Nitration in Aqueous Nitric Acid: the Rate Profile and the Limiting Reaction Rates

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Rate coefficients for the nitration of a series of quaternary ammonium ions have been used to establish a rate profile for reaction in 63.7—100% nitric acid at 25 °C and to estimate the concentration of nitronium ions in the aqueous media. The kinetics of nitration of a series of reactive aromatic compounds (mainly phenolic ethers) in aqueous nitric acid have been analysed in terms of a first-order rate coefficient and the zeroth-order rate of formation of the nitronium ion. The first-order rate coefficients approach a limiting value as the reactivity of the aromatic substrate is increased and this value is as expected for the rate-limiting formation of an encounter pair ($ArH{\cdot}NO_2^+$). The lifetime of nitronium ions in 60.4% nitric acid ($t_{\frac{1}{2}}$ *ca.* 5×10^{-8} s) has been calculated from the zeroth-order rate at 25 °C and used to show that the formation of the encounter pair ($ArH{\cdot}NO_2^+$) occurs by the diffusion together of the components, not by pre-association. The studies on the more reactive aromatic compounds were carried out in the presence of hydrazine since this was shown to prevent the nitrous-acid catalysed reactions previously observed.

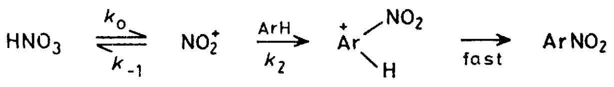
THE main features of the mechanism of nitration in nitric acid and aqueous nitric acid were established by the kinetic studies of Hughes, Ingold, and their co-workers [1] and by the later comparison of the rates of nitration and ^{18}O-exchange in aqueous nitric acid by Bunton and his co-workers.[2] Taken together, this work shows that the nitronium ion is the nitrating agent in 100% nitric acid and that it remains the nitrating agent in aqueous nitric acid, at least down to solutions containing 67% nitric acid by weight. The work also established that the nitration of unreactive aromatic compounds gave the expected first-order kinetic form [equation (1)] and that the nitration of the more reactive aromatic compounds (when present in high concentration) gave a good approximation to the zeroth-order kinetic form [equation (2)]. These two kinetic forms accord with the two possible rate-determining stages in Scheme 1 and the rate coefficients are related by equation (3).

$$\text{Rate} = k_1\,[\text{ArH}] \qquad (1)$$

$$\text{Rate} = k_0 \qquad (2)$$

$$k_1 = k_0 k_2 / k_{-1} \qquad (3)$$

Our interest in extending this work came partly from the possible use of aqueous nitric acid as a medium for studying the concurrent nitration and oxidation of aromatic substrates [3] and partly from the recent interest in the ways of forming encounter pairs ($ArH{\cdot}NO_2^+$).[4] For these purposes it was necessary to determine the rate profile for nitration in nitric acid, the limiting rate of nitration when reaction occurs on encounter, and the rate of reaction of nitronium ions with the solvent.



SCHEME 1

Kinetic Analysis.—The concentrations of the aromatic substrates that could be used in the earlier work [1,2] were restricted by the dilatometric method of analysis and the range of substrates that could be used was restricted by the prevalence of nitrous acid catalysis.[2] We have, to some extent, overcome these difficulties by using a spectrophotometric method of analysis and by using high concentrations of hydrazine to prevent nitrous-acid catalysed side reactions.[5] Some difficulties remain, particularly the necessity that the solution of the aromatic compound should be fast in comparison with the rate of reaction. Visual inspection indicates that the time of solution of the substrates now studied is too short to be significant and this is supported by the form of the kinetic runs. This condition has, however, prevented us from extending this work to a number of other aromatic systems, including benzene.

The traditional reagent for suppressing nitrous acid catalysis is urea but, as a scavenger for nitrous acid, hydrazine is more effective than urea by a factor of $>10^3$ in moderately acidic media (H_2SO_4 *ca.* 5 mol dm^{-3}).[6] The effectiveness of hydrazine come from the fact that the monoconjugate acid is feebly basic [7] but reacts with the nitrosonium ion at a rate near the encounter limit.[8] There is also a direct reaction of hydrazine with nitric acid [9] and the rate of this has been studied under our conditions (see Experimental section): the reaction rate is fortunately too slow to interfere with the nitration reactions reported here. The use of hydrazine has enabled us to extend the earlier studies to the nitration of phenols and phenolic ethers. The kinetic runs in Figure 1 show the effectiveness of hydrazine in suppressing the nitrous-acid catalysed nitration of anisole and also that the rate of the uncatalysed reaction is independent of the concentration of hydrazine.

Since the equilibrium concentration of nitronium ions in aqueous nitric acid is very small, the stationary state approximation can be applied to the reactions in Scheme 1 and yields equation (4). For concentrations of the more reactive aromatic compounds of 0.01—0.1 mol dm^{-3}, the kinetic form of the reaction is intermediate between zeroth and first and hence neither of the terms in the denominator of equation (4) is insignificant. The individual rate coefficients can be obtained by inverting equation (4) to yield equation (5) and then by plotting 1/(initial rate) against $1/[\mathrm{ArH}]_0$. The relevant data for the nitration of anisole in 60.4% nitric acid at 25 °C are given in Table 1 and plotted in Figure 2. As expected, the plot is approximately linear and a least squares analysis of the last five points * gives the following rate coefficients and standard errors: k_1 $(9.10 \pm 0.40) \times 10^{-4}$ s^{-1}; k_0 $(7.15 \pm 0.78) \times 10^{-5}$ mol dm^{-3} s^{-1}. This

$$\text{Rate} = \frac{k_0 k_1 [\mathrm{ArH}]}{k_0 + k_1 [\mathrm{ArH}]} \qquad (4)$$

$$\frac{1}{\text{Rate}} = \frac{1}{k_1[\mathrm{ArH}]} + \frac{1}{k_0} \qquad (5)$$

approach is analogous to that used by Moodie *et al.*[10] to determine the corresponding rate coefficients in other media but they were able to use excess of the aromatic compound and thus to arrange that both of the rate-determining stages in Scheme 1 gave first-order kinetics.

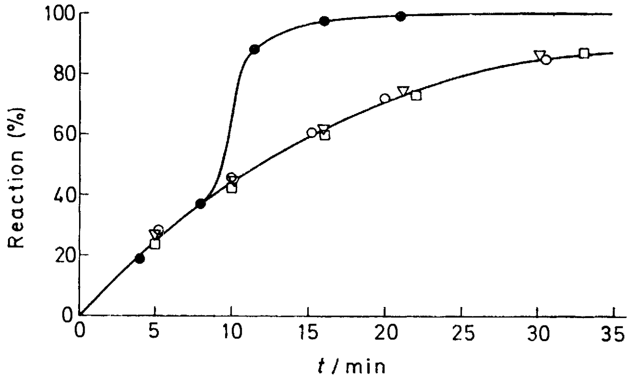


FIGURE 1 The effect of hydrazine on the rate of nitration of anisole (0.01 mol dm^{-3}) in nitric acid (60.2%) at 25 °C. Concentrations of hydrazine: ●, 0.0; □, 0.011; ▽, 0.098; ○, 0.148 mol dm^{-3}

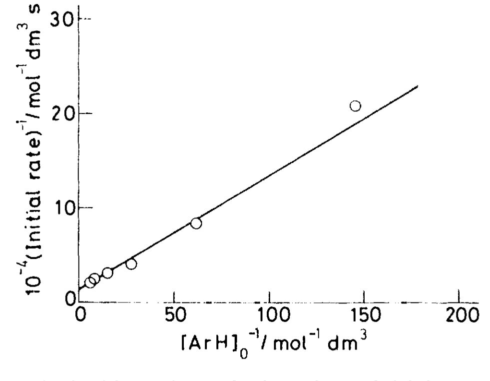


FIGURE 2 A double reciprocal plot of the initial rate against the initial concentration of the aromatic compound for the nitration of anisole in 60.4% nitric acid at 25 °C

Examples of three of the kinetic runs on the nitration of anisole are shown in Figure 3 together with the theoretical curves calculated from the above rate coefficients using the integrated form of equation (4) shown in equation (6) {with [ArH] = $(a - x)$}. The agreement between the theoretical curves and the experimental points confirms this method of kinetic analysis and shows that autocatalysis deriving from reactions catalysed by nitrous acid has been suppressed.

$$\frac{x}{k_0} - \frac{1}{k_1}\left[\ln\left(\frac{a-x}{a}\right)\right] - t = 0 \qquad (6)$$

The nitration of anisole has been studied in less detail under other conditions and the results are included in Table 1 together with those for the nitration of 3-methylanisole. In these examples, the values of the rate coefficients have been obtained by substituting in equation (4) for each pair of runs carried out under the same conditions and solving the resulting simultaneous equations for k_0 and k_1.

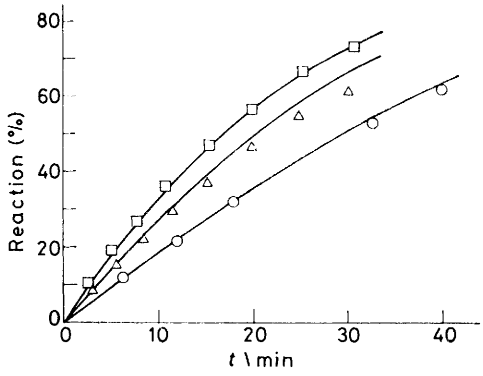


FIGURE 3 Comparison of the experimental results for the nitration of anisole in 60.4% nitric acid at 25 °C with the theoretical curves calculated from equation (6). Concentrations of anisole: 3.64×10^{-2} mol dm^{-3}, □; 6.94×10^{-2} mol dm^{-3} △; 0.146 mol dm^{-3}, ○

The Rate Profile.—The rate profile has been determined from the rates of nitration of several quaternary ammonium ions. These substrates were chosen because of the absence of strong interaction between the substituents present and the solvent. They are also sufficently deactivated to give first-order kinetics.

The resulting first-order rate coefficients are collected in Table 2. At a given acidity, the slopes of log *k versus* % nitric acid are effectively equal for different substrates and so the results can be combined to produce the rate profile shown in Figure 4. Extrapolation of the results of Lee and Millen [11] to 25 °C suggests that the concentration of nitronium ions in 100% nitric acid is 0.3 mol dm^{-3}. This result and the rate profile can be used to calculate the concentration of nitronium ions in aqueous nitric acid on the conventional assumption that the variation in the rate of nitration is determined essentially by changes in this concentration. These results are included in Table 2.

From the observed first-order rate coefficient for the nitration of the phenyltrimethylammonium ion in 100%

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* The calculation was restricted to the last five points since the errors in the points corresponding to low concentrations of the aromatic compound are relatively large and because these errors become more significant in double reciprocal plots.

nitric acid (Table 1) and the concentration of nitronium ions in 100% nitric acid (0.3 mol dm^{-3}),[11] the true second-order rate coefficient for the reaction of nitronium ions with phenyltrimethylammonium ions at 25 °C is 1.91×10^{-2} mol^{-1} s^{-1} dm^{3}. This is similar to the value obtained for this reaction in 98.9% sulphuric acid[12] (1.0×10^{-2} mol^{-1} s^{-1} dm^{3}). Exact agreement could not be expected, for the value of this rate coefficient is sensitive to medium effects and increases to 3.5×10^{-2} mol^{-1} s^{-1} dm^{3} in 90.1% sulphuric acid.

TABLE 1

Initial rates of nitration of anisole and 3-methylanisole in aqueous nitric acid and the resulting values of the limiting rate coefficients k_1 [equation (1)] and k_0 [equation (2)]

T/°C	[HNO$_3$]/%	10^2[ArH]/mol dm^{-3}	[N$_2$H$_4$]/mol dm^{-3}	10^6 Initial rate/mol dm^{-3} s^{-1}	10^5 k_0/mol dm^{-3} s^{-1}	10^3 k_1/s^{-1}
Anisole						
25	60.4	0.24	0.147	1.82		
		0.685	0.147	4.81		
		1.62	0.147	12.1		
		3.64	0.147	24.5	7.15	0.91
		6.94	0.147	32.6		
		13.4	0.147	42.9		
		14.6	0.147	46.1		
	63.7	1.16	0.147	45.1		
		20.6	0.144	156	18.3	5.16
0	63.8	2.48	0.056	5.01		
		20.1	0.055	6.54	0.68	0.76
3-Methylanisole						
25	60.4	0.993	0.147	27.6		
		10.5	0.290	59.1	6.71	4.71

Life-time of the Nitronium Ion.—In the absence of the aromatic compound, the rates of formation and hydrolysis of the nitronium ion are equal and so the first-order coefficient (k_{-1}, Scheme 1) for the hydrolysis is given by equation (7). Values of k_{-1} have been calculated from

$$k_0 = k_{-1}\,[\mathrm{NO_2}^+] \qquad (7)$$

this equation using the values of k_0 in Table 1 and a slight extrapolation of the concentrations of nitronium ions in Table 2. The results are compared with those recently obtained for reaction in aqueous sulphuric acid in Table 3. The half-life of the nitronium ion in 60.4% nitric acid at 25 °C appears to be *ca.* 5×10^{-8} s.

TABLE 2

First-order rate coefficients (k_1) for the nitration of quaternary ammonium ions in aqueous nitric acid at 25 °C and the calculated concentration of nitronium ions

[HNO$_3$]/%	Substrate	10^2[ArH]/mol dm^{-3}	k^1/s^{-1}	[NO$_2^+$]/mol dm^{-3}
100	$\mathrm{Ph\overset{+}{N}Me_3}$	1.71	5.74×10^{-3}	0.3
95.1	$\mathrm{Ph\overset{+}{N}Me_3}$	3.76	2.36×10^{-4}	1.22×10^{-2}
90.3	$\mathrm{Ph\overset{+}{N}Me_3}$	3.26	9.77×10^{-6}	5.09×10^{-4}
84.5	$\mathrm{Ph\overset{+}{N}Me_3}$	18.9	1.58×10^{-7}	8.26×10^{-6}
84.5	$\mathrm{PhCH_2\overset{+}{N}Me_3}$	2.02	3.53×10^{-3}	8.26×10^{-6}
79.8 [a]	$\mathrm{PhCH_2\overset{+}{N}Me_3}$	2.45	1.13×10^{-4}	2.67×10^{-7}
74.6 [a]	$\mathrm{PhCH_2\overset{+}{N}Me_3}$	3.19	5.13×10^{-6}	1.19×10^{-8}
74.6 [a]	p-$\mathrm{MeC_6H_4CH_2\overset{+}{N}Me_3}$	3.03	8.50×10^{-4}	1.19×10^{-8}
70.9 [a]	p-$\mathrm{MeC_6H_4CH_2\overset{+}{N}Me_3}$	4.39	6.57×10^{-3}	9.27×10^{-10}
63.7 [a]	p-$\mathrm{MeC_6H_4CH_2\overset{+}{N}Me_3}$	3.40	1.53×10^{-6}	2.17×10^{-11}
60.4				(4.7×10^{-12}) [b]

[a] In the presence of hydrazine (0.150 mol dm^{-3}). [b] Extrapolated value.

Evidence for a Limiting First-order Rate Coefficient.—The work of Moodie, Schofield, and their co-workers[13] has shown that rate coefficients for nitration by nitric acid in a number of solvents approach a limiting value as the reactivity of the aromatic substrate is increased under conditions where the reaction is first-order with respect to the aromatic compound. For reaction in 68% sulphuric acid, this limiting value is reached by the nitration of the xylenes and mesitylene. With other solvents, this limit is less clearly established but the reactivity of mesitylene appears to be within a factor of two of the limit.[4] The limiting reaction rate has been ascribed to reaction on encounter with the nitronium ion.[14]

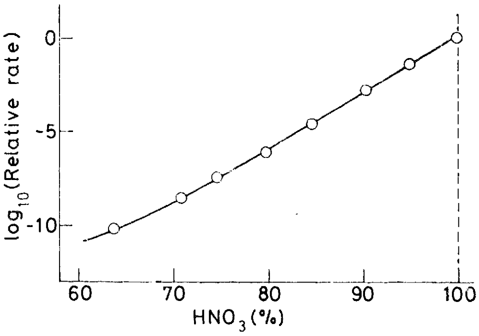


FIGURE 4 Rate profile for the nitration of quaternary ammonium ions in aqueous nitric acid at 25 °C

The extension of such studies to the nitration of the more reactive aromatic compounds in aqueous nitric acid is complicated by the nearness of the reaction rate, under our conditions, to the rate of formation of the nitronium ion. The existence of this rate-determining step imposes an additional limit on the increase in the rate of reaction with the reactivity of the aromatic substrate. To avoid this complication, the concentration of the aromatic substrate has been reduced so that, at the start of the run, the kinetics are approximately first-order. An apparent first-order rate coefficient (k_1^{obs}) has then been calculated for each run and used to calculate the initial reaction rate. This reaction rate together with the concentration of the aromatic compound and the limiting zeroth-order rate (k_0, Table 1) have then been substituted in equation (4) to give the true first-order rate coefficient (k_1). In the one example (3,5-dimethylanisole) where the initial reaction rate was found to be more than half the zeroth-order rate, this initial rate was measured directly and used as above. The resulting values of k_1 are given in Table 4 and the products formed are described in the Experimental section.

TABLE 3

Rate coefficients (k_{-1}, Scheme 1) for the reaction of nitronium ions with the solvent in aqueous nitric acid [a] and aqueous sulphuric acid [b]

HNO_3 (%)	k_{-1}/s^{-1}	H_2SO_4 (%)	k_{-1}/s^{-1}
60.4	1.5×10^7	68.3	2×10^6
63.7	8.4×10^6	80.0	$2. \times 10^4$

[a] Present work [b] Ref. 10.

TABLE 4

Observed and corrected first-order rate coefficients and initial reaction rates for the nitration of reactive aromatic compounds in aqueous nitric acid in the presence of hydrazine (0.147 mol dm^{-3}) at 25 °C

$[HNO_3]$/%	Substrate	10^2 [ArH]/mol dm^{-3}	$10^3\ k_1^{obs}$/s^{-1}	10^6 Initial rate/mol dm^{-3} s^{-1}	$10^3\ k_1$/s^{-1}
60.4	Anisole [a]				0.91
	Phenol	1.28	1.75	22.4	2.55
	$ArCH_2SO_3^-$ [b]	1.13	2.06	23.3	3.05
	Mesitylene	0.828	2.24	18.5	3.02
	4-Methylanisole [c]	1.03	2.38	24.5	3.62
	3-Methylanisole	0.993	2.77	27.5	4.50
	1,3-Dimethoxybenzene	0.868	2.89	25.1	4.45
	3,5-Dimethylanisole	1.11		37.0	6.92
63.7	Anisole	1.16	3.89	45.1	5.16
	Mesitylene	1.01	8.30	83.8	15.3

[a] For details of runs see Table 1. [b] Sodium isodurene-α^2-sulphonate. [c] Some phenolic product is also formed in this nitration: see Experimental section.

Some highly reactive aromatic compounds have also been nitrated in aqueous nitric acid under zeroth-order conditions (Table 5) but their reactivity is then no greater than that of anisole. This shows that the range of values of k_1 in Table 4 does not arise from any additional mechanism of nitration available to the most reactive compounds.

TABLE 5

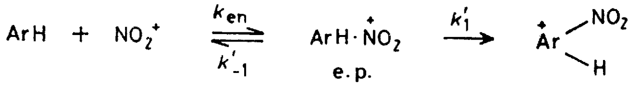
Nitration of reactive aromatic compounds under zeroth-order conditions in 63.7% nitric acid at 0 °C. $[N_2H_2]$ 0.118 mol dm^{-3}

Substrate	10^2[ArH]/mol dm^{-3}	$10^5 k_0$/mol dm^{-3} s^{-1}
Anisole	20.1	0.643
1,3-Dimethoxybenzene	19.8	0.596
1,4-Dimethoxybenzene	20.1	0.625
1,3,5-Trimethoxybenzene	19.8	0.613

Limiting zeroth-order rate (Table 1) = 0.68×10^{-5} mol dm^{-3} s^{-1} in 63.8% nitric acid.

DISCUSSION

Since the concentration of nitronium ions in aqueous nitric acid can be estimated from the rate profile, the above work provides a way of checking whether the evidence for a limiting first-order rate coefficient is consistent with the rate-determining formation of an encounter pair (e.p.). On this interpretation (Scheme 2),* the reaction rate is given in terms of the concentration of nitronium ions by equation (8) and the limiting value of the second-order rate coefficient k_2 (when $k_1' \gg k'_{-1}$) is given by k_{en}, the rate coefficient for formation of an encounter pair. The value of this rate coefficient is related to the viscosity of the medium (η) by equation (9).[4]



SCHEME 2

$$\text{Rate} = k_2\,[\text{ArH}][\text{NO}_2^+] = \frac{k_{en}k'_1}{k'_1 + k'_{-1}}\,[\text{ArH}][\text{NO}_2^+] \quad (8)$$

$$k_{en} = 8RT/3\eta \quad (9)$$

The values of k_1 (Table 4) do not reach a clearly defined limit but the similarity in these values and the diminishing effect of successive methyl substitution suggest that this rate coefficient is near a limiting value. Thus, for reaction in 60.4% acid, the replacement of one of the *meta*-hydrogen atoms in anisole by a methyl group increases the rate coefficient by a factor of five but the replacement of the second hydrogen atom by a methyl group increases the rate coefficient by a factor of only 1.52. It is easy to derive from equation (8) an expression for the relative reactivity of two compounds and then substitution of these relative reactivities (assuming a constant activation by the methyl group on the second stage of Scheme 2) gives values for the ratios k'_1/k'_{-1} of 0.143, 1.67, and 19.6 for anisole, 3-methylanisole, and 3,5-dimethylanisole together with an activating effect for the methyl group (on k'_1) of 11.7 and a limiting value of

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* Scheme 2 is an expansion of the middle stage of Scheme 1.

k_1 (Table 4) of 7.27×10^{-3} s^{-1}. The corresponding value of k_2 (from the equation $k_1 = k_2[NO_2^+]$) is 1.54×10^9 mol^{-1} s^{-1} dm^3.

From the viscosity of 60—70% nitric acid at 25 °C (1.80×10^{-3} N m^{-2} s),[15] the value of k_{en} [equation (9)] is 3.6×10^9 mol^{-1} s^{-1} dm^3. The agreement between this value and the limiting value of k_2 is greater than could reasonably be expected in view of the approximations made in deriving both quantities.* The result accords with earlier calculations based on reaction in sulphuric acid [14] and provides further support for the interpretation of the limiting reaction rate as the rate-determining formation of an encounter pair.

The reason why the limiting value of k_2 is less clearly defined for reactions in aqueous nitric acid than for those in aqueous sulphuric acid [14,16] must come, at least in part, from the difference in the viscosities of the two media. The viscosity of the aqueous sulphuric acid used (68.3%, η 8.1×10^{-3} N m^{-2} s) is *ca.* 4.5 times that of 60.4% nitric acid. This implies that k'_{-1} (Scheme 2) is greater by a factor of *ca.* 4.5 in the aqueous nitric acid and hence that it is more difficult to reach the condition for the limiting rate ($k'_1 \gg k'_{-1}$). Similar considerations have been applied to reactions in other media.[17]

The above arguments have implied that the reverse of the formation of the encounter pair ($ArH{\cdot}NO_2^+$) involves dissociation into the components, not the reaction of the nitronium ion with the solvent. This can be confirmed from the rate coefficients for these processes. Since the equilibrium constant for encounter pair formation [4] is *ca.* 0.5 mol^{-1} dm^3, the value of k'_{-1} for the dissociation of the encounter pairs in 60.4% nitric acid can be calculated to be *ca.* 7.2×10^9 s^{-1}. The corresponding rate coefficient for the reaction of the nitronium ion with the solvent (assuming no interaction within the encounter pair) is 1.5×10^7 s^{-1} (Table 3). By the principle of microscopic reversibility, this comparison also establishes that the encounter pair is formed by the diffusion together of the components and not by pre-association.[4]

The special difficulties of nitration in nitric acid have not always been recognised: in particular, the need to ensure that the solution of the substrate is fast in comparison with the time of reaction and the necessity of analysing the mixed-order kinetics obtained with the more reactive substrates. Thus, the range of reactivities of benzene and a number of monoalkylbenzenes have been reported to be within a factor of two for nitration in 75% nitric acid [18] and from this the authors have concluded that the selectivity of the electrophile for nitration in nitric acid is much less than that observed in other media. Since from the above rate profile, the value of $t_{\frac{1}{2}}$ for the nitration of mesitylene under first-order conditions in 75% nitric acid should be only 0.02 s, it is unlikely that the rate of solution of the alkylbenzenes is fast in comparison with the rate of reaction.† The problem is further complicated by the mixed-order kinetics that should be observed.[19] Because of these factors, the similarity in the observed reaction rates cannot be taken as reflecting the true reactivity of the substrates used. The work in the present paper is consistent with the other studies published previously [1,2] and with the related studies on nitration in aqueous sulphuric acid [14,16]

EXPERIMENTAL

Materials.—Nitric acid (100%) was prepared by vacuum distillation from a solution of AnalaR nitric acid (*d* 1.5) in AnalaR sulphuric acid (98%). For lower concentrations of nitric acid, this material was diluted with distilled water and the concentration determined by titration against sodium hydroxide (0.1 mol dm^{-3}) using phenolphthalein as indicator.

Solutions of nitric acid below 70% were prepared by dilution of the AnalaR acid (*d* 1.42). Hydrazinium hydrogensulphate was recrystallised from water and dried at 100 °C.

Anisole, phenol, mesitylene, 4-methylanisole, 3,5-dimethylanisole, 1,3-dimethoxybenzene, 1,4-dimethoxybenzene, and 1,3,5-trimethoxybenzene were laboratory reagents and were purified by distillation. 3-Methylanisole was prepared by the methylation of *m*-cresol with methyl sulphate. The product had b.p. 176—177 °C (lit.,[20] 177 °C) (Found: C, 78.6; H, 8.1. Calc. for $C_8H_{10}O$: C, 78.7; H, 8.3%). Sodium isodurene-α^2-sulphonate was prepared as described in the literature [21] (Found: C, 50.3; H, 5.8; S, 13.4. Calc. for $C_{10}H_{13}NaO_3S$: C, 50.8; H, 5.6; S, 13.6%). The quaternary ammonium perchlorates were available from previous studies [22] but were reanalysed (C,H,N) and shown to have satisfactory compositions.

Products.—The product compositions were determined from separate experiments carried out under the same conditions as the kinetic runs (including hydrazine where necessary) but with an increase of scale. After the time corresponding to complete reaction, the reaction mixture was poured onto ice–water and the product was isolated either by exhaustive extraction with chloroform or by removal of the solvent by vacuum distillation. The product composition was determined by 60 MHz n.m.r. spectroscopy and except where indicated corresponded to one or more of the expected mononitro-compounds. Earlier work [23] has shown that the quaternary ammonium ions give a mixture of mononitro-compounds on nitration but these product compositions were not redetermined. Other results (where the product is not obvious) were as follows: anisole, 2-nitro (54%), 4-nitro (46%); phenol, 2-nitro (77%), 4-nitro (23%); 3-methylanisole, 2-nitro (16%), 4-nitro (45%), 6-nitro (39%); 3,5-dimethylanisole, 2-nitro (44%), 4-nitro (56%); 1,3-dimethoxybenzene, 4-nitro only. For reaction at 25 °C, the product from the nitration of 4-methylanisole was 4-methyl-2-nitroanisole (49%), 4-methyl-2-nitrophenol (42%), and a third product believed to be 4-methyl-2,6-dinitro-

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* Probably the most important of these approximations is the assumption that medium effects on the rate coefficient of the reaction between the nitronium ion and the aromatic substrate can be neglected in calculating the variation in the concentration of the nitronium ion (Figure 4). It is difficult to assess the error thereby introduced but the fact that this rate coefficient for the phenyltrimethylammonium ion in 100% nitric acid differs from that in 90% sulphuric acid by less than a factor of two (see above) suggests that these medium effects are not large enough to seriously modify the significance of the above arguments. The ionic content of the two media is of course very different since, in 90% sulphuric acid, almost all the water is protonated.

† In reaction with nitric acid, toluene is less reactive than mesitylene by a factor that depends on the medium [4] but which is $\leqslant 1.8$.

phenol (8%) (*cf.* the related studies on nitration in sulphuric acid[16]).

When the amount of hydrazine present is insufficient to prevent nitrous acid catalysis, some of the product compositions are changed. Anisole still gaves the mononitro-isomers on isolation but 1,2-dimethoxybenzene and 1,4-dimethoxybenzene give only dinitration and 1,3-dimethoxybenzene and phenol give more complex products.

Kinetics.—The aromatic compound and the nitric acid (containing any necessary hydrazinium hydrogensulphate) were brought to the required temperature, mixed and shaken. At suitable time intervals, samples (1 or 2 ml) were extracted, quenched in distilled water, and further diluted to give a final volume of 50—1 000 ml (depending on the concentration of the aromatic compound). The u.v. spectra were recorded using a Perkin-Elmer 554 or a Unicam SP 800 spectrophotometer and the percentage reaction (P) was determined from the optical density at the start of reaction (A_0), at time t (A_t), and after *ca.* 15 half-lives (A_∞) using the equation $P = 100 \ (A_t - A_0)/(A_\infty - A_0)$. The wavelengths used depended on the aromatic compound but were in the range 265—350 nm. Three kinetic runs are illustrated in Figure 3.

Since nitric acid reacts slowly with hydrazine, it was necessary to determine the rate of this reaction. Portions (5 ml) were taken from a solution of hydrazine (0.1 mol dm^{-3}) in nitric acid (63.7%) at 0 °C and the concentration of hydrazine was determined volumetrically using excess potassium iodate followed by addition of potassium iodide and titration of the iodine formed.[24] The result gave a first-order coefficient of *ca.* $3 \times 10^{-7} s^{-1}$ and hence an initial rate of reaction of 3×10^{-8} mol $dm^{-3} s^{-1}$. This is less than the rate of formation of nitronium ions under these conditions (Table 1) by a factor of 200. The rate profile for the reaction of hydrazine should be much less steep than that shown in Figure 4 because of the increasing diprotonation of this substrate.

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