Clark (49) but it was found that in the range where esterification might be measurable, oxidation was appreciable, and it was not therefore suitable.

Iso-amyl alcohol was reported (28) to give practically 100% conversion to nitrate on treatment with HNO_3 and H_2SO_4 at 0°C, and also to be resistant to oxidation, so it was investigated, The nitrate was prepared by gradually adding 1 volume iso-amyl alcohol to a mixture of 1 volume concentrated HNO_3 and 3 volumes concentrated H_2SO_4 at 0°C. After a few minutes an oily layer appeared; the mixture was then added to a large volume of water, when the oil remained in suspension. It was extracted with ether, dried, the ether removed, and the oil distilled at 147°C.

The absorption spectra of the alcohol and the nitrate in water were measured, the absorption of the alcohol was negligible, apart from a slight rise at 2700 Å, when the extinction coefficient was 1·1. The nitrate absorption was stronger, although it had no distinguishing peak, and fell in a smooth curve from $\varepsilon = 33$ at 2400 Å to $\varepsilon = 1{\cdot}54$ at 3800 Å.

Further preliminary investigations were carried out involving absorption measurements on the Uvispek. The alcohol was dissolved in three different concentrations of H_2SO_4 at 0°C. viz: 65%, 75% & 90% H_2SO_4. Samples were removed after suitable time intervals and the absorption measured in the Uvispek. As thiswas not maintained at 0°C. the temperature of the solution being measured was gradually rising, but in the case of 65% & 75% H_2SO_4, this did not affect the readings, which remained constant over the time required for the measurements. The absorption of the 90% H_2SO_4 solution did begin to increase almost immediately, such that a repeated measurement at the same wavelength showed a considerable increase. In 65% H_2SO_4 the value of ε at 2900 Å increased from 0·83 to 1·04 in 30 hrs, in 75% H_2SO_4 it increased from 0·65 to 0·95 in 40 mins, and in 90% increased from 1·5 to 4·5 in 50 mins. The actual readings on the Uvispek were very low, so these values are not very accurate. It was found in nitration experiments that the reactions were complete in 23 hrs. in 65%, and 15 minutes in 75%. Within these times the alcohol absorption would only vary by a reading of •002, which was negligible.

Analytical method.

Iso-amyl nitrate is almost insoluble in water, and this insolubility made it possible to extract the ester from the reaction sample when diluted in water. A 5 c.c. sample was removed from the reaction flask, and added to 10 c.c. water. This solution became cloudy, but on shaking with hexane became clear. That the hexane did effectively extract the nitrate was checked by adding to 25% H_2SO_4 an amount of iso-amyl nitrate approximately equivalent to that likely to be produced in the reaction and shaking to dissolve as much as possible. To the mixture was added 10 c.c. hexane, and after shaking and separating the H_2SO_4 solution was examined on the Uvispek when no absorption due to iso-amyl nitrate was evident.

The reaction sample thus contained iso-amyl nitrate, iso-amyl alcohol and HNO_3. On dilution in water the resulting H_2SO_4 concentration varied from 21 - 25%, in which medium nitric acid is present as nitrate ion. A standard solution of KNO_3 in 70% H_2SO_4, at approximately the same concentration as HNO_3 in kinetic runs, was diluted in the same manner as used in the runs, and gave a peak at 2940 Å, with $\varepsilon = 7{\cdot}1$.

Shaking with hexane removed iso-amyl nitrate, the absorption of iso-amyl alcohol was negligible, so that the absorption measured by the Uvispek depended on the amount of HNO_3 present. The blank solution of HNO_3, in the corresponding concentration of H_2SO_4 used in the run, was obtained by removing 5 c.c. of the nitrating acid under the same conditions as those occurring in a run, adding to 10 c.c. water, and measuring on the Uvispek.

Prevention of Oxidation.

In a preliminary run in 70% H_2SO_4 the absorption measurements decreased in the usual way for the first 20 mins, at 40 mins there was a slight increase and after 90 mins the reading had increased beyond that of the blank HNO_3 solution. This indicated that some oxidation was occurring, it was probably very slight, as the intensity of absorption of nitrous acid solutions is far stronger than that of HNO_3. The slightest trace of nitrous acid, therefore, would upset the Uvispek readings, so that it was necessary to introduce an anti-oxidant. There are several which are effective, including urea, hydrazine sulphate, sulphanilic acid and sulphamic acid. Before using any of these in a run, their absorption between 2900 and 3000 Å was measured, since anything absorbing in that region would interfere. It was found that the first three gave appreciable readings, but that sulphamic acid was very low, giving a reading of •005 at a concentration comparable to that added to the reaction mixture. The procedure adopted was to weigh out the required amount of NH_2HSO_4 and dissolve it in the sulphuric acid medium to be used in the run. Thus the HNO_3/H_2SO_4 contained some sulphamic acid, which would destroy any HNO_2 which might have been produced; the reference solution for the Uvispek measurement was prepared from the same H_2SO_4 solution. The fact that the ε values obtained for the nitric acid blank were correct to 7•1 ± 0•1 showed that the absorption measurements were not affected, although the amount of sulphamic acid was increased in the lowest acid concentration at 0°C, and in those at 25°C. Further checks which showed that sulphamic acid did not interfere to any marked extent were provided by experiments in 75% H_2SO_4, when sulphamic acid was present in one run and absent in the other, the velocity constants obtained were 1•46 and 1•55 respectively; also the equilibrium readings remained constant over several hours, e.g. in 68% H_2SO_4 at 0°C the readings were 0•283 after 6 hrs and 0•284 after 10 hrs., and in 62•5% H_2SO_4 at 25°C were 0•305 after 3½ and 5½ hrs. Westheimer & Kharasch have stated (39) that small quantities of sulphamic acid did not affect the rate of nitration of nitrobenzene in H_2SO_4.

Experimental Procedure.

For the series of kinetic runs at 0°C, the following procedure was followed. An amount of sulphamic acid to give a 0•001 solution in H_2SO_4 was weighed out, and dissolved in the medium. The flask containing this H_2SO_4 was placed in ice in a thermos flask, and left for about 20 mins. The amount of anhydrous nitric acid necessary to give a 0·3 N concentration in 50 c.c. was weighed out into a measuring flask, and the flask filled up to the mark with H_2SO_4 at 0°C. 20 c.c. of the cooled H_2SO_4 were transferred to a 250 c.c. quickfit conical flask surrounded by ice, and the required amount of iso-amyl alcohol weighed out in a quickfit cup. This was then transferred to the flask, which was shaken for 2 minutes. Then 20 c.c. of the HNO_3 solution at 0°C were delivered, the zero time of the reaction being taken from the beginning of this addition. After being shaken, the flask was replaced in the ice bath, and samples were removed at appropriate intervals. The 5 c.c. samples were added to 10 c.c. cooled distilled water in 250 c.c. conical flasks, which were then shaken. The solution was transferred to a separating funnel and shaken with 10 c.c. hexane. After standing, the aqueous layer was run into a small dry conical flask and the HNO_3 present estimated in the Uvispek. 5 c.c. of the HNO_3 solution at 0°C were removed and added to 10 c.c. water to give the blank HNO_3 absorption measurement.

When the runs were carried out at 25°C, the same procedure was adopted, except that the original H_2SO_4 solution was left in the thermostat at 25°C for 20 mins, and the HNO_3/H_2SO_4 solution also brought to 25°C. before addition.

Isolation of the Reaction Products.

In order to prove that the reaction being followed was definitely producing iso-amyl nitrate, the reaction was carried out in 72·7% H_2SO_4 at 0°C with HNO_3 and iso-amyl alcohol in the same relative proportions but at much higher concentration than used in a kinetic run, i.e. 1·0 N HNO_3 and 0·5 N alcohol in 100 c.c. of the acid. After 15 mins the whole of the acid solution was added to 200 c.c. water, when an oil separated out. The mixture was shaken with hexane, dried, and the hexane distilled off. The weight of the residual oil, before distillation, gave a 65% yield assuming it was pure iso-amyl nitrate. On distillation the oil boiled at 145°C (b.p. iso-amyl nitrate 147°C). The density was measured with the use of a micro-pipette; it was found to be 0·988 (density iso-amyl nitrate 0·996) i.e. within 1%.

A further experiment was carried out with iso-amyl alcohol in H_2SO_4, in which ·99 gm. iso-amyl alcohol were dissolved in 50 c.c. 25% H_2SO_4, and the solution shaken with hexane. The hexane solution was dried, and then the hexane distilled off; the weight of the residue was 0·05 gm, which showed that practically all the alcohol remained unextracted. The aqueous layer was checked on the Uvispek, and gave a small but measurable reading, proving that the alcohol was in fact still in solution.

Measurement of Equilibrium Concentrations starting from Iso-amyl Nitrate.

The insolubility of the nitrate made kinetic measurements of the reverse reaction impractical, but it was possible to leave the nitrate in H_2SO_4 to reach equilibrium, which was done at two different H_2SO_4 concentrations.

The nitrate was shaken with H_2SO_4 which contained enough nitric acid to ensure that the final relative concentrations of alcohol, HNO_3 and nitrate should be similar to those reached in the forward reaction. The amount of nitric acid produced was relatively small, which meant that the change in the absorption spectra was also small, and the error correspondingly increased, e.g. in 74•6% H_2SO_4 the initial HNO_3 reading was 0•174, and the final 0•205, which corresponded to a change in concentration of •014 N ; thus agreement between equilibrium constants obtained from the forward and reverse directions within 10% was not unreasonable.

Kinetic Measurements in Perchloric Acid.

As the accuracy of the acidity function method of interpreting kinetic results was apparently doubtful, the work of Deno (16) illustrating the discrepancies which arise in nitration, another way of considering kinetic results was available. Work had been carried out by Singer & Vamplew (35) on the absorption spectrum of nitrous acid in $HClO_4$, and it was decided to see if any correlation existed between the ionisation of HNO_2 in $HClO_4$ and the rate of esterification of iso-amyl alcohol by HNO_3 in this medium.

Before the actual runs were started, various preliminary investigations similar to those carried out in H_2SO_4 were made. Thus iso-amyl alcohol was dissolved in 72% $HClO_4$ and 62•5% $HClO_4$, and the alteration in the absorption spectrum over about 60 mins noted. Whereas that in 72% increased from a reading at 2950 Å of 0•013 to 0•30 in 1 hr, that in 62•5% remained unchanged at 0•027 over the same period. Another check was made on the absorption of the alcohol in $HClO_4$ at approximately the concentration used in the kinetic runs, and this was found to be between 0•005 and 0•008. Also the spectrum of sulphamic acid in $HClO_4$ was investigated; using a concentration of 0•01 N in a reaction mixture gave a reading of 0•003. Finally the absorption spectrum of nitric acid was measured, and found to give $\varepsilon = 7{\cdot}2$; as with H_2SO_4 the ε measured in each $HClO_4$ concentration did vary between 7•0 and 7•2, but as the actual reading obtained in each run was taken as the standard for that run, the error introduced was not appreciable.

The procedure was the same as that used for H_2SO_4 runs at 25°C, the sulphamic acid being dissolved in $HClO_4$ before the nitric and alcohol solutions were made up, and the blank solution of HNO_3 prepared. Whereas with H_2SO_4 a range of 10%, i.e. from 57 - 67% could conveniently be studied, in $HClO_4$ the reasonable limits were from 55 - 62•5%.

Indicator Measurements on Triphenylcarbinol Compounds in H_2SO_4.

The first set of kinetic results were obtained at 0°C. in H_2SO_4, and as these were to be compared with the acidity function J_0, which had only been measured at 25°C, it was decided to measure a J_0 indicator at a lower temperature. The indicator had previously been prepared; the one ionising over a suitable range was 4 Cl, 4', 4", bis-(dimethylamino) triphenylcarbinyl methyl ether diperchlorate.

The procedure was as follows; a solution of 0·1 gm. indicator was dissolved in 25 c.c. 90% H_2SO_4, in which it was completely ionised. This strong solution was diluted with more 90% H_2SO_4, the solution being weighed out from a weight pipette to give a final concentration 0·0000355 N. The absorption spectrum of this solution was measured over the range 3600 - 5000 Å, so that the wavelength of the peak could be found. This concentration was rather too high to give a very accurate value of $\mathcal{E}$ at the peak, the reading being 1·77 which is outside the most accurate range of the instrument. However, as the measurement was to be repeated in a lower acid in which the carbinol still remained completely ionised, it was acceptable.

Solutions were then made up in a series of acids ranging from 69·0 to 78·6%; as before a strong solution in the appropriate acid was made up and diluted, the final solution being made up at 0°C. The concentration was varied as the proportion of ionised indicator became less, so that the absorption measurements remained within the limits 0·3 to 1·0.

It was impossible to keep the temperature in the Uvispek at 0°C, and the carbinol solution warmed up slightly when being transferred to the cell, but it was found that the temperature could be maintained at 7°C.± $\frac{1}{2}^{\circ}$. The measurements were certainly not as accurate as those of Bevan (41) but they gave a reasonably straight line when log $\frac{[R^+]}{[ROH]}$ was plotted against % H_2SO_4, except for the lowest 2 points, where ionisation was low, and gave an indication of the increased effect of temperature as % ionisation decreased.

Indicator Measurements in Perchloric Acid.

Since there has been no determination of the J_0 acidity function in $HClO_4$, it was decided to measure the ionisation of one of the J_0 indicators which had been used in H_2SO_4, and would ionise over the same range as the kinetic runs and NO^+ measurements if possible. The indicator which did overlap to a certain extent was 4-trimethylammonium triphenylcarbinyl methyl ether perchlorate, which had previously been prepared.

A concentrated solution of the carbinol in 64·2% $HClO_4$, in which it was fully ionised, was prepared by dissolving 0·137 gm. in 25 c.c. acid. Suitable amounts of this solution were added to the other $HClO_4$ media ranging from 50•4 to 60•8%. A correction was made for the alteration in the lower media by the introduction of the known weight of 64•2% $HClO_4$ from the weight pipette. The measurements were carried out at 25°C ; the complete spectrum in 64•2% $HClO_4$ was measured to find the wavelength of the peak, which occurred at 4420 Å, where the other intensities were measured. The results of plotting log $\frac{[R^+]}{[ROH]}$ against percentage acid for these indicators are shown in Graphs 8 & 9.

Calculation of Results.

The kinetic results were calculated using the equation for a second order forward reaction and first order reverse reaction

$$k_2 t = \frac{2 \cdot 303 z}{(ab - z^2)} \cdot \log \left(\frac{z}{ab} \times \frac{(ab - zx)}{z - x} \right)$$

where

Z = concentration of iso-amyl nitrate at equilibrium.

a = initial HNO_3 concentration.

b = initial iso-amyl alcohol concentration.

x = concentration of ester at time t.

Although it was not proved experimentally in this case that the reverse reaction was first order it has been shown (25) that acid hydrolysis of alkyl nitrates does obey first order kinetics and the equation fitted the results to give straight lines when

$$\log \left(\frac{z}{ab} \times \frac{(ab - zx)}{z - x} \right)$$

was plotted against time. The slope of the line was thus given by

$$\text{Slope} = k_2 \frac{(ab - z^2)}{2{\cdot}303z}$$

Details of the calculations for a typical experiment are given in Table I.

(1) Experimental Details.

Esterification in 65·3% H_2SO_4 at 25°C.

Exp: I. Wt of anhydrous HNO_3 in 50 c.c. = 0·9236 gm.

∴ concⁿ in reaction = 0·1454 N.

Wt iso-amyl alcohol in 40 c.c. = 0·2569 gm.

∴ concⁿ in reaction = ·07299 N.

Time	Uvispek Reading	HNO_3 concⁿ	Ester concⁿ x.	$\log\left(\frac{z}{ab} \times \frac{(ab - zx)}{z - x}\right)$
0	·349	·1454	0	-
10 min.	·305	·1271	·0183	·169
20 min.	·275	·1146	·0308	·376
35 min.	·259	·1079	·0375	·570
50 min.	·246	·1025	·0429	·859
70 min.	·239	·0996	·0458	1·188
90 min.	·233	·0971	·0483	-
3 hr.	·233	·0971	·0483	-

From graph, slope = $.0165 = k_2 \frac{(\cdot 1454 \times 0\cdot 07299 - 0\cdot 0483^2)}{2\cdot 303 \times 0\cdot 0483}$

$$k_2 = \frac{2\cdot 303 \times 0\cdot 0483 \times 0\cdot 0165}{0\cdot 008285}$$

$$k_2 = 0\cdot 221$$

$$\log k_2 = -\,0\cdot 655$$

Equilibrium const. = $\frac{0\cdot 0483}{0\cdot 0247 \times 0\cdot 0971}$ = 20·2

Exp: II in 65·3%.

Concentration HNO_3 = 0·1454 N.

Wt iso-amyl alcohol = 0·2465 gm.

Conc^n iso-amyl alcohol = 0·0700 N.

Time	Uvispek Reading	HNO_3 concn.	Ester conc^n x.	$\log\left(\frac{z}{ab} \times \frac{(ab - zx)}{z - x}\right)$
0	·349	·1454	-	
4	·322	·1342	·0112	·097
10	·308	·1284	·0170	·162
20	·280	·1167	·0287	·371
30	·269	·1113	·0341	·512
45	·254	·1058	·0396	·735
80	·237	·0988	·0466	-
3 hrs.	·238	·0992	-	-

Slope of graph $= 0{\cdot}0163 = \frac{k_2 \times 0{\cdot}008015}{2{\cdot}303 \times {\cdot}0466}$

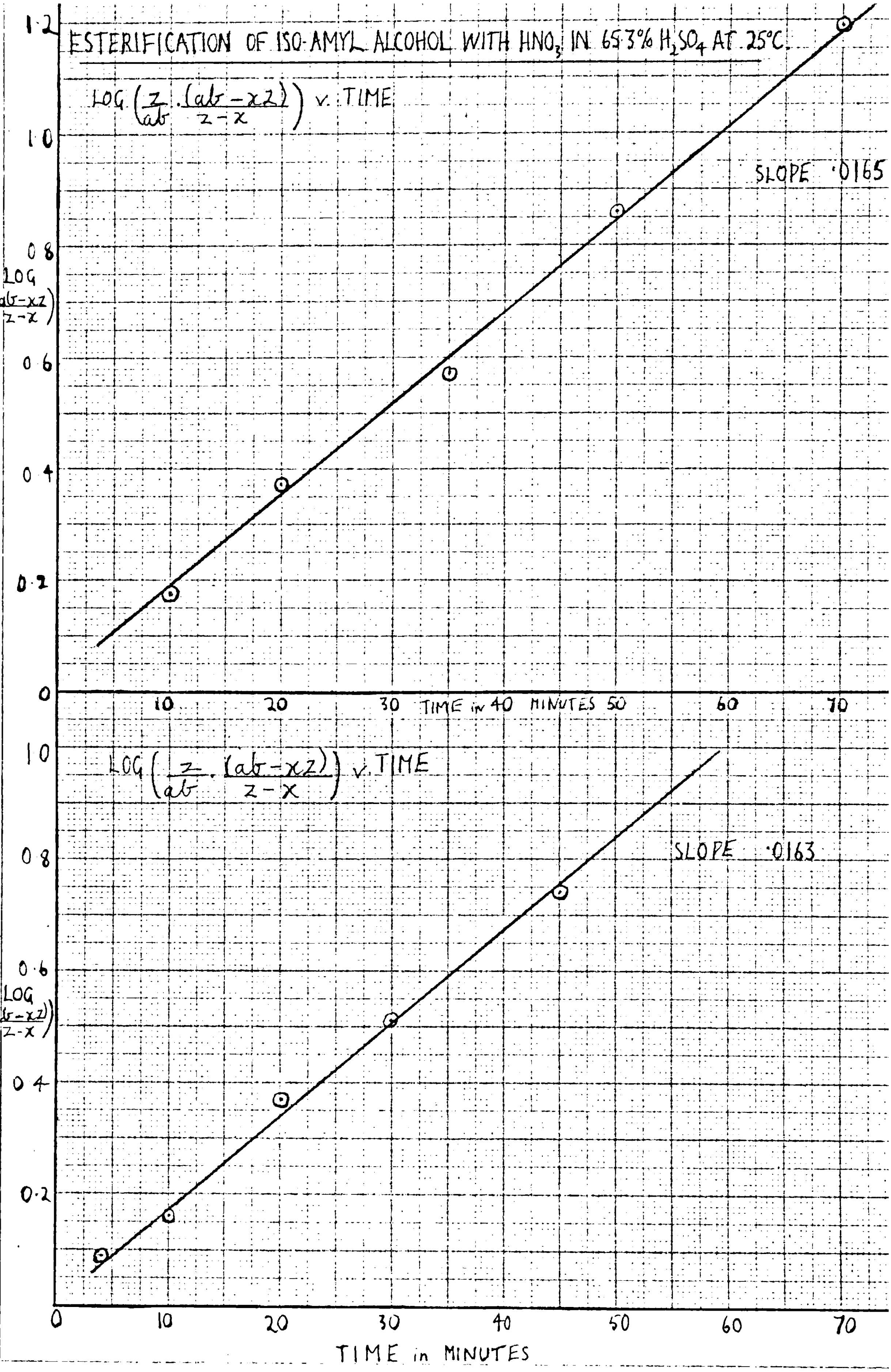
$\therefore\ k_2 = 0{\cdot}218$

$\log\ k_2 = -\ 0{\cdot}660$

Equilibrium const $= \frac{0{\cdot}0466}{0{\cdot}0234 \times 0{\cdot}0988}$

$= 20{\cdot}2$

GRAPH 1



ESTERIFICATION OF ISO-AMYL ALCOHOL WITH HNO_3 IN 65·3% H_2SO_4 AT 25°C.

Equilibrium Constants measured from initial Iso-amyl Nitrate.

Example: Exp. in 74·6% H_2SO_4.

Weight of iso-amyl nitrate in 20 c.c. = 0·111 gm.

$\therefore$ concentration = ·0417 N

Weight of anhydrous HNO_3 = 0·1314 gm.

$\therefore$ concentration = 0·0828 N

5 c.c. samples removed after 90, 110 & 140 min. and added to 10 c.c. water; nitrate extracted with hexane.

	90 min.	110 min.	140 min.
2940	0·233	0·231	0·231

$\therefore$ final HNO_3 concentration $= \frac{0{\cdot}231}{7{\cdot}1} = 0{\cdot}0975$ N

$\therefore$ amount HNO produced = 0·0975 - 0·0828

= 0·0147 N

$\therefore$ amount alcohol = 0·0147 N

$$\therefore \text{ equilibrium constant} = \frac{0{\cdot}0417 - 0{\cdot}0147}{0{\cdot}0975 \times 0{\cdot}0147}$$

$$= 18{\cdot}9$$

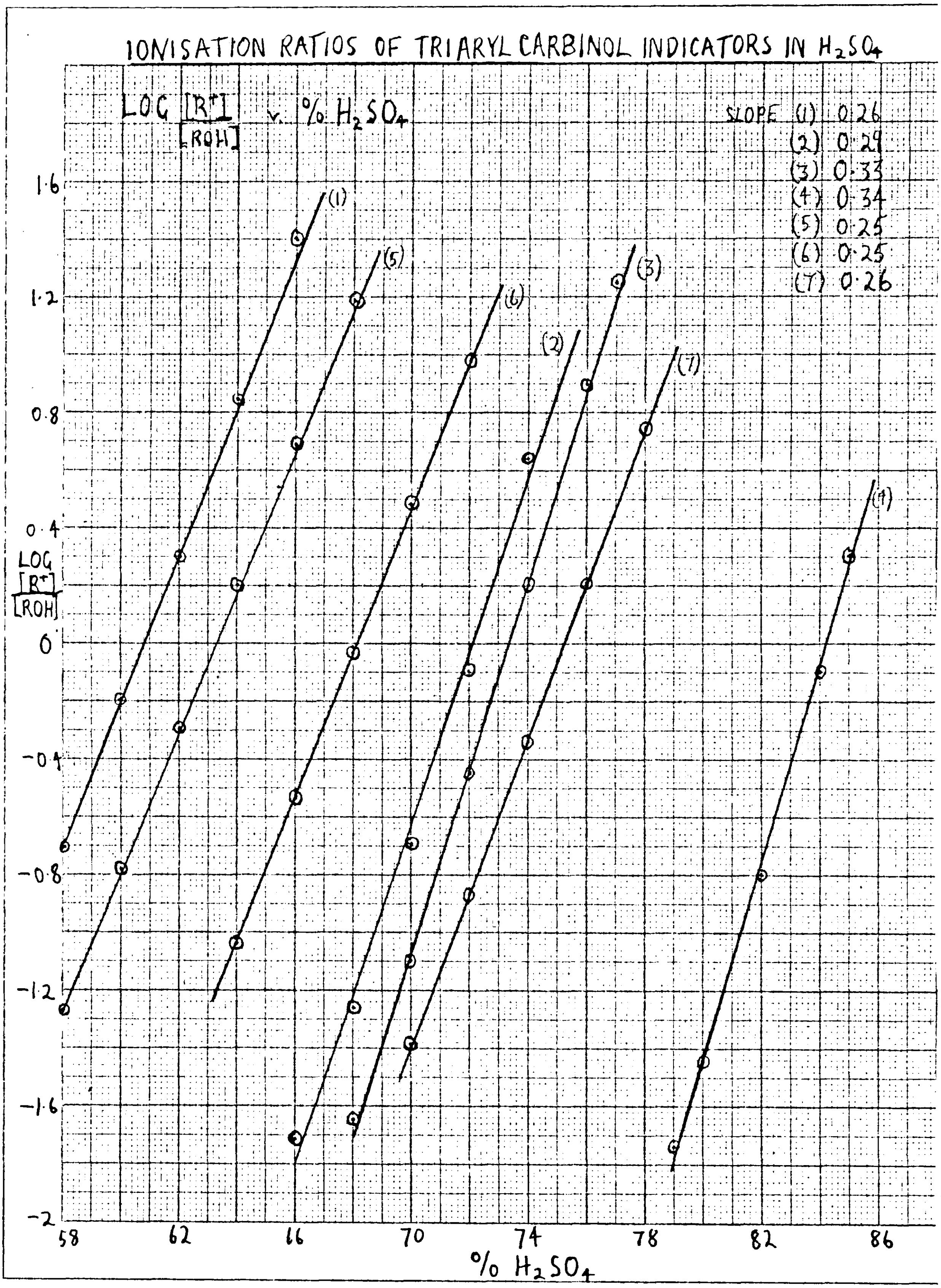
% H_2SO_4	Equil^n K from iso-amyl nitrate	Mean K	K from iso-amyl alcohol
74·6	18·9	19·7	18.3
	20·5		
69·7	13·7	13·2	12·2
	12·7		

Tables of log $\frac{[R^+]}{[ROH]}$ for various indicators.

Indicator		% H_2SO_4	log $\frac{[R^+]}{[ROH]}$
$ClO_4^-\ (Me_3{}^+N)C_6H_4.\ C(C_6H_5)_2OMe.$	(1)	60	- 0·2
		62	+ 0·31
		64	+ 0·85
$(ClO_4^-)_2(Me_3{}^+N.\ C_6H_4)_2.C.C_6H_5.OMe.$	(2)	68	- 1·26
		70	- 0·7
		72	- 0·1
$(ClO_4^-)_2(Me_3{}^+N.C.C_6H_4Cl.OMe.$	(3)	70	- 1·1
		72	- 0·45
		74	+ 0·2
$(ClO_4^-)_3(Me_3{}^+N.C_6H_4)_3.C.OMe.$	(4)	80	- 1.46
		82	- 0·8
		84	- 0.11
2-phenyl borneol	(5)	60	- 0.58
		64	+ 0·2
		68	+ 1·2
Trichlorotriphenylmethanol	(6)	64	- 1·04
		68	- 0·04
		72	+ 0·98
Dinitrotrichloromethane	(7)	70	- 1·4
		74	- 0·34
		78	+ 0·74

Indicators (1) (3) (4). Bevan (45); Indicator (2) Murray (58); Indicators (5) (6) (7). Deno (14).

GRAPH 2



IONISATION RATIOS OF TRIARYL CARBINOL INDICATORS IN H_2SO_4

Rate and Equilibrium Constants for Esterification of Iso-amyl Alcohol by HNO_3 in $HClO_4$ at 25°C

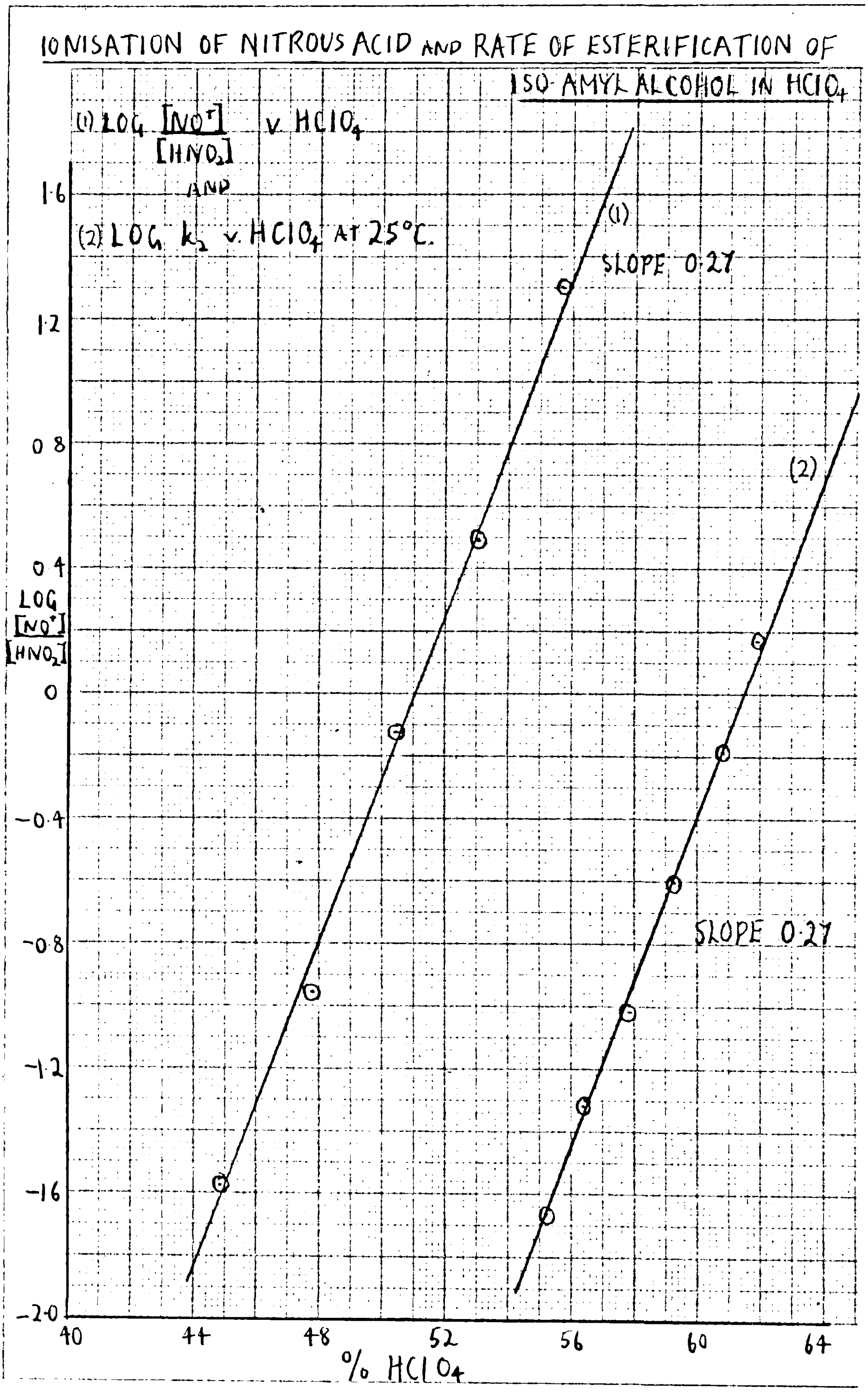
% $HClO_4$	Rate constant k_2	Mean k_2	Equil^m Const. K.	Mean K	$k_1 = \frac{k_2}{K}$	% Ester at Equil^m.
62•0	1•56	1•57	10•3	10•0	0•157	54
	1•58		9•70			
60•8	0•705	0•711	7•13	7•39	0•0963	46
	0•716		7•66			
59•3	0•275	0•271	5•96	5•93	0•0457	38
	0•267		5•90			
58•0	0•0996	0•101	4•01	4•10	0•0246	34
	0•102		4•20			
56•3	0•0513	0•0501	3•18	3•24	0•0155	28
	0•0489		3•30			
55•2	0•0222	0•0223	2•39	2•43	0•00916	25
	0•0225		2•47			

Values for log k_2 and log $\frac{[NO^+]}{[HNO_2]}$ in $HClO_4$ at 25°C.

% $HClO_4$	log k_2	log $\frac{[NO^+]}{[HNO_2]}$ *
4·5	-	- 1·55
47·9	-	- 0·945
50·4	-	- 0·118
53·0	-	+ 0·489
55·2	- 1·65	-
55·6	-	+ 1·307
56·3	- 1·30	-
58·0	- 0·996	-
59·3	- 0·567	-
60·8	- 0·148	-
62·0	+ 0·196	-

* Singer and Vamplew (35)

GRAPH 3


IONISATION OF NITROUS ACID AND RATE OF ESTERIFICATION OF ISO-AMYL ALCOHOL IN $HClO_4$
(1) LOG $\frac{[NO^+]}{[HNO_2]}$ v $HClO_4$
AND
(2) LOG k_2 v. $HClO_4$ AT 25°C.
(1)
SLOPE 0·27
(2)
SLOPE 0·27
1·6
1·2
0·8
0·4
LOG $\frac{[NO^+]}{[HNO_2]}$
0
−0·4
−0·8
−1·2
−1·6
−2·0
40
44
48
52
56
60
64
% $HClO_4$

Rate and Equilibrium Constants for Esterification of Iso-amyl alcohol by HNO_3 in H_2SO_4 at 25°C.

% $HClO_4$	Rate constant k_2	Mean K_2	Equilm Const.K.	Mean K	$k_1 = \frac{k_2}{K}$	% Ester at Equil^m.
67•0	0•312	0•315	18•9	19•5	0•0162	65
	0•318		20•1			
66•0	0•254	0•252	23•4	22•4	0•0113	68
	0•249		21•3			
65•3	0•218	0•219	20•2	20•2	0•0108	66
	0•221		20•2			
63•5	0•0948	0•0938	14•3	13•5	0•00695	56
	0•0928		12•7			
62•4	0•0514	0•0504	7•91	8•31	0•00606	48
	0•0494		8•72			
60•0	0•0170	0•0172	5•85	5•60	0•00307	42
	0•0174		5•35			
57•7	0•00744	0•00732	3•93	3•71	0•00198	38
	0•00720		3•48			

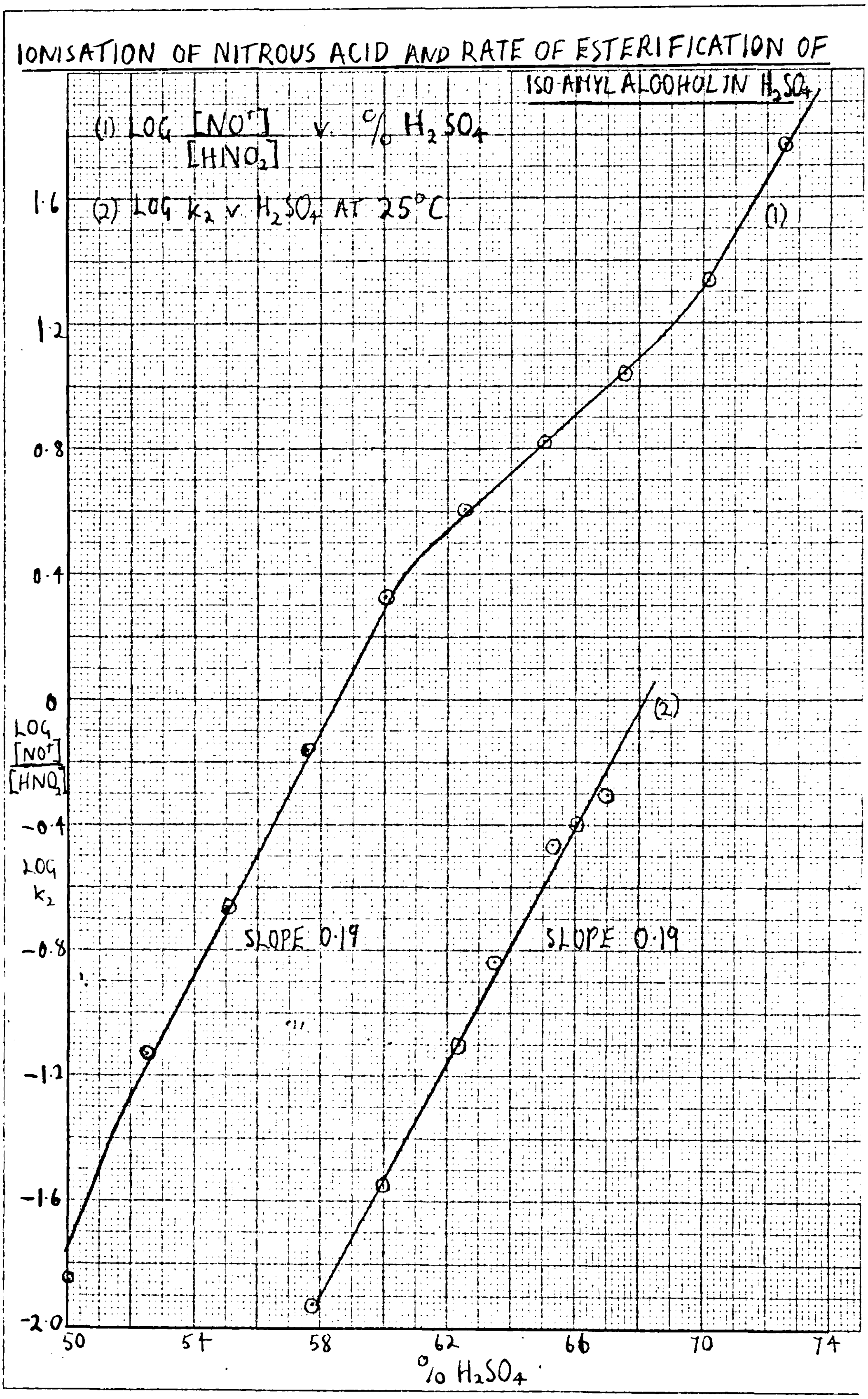
Values for log k_2 for esterification of Iso-amyl alcohol with HNO_3; log $\frac{[NO^+]}{[HNO_2]}$ and log $\frac{[NO^+]}{[HNO_2 + H_2NO_2^+]}$ in H_2SO_4 at 25°C.

% H_2SO_4	log k_2	log $\frac{[NO^+]}{[HNO_2]}$ (1)	log $\frac{[NO^+]}{[HNO_2 + H_2NO_2^+]}$ (2)
50		- 1·86	- 2·00
52·5		- 1·13	- 1·38
55		- 0·665	- 1·06
57·5		- 0·160	- 0·659
57·7	- 2·14	-	-
60·0	- 1·76	0·323	- 0·158
62·4	- 1·30	-	-
62·5	-	0·602	0·140
63·5	- 1·03	-	-
65·0	-	0·817	0·346
65·3	- 0·66	-	-
66·0	- 0·599	-	-
67·0	- 0·502	-	-
67·5		1·04	0·525
70·0		1·32	0·720
72·5		1·77	0·908
75·0		2·27	1·196

(1) Bayliss and Watts (36)

(2) Dr. Singer private communication, i.e. suggestion that $H_2NO_2^+$ may not be real but represent loss of HNO_2 or faulty analysis.

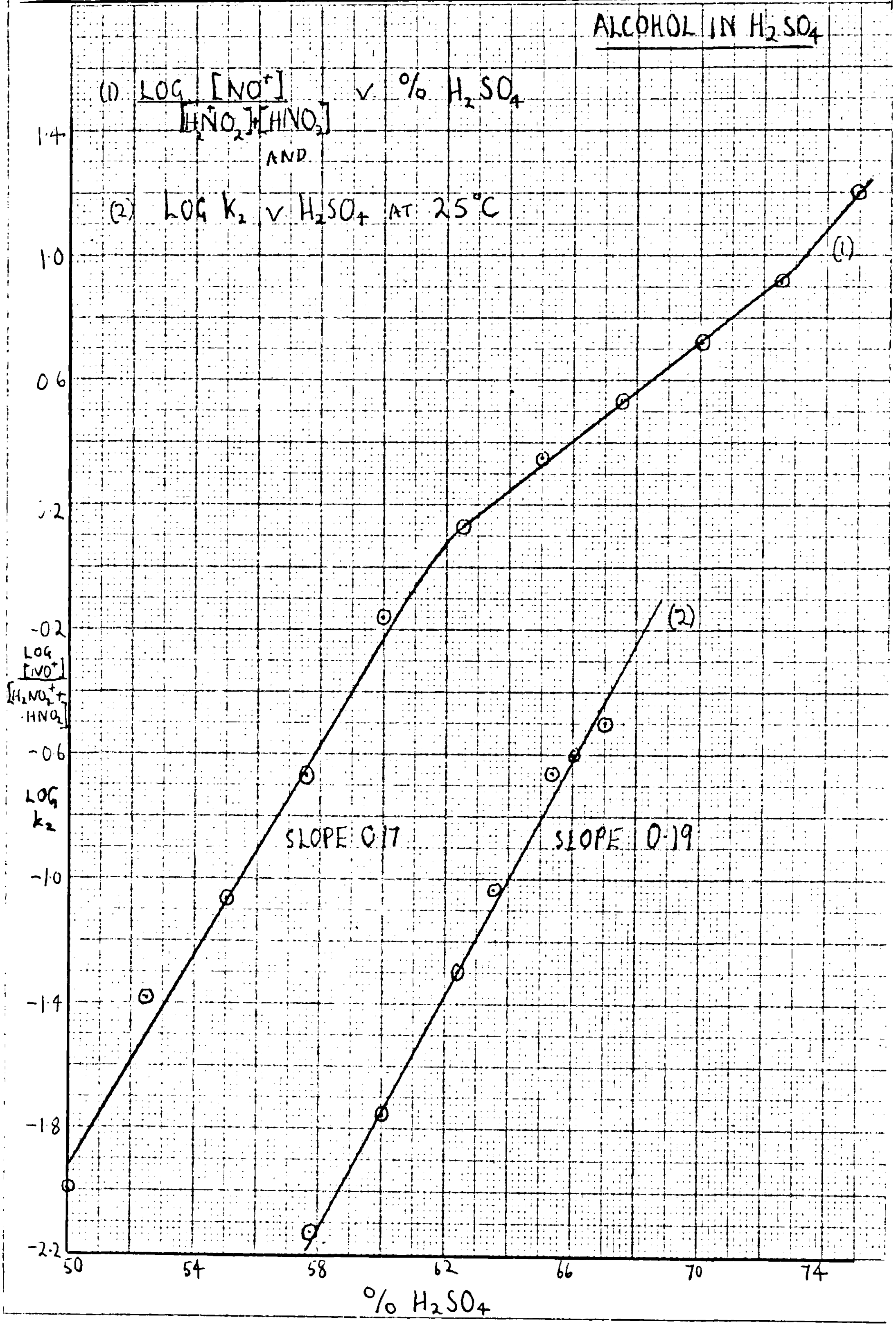
GRAPH 4



IONISATION OF NITROUS ACID AND RATE OF ESTERIFICATION OF ISO-AMYL ALCOHOL IN H_2SO_4

GRAPH 5

IONISATION OF NITROUS ACID AND RATE OF ESTERIFICATION OF ISO-AMYL ALCOHOL IN H_2SO_4



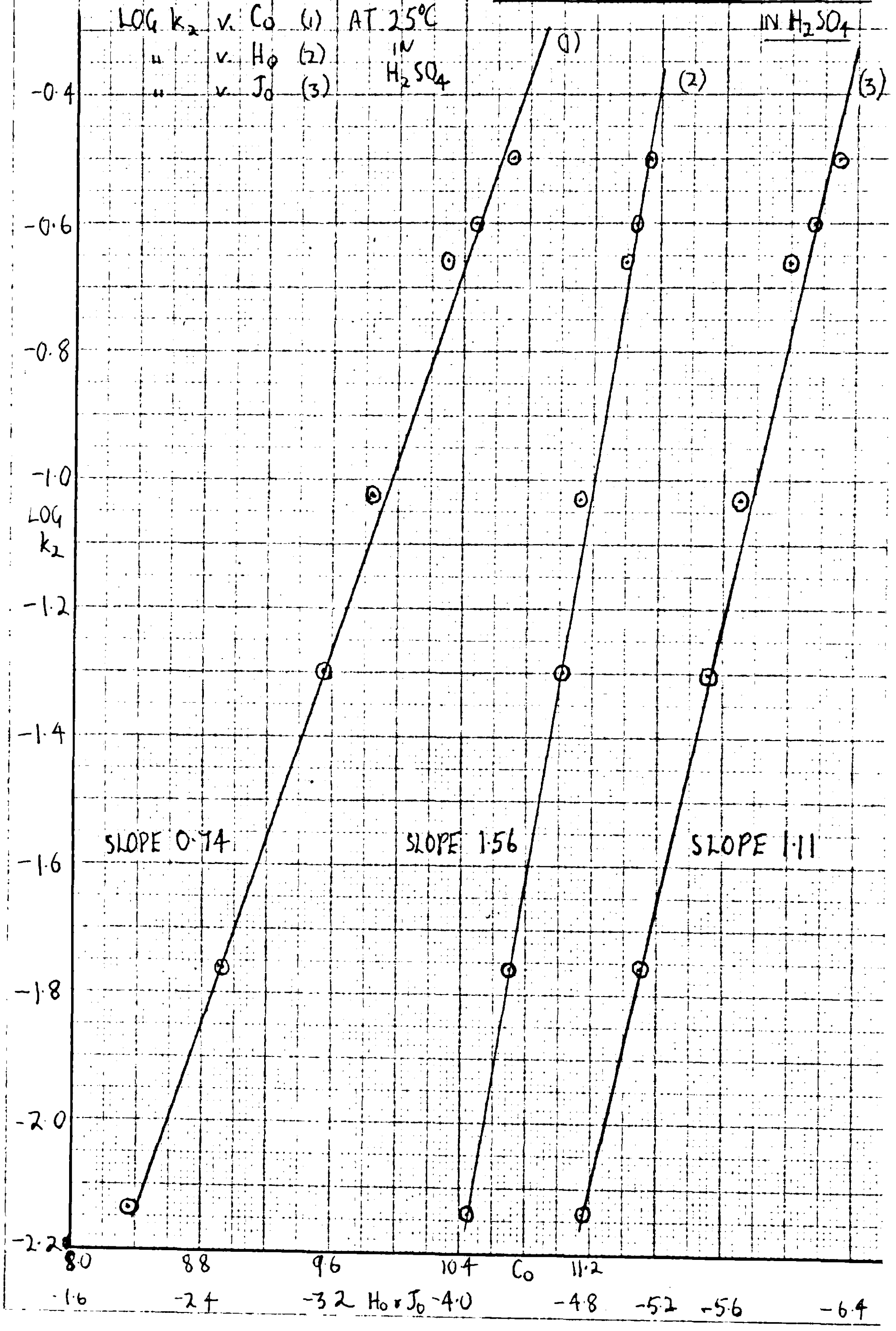
Values of log k_2 in H_2SO_4 at 25°C. and Acidity Functions
Co, *Jo and Ho.

% H_2SO_4	k_2	log k_2	Co	Jo calc.	Ho.
67·0	0·315	- 0·502	10·72	- 6·3	- 5·15
66·0	6·252	- 0·599	10·47	- 6·15	- 5·05
65·3	0·219	- 0·660	10·30	- 6·0	- 4·98
63·5	0·0938	- 1·03	7·82	- 5·7	- 4·72
62·4	0·0504	- 1·30	9·55	- 5·5	- 4·62
60·0	0·0172	- 1·76	8·92	- 5·1	- 4·3
57·7	0·00732	- 2·14	8·35	- 4·75	- 4·05

* Gold and Hawes (13)

GRAPH 6

RATE OF ESTERIFICATION OF ISO-AMYL ALCOHOL COMPARED WITH ACIDITY FUNCTIONS C_0, H_0, J_0 IN H_2SO_4

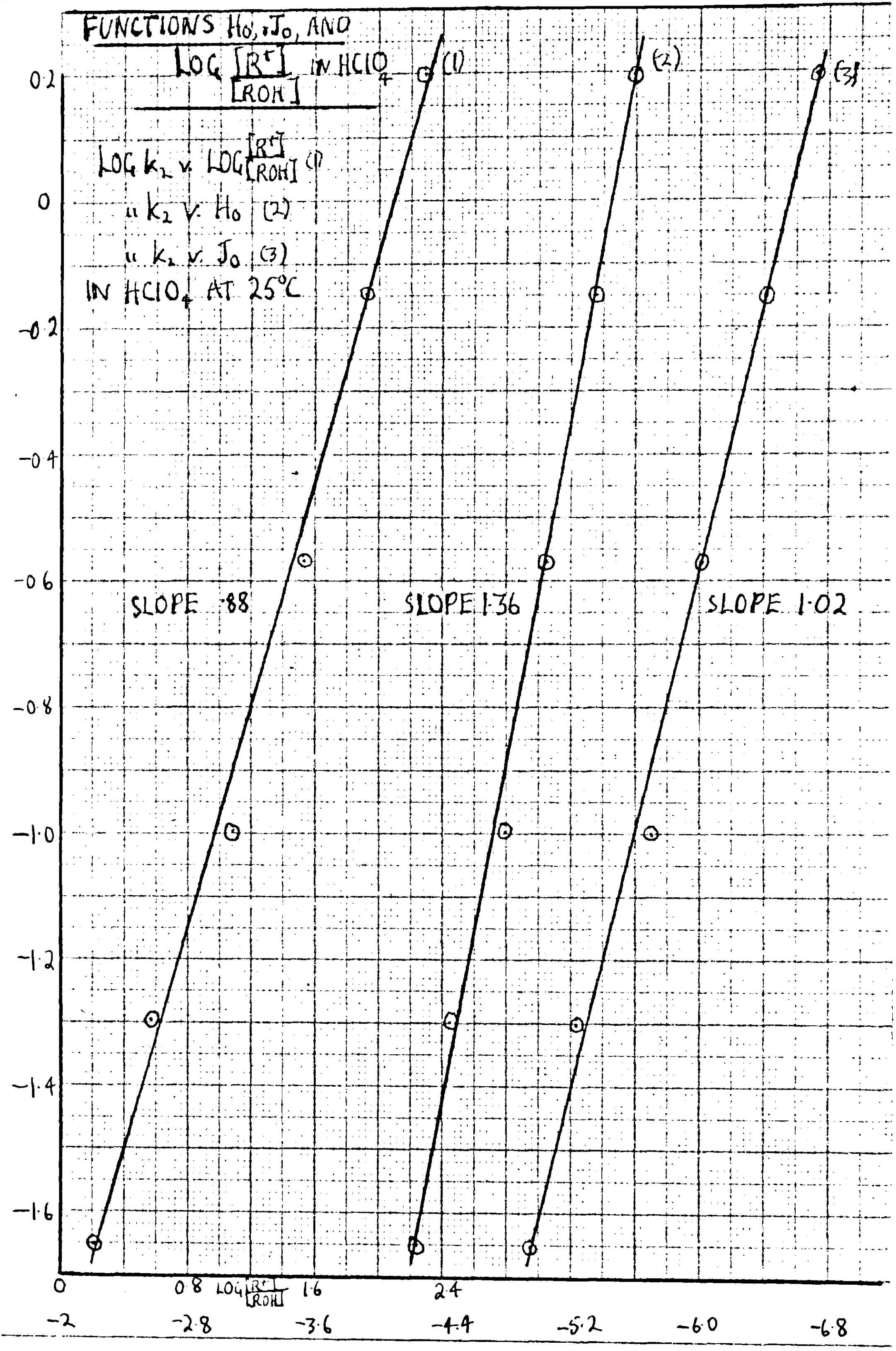


Values of log k_2 in $HClO_4$ at 25°C, Acidity Functions Ho, Jo, and log $\frac{[R^+]}{[ROH]}$ for 4-trimethylammoniumtriphenylcarbinyl methyl ether perchlorate in $HClO_4$.

% $HClO_4$	Rate const.	log k_2	Ho	Jo	log $\frac{[R^+]}{[ROH]}$
62	1·57	0·196	- 5·6	- 6·77	2·31
60·8	0·711	- 0·148	- 5·34	- 6·43	1·94
59·3	0·271	- 0·567	- 5·04	- 6·03	1·48
58·0	0·101	- 0·996	- 4·78	- 5·68	1·08
56·3	0·0501	- 1·30	- 4·44	- 4·23	0·56
55·2	0·0223	- 1·65	- 4·23	- 4·96	0·22

GRAPH 7

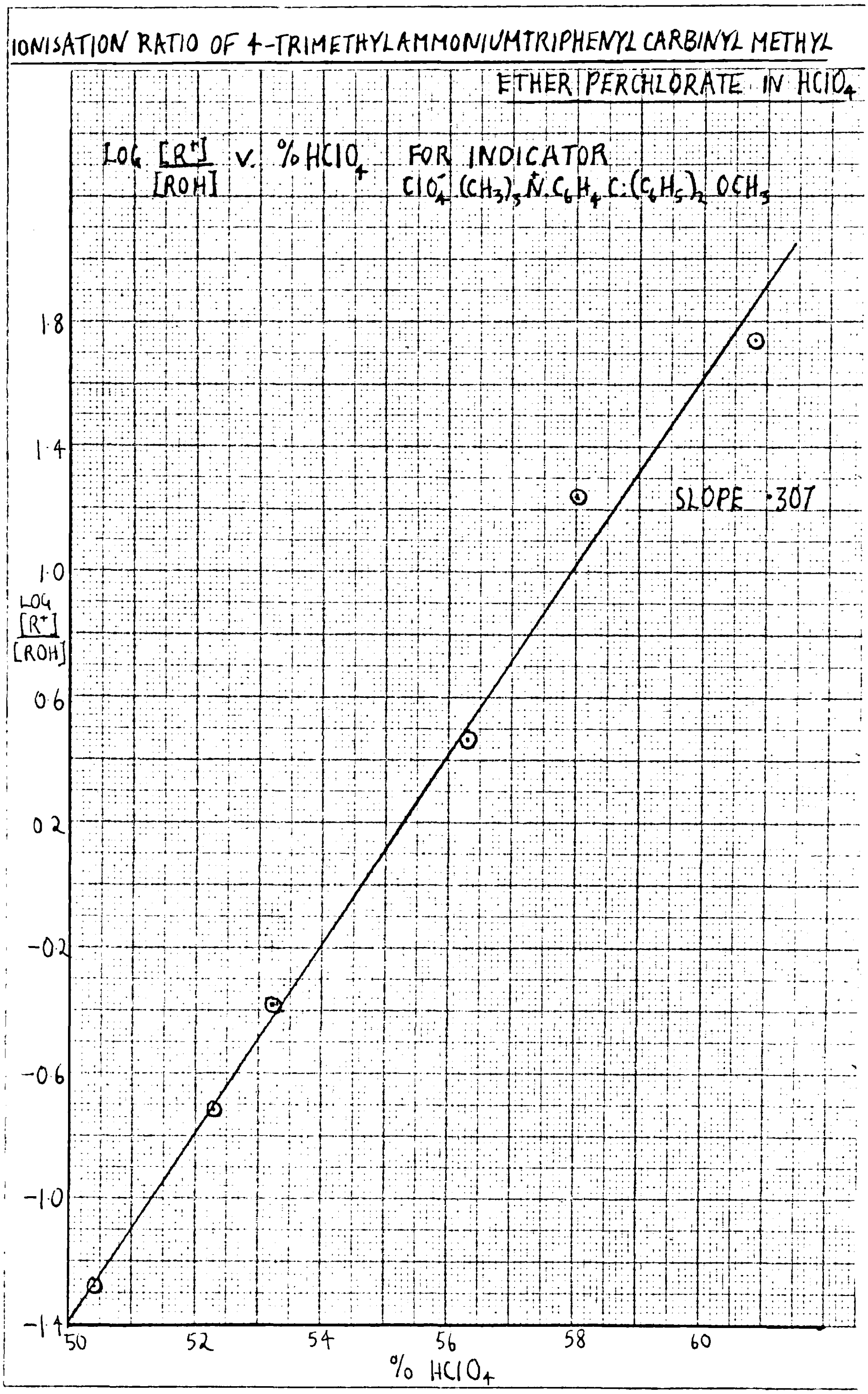
RATE OF ESTERIFICATION OF ISO-AMYL ALCOHOL COMPARED WITH ACIDITY



Results of Indicator Measurements at 25°C. in $HClO_4$ on 4-Trimethylammoniumtriphenylcarbinyl methyl ether perchlorate.

% $HClO_4$	Uvispek Reading	Concentration $\times 10^{+4}$	$\varepsilon \times 10^{-4}$	$\log \frac{[R^+]}{[ROH]}$
50•4	0•202	1•198	0•1687	- 1•283
52•3	0•433	•7946	0•545	- 0•720
53•2	0•469	•4752	0•987	- 0•390
55•2	0•877	•4093	2•143	0•229
56•3	0•955	•3791	2•520	0•453
58•0	0•673	•2088	3•222	1•243
60•8	1•420	•4244	3•346	1•742
64•16	1•227	•3602	3•406	-

GRAPH 8


IONISATION RATIO OF 4-TRIMETHYLAMMONIUMTRIPHENYL CARBINYL METHYL ETHER PERCHLORATE IN $HClO_4$

Results of Indicator Measurements at 7°C.

Indicator 4-Cl-4':4''-bis(dimethylamino)triphenyl carbinyl methyl ether diperchlorate.

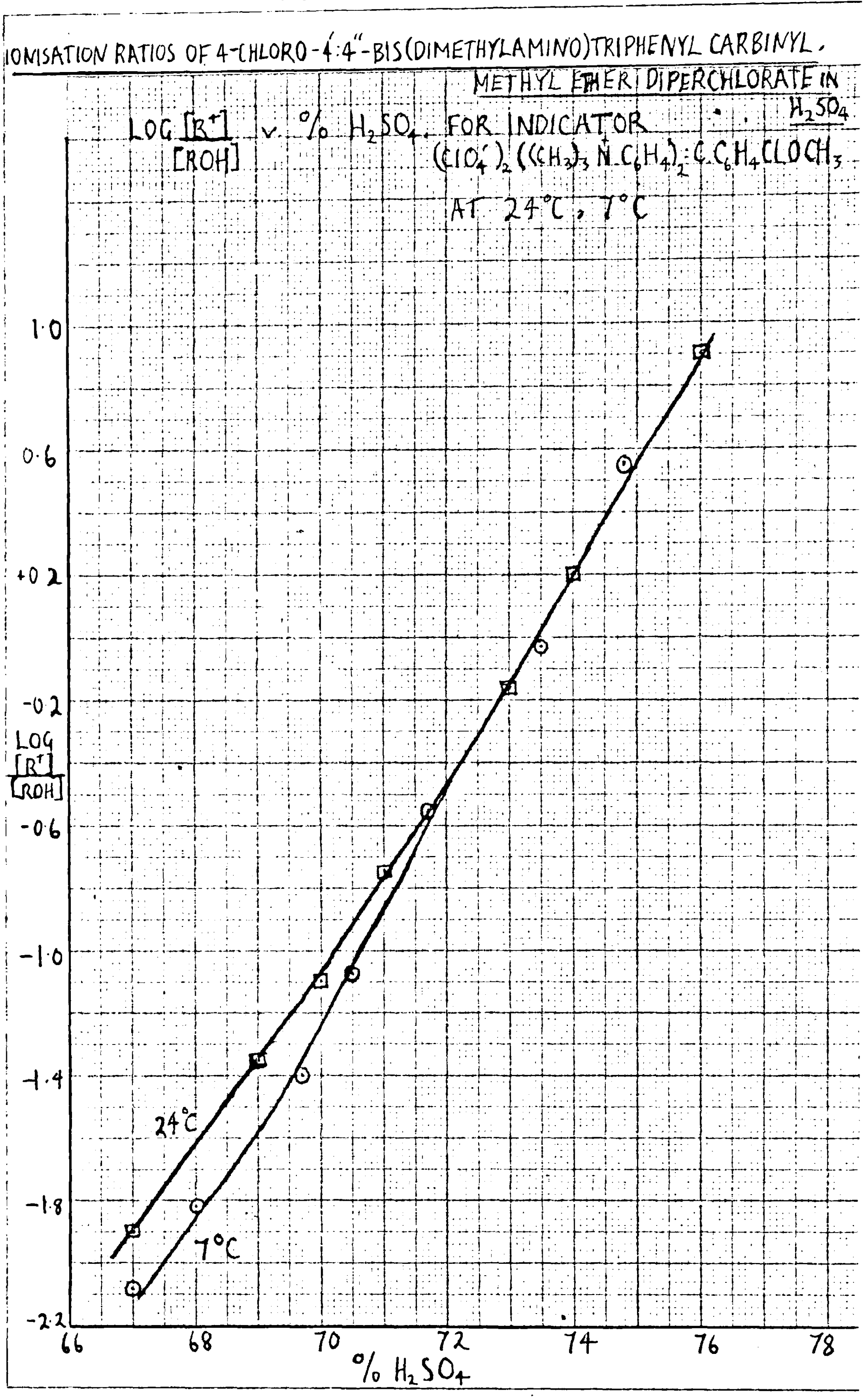
% H_2SO_4	Uvispek Reading	Conc^n x 10^{+3}	ε x 10^{-4}	R^+x 10^{+4}	log $\frac{[R^+]}{[ROH]}$
67·0	0·850	1·948	0·0436	·162	- 2·076
68·0	0·780	·990	0·0787	·149	- 1·817
69·7	0·275	·137	0·0200	·0525	- 1·400
70·5	0·590	·134	0·440	·113	- 1·072
71·7	0·604	·0526	1·143	·115	- 0·552
73·5	0·980	·0387	2·530	·187	- 0·029
74·8	1·04	·0254	4·099	·118	- 0·548
78·6	0·567	·0108	5·241		

Values of log $\frac{[R^+]}{[ROH]}$ for 4-Chloro-4':4''-Bisdimethylaminotriphenyl carbinyl methyl ether diperchlorate in H_2SO_4 at 24°C and 7°C.

% H_2SO_4	log $\frac{[R^+]}{[ROH]}$ * at 24°C.	log $\frac{[R^+]}{[ROH]}$ at 7°C.
67•0	- 1•90	- 2•076
68•0	-	- 1•817
69•0	- 1•35	-
69•7	-	- 1•40
70•0	- 1•10	-
70•5	-	- 1•072
71•0	- 0•75	-
71•7	-	- 0•552
73•0	- 0•16	-
73•5	-	- 0•029
74•0	0•20	-
74•8	-	0•548
76•0	0•90	-

* Log $\frac{[R^+]}{[ROH]}$ from Bevan (48)

GRAPH 9



IONISATION RATIOS OF 4-CHLORO-4′:4″-BIS(DIMETHYLAMINO)TRIPHENYL CARBINYL. METHYL ETHER DIPERCHLORATE IN H_2SO_4

LOG $\frac{[R^+]}{[ROH]}$ v. % H_2SO_4. FOR INDICATOR $(ClO_4')_2((CH_3)_3\overset{+}{N}C_6H_4)_2 : C.C_6H_4ClOCH_3$

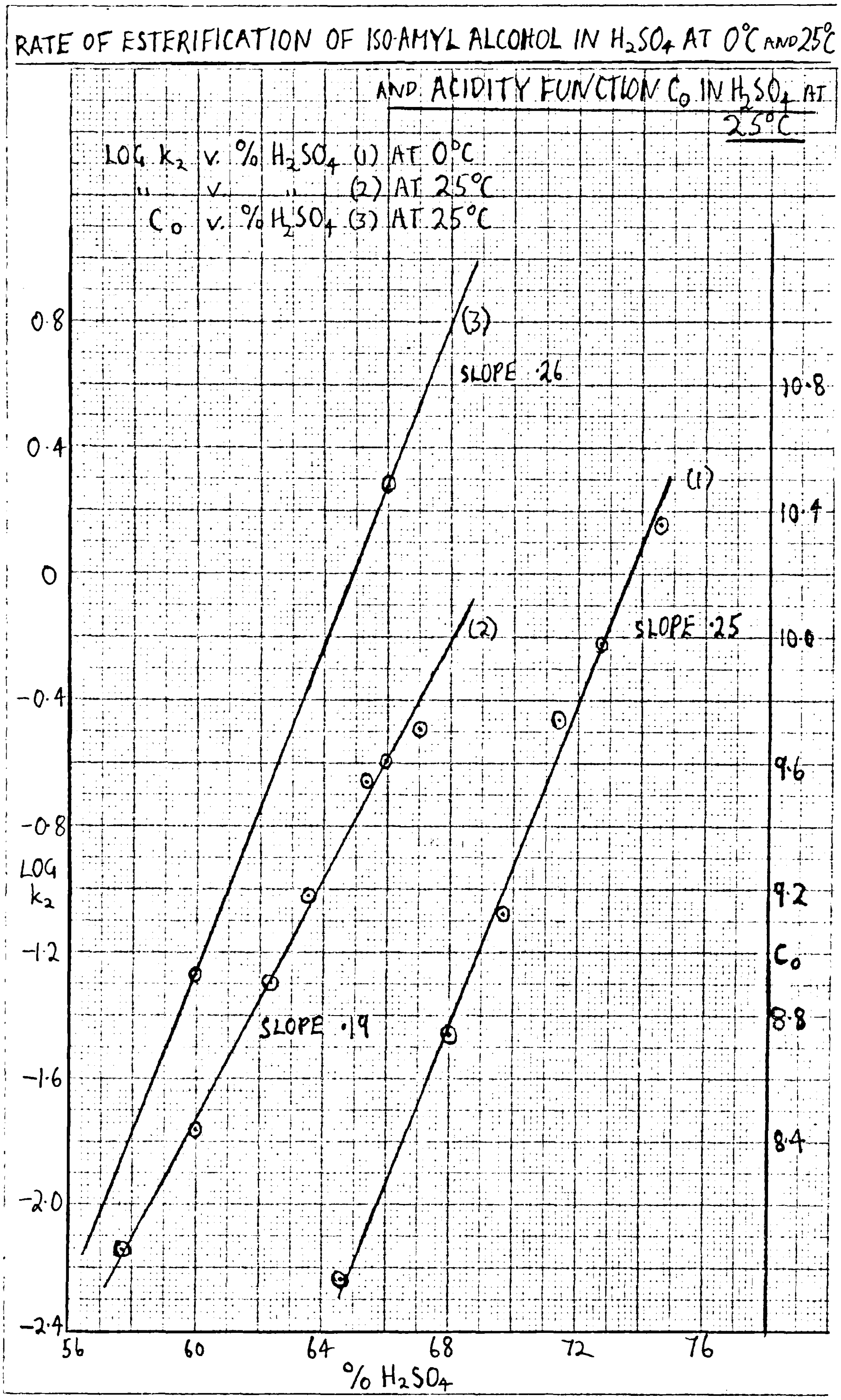
AT 24°C, 7°C

Rate and Equilibrium Constants for esterification of iso-amyl alcohol by HNO_3 in H_2SO_4 at $0^{\circ}C$.

% H_2SO_4	Rate constant k_2	Mean k_2	Equil^m Const.K.	Mean K	$k_1 = \frac{k_2}{K}$	% Ester at Equil^m	Log k_2
74·6	1·53	1.49	19·2	18·3	0·0815	66	- 0·173
	1·46		17·4				
72·7	0·585	0·594	15·0	15·1	0·0394	63	- 0·226
	0·603		15·2				
71·4	0·343	0·345	14·7	14·5	0·0238	62	- 0.462
	0·348		14·3				
69·7	0·0879	0·0867	11·9	12·2	0·00710	59	- 1·062
	0·0856		12·5				
68·0	0·0351	0·0345	10·7	10·8	0·00320	55	- 1·462
	0·0340		10·9				
64·6	0·00594	0·00596	8·51	8·20	0·000727	49	- 2·225
	0·00598		7·89				

GRAPH 10

RATE OF ESTERIFICATION OF ISO-AMYL ALCOHOL IN H_2SO_4 AT 0°C AND 25°C AND ACIDITY FUNCTION C_0 IN H_2SO_4 AT 25°C

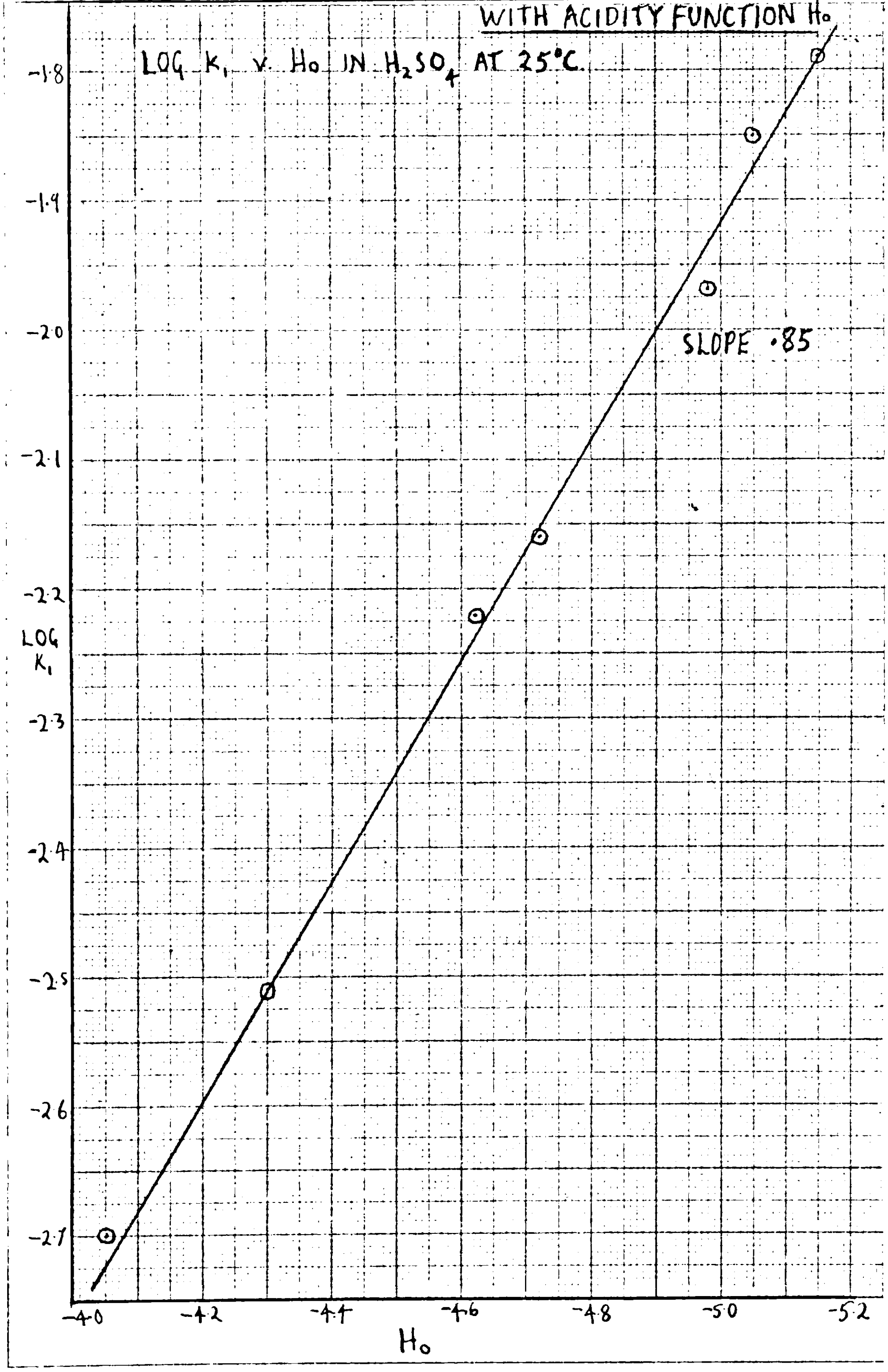


Log k_1 for hydrolysis of iso-amyl nitrate in H_2SO_4 at 25°C, and corresponding values of Ho.

% H_2SO_4	k_1	log k_1	Ho
67•0	0•0162	- 1•79	- 5•15
66•0	0•0113	- 1•95	- 5•05
65•3	0•0108	- 1•97	- 4•98
63•5	0•00695	- 2•16	- 4•72
62•4	0•00606	- 2•22	- 4•62
60•0	0•00307	- 2•51	- 4•30
57•7	0•00198	- 2•70	- 4•05

GRAPH 11

RATE OF HYDROLYSIS OF ISO-AMYL NITRATE IN H_2SO_4 AT 25°C COMPARED WITH ACIDITY FUNCTION H_0



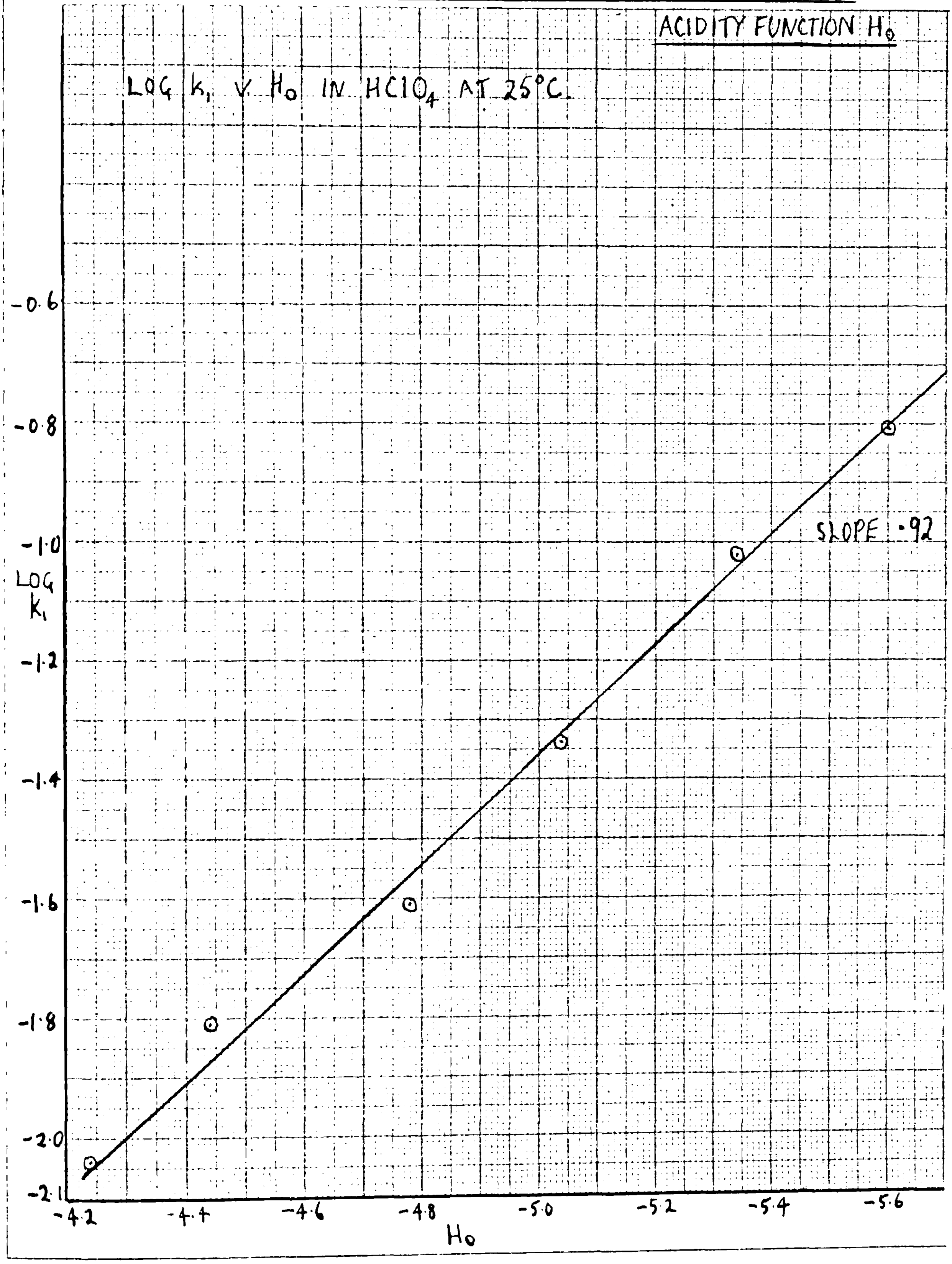
Log k_1 for hydrolysis of iso-amyl nitrate in $HClO_4$ at 25°C, and corresponding values of Ho.*

% $HClO_4$	k_1	log k_1	Ho
62•0	0•157	- 0•804	5•6
60•8	0•0963	- 1•02	5•34
59•3	0•0457	- 1•34	5•04
58•0	0•0246	- 1•61	4•78
56•3	0•0155	- 1•81	4•44
55•2	0•00916	- 2•04	4•23

Values of Ho* from unpublished results J.C.Lockhart.

GRAPH 12

RATE OF HYDROLYSIS OF ISO-AMYL NITRATE IN $HClO_4$ AT 25°C COMPARED WITH ACIDITY FUNCTION H_0



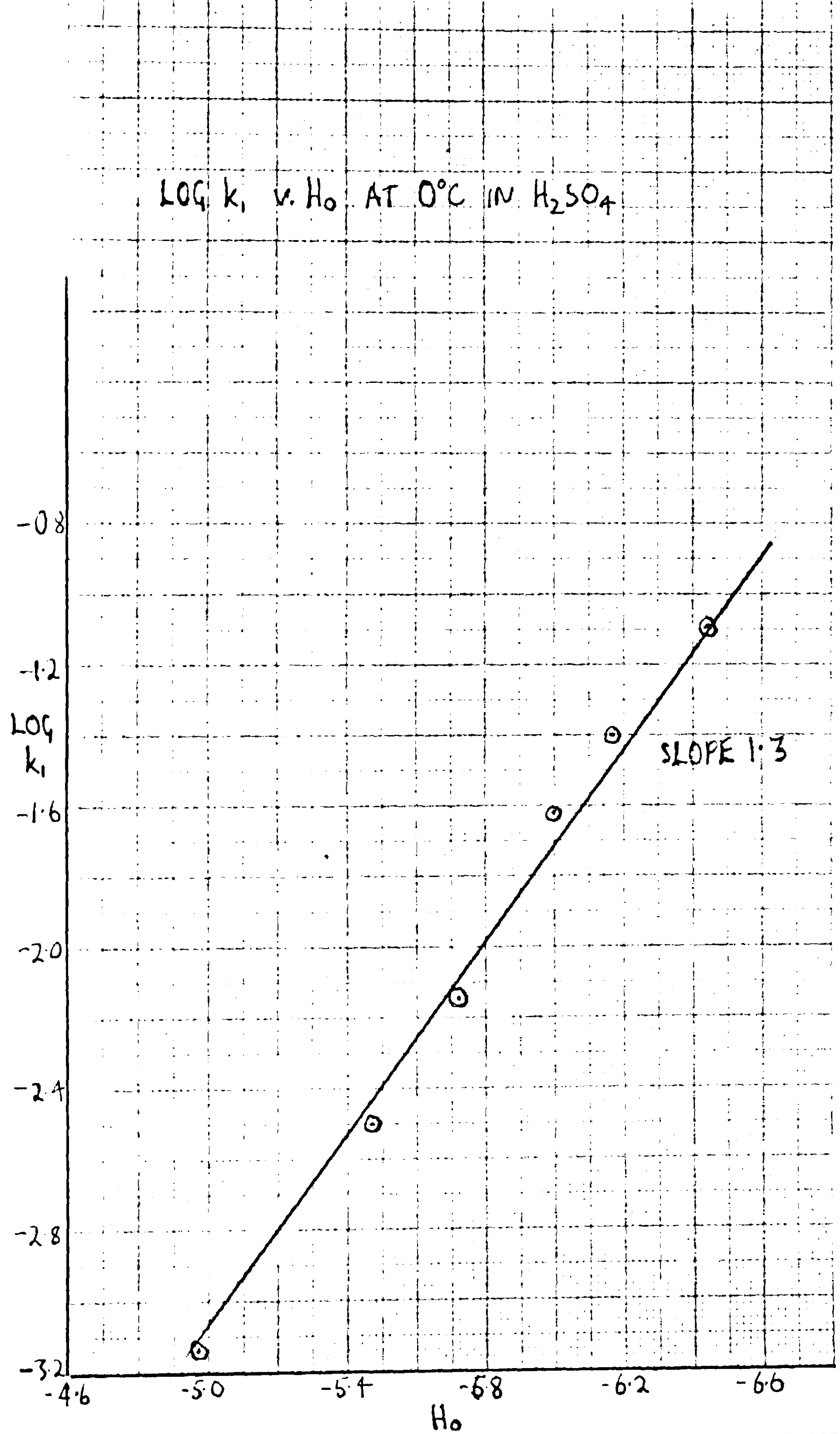
Log k_1 for hydrolysis of iso-amyl nitrate in H_2SO_4 at 0°C, and corresponding values of Ho.

% H_2SO_4	k_1	log k_1	Ho
74•6	0•0815	- 1•089	- 6•44
72•7	0.0394	- 1•404	- 6•16
71•4	0•0238	- 1•623	- 5•97
69•7	0•0071	- 2•149	- 5•72
68•0	0•0032	- 2•495	- 5•47
64•6	0•000727	- 3•138	- 4•97

GRAPH 13

RATE OF HYDROLYSIS OF ISO-AMYL NITRATE IN H_2SO_4 AT 0°C

COMPARED WITH ACIDITY FUNCTION H_0



Results of O-nitration of 2:4-dinitrobenzyl alcohol at 0°C.

% H_2SO_4	HNO_3 Initial Conc^n^.	2:4-diNO_2 benzyl alcohol Initial Conc^n^.	Time	% Nitrate Ester	% Sulphate Ester
93	0•1 N	0•1 N	7 min.	3•7	86
			4 hr.	4•1	85
87	0•1 N	0•1 N	6 min.	19	43
			3 hr.	4	80
77	0•1 N	0•1 N	4 min.	12	2•6
			69 hr.	11	35
73	0•1 N	0•1 N	7 min.	7	3
			4 hr.	8	8
70	0•1 N	0•1 N	7 min.	6	1•4
			4 hr.	5	4
65	0•1 N	0•1 N	7 min.	0	0
			4 hr.	2	0
65	2•0 N	0•08 N	4 min.	2	-
			14 min.	12	-
			30 min.	17	-
			2 hr.	21	-
65	3•0 N	0•075 N	20 min.	49	-
			35 min.	37	-
65	4•0 N	0•1 N	45 min.	55	-
			75 min.	60	-

Results of O-nitration of 2:4-dinitrobenzyl alcohol at 0°C.

% H_2SO_4	HNO_3 Initial Conc^{n}.	2:4-diNO_2 benzyl alcohol Initial Conc^{n}	Time	% Nitrate Ester	% Sulphate Ester
60	4 N	0·075 N	2 min	55	-
			32 min	60	-
55	4 N	0·05 N	5 min	32	-
			35 min	38	-
55	4·5 N	0·1 N	5 min	39	-
			45 min	40	-
At 20°C.					
	4 N	0·1 N	20 min	23	-
			35 min	34	-
			50 min	43	-

Starting with 2:4-dinitrobenzyl nitrate at 0°C.

% H_2SO_4	Nitrate Ester Initial Conc^{n}.	Time	% Nitrate Ester	% Sulphate Ester
87	0·1 M	6 min	10	74
		3 hr.	9	78
77	0·1 M	100 min.	9·7	18·4
		130 min.	9·4	16·8
75	0·1 M	3½ hr.	5·6	25
		4½ hr.	5·5	26

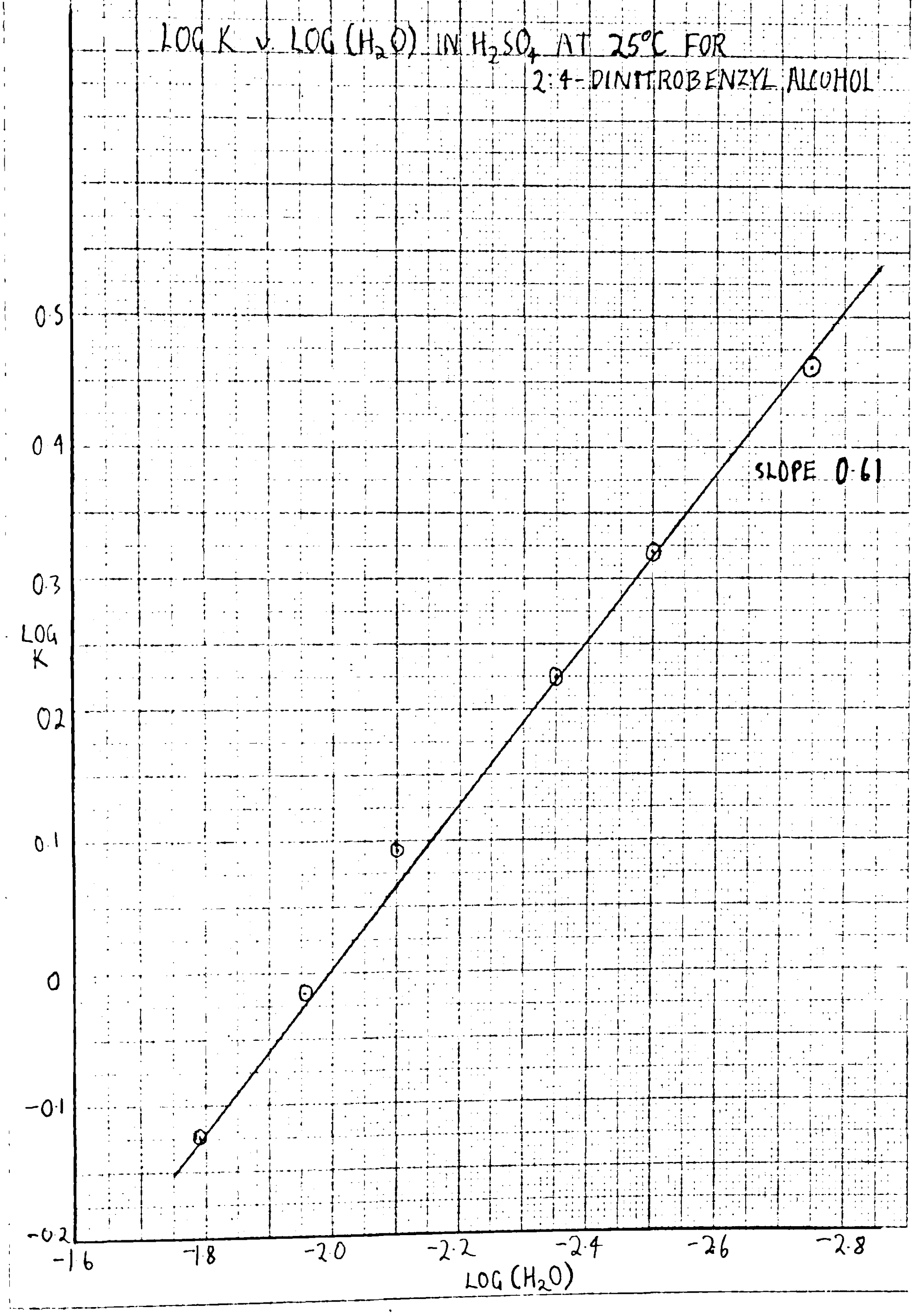
Equilibrium Constants for O-nitration of 2:4-dinitrobenzyl alcohol in H_2SO_4 at 25°C and corresponding values of log (H_2O).

% H_2SO_4	$K = \frac{[\text{2:4-diNO}_2\text{benzyl NO}_3]}{[\text{2:4-diNO}_2\text{benzyl alcohol}][\text{HNO}_3]}$	log K	log (H_2O) *
84•89	2•87	0•458	- 1•75
82•52	2•08	0•318	- 1•95
80•69	1•67	0•223	- 2•1
78•56	1•23	0•090	- 2•35
76•79	0•95	- 0•0223	- 2•5
74•64	0•70	- 0•152	- 2•75

* Log (H_2O) from Gold and Hawes (13)

GRAPH 14

EQUILIBRIUM CONSTANT FOR ESTERIFICATION OF 2:4-DINITROBENZYL ALCOHOL IN H_2SO_4 COMPARED WITH ACTIVITY OF H_2O

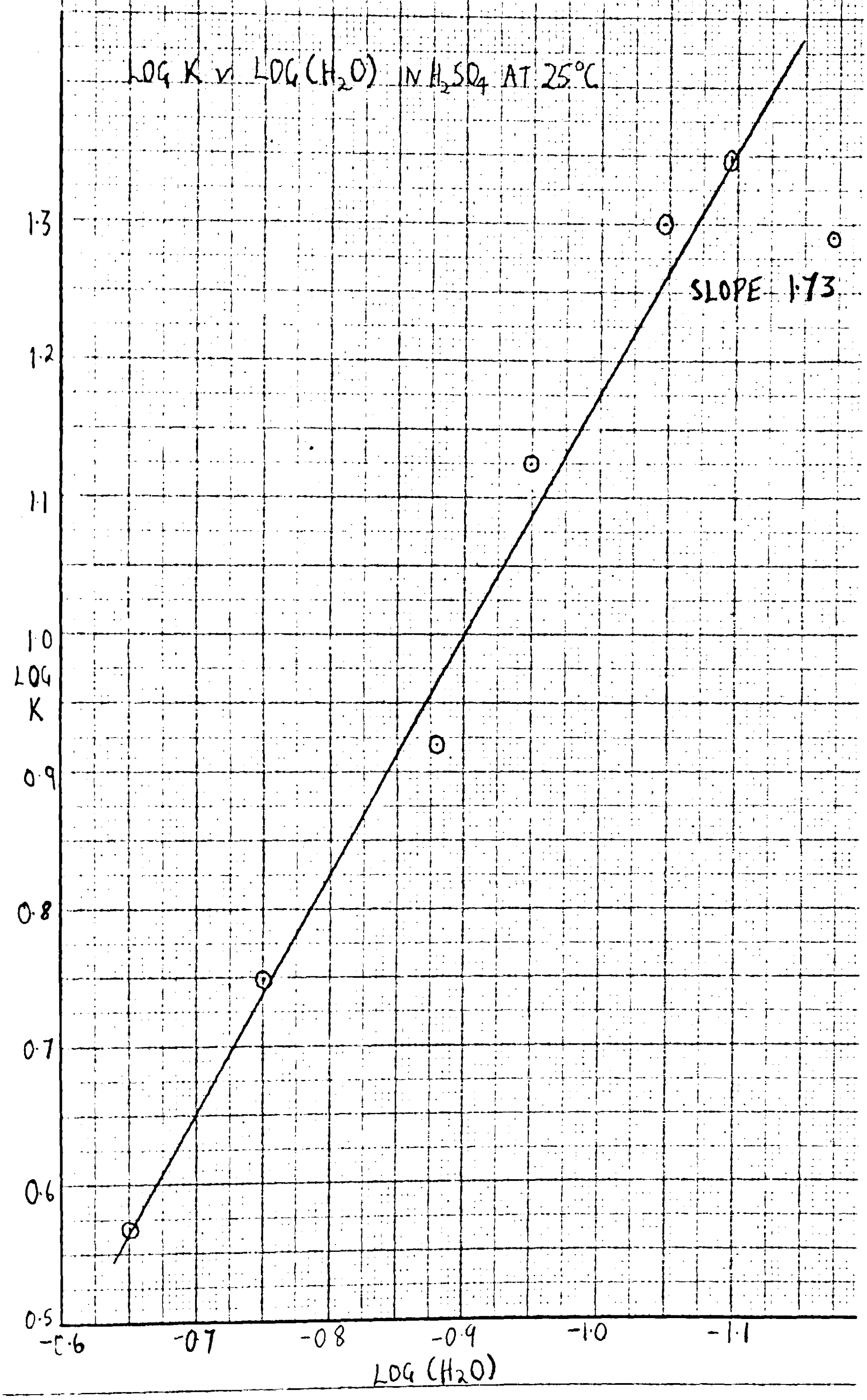


Equilibrium Constants for O-nitration of iso-amyl alcohol in H_2SO_4 at 25°C. and corresponding values of log (H_2O).

% H_2SO_4	$K = \frac{[\text{Iso-amyl } NO_3]}{[\text{Iso-amyl alcohol}]\,[HNO_3]}$	log K	log (H_2O)
67•0	19•5	1•29	- 1•17
66•0	22•4	1•35	- 1•10
65•3	20•2	1•305	- 1•05
63•5	13•5	1•13	- 0•95
62•4	8•31	0•920	- 0•88
60•0	5•60	0•748	- 0•75
57•7	3•71	0•569	- 0•65

GRAPH 15

EQUILIBRIUM CONSTANT FOR ESTERIFICATION OF ISO-AMYL ALCOHOL IN H_2SO_4 COMPARED WITH ACTIVITY OF WATER



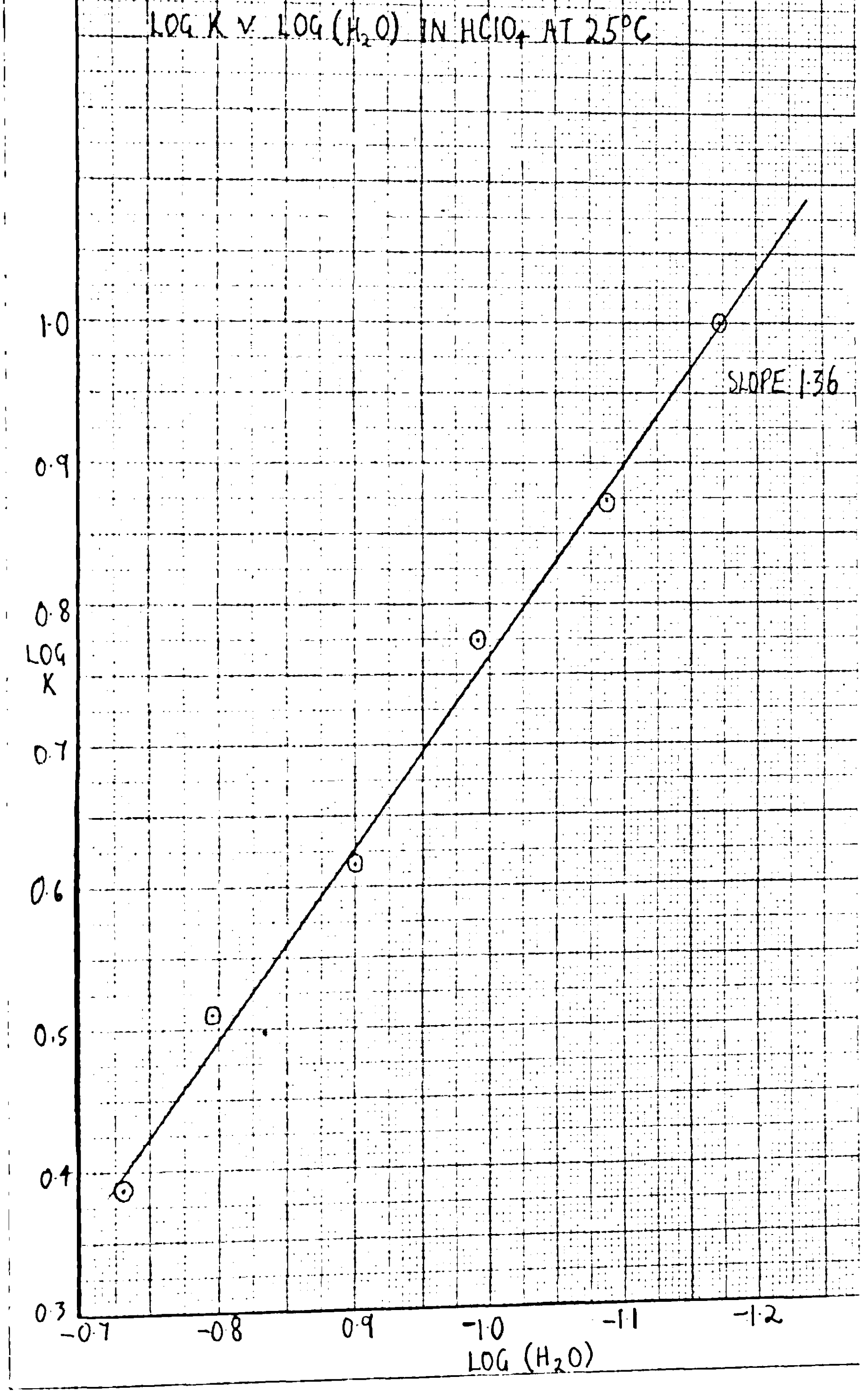
Equilibrium Constants for O-nitration of iso-amyl alcohol in $HClO_4$ at 25°C. and corresponding values of log $(H_2O)^*$

% $HClO_4$	K	log K	log (H_2O)
62•0	10•0	1•00	- 1•175
60•8	7•39	0•869	- 1•09
59•3	5•93	0•773	- 0•99
58•0	4•10	0•613	- 0•90
56•3	3•24	0•510	- 0•795
55•2	2•43	0•386	- 0•73

* Log (H_2O) from Robinson & Baker (44)

GRAPH 16

EQUILIBRIUM CONSTANT FOR ESTERIFICATION OF ISO-AMYL ALCOHOL IN $HClO_4$ COMPARED WITH ACTIVITY OF H_2O



Calculation of Activation Energies for Esterification of Iso-amyl Alcohol by HNO_3 in H_2SO_4.

Measurements of velocity constants for the iso-amyl alcohol esterification in H_2SO_4 overlapped between 64•6 and 67% H_2SO_4, and 3 values were therefore taken from the log k_2 v. H_2SO_4 plots at 65, 66, and 67%.

Equation used

$$\log \frac{k_2}{k_1} = - \frac{E}{2{\cdot}303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

% H_2SO_4	log k_2	log k_1	E
65•0	- 0•80	- 2•16	20,270 cals.
66•0	- 0•61	- 1•91	19,375 cals.
67•0	- 0•43	- 1•66	18,335 cals.

Usefulness of Acidity Functions.

The interpretation of results obtained depends to a considerable extent on their correlation with acidity functions so that consideration of the accuracy and validity of the latter is desirable. If the two acidity scales, H_o and J_o, the former is more well-established as a useful means of studying mechanisms, and since some of the assumptions involved apply also to the J_o scale, they will be discussed first.

As outlined in the introduction, the H_o scale can be expressed by

$$H_o = pK_A + \log \frac{CB}{C_{BH^+}}$$

$$\text{or} \quad H_o = - \log \frac{a_{H^+} f_B}{f_{BH^+}}$$

where pK_A is the negative log of the acidity constant;

C_B and C_{BH^+} the concentrations of the unionised and ionised forms of the indicator respectively, and f_B and f_{BH^+} the activity coefficients of the two forms; a_{H^+} the activity of the hydrogen ion.

As f_B and f_{BH^+} are taken to be unity in dilute aqueous solution, in this limiting case $H_o \rightarrow pH$. The establishment of the scale involves the fundamental assumption that for any two indicators

$$\frac{f_B}{f_{BH^+}} = \frac{f_C}{f_{CH^+}} \quad \text{in the same medium.}$$

There is the possibility that the influence of electrolytes on the activity coefficients might vary, although the indicators used are mainly similar in type. In that case the rates f_B/f_C would vary with electrolyte, and only if the acidity coefficient ratio for the two ions, f_{BH^+}/f_{CH^+} varied in exactly the same way would the ratios be exactly equa: This variation has been observed in studies of the indicators themselves (14), so that the discrepancy is likely to be more pronounced when the reactant species involved in a rate study are considerably different from a Hammett indicator, e.g. in the hydrolysis of methylal. Eaborn (46) has shown that even for the related bases p- and o-nitroaniline in aqueous methanol the plot of $\log\frac{[R^+]}{[ROH]}$(para) v. $\log\frac{[R^+]}{[ROH]}$(ortho) gives a line of slope 0·82. He has also investigated some of indicators which made up the Hammett scale, and found further discrepancies. Deno determined activity coefficients in H_2SO_4 (47) of various compounds including triphenylcarbinol, and found that up to 60% H_2SO_4 $d \log f_B/d\%H_2SO_4$ stayed almost constant, and close to zero, but above that percentage some compounds showed a rapid decrease in $\log f_B$, and the effect varied with the compound.

Thus the H_o scale appears to have a practical value, though there are factors which could be taken into consideratio if more information were available, for example on activity coefficients and transition slates. The fact that a considerable number of reactions do follow H_o indicates that the agreement is not merely fortuitous, but that the possible discrepancies are not in these cases large enough to affect the results.

When the J_0 acidity scale is considered, there is less information available, and some wide discrepancies. The J_0 scale as originally introduced was

$$J_0 = pK_{R^+} - \log \frac{[R^+]}{[ROH]}$$

where pK_{R^+} is the negative log of the equilibrium constant for the equation $H_2O + R^+ = ROH + H^+$, and R is an indicator of the triaryl-carbinol type, ionising in sulphuric acid as

$$ROH + 2H_2SO_4 = R^+ + H_3O^+ + 2HSO_4^-$$

As mentioned in the introduction, this involved certain assumptions which are questionable. In the course of their derivation Gold and Hawes obtained the equation

$$K_{ROH} = \frac{[R^+]}{[ROH]} \frac{(H_2O)}{h_0} \cdot \frac{f_{R^+}}{f_{ROH_2^+}}$$

and assumed that $\frac{f_{R^+}}{f_{ROH_2^+}} = 1$, thus arriving at the equation

$$J_0 = pK_{ROH} + \log \frac{[ROH]}{[R^+]}$$

The ratio $\frac{f_{R^+}}{f_{ROH_2^+}}$ was obtained by equating $\frac{f_{BH^+}}{f_{B^+}} = \frac{f_{ROH_2^+}}{f_{ROH}}$

where B is a Hammett base, and it has been shown thet this is not always true. Deno (14) stated as a result of further experimental work that the ratio $f_{R^+}/f_{ROH_2^+}$ could not be ignored, and included it in the expression

$$C_0 = J_0 + \log \frac{f_{R^+}}{f_{ROH_2^+}}$$

The C_o scale was obtained by measuring the ionisation of a series of indicators, and a comparison was made with J_o calculated from the sum of $H_o + \log {}^{a}H_2O$. Up to 80% the difference between the two scales constantly increased, but above this remained at 4·92. In this region the activity coefficients of ions are constant, and the assumption that $fR^+/fROH_2^+ = 1$ is valid providing dilute solution in sulphuric acid is chosen as the standard state.

Gold and Hawes (13) plotted the neutral indicator 4:4':4"-trinitrotriphenylcarbinol against their calculated J_o, and obtained a slope of 1·16, which they considered reasonable.

Quite apart from differences caused by the inclusion or otherwise of activity coefficient ratios, there appeared to be considerable discrepancies in the ratio log $[R^+] / [ROH]$ for indicators used. A graph (No.2) of various indicators measured by Bevan (45), Murray (58) and Deno et al (14) showed that over a range from 60% to 86% H_2SO_4, slopes of log $[R^+]/[ROH]$ v. H_2SO_4 varied from 0·25 to 0·34. In one or two cases indicators measured over approximately the same range of acid varied from 0·26 to 0·33. That the variation in slope was not due to different charge types was shown by the slopes of trinitrotriphenylcarbinol and $(Me_3\overset{+}{N}.C_6H_4)_3.C.OMe(ClO_4^-)_3$, with 0 and 3 charges respectively, which agreed very well. It would appear that by judicious choice of indicators, an acidity scale could be produced to fit the kinetic rate observed. For example, plotting d log k/d%H_2SO_4 for the nitration of nitrobenzene (14) gives a slope 0·39; dJ_o/d%H_2SO_4 (48) slope 0.32. and dC_o/d%H_2SO_4 (14) slope 0·26. Thus the nitration relative to J_o is 1·2, which would indicate similarity of mechanism, whereas relative to C_o it is 1·5 which is inconclusive.

The argument used to explain variations in the Hammett indicators, i.e. that the ratio f_B/f_C may not vary as f_{BH^+}/f_{CH^+} could also be applied to these indicators, although many of the indicators are similar in structure. One explanation of nitration discrepancies put forward by Deno et al (16) is that NO_2^+ differs in such a pronounced manner in structure from the indicators that variations are likely.

Another reason for deviations between d log k/d%H_2SO_4 and dC_o/d%H_2SO_4 from 65-80% suggested by Deno is that activity coefficients for a variety of oxygen containing compounds undergo sharp changes in this region, as shown by sharply changing solubilities, in contrast to the other regions where activity coefficients appear to be constant. On the other hand, comparison of indicators above 80% continues to show variation, in fact as Graph 2 shows, it is greatest above 80%.

However, since the J_o scale has a slope approximately twice as great as H_o it can give some guide to the mechanisms in sulphuric acid. H_o has been measured in

$HClO_4$, but a corresponding J_o scale has not been producec. In the course of this research an indicator ionising over the same range as kinetic runs was measured at 25°C, giving a result similar to that in H_2SO_4, i.e. $d \log \frac{|R^+|}{|ROH|} / d\% HClO_4$ was greater than $d \, (H_o + \log {}^{a}H_2O)/d\% HClO_4$. However, one isolated indicator is not an altogether reliable guide to the general acidity scale, and further information would be useful.

Formation and Mechanism of Nitrating Entities.

Although very little work on the mechanism of esterification of alcohols by nitric acid in strong acids has been carried out previously, the condition of nitric acid in H_2SO_4, and to a lesser extent $HClO_4$, has been studied very thoroughly from the point of view of aromatic nitration. The rate of aromatic nitration in sulphuric acid must depend to some extent on the condition of the aromatic compound in such media, and Gillespie (50) states that most compounds that are soluble in H_2SO_4 behave as bases in that solvent, taking up a proton and forming a hydrogen bond complex which can partially or wholly ionise to the conjugate acid.

$$B + H_2SO_4 \rightleftharpoons BHSO_4H \rightleftharpoons BH^+ + HSO_4^-$$

Whether this general pattern can be applied to alcohols in H_2SO_4 is questionable, for cryoscopic measurements (51) on alcohols in concentrated H_2SO_4 failed to give any decisive evidence for the presence of alkyloxonium ions, and the situation is often complicated by olefin formation or secondary reactions. Gillespie and Millen (53) noted that since $BHSO_4H$ and BH^+ will have depressed nuclear reactivity towards electrophilic reagents, nitration rate might often depend on the amount of free base B, and incompleteness of the conversion into BH^+. This could be a contributary cause to the fact that rates of nitration are first increased, and then decreased by the progressive addition of water, since small amounts of water may reverse the equilibrium increasing the relative amount of the more reactive form of the compound. The effect of larger amounts of water have been illustrated by the retardation of nitration in nitric acid and nitromethane, when it is considered to reverse the reaction step

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O$$

In the presence of considerable quantities of water, another reversible process can also be involved, i.e.

$$HNO_3 + H_3O^+ \rightleftharpoons NO_2^+ + 2H_2O$$

while with sufficient water, the nitronium ion is practically destroyed.

Whether the actual mechanism of nitration by the nitronium ion is a bimolecular or termolecular reaction has been discussed in some detail, the two schemes being either

$$NO_2^+ + ArH \longrightarrow ArHNO_2^+ \qquad \text{Slow}$$

$$ArHNO_2 \longrightarrow ArNO_2 + H^+ \qquad \text{Fast}$$

or

$$NO_2^+ + ArH + B^- \longrightarrow ArNO_2 + HB$$

which is base-accelerated.

In the second case the proton-loss has kinetic importance, but the work of Melander (52) showed that this did not take part in the rate determining step. He nitrated toluene with HNO_3/H_2SO_4, in which the hydrogen in the toluene nucleus was replaced by tritium in the 2, 3, and 4 positions respectively. He found that 50% of the tritium was replaced in the ortho-position, which showed that nitration proceeded at the same velocity irrespective of whether tritium or hydrogen occupied the ortho-position. In view of the great difference in mass, and therefore in zero-point energy of the original bond, the velocities should be different if the splitting off of the hydrogen takes part in the rate-determining step. The conclusion is therefore that the addition of NO_2^+ is the rate-determining step, followed by a rapid splitting off of hydrogen. Hughes (11) considered that the bimolecular process is the correct one, since it agrees with the experimentally observed fact that rates of nitration in highly polar H_2SO_4 are very great compared with those in moderately polar organic solvents. If the nitration process contained any essential step which theory required to be strongly retarded as the medium is made more polar, this would not be the case, and therefore the termolecular process does not hold. This argument has been followed in organic solvents by noting changes in reaction order, which support the bimolecular mechanism, and this should be equally applicable to esterification.

No specific mechanism has been produced for nitration by the nitracidium ion, $H_2NO_3^+$, though there is definite evidence of its existence as an intermediate stage in the production of NO_2^+ (11). Halberstadt, Hughes and Ingold, (10) considering nitrating agents in aqueous nitric acid stated that they could not distinguish between the possibility of nitration by extremely minute amounts of NO_2^+ which might survive in equilibrium with a great excess of water and nitration by larger equilibrium amounts of $H_2NO_3^+$ in these conditions.

These authors also investigated mixtures of HNO_3, $HClO_4$ and H_2O, although the concentration of $HClO_4$ was lower than that used in the esterification experiments, and the concentration of HNO_3 higher. The Raman spectra showed that in a solution of 72 mol. per cent H_2O, 17 mol. per cent HNO_3, and 11 mol. per cent $HClO_4$, no trace of NO_2^+ was detectable, that perchloric acid was completely converted to perchlorate ion, and that the spectrum of the nitric acid molecule was strongly developed. The spectrum of the nitrate ion was quite weak, only 4% of the total nitric acid being present as nitrate ion. The fact that no nitracidium ion was observed was explained by the fact that such ions change their protons too frequently to yield well-defined vibrational levels.

Some nitrations of 2-phenylethyl sulphonic acid were carried out in aqueous $HClO_4$, it was found that there was a fairly narrow region, between 8 - 11 mol. per cent

$HClO_4$, in which nitration was measurable, and that there was a threshold of reactivity above which the rate rises to high values for a small increase of $HClO_4$. This was explained by the fact that Hydrogen ion and the nitric acid molecule form monohydrates H_3O^+ and H_2O--$HONO_2$. As the amounts of $HClO_4$ and HNO_3 are increased, the activity of water will decrease because the available water has been bound in these hydrates, the protons derived from $HClO_4$ will combine with water rather than with nitric acid, but a point is reached at which the nitric acid can compete more effectively for the protons. It is at this point that the sharp increase in nitration rate is attributed to the sharp increase in $H_2NO_3^+$. However, as this is a stage in the production of nitronium ions, there is the possibility that it may decompose to give NO_2^+ and H_2O, although in more aqueous solutions this step seems less likely to occur.

The possibility of the nitric acid molecule acting as nitrating agent seems feasible in more aqueous solutions, for it is present in relatively large proportion. For a long time the 'addition-elimination' theory was used to explain aromatic nitration, which regarded it as taking place by the addition of an HNO_3 molecule to a double bond in the benzene nucleus, followed by elimination of H_2O. This has been disproved, and it is now accepted that the NO_2 group from the nitrating agent becomes attached to a carbon atom. NO_2OH is only a weak nitrating agent, corresponding to the weak electron affinity of the OH group.

Evidence against the HNO_3 molecule as nitrating agent even in aqueous H_2SO_4 with HNO_3 largely present as molecules was given by Halberstadt, Hughes and Ingold (10). Since the nitration of sodium toluene w-sulphonate was accelerated by strong acids they concluded that a proton uptake was involved, and that the HNO_3 molecule itself was not the nitrating agent.

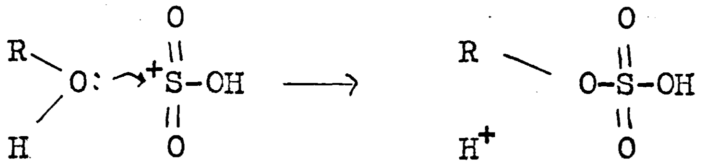
The rate of nitration of p-tolyltrimethylammonium ion was studied in 75-82% H_2SO_4, and no relationship was found between the rate constant and the vapour pressure of HNO_3. There is no information on the subject of esterification, but the general conclusion is that the nitric acid molecule is a very much weaker nitrating agent than either $H_2NO_3^+$ or NO_2^+, the sequence given by Gillespie & Millen (53) being, in the order of increasing nitrating power,

$$EtO.NO_2 < HO.NO_2 < AcO.NO_2 < NO_3.NO_2 < ClNO_2 < H_2O^+NO_2 < NO_2^+.$$

Sulphuric Acid Esterification and Equilibrium Constants.

The equilibrium constants for the nitric acid esterification of iso-amyl alcohol in H_2SO_4 were measured in the course of kinetic runs, while those for 2:4-dinitrobenzyl alcohol were measured only after equilibrium with the sulphate ester had been attained, no satisfactory method of following the rate of HNO_3 esterification having been found.

The sulphuric acid esterification of 2:4-dinitrobenzyl alcohol was investigated very thoroughly by Clark and Williams (40). In spite of the uncertainties of the molecular condition of alcohols in aqueous H_2SO_4 media, and the ionisation of water and sulphuric acid, they concluded that sulphation must be brought about by a nucleophilic attack of the alcohol on the sulphur of the acid, e.g.



though the actual entities involved might be ROH or ROH_2^+, and HSO_3^+, $H_3SO_4^+$, H_2SO_4, HSO_4^- or $SO_4^=$. The Raman spectra of Woodward and Horner (55) indicates that between 65 and 85% H_2SO_4 fairly complete ionisation to H_3O^+ and HSO_4^- occurs, but relatively little ionisation to $SO_4^=$.

Clark and Williams considered their results from the point of view of the various mechanisms possible, and concluded that the best interpretation was that of compound formation between alcohol and bisulphate ion, thus

$$ROH + HSO_4^- \rightleftharpoons ROH.HSO_4^- \qquad (1)$$

$$ROH.HSO_4^- + H^+ \rightleftharpoons ROH.HSO_4^-.H^+ \qquad (2)$$

$$ROH.HSO_4^-.H^+ \longrightarrow RHSO_4 + H_2O \qquad (3)$$

in which equilibria (1) and (2) are rapidly established, and the unimolecular decomposition (3) determines the rate. The measurements of equilibrium constants at 25°C. show that at 65% H_2SO_4, the time taken for 10% sulphation to reach equilibrium is 20 hrs, while in 75% H_2SO_4 30% sulphation takes 3 hrs.

The results obtained during the investigation of the nitration indicated that in 75% H_2SO_4 nitration was complete in 7 mins, and while in 65% H_2SO_4 under certain conditions a possibly measurable rate was observed; this was completed in 2 hrs. at $0^\circ C$. The two main disadvantages to this reaction were that (1) the nitric acid esterification was too fast to be measurable in the stronger acids, and (2) in much lower acids the amount of nitrate formed was very small, though in this region there would obviously be no interference from the sulphation.

An attempt was made to establish the mechanism from a study of the equilibrium results for 2:4-dinitrobenzyl alcohol, using the equation

$$ROH + NO_2^+ + H_2O \rightleftharpoons RNO_3 + H_3O^+$$

where the equilibrium constant K is given by

$$K = \frac{[RNO_3]\,[H_3O^+]}{[ROH][NO_2^+]\,(H_2O)} \cdot \frac{fRNO_3 \cdot fH_3O^+}{fROH\; fNO_2^+}$$

This can be written

$$K = \frac{[RNO_3][H_3O^+]}{[ROH]\,(H_2O)} \cdot \frac{[HNO_3]}{[NO_2^+]} \; \frac{1}{[HNO_3]} \cdot \frac{fRNO_3\; fH_3O^+}{fROH\; fNO_2^+}$$

and the factor $\frac{[HNO_3]}{[NO_2^+]}$ equated with $\frac{[R'OH]}{[R'^+]}$ where R′OH is a triarylcarbinol indicator.

By taking logs the value of log K should be equal to the sum of the terms

$$\log[RNO_3] - \log[ROH] - \log[HNO_3] + \log [R'OH]/[R^+] - Ho$$

but the sum of these terms gradually decreased from 75-85% H H_2SO_4. This was possibly due to inaccuracies in the acidity scales, and omission of activity coefficient terms.

Considering the reaction simply, it can be expressed

$$ROH + HNO_3 \rightleftharpoons RNO_3 + H_2O$$

The empirical equilibrium constant is thus

$$K_o = \frac{[RNO_3]\,(H_2O)}{[ROH]\,[HNO_3]} \cdot \frac{f_{RNO_3}}{f_{ROH}\,f_{HNO_3}}$$

The experimental constant can be defined by

$$K = \frac{[RNO_3]}{[ROH]\,[HNO_3]}$$

Thus $\log K = \log K_o + \log a_{H_2O} + \log \cdot \frac{f_{RNO_3}}{f_{ROH}\,f_{HNO_3}}$

There is therefore some reason to expect log K to vary linearly with log a_{H_2O} if the activity coefficient term is constant, or very small. The following tables give the sums of log K + log a_{H_2O} in H_2SO_4 and $HClO_4$ for iso-amyl alcohol, and 2:4-dinitrobenzyl alcohol in H_2SO_4.

Esterification of Iso-amyl alcohol with HNO_3				Esterification of 2:4-dinitrobenzyl alcohol with HNO_3	
% H_2SO_4	$\log K + \log a_{H_2O}$	% $HClO_4$	$\log K + \log a_{H_2O}$	% H_2SO_4	$\log K + \log a_{H_2O}$
67	0.12	62	- 0·175	84·9	- 2·29
66	0·25	60·8	- 0·22	82·5	- 2·18
65·3	0·255	59·3	- 0·22	80·7	- 2·13
63·5	0.20	58·0	- 0·287	78·6	- 2·01
62·4	0·05	56·3	- 6·285	76·8	- 1·97
60·0	0·0	55·2	- 0·34	74·6	- 1·90
57·7	- 2·1				

The sum of log K + log a_{H_2O} for iso-amyl alcohol varies considerably, but those for 2:4-dinitrobenzyl alcohol are nearly constant. The fact that the activity coefficient term has been ignored probably has more effect on the results of the measurements in lower acid ranges.

The slopes of the graphs for log K v. log a_{H_2O} (Graphs 14,15,16) also show a wide variation, from 1·73 for iso-amyl alcohol in H_2SO_4 to 1·36 for the same alcohol in $HClO_4$, and 0·61 for 2:4-dinitrobenzyl alcohol in H_2SO_4.

It is therefore difficult to draw any conclusion about the mechanism of the esterification from equilibrium results alone.

Correlation of Results with Acidity Functions.

Although the interpretation of results by their comparison with existing acidity functions has been shown to fall short of complete reliability, it does afford a general guide to the type of mechanism.

Dealing first with the H_2SO_4 scales, there are three variations of the scale referring to 'secondary bases', being Jo from Gold and Hawes (13) which is calculated from Jo = Ho + log $^{a}H_2O$; Jo measured from indicators by Bevan (48) and Co also measured from indicators by Deno et al (14). As Deno constructed his scale from a wider range of indicators, results have been compared with this rather than Jo (Bevan.) The Jo scale has ignored the log $\frac{f_{BH^+}}{f_B}\ \frac{f_{ROH}}{f_{R^+}}$ term; this was discussed on page 3 when the ratio is written as log $f_{R^+}/f_{ROH_2^+}$. Deno (47) has shown that the ratio of f_{BH^+}/f_{R^+} where BH^+ is the cation of a typical Hammett indicator, and R^+ is a tertiary carbonium ion, does not stay constant, but increases rapidly, with increasing H_2SO_4 concentration. It can be argued that observations which apply to a tri-aryl carbonium ion do not necessarily hold equally for another monovalent cation of different use and charge distribution.

A consideration of the slopes of the graphs gives an indication of the mechanism, as the relationships derived below show. If the nitrating agent were $H_2NO_3^+$ produced by the reaction

$$HNO_3 + H^+ \longrightarrow H_2NO_3^+ \qquad (1)$$

the esterifying process would be

$$ROH + H_2NO_3^+ \rightleftharpoons RONO_2 + H_3O^+ \qquad (2)$$

Then if K = equilibrium constant for equation (1)

$$K = \frac{a_{H_2NO_3^+}}{a_{H^+} \times a_{HNO_3}}$$

$$\therefore \quad [H_2NO_3^+]\, f_{H_2NO_3^+} = K a_{H^+}\, [HNO_3]\, f_{HNO_3}$$

where HNO_3 = concentration of free molecular HNO_3.

From equation (2) the theoretical rate is given by

$$\frac{-d\,[HNO_3]_T}{dt} = k_a [ROH][H_2NO_3^+] \cdot \frac{f_{ROH}\, f_{H_2NO_3^+}}{f_x}$$

where $[HNO_3]_T$ = total of all forms of nitric acid present

ko = theoretical rate constant.

f_x = activity coefficient of the transition state complex.

Assuming that the activity coefficient ratio $\frac{f_{ROH}\, f_{H_2NO_3^+}}{f_x}$ is constant over the range of media investigated,

$$-\frac{d\,[HNO_3]_T}{dt} = K k_o [ROH][HNO_3] \frac{a_{H^+}\, f_{HNO_3}}{f_{H_2NO_3^+}}$$

$$= K k_o [ROH][HNO_3]\, h_o$$

where $h_o = \dfrac{a_{H^+} \cdot f_{HNO_3}}{f_{H_2NO_3^+}}$

and $-\log_{10} h_o = H_o$

Experimentally $-\frac{d[HNO_3]_T}{dt} = k_2[ROH][HNO_3]_T$

where k_2 = experimental rate constant.

If $[H_2NO_3^+] \ll [\text{Total } HNO_3]$

$$-\frac{d[HNO_3]_T}{dt} = k_2[ROH][HNO_3]$$

and $k_2[ROH][HNO_3] = K\,k_o[ROH][HNO_3]ho$

$$k_2 = K\,k_o ho$$

$$\therefore \quad \log k_2 = \log K\,k_o - Ho.$$

This implies that a linear relationship should exist between $\log k_2$ and Ho with unit slope, but this was not observed.

The derivation of the corresponding relationship between $\log k_2$ and Jo was given in the introduction (page 8), where it was shown that if nitric acid ionised in H_2SO_4 as

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (3)$$

$$\log k_2 = \log k + \log \frac{[NO_2^+]}{[NO_2OH]} \qquad (4)$$

and for a triarylcarbinol indicator ionising as

$$ROH + 2H_2SO_4 = R^+ + H_3O^+ + 2HSO_4^- \qquad (5)$$

$$Jo = pK_R - \log \frac{[R^+]}{[ROH]} \qquad (6)$$

Sin ce the ionisations in equations (3) and (5) are the same, equation (6) can be written as

$$Jo = pK_{NO_2OH} - \log \frac{[NO_2^+]}{[NO_2OH]} \qquad (7)$$

and from (7) and (4)

$$\log k_2 = \log k + pK_{NO_2OH} - Jo.$$

The slopes of $\log k_2$ v. Co and $\log k_2$ v. Jo are 0•74 and 1•11 respectively (Graph 6), while $\log k_2$ v. Ho gives 1•56, which indicate that the NO_2^+ mechanism is operating.

Measurements in Perchloric Acid.

There is not a great deal of information available on velocity measurements or acidity scales in $HClO_4$, although reactions in this acid should be simplified to some extent by the fact that ionisation is limited to the formation of H_3O^+ and ClO_4^-. The values of Ho used are taken from the results of Lockhart (54), and the activity of water in $HClO_4$ from vapour pressure measurements of Gold and Hawes (13).

As previously mentioned, no Jo scale has been measured experimentally, but an indicator was used which covered a suitable range to give an indication of the probable slope of $\log [R^+] / [ROH]$. In this case, the $\log k_2$ v. $\log [R^+] / [ROH]$ plot gave a slope of 0•88, (Group 7) and $\log k_2$ v. Jo gave 1•04, the variation being much smaller than that observed in H_2SO_4, and both are nearer to unit slope. However, the slope against Ho is not so markedly different, being 1•36, but there is not such a large difference between Ho and Jo in $HClO_4$ as there is in H_2SO_4, so that here again NO_2^+ mechanism is indicated.

The Effect of Temperature Variation.

The esterification in H_2SO_4 was carried out at 0°C. and 25°C; the measurements at 0°C. were made in a higher range of H_2SO_4/H_2O mixtures, and there was less likelihood of any reaction between H_2SO_4 and the alcohol occurring during the course of the nitric acid esterification.

The acidity function Jo in H_2SO_4 determined by indicator measurements has only been carried out at 25°C, although the Ho scale has been measured over a wide temperature range (56) and found to vary very little with temperature differences of 80°C. The log k_2 v. % H_2SO_4 plots showed a distinct variation in slope at the two temperatures (Graph 10) so that the measurement of a Jo indicator at 0°C seemed advisable. It was not possible to carry out measurements at 0°C, but the ionisation at $7^\circ \pm \frac{1}{2}{}^\circ$C. was investigated.

The result of ionisation ratio measurements for 4-chloro-4 : 4"-bisdimethylaminotriphenyl carbinyl methyl ether diperchlorate are shown on Graph 9, from which it would appear that above 20% ionisation, the temperature effect is not appreciable, but when the amount of ionisation is small, the variation in temperature becomes increasingly important. Since the ionisation of HNO_3 to NO_2^+ is very small indeed, it is to be expected that the slopes of velocity constants against sulphuric acid should show a difference between 0° and 25°C.

It is not possible to conclude from one set of measurements what the slope of the acidity scale would be at a lower temperature, and it would appear to depend on the range of ionisation included, since the temperature effect is much more marked from 5 - 20% ionisation than from 20% upwards in this case. As the measurements were not made with any great accuracy, it is not advisable to place much reliance on these results, but the fact that log k_2 at 0°C and Co at 25°C have parallel slopes may have some significance, and at least indicate that the mechanism is far removed from an Ho type.

Correlation of Nitric Acid Esterification with Ionisation of Nitrous Acid.

The purpose of Singer & Vamplew's investigation (35) of the spectrum of HNO_2 in $HClO_4$ was to measure the equilibrium between NO^+ and nitrous acid in aqueous $HClO_4$ spectroscopically. This involved independent measurements of NO^+ and molecular nitrous acid, and led to the conclusion that there was no indication of a third entity such as $H_2NO_2^+$.Nitrous acid presumably ionises in the same way as HNO_3, i.e.

$$HNO_2 + HClO_4 \rightleftharpoons H_2NO_2^+ + ClO_4^-$$

$$H_2NO_2^+ \longrightarrow NO^+ = H_2O.$$

with $H_2NO_2{}^+$ as an intermediate stage, but careful consideration of the results indicated that the spectrum was due only to NO^+ and HNO_2.

There are certain practical difficulties in the estimation, due to the volatility of nitrous acid solutions. This was overcome as far as possible by using closed optical cells for absorption measurements, and removing samples before and after filling the cell, to be estimated for nitrous acid independently. The average of the two values, which varied between 5 and 10%, was taken as the concentration of analytical nitrous acid in the cell solution.

The NO^+ ion gave a peak at 2600 Å, which was at a maximum in 58% $HClO_4$; the absorption measured thus gave the ε value for NO^+, so that measurements of the intensity at x% $HClO_4$ could be converted to NO^+. The nitrous acid peak at 3700 Å was also measured, and another at 3840 Å, the two agreeing fairly well.

From the tables given by Singer and Vamplew it is possible to obtain values for $\log [NO^+] / [HNO_2]$ from 45-55·6% $HClO_4$, where $[HNO_2]$ is the concentration of molecular nitrous acid. It was possible to measure $\log k_2$ for the nitric acid esterification of iso-amyl alcohol in 55-62% $HClO_4$ at 25°C. The fact that $\log [NO^+]/[HNO_2]$ v. % $HClO_4$ is exactly parallel to $\log k_2$ v. % $HClO_4$ indicates clearly that the nitrating entity in esterification is NO_2^+. This conclusion is reached by the following considerations -

The esterification followed experimentally is

$$ROH + HNO_3 \rightleftharpoons RONO_2 + H_2O$$

Thus the overall rate of reaction is given experimentally by

$$r = k_2 [ROH][HNO_3]_T - k_1 [RONO_2]$$

where $[HNO_3]_T$ = stoichiometric concentration of nitric acid. Theoretically, if the nitronium ion is responsible for the esterification, the forward rate is given by

$$r = k_o [NO_2^+][ROH] \frac{f_{NO_2^+} f_{ROH}}{f_x}$$

where f_x is the activity coefficient of the transition complex.

By equating the experimental and theoretical forward rates

$$k_2 [ROH][HNO_3]_T = k_o [NO_2^+][ROH] \frac{f_{NO_2^+} f_{ROH}}{f_x}$$

Assuming that the activity coefficient term remains constant in the range of media studied,

$$k_2 = \frac{k_o [NO_2^+]}{[HNO_3]_T}$$

Since the extent of ionisation of nitric acid to NO_2^+ is very small, it can be concluded that

$$[HNO_3]_T = [HNO_3]$$

where $[HNO_3]$ = concentration of molecular HNO_3.

$$\therefore k_2 = k_o \frac{[NO_2^+]}{[HNO_3]}$$

$$\text{and } \log k_2 = \log k_0 + \log \frac{[NO_2^+]}{[HNO_3]} \qquad (1)$$

Since nitric and nitrous acids ionise in the same way, i.e.

$$HNO_3 + 2HClO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2ClO_4^-$$

$$HNO_2 + 2HClO_4 \rightleftharpoons NO^+ + H_3O^+ + 2ClO_4^-$$

the following relation can be obtained.

$$\log \frac{[NO_2^+]}{[HNO_3]} - \log \frac{[NO^+]}{[HNO_2]} = \text{const.}$$

Therefore equation (1) can be written

$$\log k_2 = \log k_0 + \log \frac{[NO^+]}{[HNO_2]} + \text{const.}$$

Thus if NO_2^+ is the esterifying agent, the graphs of $\log k_2$ and $\log [NO^+]/[HNO_2]$ against % $HClO_4$ should be parallel. Graph 3 shows that they are exactly parallel, which is the essential criterion that the nitrating entity in $HClO_4$ is NO_2^+.

Measurements of the Ionisation of Nitrous Acid in H_2SO_4.

The ionisation of nitrous acid in H_2SO_4 has been investigated spectroscopically by Bayliss & Watts (36) and it is interesting to compare their account with that of Singer and Vamplew. To begin with, the latter's paper states that quantitative spectrophotometric analysis of the absorption spectra of nitrous acid in H_2SO_4 is almost impossible due to the displacement of the maximum for NO^+ from λ = 2550 Å to 2300 Å in 60-90% H_2SO_4, and in more aqueous media displacements also occur in the region of the maxima of nitrous acid. Bayliss & Watts show this variation in a graph, but take $\varepsilon_{max} = 3850$ at 2200 Å, and presumably make allowances for the variation.

They do not appear to have made any correction for the loss of HNO_2 by volatility, which Singer & Vamplew found a major experimental difficulty in H_2SO_4, but state that solutions of sodium nitrite in H_2SO_4 were surprisingly stable except in the region 55-60%. Thus there could possibly be an error in their standard measurements, since they only measured the nitrous acid spectroscopically, and did not estimate it independently as did Singer & Vamplew. Bayliss and Watts state that by cooling the solvent to - 10°C and adding weighed amounts of $NaNO_2$ they prevented decomposition. The spectra measurements were interpreted in the following manner. In 95% H_2SO_4, all nitrous acid is present in the form of NO^+, thus ε max is obtained for NO^+. In 30%, it is completely molecular nitrous acid, giving ε max for HNO_2. In between, where the two are superimposed, their contributions are separated by extrapolating the NO^+ spectrum to lower frequencies. Since for the spectrum of nitrous acid solutions up to M/30 were used, it was necessary to dilute these solutions to M/3000 for NO^+ spectra.

The next major difference between the work in $HClO_4$ and H_2SO_4 is that whereas Singer & Vamplew found no evidence for the $H_2NO_2^+$ ion, since the NO^+ and molecular HNO_2 concentrations corresponded, Bayliss & Watts noted a discrepancy which rose to a maximum between 50 and 65% H_2SO_4, and which they accounted for by the existence of $H_2NO_2^+$ which does not contribute to the spectra. The concentration of $H_2NO_2^+$ present was found by subtracting from the total initial amount of nitrous acid the sum of spectroscopically measured NO^+ and molecular HNO_2. They suggested that

$$(1) \quad HNO_2 + H_3O^+ \rightleftharpoons H_2NO_2^+ + H_2O$$

$$(2) \quad H_2NO_2^+ \rightleftharpoons NO^+ + H_2O$$

For (2) the equilibrium is

$$K_2 = \frac{(NO^+)\ (H_2O)}{(H_2NO_2^+)}$$

Assuming that the activity coefficients of $H_2NO_2^+$ and NO^+ are equal

$$\frac{[NO^+]}{[H_2NO_2^+]} = \frac{K_2}{(H_2O)}$$

and a plot of $\frac{[NO^+]}{[H_2NO_2^+]}$ v. $\frac{1}{(H_2O)}$ should be linear.

It was found to be so from 60-80% H_2SO_4, but failed below 60%, where the spectrum of NO^+ is inaccurate. From 80-65% H_2SO_4 the percentage of $H_2NO_2^+$ increases from 3% to 20%, but from 65-55% H_2SO_4 it increased from 20% to 55%, so that the region in which linearity fails is the one in which there is theoretically most $H_2NO_2^+$ present. For equation (1) the relation

$$\frac{[H_2NO_2^+]\cdot}{[HNO_2]} = \text{const } (H_2SO_4)$$

was found to hold between 40 and 50% H_2SO_4.

Considering the fact that there may be error in the standard ε values from initial loss of nitrous acid; that displacement of the NO^+ maximum in H_2SO_4 solutions complicates the absorption spectra, and that below 60% solutions are admittedly less stable, the correlation of results of esterification in H_2SO_4, and nitrous acid ionisation is not conclusive.

Comparison of Results in H_2SO_4.

When the values for log $[NO^+]/[HNO_2]$ in $HClO_4$ were plotted against % acid, a straight line was obtained from 45-55% H_2SO_4, representing a range of conversion of HNO_2 to NO^+ from 3% to 95%. When the results obtained by Bayliss & Watts for log $[NO^+]/[HNO_2]$ in H_2SO_4 were plotted against % acid, a straight line over the whole range of ionisation was not obtained. Since there is some uncertainty about the composition of the nitrous acid solution, the results were plotted in 2 different ways, graphs 4 & 5. First the values of log $[NO^+]/[HNO_2]$ were calculated, where $[HNO_2]$ was taken as the concentration of molecular nitrous acid found from the absorption spectra. Secondly, log $[NO^+]/[HNO_2 + H_2NO_2^+]$ was calculated, where $[HNO_2 + H_2NO_2^+]$ was obtained as the concentration of remaining nitrous acid after subtracting the NO^+ actually measured. In both cases the same form of curve was obtained from log $[NO^+]/[HNO_2]$ v. % H_2SO_4 and log $[NO^+]/[HNO_2 + H_2NO_2^+]$ v. % H_2SO_4. Over the range 50-62% H_2SO_4 both plots gave straight lines which were almost parallel to the plot of log k_2 v. % H_2SO_4 for the esterification of iso-amyl alcohol.

From 50-62% H_2SO_4 the percentage of NO^+ varies from 1-60%, above 62% H_2SO_4 the ionisation graphs show a distinct change in slope, but whether this is because measurements made in the higher acid range are more accurate, or some other factor is affecting the results, it is impossible to say.

The same argument applies in the case of H_2SO_4 as in $HClO_4$, i.e. that log k_2 should be parallel to log $[NO^+]/[HNO_2]$ if the nitronium ion is the nitrating agent. Since the amount of NO_2^+ present is known to be very small, it is reasonable to compare results with the range of H_2SO_4 in which the nitrosonium ion is present from 1% to 60%.

Within this range, log $[NO^+]/[HNO_2]$ v. % H_2SO_4 and log k_2 have the same slope of 0·19, while log $[NO^+]/[HNO_2 + H_2NO_2^+]$ v. % H_2SO_4 and log k_2 v. % H_2SO_4 have slopes of 0·17 and 0·19 respectively.

Thus it can be concluded that the nitronium ion is also responsible for esterification in H_2SO_4, with the reservation that the NO^+ ionisation results may include considerable error.

Mechanism of Hydrolysis.

It was not possible to measure the reverse reaction owing to the insolubility of iso-amyl nitrate, but values of k_1 have been obtained from k_2 and the equilibrium constant K. The values of K are less accurate than those of k_2, since by the method of obtaining it a small error in the equilibrium reading is magnified. This is best illustrated by taking examples of the calculation involved, the equilibrium being expressed by

$$K = \frac{a-b}{b[c-(a-b)]} = \frac{[\text{Nitrate ester}]}{[\text{Nitric Acid}][\text{Alcohol}]}$$

where a = initial nitric acid concentration

b = final nitric acid concentration

c = initial alcohol concentration.

Taking two sets of typical figures, with b the equilibrium HNO_3 concentration varied by 1%, i.e. from 1·00 N to 1·01 N, the following results are obtained, where

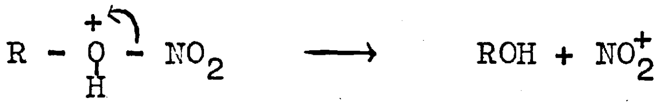
a = 1·5 N and c = 0·70 N.

$$K_1 = \frac{1\cdot50 - 1\cdot00}{1\cdot00(0\cdot70-0\cdot50)} \quad \text{and} \quad K_2 = \frac{1\cdot50 - 1\cdot01}{1\cdot01(0\cdot70-0\cdot49)}$$

$$K_1 = 2\cdot5 \quad \text{and} \quad K_2 = 2\cdot31$$

Thus an error of 1% in the equilibrium concentration becomes an error of 8% in the equilibrium constant.

As outlined in the introduction, the hydrolysis of nitrates can be a complicated procedure, with possibly two or three different mechanisms operating. As alkyl nitrates in concentrated H_2SO_4 are effective nitrating agents (28) the formation of NO_2^+ has been postulated. In this case proton addition to the oxygen atom occurs, to give the resulting fission to ROH and NO_2^+



$$R - \underset{H}{\overset{+}{O}} - NO_2 \longrightarrow ROH + NO_2^+$$

If proton uptake occurs, then

$$RNO_3 + H^+ \rightleftharpoons RHNO_3^+$$

$$RHNO_3^+ \rightleftharpoons ROH + NO_2^+$$

The theoretical rate is given by

$$r = k_o \left[RHNO_3^+ \right] \frac{f_{RHNO_3^+}}{f_x} \qquad (1)$$

where f_x is the activity coefficient of the transition complex, and $f_{RHNO_3^+}$ is the activity coefficient of $RHNO_3^+$.

The experimental rate is given by

$$r = k_1 \left[RNO_3 \right]_T \qquad (2)$$

where $\left[RNO_3 \right]_T$ is the stoichiometric concentration of nitrate ester. Combination of (1) and (2) gives

$$k_1 = k_o \frac{\left[RHNO_3^+ \right]}{\left[RNO_3 \right]_T} \cdot \frac{f_{RHNO_3^+}}{f_x}$$

Since the two activity coefficient terms are very similar, the transition state being an activated complex of the protonated nitrate, let it be assumed that $f_{RHNO_3^+} = f_x$

$$\text{then} \quad k_1 = k_0 \frac{[RHNO_3^+]}{[RNO_3]_T}$$

If the amount of $RHNO_3^+$ formed is very small, then $[RNO_3]_T$ can be replaced by $[RNO_3]$ which represents the concentration of unionised nitrate ester, and

$$\log k_1 = \log k_0 + \log \frac{[RHNO_3^+]}{[RNO_3]}$$

Treating RNO_3 as a Hammett indicator

$$Ho = \log K_{RHNO_3^+} - \log \frac{[RHNO_3^+]}{[RNO_3]}$$

$$\text{if} \quad \frac{f_{BH^+}}{f_B} \times \frac{f_{RNO_3}}{f_{RHNO_3^+}} = \text{const.}$$

where f_{BH^+}/f_B is the ratio of activity coefficients of a Hammett indicator B and its conjugate acid BH^+.

$$\therefore \log k_1 = \log k_0 - Ho + \text{const.}$$

In considering the hydrolysis of sulphate esters, Clark (57) decided that the first stage was the uptake of a proton by the ester, which was a fast process, but since the slope of $\log k_r$ plotted against Ho gave a slope of 0·45, he concluded that the rate-determining step was a bimolecular reaction of the protonated ester with a water molecule. The equation thus obtained for the rate of hydrolysis was

$$\log k_r = \text{const.} + \log (H_2O) - Ho$$

where k_r = velocity constant for the hydrolysis, and on plotting $\log k_r - \log (H_2O)$ against Ho, a slope of $-1{\cdot}1$ was obtained.

For the hydrolysis of iso-amyl nitrate in H_2SO_4 at 25°C, the slope of log k_1 v. Ho is 0•85, while at 0°C it is 1•3; in $HClO_4$ at 25°C the slope is 0•92 (Graphs 11,12,13). These values indicate that the hydrolysis probably involves the rapid uptake of a proton to give the complex $RHNO_3^+$, which then splits up in the rate-determining step to give ROH and NO_2^+.

Activation Energies for the Nitric Acid Esterification of Iso-Amyl Alcohol.

From the measurements of esterification of iso-amyl alcohol at 0°C and 25°C it is possible to calculate the energy of activation, using an integrated form of the Arrhenius equation for two temperatures.

The measurements at the two temperatures were not made in identical H_2SO_4 media, but between 65% and 67% results for log k_2 were obtainable at both temperatures from the log k_2 v. % H_2SO_4 plots. The values decreased from 20,270 cals in 65% H_2SO_4 to 18,335 cals in 67% H_2SO_4, but more extensive measurements in a wider range of media would be necessary to decide if this decrease is significant.

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