Electrophilic Aromatic Substitution. Part 17.[1] Products, Kinetics, and Mechanism of Nitration in Trifluoroacetic Acid

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Benzene, chlorobenzene, toluene, and the di- and tri-methylbenzenes are mononitrated quantitatively at a rate convenient for kinetic study at 25 °C in trifluoroacetic acid containing nitric acid and up to 1 mol dm^{-3} of water. Product yields suggest that the consequence of *ipso*-attack of nitronium ion is migration of the nitro-group to an unsubstituted position. The formation of the nitryl cation can be rate-limiting. When it is not, rate limitation by a step which is insensitive to the nature of sufficiently reactive aromatic compounds is observed. The level of reactivity at which this limiting rate is observed is compared with that found in seven other media.

TRIFLUOROACETIC ACID has high acidity with regard to the H_R acidity function,[2] and it is also a good solvent for many aromatic compounds. This unusual combination of properties make it potentially a useful medium for aromatic nitration. No kinetic studies have been reported, but Brown and Wirkalla[3] have reported isomer ratios in the nitration of toluene, and have found by the competition method that this compound is 29 times more reactive than benzene. Solutions of sodium nitrate in trifluoroacetic acid have been shown to nitrate benzene and toluene, giving good yields of mononitro-compounds, though toluene was reported to yield small amounts of unidentified phenolic products.[4]

In this preliminary study of nitration in trifluoroacetic acid we had three main aims: (*a*) to establish whether the effective electrophile could be identified as the nitronium ion, by, for example, observing conditions under which formation of the electrophile were rate-limiting; (*b*) to seek for a limit to differentiable reactivity of the nitronium ion with reactive aromatic compounds, as found in other media[5-8] and to compare amongst the media the level of reactivity at which this limit occurs; and (*c*) to establish the consequences of *ipso*-attack.[9]

Relevant physicochemical studies of trifluoroacetic acid include the demonstration by conductimetric measurements that water acts as a very weak base in trifluoroacetic acid,[10] so that stoicheiometric and actual concentrations of water are likely to be closely similar. Ion pairing and higher aggregation is extensive.[11]

EXPERIMENTAL

Materials.—Commercial trifluoroacetic acid (99%) was fractionally distilled from concentrated sulphuric acid[12] (10% v/v). Titration revealed a purity of 100 ($\pm$0.1)%. Used trifluoroacetic acid was recovered by two such distillations. Each batch of new or used trifluoroacetic acid thus purified was checked by comparing rate constants for nitration of benzene under standard conditions. Good reproducibility was obtained provided that the concentration of water added was >0.1 mol dm^{-3}. Progressively poorer reproducibility was observed with lower concentrations of water, which we attribute to small (<0.01 mol dm^{-3}) but variable and unknown concentrations of water in the purified acid. (The Karl Fischer reagent proved unsuitable for estimation of water in this medium.) For this reason all our results relate to aqueous trifluoroacetic acid in which $[H_2O] > 0.1$ mol dm^{-3}, rendering the effects of adventitious water negligible.

Nitric acid was purified as previously described.[6] Aromatic substrates were fractionally distilled and their purities checked by g.l.c. Nitro-compounds were available from previous work.[13,14]

Kinetic Measurements.—A small volume (*ca.* 10 mm^3) of a solution of aromatic substrate in trifluoroacetic acid was transferred by syringe at zero time to an optical cell of 1 cm path length containing a solution of nitric acid in aqueous trifluoroacetic acid at 25 °C in the thermostatted cell compartment of a Pye–Unicam SP 1800 spectrophotometer. The change of absorbance with time at a selected wavelength was monitored.

Product Analysis.—A solution of aromatic substrate in trifluoroacetic acid was prepared and a portion (typically 1 cm^3) was added to trifluoroacetic acid (25 cm^3) containing the required concentrations of water and nitric acid (the latter in at least 10-fold excess over substrate) at 25 °C. The mixture was shaken vigorously and then left for at least 10 half-lives. It was quenched in sodium hydroxide solution (500 cm^3; 1 mol dm^{-3}), a known amount of reference standard was added, and the mixture was extracted 10 times with dichloromethane (120 cm^3 in all). The combined extracts were dried ($MgSO_4$) and freed from solvent by fractional distillation (20 cm glass column packed with glass helices). The residue was analysed by g.l.c., under conditions reported previously.[13,14]

Competition Experiments.—A solution in trifluoroacetic acid of the two aromatic substrates, typically with a five-fold excess of the less reactive and with a total concentration of 0.03—0.03M, was brought to 25 °C. A portion

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[1] J. W. Barnett, R. G. Coombes, J. S. Golding, R. B. Moodie, K. Schofield, G. D. Tobin, and J. B. Weston, *J.C.S. Perkin II*, 1977, 248.

[2] U. A. Spitzer, T. W. Toone, and R. Stewart, *Canad. J. Chem.*, 1976, **54**, 440.

[3] H. C. Brown and R. A. Wirkkala, *J. Amer. Chem. Soc.*, 1966, **88**, 1447.

[4] U. A. Spitzer and R. Stewart, *J. Org. Chem.*, 1974, **39**, 3936.

[5] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800.

[6] J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1969, 1.

[7] J. W. Barnett, R. B. Moodie, K. Schofield, P. G. Taylor, and J. B. Weston, unpublished work.

[8] H. W. Gibbs, R. B. Moodie, and K. Schofield, unpublished work.

[9] R. B. Moodie and K. Schofield, *Accounts Chem. Res.*, 1976, **9**, 287.

[10] M. G. Harriss and J. B. Milne; *Canad. J. Chem.*, 1971, **49**, 1888.

[11] M. G. Harriss and J. B. Milne, *Canad. J. Chem.*, 1971, **49**, 3612; 1972, **50**, 3789.

[12] C. Eaborn, P. M. Jackson, and R. Taylor, *J. Chem. Soc.* (*B*), 1966, 613.

[13] J. W. Barnett, R. B. Moodie, and K. Schofield, and J. B. Weston, *J.C.S. Perkin II*, 1975, 648.

[14] R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1970, 347.

(typically 1 cm^3) of a solution of nitric acid in trifluoroacetic acid was added to give a final nitric acid concentration less than that of the minor aromatic component. The flask was shaken vigorously. Quenching, extraction and g.l.c. analyses were carried out as above.

RESULTS

Products.—These are given in Table 1. In all cases yields of mononitro-compounds were quantitative within experimental error. Isomer proportions varied little over the ranges of water concentrations studied.

Kinetics.—With the nitric acid in considerable excess over the aromatic substrate, the orders of reactions varied between the limits of zero and unity. Zero-order character increased with increasing concentration and reactivity of the aromatic compound, and decreased with increasing concentration of water. This behaviour is found in many other media [6,7,15] and can similarly be ascribed to the intermediacy of nitronium ion, formation or further reaction of which can be rate-limiting as in the scheme (1) (solvent species and water not included; AR = aromatic substrate). This scheme is sufficient for the kinetic analysis which follows; a more detailed description of the mechanism is developed in the Discussion section. Application of the steady-state approximation with respect to the concentration of the nitronium ion leads to equation (2). Integration leads to equation (3), in which y and k_2 are defined as shown, and A_0, A_∞, and A are the initial and final absorbance and the absorbance at time t, respectively.

TABLE 1

Yields of nitro-compounds from nitration in aqueous trifluoroacetic acid at 25 °C

Substrate[a]	$[H_2O]$/ mol dm^{-3}	Yields of isomers[b] (%)			Aggregate yield[b] (%)
Chlorobenzene		*x*-Nitrochlorobenzene			
		$x = 2$	$x = 4$		
	0.56	34.5	65.5		100
	1.00	34.5	65.5		100
Benzene		Nitrobenzene			
	0.56	100			100
	1.00	98			98
Toluene		*x*-Nitrotoluene			
		$x = 2$	$x = 3$	$x = 4$	
	0.56	55.4	3.3	41.2	100
	1.11	56.8	2.2	41.3	100
1,2-Dimethylbenzene		1,2-Dimethyl-*x*-nitrobenzene			
		$x = 3$	$x = 4$		
	0.22	59.2	38.6		98
	0.56	59.1	39.3		98
	0.78	58.2	38.9		97
	1.00	58.6	39.1		98
1,3-Dimethylbenzene		1,3-Dimethyl-*x*-nitrobenzene			
		$x = 2$	$x = 4$		
	0.56	14.0	86.0		100
	1.00	13.5	86.5		100
1,4-Dimethylbenzene		1,4-Dimethyl-2-nitrobenzene			
	0.22	100			100
	0.56	101			101
	0.78	100			100
	1.00	100			100
1,3,5-Trimethylbenzene		1,3,5-Trimethyl-2-nitrobenzene			
	0.56	100			100
	1.00	100			100
1,2,4-Trimethylbenzene		1,2,4-Trimethyl-*x*-nitrobenzene			
		$x = 3$	$x = 5$	$x = 6$	
	0.56	8.6	48.2	41.5	98
	1.00	8.9	48.7	40.7	98
1,2,3-Trimethylbenzene		1,2,3-Trimethyl-*x*-nitrobenzene			
		$x = 4$	$x = 5$		
	0.56	88.8	13.1		102
	1.00	87.3	12.7		100

[a] [AR] *ca.* 10^{-3} mol dm^{-3}. [b] Based on initial substrate; ±2%.

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

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

$$-d[AR]/dt = k_1[HNO_3][AR]/\{(k_{-1}/k_r) + [AR]\} \qquad (2)$$

$$\frac{t}{1-y} = \frac{1}{k_2[HNO_3]}\left\{\frac{\ln y}{1-y}\right\} + \frac{[AR]_0}{k_1[HNO_3]} \qquad (3)$$

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

$$k_2 = k_1k_r/k_{-1} \qquad (4)$$

In each run a series of values of y and t were obtained by spectrophotometric observation at a suitable wavelength. Plots of the quantity on the left-hand side of equation (3) against the quantity in curly brackets on the right-hand side showed excellent linearity except in the case of toluene, where slight downward curvature was sometimes apparent at the extremes of the plots. From slope and intercept, values of k_2 and k_1 were derived; these are in Table 2 and are noticeably less regular in the case of toluene for the reason just mentioned.

The quantity k_2 is [see equation (4) and scheme (1)] the ' true ' second-order rate constant for nitration (that which would be observed if nitric acid and nitronium ion were in equilibrium throughout the reaction); k_1 is the first-order rate constant for conversion of nitric acid into nitronium ion when the latter is completely scavenged by aromatic substrate, and should be independent of the concentration and nature of the substrate except insofar as these might change the nature of the medium.[16]

If the reaction showed good first-order kinetics, as with chlorobenzene at all concentrations of water, and benzene at the higher concentrations of water, values of k_2 were obtained by dividing the observed first-order rate constant derived from the normal ' infinity ' plot by the concentration of nitric acid. These values also are in Table 2.

In some runs much higher concentrations of toluene (0.2—0.3 mol dm^{-3}) were used, forcing the reaction to zero order in substrate [see equation (2)]. The substrate under these conditions was in much higher concentration than nitric acid, and k_1 was obtained directly from the first-order plot. The values of k_1 obtained in this way were 10—20% lower than those obtained as described above (Table 2), a difference which we attribute to a medium effect.[16] Apart from this values of k_1 are seen to be satisfactorily independent of the aromatic substrate.

DISCUSSION

The Nitronium Ion, its Precursor, and the Relative Reactivity of Water.—If k_1 (substrate-independent) is divided by the values of k_2 for benzene (k_2^{bz}) the quantity

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[15] J. W. Chapman and A. N. Strachan, *J.C.S. Chem. Comm.*, 1974, 293.

[16] N. C. Marziano, J. H. Rees, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 600.

TABLE 2

Rate constants k_1 and k_2 (see text) for nitration in trifluoroacetic acid at 25 °C

$[H_2O]$/ mol dm^{-3}	$10^2[HNO_3]$/ mol dm^{-3}	10^4k_1/s^{-1}	k_2/ dm^3 mol^{-1} s^{-1}
Chlorobenzene[a]			
0.10	20		0.080
0.20	20		0.046
0.30	20		0.026
0.40	20		0.015 5
0.51	20		0.010 8
0.65	21		0.007 8
0.86	20		0.005 1
1.02	20		0.003 7
Benzene[a]			
0.10[b]	2.1[b]	7.3[b]	1.41[b]
0.22[c]	2.1[c]	5.0[c]	0.41[c]
0.36[d]	2.1[d]	6.2[d]	0.20[d]
0.45	1.98		0.151
0.56	1.98		0.118
0.57[e]	2.0[e]	5.5[e]	0.100[e]
0.60	4.8		0.108
0.70	0.8		0.098
0.78	1.98		0.073
0.80	9.6		0.070
0.90	11.1		0.063
1.00	1.98		0.050
Toluene[a]			
0.10	0.50	5.0	42
0.10[f]	1.70[f]	4.5[f]	
0.17	0.11	6.7	18.6
0.17	0.10	3.9	15.5
0.17	1.99	4.8	
0.20	0.50	4.7	13.5
0.20[g]	1.78[g]	4.4[g]	
0.21[f]	1.70[f]	3.4[f]	
0.22	0.11	6.0	11.0
0.25	0.20	4.4	
0.28	0.50	4.2	8.1
0.35[f]	1.70[f]	3.2[f]	
0.35[g]	1.70[g]	3.7[g]	
0.40	1.26	4.1	5.7
0.49[f]	1.70[f]	3.2[f]	
0.55[g]	1.70[g]	3.4[g]	
0.55	2.50	4.8	3.8
0.57	1.03	2.9	3.4
0.61	0.46	3.2	3.0
0.66[f]	1.70[f]	3.1[f]	
0.71	0.46	4.1	2.5
0.79	1.26	3.1	2.2
0.81[f]	1.70[f]	2.9[f]	
0.91[c]	1.70[g]	3.0[g]	
0.91	0.46	3.3	1.79
1.01	0.46	3.4	1.50
o-Xylene[a]			
0.51	0.30	3.6	11.5
0.59	0.30	3.4	9.8
0.69	0.30	3.5	7.7
0.79	0.30	3.6	6.5
0.89	0.30	3.5	5.6
1.00	0.30	3.3	4.1
m-Xylene[a]			
0.49	0.30	4.2	13.4
0.59	0.30	3.7	9.9
0.69	0.3	3.7	8.5
0.79	0.30	3.7	6.6
0.89	0.30	3.4	5.9
0.99	0.30	3.4	5.0
p-Xylene[a]			
0.50	0.30	3.7	15.2
0.59	0.30	3.8	10.5
0.69	0.30	3.6	9.1
0.79	0.30	4.1	7.2
0.89	0.30	3.5	6.3
0.99	0.30	3.4	5.3
1,2,4-Trimethylbenzene[a]			
0.50	0.31	3.5	16.4
0.60	0.30	3.6	11.5
0.70	0.31	3.3	9.6
0.80	0.31	3.5	7.5
0.90	0.30	3.6	6.4
1.00	0.30	3.5	6.3
1,3,5-Trimethylbenzene[a]			
0.50	0.31	3.6	11.3
0.60	0.31	3.7	8.7
0.70	0.31	3.7	7.0
0.80	0.31	3.7	5.5
0.90	0.31	3.6	4.9
1.00	0.30	3.5	4.4
1,2,3-Trimethylbenzene[a]			
0.50	0.30	3.4	16.6
0.61	0.32	3.7	13.5
0.71	0.32	3.5	10.5
0.81	0.32	3.3	7.7
0.92	0.32	3.3	6.6
1.00	0.32	3.5	4.9

[a] [AR] $\simeq 10^{-4}$ mol dm^{-3} and measurements at 290 nm unless otherwise indicated. [b] [AR] = 5×10^{-4} mol dm^{-3}. [c] [AR] = 10^{-3} mol dm^{-3}. [d] [AR] = 1.5×10^{-3} mol dm^{-3}. [e] [AR] = 2×10^{-3} mol dm^{-3}. [f] [AR] = 0.3 mol dm^{-3}; measurements at 390 nm. [g] [AR] = 0.2 mol dm^{-3}; measurements at 390 nm.

(k_{-1}/k_r) is obtained [equation (4)], and is proportional to the concentration of water (Figure 1). If water remains largely unprotonated,[10] this proportionality can be understood if the step with rate constant k_{-1} is a bimolecular reaction between nitronium ion and water: $k_{-1} = k'_{-1}[H_2O]$. The ratio of reactivities towards nitryl cation of water and benzene (k'_{-1}/k_r) is the slope of the line in Figure 1 and has the value 0.0064. This agrees satisfactorily with an independent and much less direct estimate: 2-phenylethanesulphonate ion and benzene are known from studies of nitration in sulphuric acid [17] to have closely similar reactivities towards the nitronium ion, and in aqueous nitric acid [18] the estimated reactivity of water relative to that of 2-phenylethane-

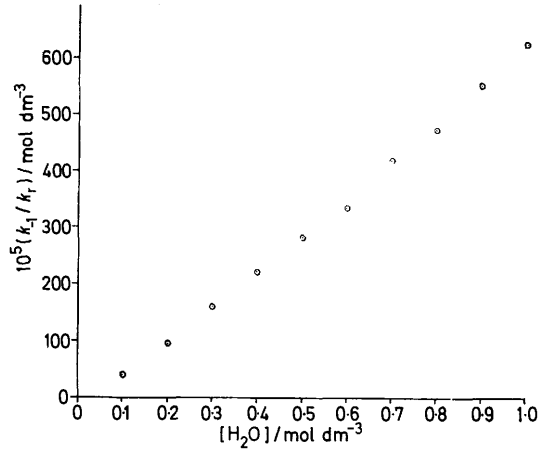

FIGURE 1 Plot of $(10^5k_{-1}/k_r)$/mol dm^{-3} *vs.* $[H_2O]$/mol dm^{-3}

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[17] R. B. Moodie, K. Schofield, and T. Yoshida, *J.C.S. Perkin II*, 1975, 788.

[18] C. A. Bunton and E. A. Halevi, *J. Chem. Soc.*, 1952, 4917.

sulphonate ion varies between 0.004 and 0.01 depending upon the concentration of nitric acid.

The reactivity of chlorobenzene relative to that of benzene (*i.e.* the ratio of values of k_2) is in the range 0.056—0.075 (Table 2 and Figure 2) and this is similar to the value (0.064) observed[14] for nitration in 68% H_2SO_4, a medium in which nitration is known to be effected by nitronium ion.

The observations can therefore be ascribed to nitration by nitronium ion, formed by dehydration of nitric acidium ion. The first step in scheme (1) is more completely described by scheme (5) (HA is trifluoroacetic

$$\mathrm{HA} + \mathrm{HNO_3} \overset{K}{\rightleftharpoons} \mathrm{H_2NO_3^+} + \mathrm{A^-} \qquad (5)$$

$$\mathrm{H_2NO_3^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO_2^+} + \mathrm{H_2O}$$

acid). Possible complications arising from ion pairing are discussed later.

Variation of k_1 and k_2 with the Concentration of Water.—The insensitivity of k_1 {which in terms of scheme (5) is equal to $KK_ik_1[H^+]$, where K_i is the ionic product of trifluoroacetic acid[10]} to the concentration of water (Table 2) is not surprising in view of the very small change in the acidity function H_0 in this range[2] (H_0 *decreases* by 0.06 in the range $[H_2O] = 0.1$—1.0 mol dm^{-3}).

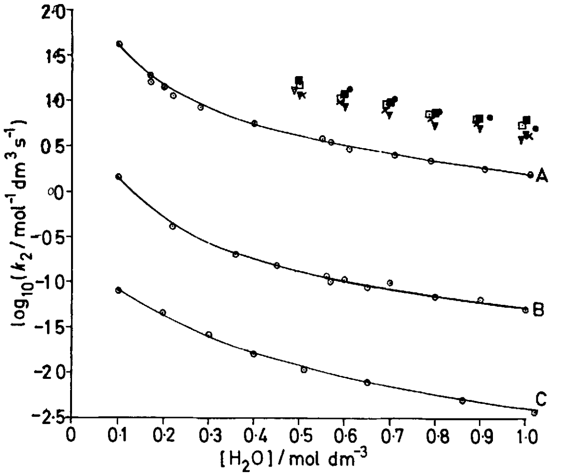

FIGURE 2 Rate profiles [$\log_{10}(k_2/\mathrm{mol^{-1}\,dm^3\,s^{-1}})$ *vs.* $[H_2O]$/mol dm^{-3}; curve A: toluene, curve B: benzene, curve C: chlorobenzene. Crosses: *o*-xylene, open triangles: *m*-xylene, open squares: *p*-xylene, full triangles: mesitylene, full circles: hemimellitene, full squares: pseudocumene

The profiles of log k_2 for the various substrates (Figure 2) are parallel and reveal a much greater dependence upon water concentration. In aqueous sulphuric acid, log k_2 for many substrates increases linearly and with approximately unit slope when plotted against the acidity function $-(H_R + \log a_\omega)$, where a_ω is the activity of water.[19] The activity of water in aqueous trifluoroacetic acid is not known, but H_R increases[2] by 0.15 when $[H_2O]$ goes from 0.1 to 1.0 mol dm^{-3} in trifluoroacetic acid, and if water behaves approximately according to Henry's law, log a_ω probably increases by about 1 in the same range giving an estimated change of $-(H_R + \log a_\omega)$ of 1.15. The observed change in log k_2 over the same range is about 1.4 (Figure 2). The dependence upon acidity of k_2 is thus seen to be broadly similar to that found in other media.

Limiting Value of k_2.—For di- and tri-methylbenzenes values of k_2 (Figure 2) are all closely similar, and such differences as there are are not in the expected order of reactivities. Thus the rate of reaction of nitronium ion with aromatic substrate is limited by a step which is insensitive to the nature of the aromatic compound, provided that the latter is significantly more reactive than toluene. Similar behaviour has been observed before with nitrations in sulphuric acid, where the limiting rate corresponds quite closely with the calculated rate of encounter between nitronium ion and substrate.[5] We digress briefly to consider this calculation. It requires (*a*) an estimate of the equilibrium fraction, I, of nitric acid ionised to nitronium ion as in (6); and

$$I = [NO_2^+]/[HNO_3]_{\mathrm{stoich}} \qquad (6)$$

(*b*) an estimate of the rate constant, k_{enc}, of an encounter-limited bimolecular process. The calculated k_2 value is then obtained from equation (7). According to an

$$k_2 = Ik_{\mathrm{enc}} \qquad (7)$$

approximate theory,[20] k_{enc} may be estimated by using the relation (8) in which η is the viscosity of the medium.

$$k_{\mathrm{enc}} = 8RT/3\eta \qquad (8)$$

It is very difficult to estimate I. In 68.3% H_2SO_4, I can be assigned a value of about[5] 10^{-8} because observed second-order rate constants for nitration are estimated from observed dependences upon acidity to be smaller by about this factor than they are in >90% H_2SO_4 in which $I \simeq 1$. From equations (7) and (8) the value of k_2 for an encounter-limited nitration in 68.3% H_2SO_4 is estimated to be about 6 dm^3 mol^{-1} s^{-1}, in satisfactory agreement in view of the approximate, order-of-magnitude, nature of the calculations, with the observed limiting value of k_2 typified by that of mesitylene, of 2 dm^3 mol^{-1} s^{-1}.

Similar observations of a limiting rate in aqueous perchloric acid[5] and in ternary mixtures of nitric acid, water, and tetramethylene sulphone or nitromethane[2] have been ascribed analogously to rate limitation by diffusion. The present results for nitration in trifluoroacetic acid, and unpublished results for aqueous phosphoric[8] and methanesulphonic[7] acids, make it possible to compare observed values of k_2 for mesitylene (k_2^{mes}) in seven different media, in all of which this compound is nitrated at a limiting rate.

In media other than aqueous sulphuric acid it is not possible to estimate I because conditions under which $I = 1$ have not been achieved, so in Table 3 we compare

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[19] R. B. Moodie, K. Schofield, and P. J. Thomas, following paper.

[20] E. F. Caldin, 'Fast Reactions in Solution,' Blackwell, Oxford, 1964.

k_2^{mes} with k_2^{bz}. Since values of k_2^{bz} fall below the limiting value it is certain that the rate of nitration of benzene is not significantly limited by encounter (except to some extent in phosphoric acid) and that the dependence upon the medium of k_2^{bz} can be expressed by the Bronsted–Bjerrum rate equation (9). In (9) the parameters y are activity coefficients and k is the

$$k_2^{bz} = Ik(y_{NO_2}y_{bz}/y^{\ddagger}) \qquad (9)$$

second-order rate constant for reaction of nitronium ion and benzene in any arbitrarily chosen standard solvent in which the activity coefficients are unity.

If the limiting rate is an encounter rate, equation (10)

$$k_2^{mes}/k_2^{bz} = (\text{constant}/\eta)/(y_{NO_2}y_{bz}/y^{\ddagger}) \qquad (10)$$

follows. Table 3 shows that k_2^{mes}/k_2^{bz} is not inversely proportional to viscosity. However when a range of concentrations of aqueous sulphuric acid only is considered the expected inverse relationship between k_2^{mes}/k_2^{bz} and viscosity *is* observed.[5] The same is found within a range of concentrations of aqueous phosphoric acid.[8] This makes it likely that the limiting rate is correctly identified as a diffusion-controlled one, and that the inadequacy of viscosity as a guide to the level of reactivity at which diffusion control sets in when comparison is made amongst widely different media (Table 3) is due to variations in activity coefficients [equation (10)]. Where the solubility of benzene is low enough to give an inverse measure of its activity coefficient, it is included in the Table and is seen not to be a sufficient explanation of the variations of k_2^{mes}/k_2^{bz}. This leaves the function $y_{NO_2^+}/y^{\ddagger}$), which is not measurable, but might well vary because of differences in solvation and of ionic aggregation (see below). We are unable to resolve this problem further at present.

TABLE 3

Comparison amongst seven media of the level of reactivity at which the limiting rate of nitration is observed; all data relate to 25 °C

Medium	CF_3CO_2H [a]	HNO_3–H_2O–CH_3NO_2 [b,c]	61.1% $HClO_4$ [d,e]	HNO_3–H_2O–$[CH_2]_4SO$ [c,f]	68.3% H_2SO_4 [d,e]	88.0% $MeSO_3H$ [d,g]	85.7% H_3PO_4 [d,h]
η/cP [i]	0.86 [j]	1.1 [c]	2.7	4.2 [c]	8.1	18 [g]	43
k_2^{mes}/dm^3 mol^{-1} s^{-1}	11.3	1.02×10^{-3}	6.5	1.2×10^{-4}	2.1	1.7	0.003 9
k_2^{bz}/dm^3 mol^{-1} s^{-1}	0.135	2.5×10^{-6}	0.083	3.4×10^{-7}	0.058	0.003 1	0.001 2
k_2^{mes}/k_2^{bz}	84	410	78	350	36	550	3
Solubility of benzene (mol dm^{-3})	High [k]	High	0.015 [g]	High	0.009 8	0.182 [g]	0.015 6 [h]

[a] Containing 0.5 mol dm^{-3} of water. [b] $[HNO_3]$ = 8.5 mol dm^{-3} in nitromethane containing 15% by weight of water. [c] Ref. 6. [d] Percentage by weight of acid in the aqueous acid. [e] Ref. 5. [f] $[HNO_3]$ = 8.54 mol dm^{-3} in $[CH_2]_4SO$ containing 7.59 by weight of water. [g] Ref. 7. [h] Ref. 8. [i] From Landolt-Börnstein, 'Zahlenwerte und Funktiosen,' Springer Verlag, Berlin, 1969, unless otherwise indicated. [j] Ref. 10. [k] Completely miscible.

TABLE 4

Competition experiments in trifluoroacetic acid at 25 °C containing 0.55 mol dm^{-3} of water

Substrates	[Total substrate] mol dm^{-3}	$10^2[HNO_3]$ mol dm^{-3}	No. of experiments	R [a] (competition)	R [b] (kinetics)
Mesitylene, toluene	0.29	1.8	2	4.1 (±0.2)	2.8 (±0.2)
	0.025	0.2	2	3.9 (±0.2)	
p-Xylene, toluene	0.26	1.9	5	5.0 (±0.2)	3.7 (±0.2)
	0.029	0.19	4	5.3 (±0.2)	
Toluene, benzene	0.3	1.0	5	29 (±2)	30 (±0.2)

[a] Mean value from the number of experiments indicated of the ratio of reactivities of the two aromatics, deduced by using method A of S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 1256. [b] Ratio of reactivities deduced from kinetics; ratio of values of k_2 in trifluoroacetic acid containing 0.5 ml dm^{-3} water.

TABLE 5

Comparison of yields of isomers with those found in 54 and 79% H_2SO_4

	x-Nitrochlorobenzene			*x*-Nitrotoluene			1,2-Dimethyl-*x*-nitrobenzene		1,3-Dimethyl-*x*-nitrobenzene			1,2,4-Trimethyl-*x*-nitrobenzene			1,2,3,-Trimethyl-*x*-nitrobenzene	
	$x = 2$	$x = 3$	$x = 4$	$x = 2$	$x = 3$	$x = 4$	$x = 3$	$x = 4$	$x = 2$	$x = 4$	$x = 5$	$x = 3$	$x = 5$	$x = 6$	$x = 4$	$x = 5$
54 (±1)% H_2SO_4 [13]				61	4	31	12	23	17	74	2	9	34	3	41	9
CF_3CO_2H	34	0	66	57	2	41	59	39	14	86	0	9	49	41	87	13
79 (±1)% H_2SO_4 [13]	36 [a]	1 [a]	63 [a]	59	4	37	56	43	17	77	2	12	50	38	80	17

[a] 74% H_2SO_4, ref. 14.

Competition Experiments.—The reactivity of toluene relative to that of benzene (Table 4), agrees well with that obtained from kinetic data, but those of mesitylene and *p*-xylene, both relative to toluene, are greater by 30—40%, a discrepancy too great to be accounted for by the combined experimental error of the two methods. The ratio of reactivities of mesitylene and *p*-xylene which can be deduced from the competition results is however in satisfactory agreement with the kinetic results, and again clearly shows that a limiting rate has been reached. Mesitylene, though intrinsically more reactive, reacts marginally more slowly than *p*-xylene.

The failure of the competition experiments to give the same answer with regard to the reactivities of mesitylene and of *p*-xylene relative to that of toluene is puzzling. One possible explanation is that the nitronium ion is second-order rate constant for reaction of nitronium ion formed predominantly from ion-paired, not free, nitric acidium ion, and is itself initially ion-paired. With the less reactive substrates and at the lower aromatic concentration used for kinetic studies, there may be time for this to dissociate to equilibrium with free nitronium ion, but with the more reactive substrates, or at the higher concentrations used in the competition experiments, the ion-pair dissociation equilibrium may not be established before further reaction of the initially formed ion-paired nitronium ion with aromatic substrate.

Product Yields.—These are compared in Table 5 with those obtained in media in which *ipso*-attack [9] is known to be followed either by capture (54% H_2SO_4) or by migration (79% H_2SO_4). It is seen that there is a much closer comparison with results for the more concentrated aqueous sulphuric acid, and this together with the observation of quantitative aggregate yields of mononitro-compounds (Table 2) shows that this is a medium in which *ipso*-attack is followed by migration. The small quantities of phenolic products observed by Stewart [4] indicate that *ipso*-capture may intrude if sodium nitrate, rather than nitric acid, is used in this medium.

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