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

By T. G. Bonner and D. E. Frizel.

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

The elegant test for the operation of the nitronium mechanism in *C*-,[1] *N*-, and *O*-nitration [2,3] based on the demonstration of zeroth-order kinetics for sufficiently reactive substrates is decisive in the case of nitration by excess of nitric acid in a relatively weak acidic environment. Under such conditions the rate-controlling step becomes the dissociation of the nitric acidium ion $H_2NO_3^+$ to nitronium ion, NO_2^+ (nitryl cation), which is consumed rapidly and completely by the substrate. In a strongly acidic solvent this test is inapplicable as the nitronium ion is formed in a rapidly established equilibrium, and although its

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[1] Hughes, Ingold, and Reed, *J.*, 1950, 2400.
[2] Blackall and Hughes, *Nature*, 1952, **170**, 972.
[3] Hughes, Ingold, and Pearson, *J.*, 1958, 4357; Blackall, Hughes, Ingold, and Pearson, *J.*, 1958, 4366.

presence can be inferred and its potency assumed there is the necessity of proving that it is the active nitrating agent in this particular situation, particularly since it may be present in such minute concentrations that direct detection by physical methods is impossible.

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

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

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

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

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

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

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

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

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

More useful general forms of eqn. (4) are based on the definition of acidity functions, *viz.*,

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[4] Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871.

[5] Lowen, Murray, and Williams, *J.*, 1950, 3318.

[6] Murray and Williams, *J.*, 1950, 3322.

[7] Bonner and Williams, *Chem. and Ind.*, 1951, 820.

[8] Simkins and Williams, *J.*, 1953, 1386.

[9] Hardy-Klein, *J.*, 1957, 70.

H_R,[5] J_0,[10] and C_0 [11] related to the ionisation of triphenylmethanol indicators. They are of the type shown in eqn. (6), which appears to have received the widest application.

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

where

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

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

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

or alternatively

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

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

The evidence concerning condition (*a*) is conflicting. Table 1 gives the value of d log Q/d %H_2SO_4 for four indicators (I—IV) reported by Deno *et al.*[11] and six (IV-IX) by Williams *et al.*[6,13] which collectively cover the range 60—90% sulphuric acid. The differences in the values of the gradients between the two groups are apparent; in addition, the results for (IV) which is common to both groups differ appreciably. In a detailed examination of the applicability of eqn. (8) to nitration data, Deno and Stein [12] found that the equality of the gradients for log k and C_0 was maintained up to 62% sulphuric acid but above this acidity considerable divergence ensued, *e.g.*, for the nitration of nitrobenzene in 80—87·5% sulphuric acid the value of d log k/d %H_2SO_4 is 0·39 while d C_0/d %H_2SO_4 is 0·26. The previously employed test of the nitronium-ion mechanism with eqn. (4) or (6) would give a satisfactory result of 1·18 for the slope of log k against log Q for indicator

TABLE 1.

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

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

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[10] Gold and Hawes, *J.*, 1951, 2102; Gold, *J.*, 1955, 1263.

[11] Deno, Jaruzelski, and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

[12] Deno and Stein, *ibid.*, 1956, **78**, 578.

(VIII) but the less acceptable result of 1·50 for the similar plot of log k against C_0. Differences in ionisation characteristics of the type evident in Table 1 are usually attributed to a difference in the activity coefficient functions d log (f_{Z^+}/f_{ZOH})/d %H_2SO_4 arising from variation in charge type or molecular size. The difficulty of prediction in this matter is evident from the fact that while there are marked differences between the singly, doubly, and triply charged types of the lower group there are none between the uncharged types of the upper group and the singly charged indicator (V). It is possible that this factor may depend on the range of media in which comparisons are made and it has been pointed out that activity coefficients of a variety of oxygen-containing compounds change rapidly over the range 65—80% sulphuric acid.[12] This may be a particularly vulnerable region but the deviations are also apparent in higher acidities and it has been recently shown for certain compounds that d (log f)/d %H_2SO_4 changes very rapidly above 80% sulphuric acid.[14]

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

TABLE 2.

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

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

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

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

aqueous sulphuric acid.[17] As a result of these reports, data were available on the ionisation ratio $[NO^+]/[HNO_2]$ over the range 45—56% perchloric acid and 50—75% sulphuric acid. Several alcohols were investigated to select a suitable one for measurement of *O*-nitration rates in a near or overlapping range of media, and isopentyl alcohol was found to be the most satisfactory. It is rapidly and almost quantitatively converted into its nitrate ester

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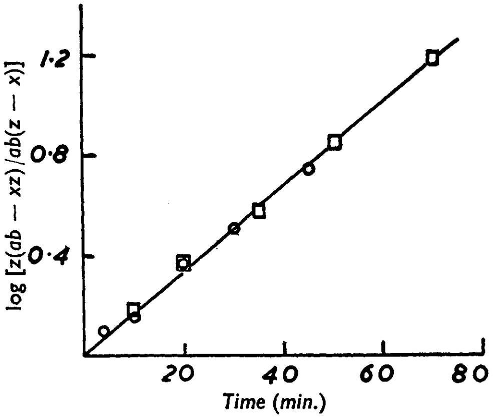
[13] Williams and Bevan, *Chem. and Ind.*, 1955, 171.
[14] Deno and Perizollo, *J. Amer. Chem. Soc.*, 1957, **79**, 1345.
[15] Bevan, unpublished work.
[16] Singer and Vamplew, *J.*, 1956, 3971.
[17] Bayliss and Watts, *Austral. J. Chem.*, 1956, **9**, 319.

with a mixture of nitric and sulphuric acid at 0° with no apparent oxidation.[18] At 0° and 25° measurable rates of nitration were obtained within the range of 57—75% sulphuric acid with attainment of an unchanging equilibrium in a reasonably short time. The comparable range for perchloric acid at 25° was 55—62·5% acid. In both media, the extremely small amount of oxidation of the alcohol which was detected was eliminated by addition of 0·001M-sulphamic acid. With fixed initial concentrations of isopentyl alcohol (0·07M) and nitric acid (0·15M) the experimental rate equation corresponded to a second-order forward reaction (the *O*-nitration) opposed by a first-order reverse reaction (hydrolysis of isopentyl nitrate). The nitration rate constant, k, was calculated from eqn. (11) where

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

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

FIG. 1.



In all rate measurements the plot of log $[z(ab - zx)/ab(z - x)]$ against t was a straight line from the slope of which k was calculated (see Fig. 1 for a duplicated typical experiment). The rate constants obtained for *O*-nitration in aqueous perchloric acid and sulphuric acid are given in Table 3 together with the percentage conversion of the alcohol into nitrate

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

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

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

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

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[18] Chapman and Smith, *J.*, 1867, 581; Boschan, Merrow, and van Dolah, *Chem. Rev.*, 1955, **55**, 485.

at equilibrium. The test for the nitronium-ion mechanism in perchloric acid is that equation (12) should be satisfied, it being assumed that d log $(f_{NO_2^+}/f_{HNO_3})$/d %$HClO_4$ and

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

d log (f_{NO^+}/f_{HNO_2})/d %$HClO_4$ are closely similar. The plots of log *k* and of log ($[NO^+]/[HNO_2]$) against percentage of perchloric acid are shown in Fig. 2. The best line through each set of points being taken, both gradients are 0·27. It is possible to discern a slight curvature in the plot of log *k*, and if this is assumed to be real an increase in gradient from 0·27 to 0·30 with increasing acidity is evident. Discounting the highest point on the log $[NO^+]/[HNO_2]$ line, since it corresponds to more than 95% ionisation and is therefore liable to considerable inaccuracy, we cannot decide, with the limited data, whether any similar curvature occurs in this case. It is clear, however, that in the absence of more accurate ionisation measurements the correspondence required by eqn. (12) and by the similar equations (4), (6), (8), and (9) may not be closer than 10% even in the most favourable circumstances. For comparison, some ionisation ratios for indicator (V) (Table 1) were measured in 50—56% perchloric acid and log ($[Z^+]/[ZOH]$) is included in Fig. 2. Again, more data are desirable bnt the best line has a gradient of 0·31 which is close enough to that of the log *k* value to provide an acceptable proof of the nitronium-ion mechanism. Divergences of this order have been recognised for some time in applications of eqn. (5).[19]

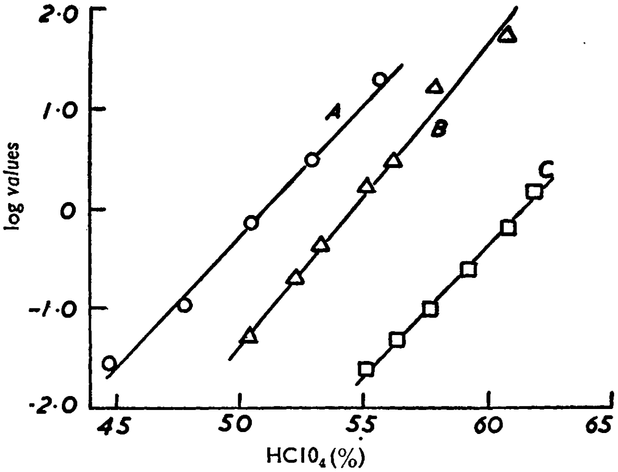

FIG. 2.

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

The application of a similar equation to (12) to the results obtained in sulphuric acid is more complicated. Bayliss and Watts[17] do not mention the difficulties noted in this medium by Singer and Vamplew[16] of (i) a large shift in the position of the maximum in the absorption spectrum of the nitrosonium ion with change in acidity, and (ii) appreciable loss of nitrous acid in aqueous acid solutions; these difficulties led the latter authors to abandon sulphuric acid in favour of perchloric acid for their studies. Further, although the latter authors found no evidence in perchloric acid for a third entity such as $H_2NO_2^+$, since the sum of the nitrosonium ion and molecular nitrous acid concentrations corresponded to the initial amount of nitrous acid determined by chemical analysis, Bayliss and Watts found a discrepancy between the two amounts which rose to a maximum between 50% and 65% sulphuric acid which they accounted for by postulating the existence of the $H_2NO_2^+$ ion. In view of this uncertainty about the composition of nitrous acid solutions in sulphuric acid, two different procedures have been employed to obtain

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[19] Long and McIntyre, *J. Amer. Chem. Soc.*, 1954, **76**, 3240; Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

d log (NO^+/HNO_2)/d $\%H_2SO_4$; first, values of log $[NO^+]/[HNO_2]$ were calculated in which $[HNO_2]$ was the figure quoted as the concentration of molecular nitrous acid found directly by absorption spectra measurement. Secondly, log $([NO^+]/[HNO_2]_T)$ was evaluated, where $[HNO_2]_T$ is the sum of the values given for $[HNO_2]$ and $[H_2NO_2^+]$, *i.e.*, the figure obtained by subtracting the spectroscopically determined NO^+ from the initial total nitrous acid concentration; this is in effect what the molecular nitrous acid concentration would be if no $H_2NO_2^+$ or any other third form of nitrous acid were present. As shown in Fig. 3, in both cases the plot of log (ionisation ratio) against the percentage of sulphuric acid follows the same course; a straight line is obtained over the range 50—62% sulphuric acid over which the ionisation to nitrosonium ion increases to 60%, followed by a sharp change of slope at higher acidities where the rapid increase in conversion of nitrous acid into nitrosonium ion increases the error in evaluating the ionisation ratio. The significant result is that over the range 50—62% sulphuric acid the gradients for log $([NO^+]/[HNO_2])$ and log $([NO^+]/[HNO_2]_T)$ are 0·19 and 0·17 respectively while d log k/d $\%H_2SO_4$ is 0·19. Although there may be some uncertainty in the interpretation of the ionisation data, the closeness of these values is acceptable evidence of the nitronium-ion mechanism for this region of sulphuric acid-water mixtures. A comparison of the nitration rates with the ionisation ratios of triphenylmethanol type indicators shows that much greater divergences exist, since both d C_0/d $\%H_2SO_4$ and d log $Q/\%H_2SO_4$ for indicator (V) have a value of 0·26; otherwise expressed, a plot of log k against C_0 [or log Q for (V)] would have a gradient of 0·64 instead of unity. It is a coincidence that at 0° d log k/d $\%H_2SO_4$ is 0·25, and this large difference from the value at 25° underlies the necessity, often disregarded, of comparing kinetic and ionisation data at the same temperature.

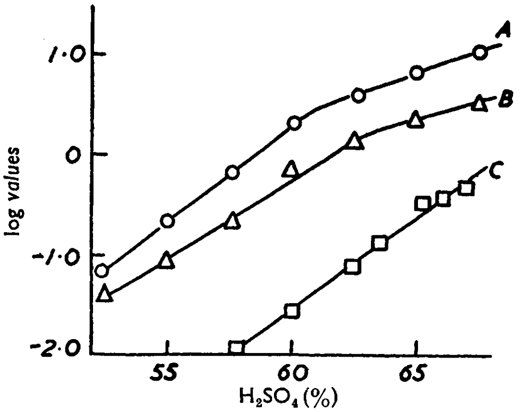

FIG. 3.

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

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

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[20] Bonner and Lockhart, *J.*, 1958, 3852.

EXPERIMENTAL

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

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

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

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

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

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

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