Electrophilic Aromatic Substitution. Part 21.[1] Rate Constants for Formation of Nitronium Ion in Aqueous Sulphuric, Perchloric, and Methanesulphonic Acids

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Studies of the kinetics of nitration of anisole in 66—80% H_2SO_4, 64—70% $HClO_4$, and 88—97% CH_3SO_3H, and of toluene in 74—79% H_2SO_4 are reported. Concentrations of the aromatic compound were high enough for the reaction to be less than first-order in them. Rate constants for formation of the nitronium ion are reported, and rate constants for the reverse reaction estimated. It is suggested that the reaction is a one-step process.

It is well known from studies of the kinetics of nitration of aromatic compounds in various media,[2] that the order of the reaction in the aromatic compound can change from unity to zero both with an increasing concentration and reactivity of it, and decreasing concentration of water. This is rationalised by the Scheme (in which solvent species are not included) and the rate equation (1) derived using the steady-state approximation with respect to the concentration of nitronium ion (AR = aromatic substrate).

$$HNO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2^+$$

$$AR + NO_2^+ \xrightarrow{k_r} \text{products}$$

Scheme

$$\frac{-d[HNO_3]}{dt} = \frac{-d[AR]}{dt} = \frac{k_1k_r[HNO_3][AR]}{k_{-1} + k_r[AR]} \quad (1)$$

This paper reports the measurement of k_1, the rate constant for formation of nitronium ion from solute nitric acid, in aqueous sulphuric, perchloric, and methanesulphonic acids. Values of k_1 for aqueous sulphuric acid (74.7—81.5%) have previously been reported by Chapman and Strachan.[3] Our results are not in quantitative agreement with theirs.

With sufficiently low concentrations of aromatic substrate the reaction is first order in both nitric acid and aromatic substrate [see equation (1)]. This is the situation which normally obtains in these media, even with aromatic compounds sufficiently reactive to react upon encounter with the nitronium ion,[4] because with most such substrates low solubilities make low concentrations unavoidable. Under such circumstances only k_2 [equation (2)] can be determined.

$$k_2 = k_1k_r/k_{-1} \quad (2)$$

It is convenient to combine equations (1) and (2) to give (3).

$$\frac{-d[HNO_3]}{dt} = \frac{-d[AR]}{dt} = \frac{k_1k_2[HNO_3][AR]}{k_1 + k_2[AR]} \quad (3)$$

Provided that the concentration of the aromatic substrate can be made high enough for k_2[AR] not to be negligible compared to k_1 in the denominator on the right of equation (3), k_1 can be determined. The substrate we chose for this study was anisole, because its reactivity[5] and solubility are sufficiently high for the purpose. Toluene, the substrate used by Chapman and Strachan,[3] was also used for the measurement of k_1 in aqueous sulphuric acid. Products from the nitration of both substrates have previously been reported.[5,6]

EXPERIMENTAL

Materials.—Sulphuric acid (98%) and perchloric acid (72%) were AnalaR reagents. Concentrations of diluted acids were determined as previously described.[4,7] Commercial methanesulphonic acid (99%) was fractionally distilled under reduced pressure. A sample (500 cm^3) typically gave a forerun (20 cm^3) after which material was collected for use (250 cm^3, b.p. 140 °C at 0.15 mmHg). Titrimetric assay with standard base of some acid prepared in this way gave a purity of $>99.8\%$. For dilution use was made of inverted U tubes, into the arms of which the required amounts of acid and water respectively were weighed; the apparatus was stoppered and cooled before the contents were mixed. That consistent concentrations were achieved by this method was checked by measuring the rate constant for nitration of toluene dissolved in each sample. Nitric acid was purified as previously described.[8] Anisole and toluene were purified by distillation.

Solubilities.—Excess of aromatic substrate was vigorously stirred with aqueous sulphuric acid for 15 min at 25 °C. The acid layer was separated and centrifuged for 5 min. A sample was taken from the middle of the solution and the concentration of the aromatic substrate determined by comparison of the absorbance after appropriate dilution with the absorbance–concentration plot determined previously.

Kinetics.—For the faster reactions a Nortech SF 3A stopped-flow spectrophotometer combined with a Datalab DL 901 transient recorder was employed to monitor the variations of transmittance with time. For the slower reactions a Pye–Unicam SP 1800 spectrophotometer was used, as previously described.[9]

RESULTS

Solubilities of Anisole and Toluene in Aqueous Sulphuric Acid.—These results are given in Table 1. Values for the more concentrated acid are less accurate because of concurrent sulphonation, although the extent of this was small[10] during the time taken to make the measurement. The solubility of toluene at the lower acidity is in approximate agreement with literature data.[10,11] However, we were not able to achieve reproducible results in the kinetic studies when the concentration of toluene was, as in the previous work,[3] at or close to this solubility limit. It is our view that true homogeneity in such 'solutions' is difficult or impossible to achieve. Mechanical shaking of toluene, enough to make a solution of concentration 2×10^{-3} mol dm^{-3}, with 78% H_2SO_4, for 15 min led to a turbid solution. Although this turbidity was apparently due to bubbles it was very slow to clear, unlike that in a solution of nitric acid in sulphuric acid shaken in the same way. No difficulties in obtaining reproducible kinetics were encountered with solutions of anisole, or of toluene at substantially lower concentrations, as used in the kinetic studies reported below. Solubilities in aqueous perchloric and methanesulphonic acids were not determined, but solubilities of organic compounds in these media are generally higher than in aqueous sulphuric acid.[12] With anisole at the concentrations used we had no doubt about the homogeneity of the solutions.

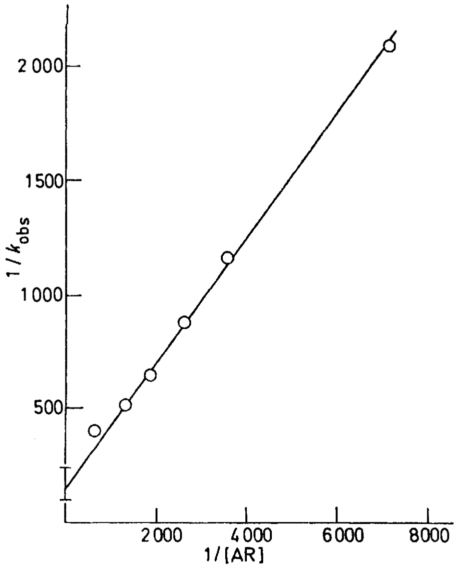


FIGURE 1 Plot of $1/k_{obs.}$ *vs.* $-1/[AR]$ for the nitration of anisole in 69.7% H_2SO_4. (For explanation of error bar see footnote *b* of Table 2)

TABLE 1

Solubilities in aqueous sulphuric acid at 25 °C

	% H_2SO_4	Solubility/mol dm^{-3}
Anisole	73.5	0.039
	77.5	0.07 [a]
Toluene	73.5	0.0028 [b]
	77.5	0.004 [a]

[a] Approximate figures; some sulphonation of the aromatic during equilibration being unavoidable. [b] See text concerning the significance of this figure.

Kinetic Studies.—With neither substrate and in none of the media was it possible to make the concentration of aromatic substrate large enough for the inequality $k_2[AR] \gg k_1$ to hold. Accordingly k_1 was determined by one of the following methods.

(a) With $[AR] \gg [HNO_3]$, the reaction follows a first-order course with rate constant $k_{obs.}$. Equation (4) follows from equation (3): k_1 was deduced, either directly from equation (4) using a value of k_2 determined independently, or from the intercept of a plot of $(1/k_{obs.})$ *vs.* $-(1/[AR])$. Such a plot is shown in Figure 1.

$$\frac{1}{k_{obs.}} = \frac{1}{k_2[AR]} + \frac{1}{k_1} \qquad (4)$$

(b) With $[HNO_3] \gg [AR]$ equation (6) derived by integration of equation (4), was used as previously[9] to determine k_1 and k_2. This method is more accurate than that[3] of using the initial part of the absorbance-time curve to determine k_1 and the latter part to determine k_2. y is

$$\frac{t}{1-y} = -\frac{1}{k_2[HNO_3]}\frac{\ln y}{1-y} + \frac{[AR]_0}{k_1[HNO_3]} \qquad (5)$$

$$y = [AR]/[AR]_0 = (A_\infty - A)/(A_\infty - A_0)$$

defined as shown and A_0, A_∞, and A are the initial and final absorbances and the absorbance at time t respectively.

Values of k_1 and k_2 are given in Table 2. Whether method (a) or (b) was used to derive these values is obvious from the relative concentrations of nitric acid and aromatic substrate. The ratio k_1/k_2 for anisole represents the concentration of anisole which would lead to equal partitioning of the nitronium ion between regression to nitric acid and forward reaction to products. This ratio changes from *ca.* 8×10^{-3} mol dm^{-3} in 66% H_2SO_4 to *ca.* 2×10^{-4} mol dm^{-3} in 80% H_2SO_4.

DISCUSSION

The dependence of log k_1 upon the acidity function H_0 is an approximately linear one in each of the aqueous acid systems (Figure 2). The agreement between the values of k_1 obtained using anisole and those obtained using toluene is seen to be satisfactory, though as explained in the results section the former are probably the more reliable. Values of d(log k_1)/d($-H_0$) are 1.5 (H_2SO_4), 1.1 ($HClO_4$), and 1.0 (CH_3SO_3H). For the ionisation of triarylcarbinols (a rather similar reaction), values of d(log k_1)/d($-H_0$) are in the same range (1.0 to 1.5).[13]

In considering the mechanism of the ionisation of nitric acid it is convenient to focus attention on the reverse step, the hydration of the nitronium ion. This may be done by combining present data with observed

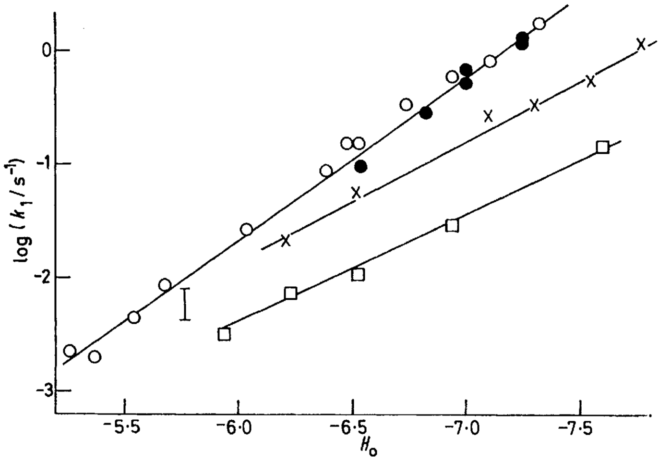


FIGURE 2 Plot of log (k_1/s^{-1}) *vs.*—the acidity function H_0. ○ = sulphuric acid, × = perchloric acid, □ = methanesulphonic acid. Full circles relate to the use of toluene as scavenging aromatic, in all other cases anisole was used. (For explanation of error bar see footnote *b* of Table 2)

second-order rate constants[4,7] for the nitration of benzene, k_2^{bz}. Equation (6) follows from equation (2).

TABLE 2

Rate constants k_1 and k_2 (see text) in aqueous acids at 25 °C

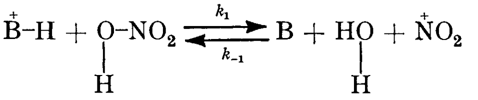
% Acid	10^3[AR]/mol dm^{-3}	10^3[HNO$_3$]/mol dm^{-3}	k_1/s^{-1}	k_2/mol^{-1} dm^3 s^{-1}
Toluene in aqueous sulphuric acid				
74.5	0.20—1.03	0.047	0.094	118
76.2	0.25—0.67	0.040	0.29	680
77.3	0.74	0.14	0.66	1 860 [a]
	0.41	0.077	0.52	1 860 [a]
78.8	0.70	0.12	1.20	6 600 [a]
	0.35	0.065	1.28	6 600 [a]
Anisole in aqueous sulphuric acid				
66.4	0.1	6.2		0.30
66.4	6.2	0.1	0.0023	0.30 [a]
67.2	5.8	0.1	0.0020	0.48
68.3	0.1	6.7		1.11
68.3	6.7	0.1	0.0045	1.11 [a]
69.2	0.1	6.6		1.78
69.2	5.9	0.1	0.0087	1.78 [a]
69.7	0.14—1.52	0.026	0.0045—0.0084 [b]	3.6
69.8	0.03	0.14—7.2		3.4
71.6	9.9	0.60	0.026	8.5 [a]
73.9	9.9	0.48	0.088	63 [a]
74.5	9.9	0.60	0.15	100
74.8	1.39	21	0.14	148
74.8	1.39	7.5	0.16	120
74.8	1.39	0.1	0.14	130 [a]
76.2	1.43	10.7	0.32	560
76.2	1.43	16.4	0.33	650
77.5	1.43	13.5	0.60	1 200
78.5	0.04	0.26		3 200
78.5	9.9	0.60	0.78	3 200 [a]
78.5	5.0	0.60	0.79	3 200 [a]
78.5	1.48	0.26	0.88	3 200 [a]
79.9	9.9	0.60	1.77	10 000 [c]
Anisole in aqueous perchloric acid				
64.0	1.46	14.7	0.022	
64.0	1.46	0.147	0.021	43
65.2	1.44	12.5	0.056	
65.2	1.44	0.125	0.057	115
67.5	1.58	14.3	0.25	2 560
68.3	1.44	15.0	0.33	
68.3	1.44	0.150	0.33	4 100
69.3	1.43	15.4	0.56	
69.3	1.43	0.154	0.54	10 500
70.1	1.27	0.155	1.16	9 × 10^4
Anisole in methonesulphonic acid				
88.0	6.6	37	0.0033	0.61
89.5	5.1	23	0.0077	1.53
91.0	2.8	36	0.0109	8.9
93.2	1.40	18.8	0.030	47
97.0	1.38	16.7	0.147	1 350

[a] Interpolated values using present data and those from refs. 3 and 4. [b] The intercept of the double-reciprocal plot was subject to considerable error because the reaction was largely first-order in aromatic under the conditions. (See error bar in Figures 1, 2, and 3). [c] Value obtained by short extrapolation of the rate profile.

In (6) k_r^{bz} is the specific rate constant for the reaction of benzene with the nitronium ion. Since this reaction is

$$k_1/k_2^{bz} = k_{-1}/k_r^{bz} \qquad (6)$$

not diffusion controlled,[4] k_r^{bz} will be independent of viscosity, and can be expected to vary little with acidity. There is independent evidence that k_r^{bz} is not strongly medium dependent.[14] Variation of k_1/k_2^{bz} then indicates the medium dependence of k_{-1}, the rate constant for the hydration of the nitronium ion. A plot of log (k_1/k_2^{bz}) *vs.* —log (activity of water) of the data relating to H_2SO_4 (Figure 3) is linear with a slope of 1.95. Thus it appears that two water molecules are needed to hydrate the nitronium ion, and a satisfactory picture of the reaction is (7), in which BH^+ and B are hydronium ion and water respectively. The role of the second water molecule B



$$\overset{+}{B}\text{-H} + \underset{\displaystyle H}{\underset{|}{O}}\text{-NO}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + H\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}} + \overset{+}{N}O_2 \qquad (7)$$

in the hydration step is that of a general-base catalyst. There are several other cases in which attack of water on an electrophilic centre in aqueous solution is thought to be subject to general base catalysis by water or other species.[15]

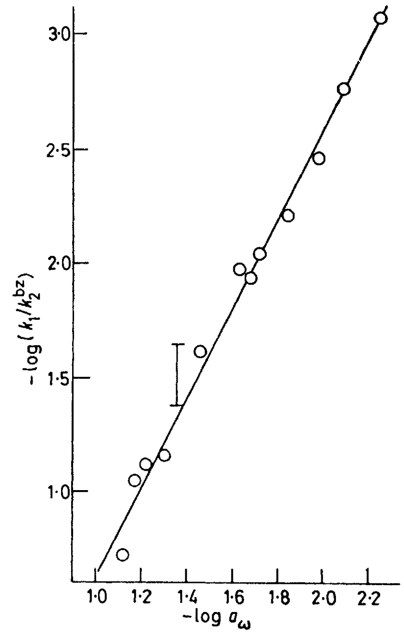


FIGURE 3 Plot of log $[(k_1/k_2^{bz})$/mol dm$^{-3}]$ *vs.* — log (activity of water) for sulphuric acid. (For explanation of error bar see footnote *b* of Table 2)

An apparent difficulty is that in other media (notably the binary solvent systems HNO_3–CH_3NO_2 and HNO_3–CH_3CO_2H) the formation of nitronium ion has been held to occur in two steps as in (8) and (9).[16] The evidence

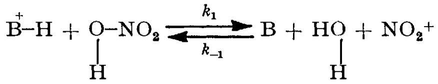
$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \qquad (8)$$

$$H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+ \qquad (9)$$

has been summarised;[2] in particular the effect of added nitrate ion on the rate constants for nitrations which are zeroth order in aromatic (depression of the rate constant without change in order) could thus readily be explained. For these media too, equation (7) with B a solvent species, (HNO_3, CH_3NO_2, or CH_3CO_2H), provides an alternative and satisfactory explanation of the observations. The effect of nitrate ion is to depress the concentration of the protonated solvent molecule BH^+. If this is protonated nitric acid, the form with the two protons on different oxygen atoms [which cannot be the direct precursor of the nitronium ion as in (9)] is implied because it is likely to be predominant. (Carboxylic acids are protonated predominantly on carbonyl oxygen.[17]) The implication of equation (7) is that the alternative form, with both protons on the same oxygen, is too unstable to exist. The linear dependence of k_{-1} upon the concentration of water in trifluoroacetic acid [9] is accommodated by equation (8) with B being a solvent molecule.

In summary, equation (8), with BH^+ and B identified as in Table 3, gives a satisfactory and coherent explanation of all the observations.

TABLE 3



$$\overset{+}{B}\text{–}H + \underset{\displaystyle H}{\underset{|}{O}}\text{–}NO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + H\underset{\displaystyle H}{\underset{|}{O}} + NO_2^+$$

Nitration medium	BH^+	B
Aqueous H_2SO_4, $HClO_4$, and CH_3SO_3H	H_3O^+	H_2O
Trifluoroacetic acid	$CF_3C(OH)_2^+$	CF_3CO_2H
HNO_3–CH_3CO_2H	$(HO)_2NO^+$ or $CH_3C(OH)_2^+$	HNO_3 or CH_3CO_2H
HNO_3–CH_3NO_2	$(HO)_2NO^+$ or $CH_3NO_2^+H$	HNO_3 or CH_3NO_2

The reactivity of water relative to that of benzene towards the nitronium ion, deduced previously,[9] now loses some significance because it depends upon the nature and concentration of B in the solvent in question.

The absolute magnitude of the rate constant k_{-1} can be estimated as follows: benzene reacts with nitronium ion at 1/36th the rate of encounter in 68.3% H_2SO_4, in which medium the bimolecular rate constant for encounter is estimated to be[4] *ca.* 6×10^8 mol^{-1} dm^3 s^{-1}. Use of equation (6) and Figure 3 then gives a value for k_{-1} of 2×10^6 s^{-1} in this medium. By extrapolation, values of k^{-}_{1} of 5×10^8 s^{-1} in water, and 2×10^4 s^{-1} in 80% H_2SO_4 can be deduced.

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