Electrophilic Aromatic Substitution. Part XV.[1] The Kinetics, Mechanism, and Products of Nitrodebromination in Sulphuric Acid

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The kinetics of nitration in sulphuric acid of *o*- and *p*-dibromobenzene, *p*-bromo- and *p*-chloro-toluene, 2-bromo-*m*-xylene, and *p*-bromochlorobenzene are reported. For these compounds and for bromobenzene and *p*-bromofluorobenzene the yields of products formed over a range of acidities have been determined. Nitrodebromination was not detected with *o*-dibromobenzene and 2-bromo-*m*-xylene, but was a major outcome of nitrating *p*-dibromobenzene, *p*-bromotoluene, and *p*-bromochlorobenzene. The degree of nitrodebromination increased with increasing dilution of the sulphuric acid and evidence is provided to show that Wheland intermediates formed at brominated carbon atoms (W_i^{Br}) are either debrominated or rearranged by nitro-group migration. There is no intramolecular migration of bromine and little or no nucleophilic capture of the Wheland intermediates.

When methyl groups are present *ipso*-nitration at C(Me) occurs and is followed by nucleophilic capture by water and by nitro-group migration in proportions which varied with the acidity. Nitrodechlorination was not observed, but even if attack at C(Cl) is assumed to occur a choice between subsequent decomposition of the Wheland intermediate to its components and nitro-group migration cannot be made. In *p*-dibromobenzene the C(Br) positions are at least as reactive as the C(H) positions.

As part of a general study of nitrodehalogenation, we report here some experiments on nitrodebromination. Few mechanistically authenticated examples of nitrodehalogenation are to be found in the literature. Many examples of the displacement of halogen in nitration solutions, from polysubstituted phenols and phenol ethers have been noted,[2] but most are mechanistically ambiguous and may involve at least some nitrosodehalogenation.[3] Generally however, the evidence supports the view that the ease of halogen displacement increases from chlorine to bromine to iodine.

As regards nitrodebromination, most observations relate to activated substrates.[2,4] Thus *p*-bromoanisole, nitrated in acetic anhydride containing urea, gave 31% of *p*-nitroanisole, together with 2-bromo-4-nitroanisole, 4-bromo-2-nitroanisole, and 2,4-dibromoanisole.[5] Under similar conditions, in ' the absence of nitrous acid ' 4-bromo-2,6-dimethylanisole underwent some nitrodebromination.[6] Curious ' rearrangements ' have been recorded in reactions of this kind, but the polybromo-compounds isolated are probably formed by brominations following expulsion of a brominating agent in the nitrodebromination step. Examples of such ' rearrangements ' are the formation of 2,6-dibromo-4-nitroanisole when 2,4-dibromoanisole is treated with colourless nitric acid,[7] and of 2-bromo-3-methyl-4,6-dinitrophenol from 4-bromo-3-methylphenol.[8] Nitrodebromination was the sole outcome of treating 4-bromo-2,6-dialkylphenols with nitric acid in acetic acid,[9] and it also occurred with 2,6-dibromo-4-methylphenol;[10] the possibility that nitrosodebromination may have been the primary process is, of course, especially strong in such instances.

True nitrodebromination is much more likely to be occurring when deactivated substrates are involved. One of the products from nitrating 1,2,4,5-tetrabromobenzene in sulphuric acid was hexabromobenzene,[11] formed by nitrodebromination to give a brominating reagent which reacted with the starting material.

Barnish and Gibson[12] noted the formation of some *p*-bromonitrobenzene when *p*-dibromobenzene was nitrated in 70% nitric acid, and an earlier paper from this laboratory[13] reported the kinetics and products of

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[2] H. Barbier *Helv. Chim. Acta* 1928, **11**, 157; D. V. Nightingale, *Chem. Rev.*, 1947, **40**, 117.

[3] A. R. Butler and A. P. Sanderson, (*a*) *J. Chem. Soc.* (*B*), 1971, 2264; (*b*) *J.C.S. Perkin II*, 1972, 989; (*c*) 1974, 1671; (*d*) p. 1784; (*e*) K. Olsson and P. Martinson, *Acta Chem. Scand.*, 1972, **26**, 3549; (*f*) K. Olsson, *ibid.*, 1974, **B28**, 322; 1975, **B29**, 405.

[5] C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, 1971, **93**, 3389.

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[11] C. L. Jackson and F. B. Gallivan, *Amer. Chem. J.*, 1896, **18**, 250.

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

nitration of *p*-dibromobenzene in sulphuric acid. 2,5-Dibromonitrobenzene and *p*-bromonitrobenzene were formed in a ratio which varied from 3.8 to 200 in the acidity range 68—90% sulphuric acid, lower acidities favouring nitrodebromination. The nature of the substrate, the conditions used, and the observed kinetics make it highly probable that true nitrodebromination was being observed. This paper describes work on a range of substituted bromobenzenes, aimed at defining the effect of structure and solvent composition on the process of nitrodebromination.

EXPERIMENTAL

Materials.—Sulphuric acid, nitrobenzene, and urea were AnalaR reagents. Sulphuric acid concentrations were determined by density measurements. Nitric acid was prepared by vacuum distillation of a mixture of fuming nitric acid and an equal volume of concentrated sulphuric acid, and stored at −10 °C

p-Dibromobenzene, m.p. 88—89 °C (from EtOH), *p*-bromochlorobenzene, m.p. 67 °C (from EtOH), *p*-dichlorobenzene, m.p. 51—52 °C (from MeOH), 2,5-dibromonitrobenzene, m.p. 82—84 °C (from MeOH), 1-bromo-4-chloro-2-nitrobenzene, m.p. 70 °C (from MeOH), 2,5-dichloronitrobenzene, m.p. 54—55 °C (from EtOH), 4-bromo-2-nitrotoluene, m.p. 47 °C (from MeOH), 4-bromo-3-nitrotoluene, m.p. 34 °C (from MeOH), 2,3-dichloronitrobenzene, m.p. 60—62 °C (from EtOH), 3,4-dichloronitrobenzene, m.p. 42—43 °C (from EtOH), *o*-bromonitrobenzene, m.p. 42 °C (from MeOH), *m*-bromonitrobenzene, m.p. 56 °C (from MeOH), *p*-bromonitrobenzene, m.p. 127 °C (from MeOH), 4-chloro-2-nitrotoluene, m.p. 38 °C (from MeOH), *p*-chloronitrobenzene, m.p. 83 °C (from EtOH), *p*-nitrotoluene, m.p. 54.5 °C (from EtOH), 5-nitropseudocumene, m.p. 70.5 °C (from EtOH), nitromesitylene, m.p. 43—44 °C (from EtOH), and *m*-dinitrobenzene, m.p. 89—90 °C (from EtOH) were purified by recrystallisation from the solvent indicated.

o-Dichlorobenzene, b.p. 177 °C, *o*-dibromobenzene, b.p. 103 °C at 14 mmHg, 2-bromo-*m*-xylene, b.p. 89 °C at 14 mmHg, *p*-bromofluorobenzene, b.p. 153 °C, bromobenzene, b.p. 153 °C, and *p*-chlorotoluene, b.p. 106 °C at 14 mmHg, were purified by distillation.

Fluoronitrobenzenes, *p*-bromotoluene, 2-nitro-*m*-xylene, 4-chloro-3-nitrotoluene, and nitro-*p*-xylene were obtained from commercial sources.

2-Bromo-1,3-dimethyl-4-nitrobenzene, m.p. 57 °C, and 2-bromo-1,3-dimethyl-5-nitrobenzene, m.p. 101 °C, were obtained by g.l.c. (Pye 105 instrument, fitted with a 15 ft column of 15% Silicone SE-30 on Chromosorb W, nitrogen flow rate 100 ml min^{-1}, column temperature 182 °C) from the mixture formed by nitrating 2-bromo-*m*-xylene with nitric acid in 79.4% sulphuric acid.

1-Bromo-4-fluoro-2-nitrobenzene, m.p. 40 °C (from MeOH), and 1-bromo-4-fluoro-3-nitrobenzene, m.p. 19 °C [from light petroleum (b.p. 40—60 °C)], were obtained by g.l.c. (Pye 105 instrument fitted with a 15 ft column of 15% Silicone SE-30 on Chromosorb W, nitrogen flow rate 100 ml min^{-1}, column temperature 159 °C) from the mixture formed by nitrating *p*-bromofluorobenzene with nitric acid in 94.5% sulphuric acid.

1,2,4-*Tribromobenzene*.—2,4-Dibromoaniline (5 g) was heated under reflux for 2 h with hydrobromic acid (47%; 25 ml). The stirred mixture was cooled to 0 °C and sodium nitrite (1.5 g) in water (25 ml) was added dropwise over 30 min. The solution was filtered into another prepared from copper(I) bromide (6.9 g) in hydrobromic acid (25 ml). This mixture was heated on a steam bath for 2 h, cooled in ice, and extracted with ether (3 × 50 ml). The extracts were washed with water (2 × 25 ml) and dried ($MgSO_4$). The ether was evaporated to yield a brown oil, which was distilled, b.p. 85—90 °C at 0.04 mmHg, and crystallized from ethanol to form white needles (2.9 g), m.p. 44.5 °C.

2,4-*Dibromonitrobenzene*.—*m*-Dibromobenzene (5 g) was mixed with a solution of nitric acid (1.1 ml; *d* 1.5) in sulphuric acid (15 ml; 81.9%) at 0 °C. The mixture was allowed to warm up to room temperature with vigorous stirring. After 5 h the mixture was poured into water, when a pale yellow precipitate was formed. The mixture was neutralized with sodium carbonate and then extracted with ether to yield a pale yellow solid. The crude material was purified by recrystallization from methanol, to yield pale yellow needles (4.8 g), m.p. 61 °C.

3-*Bromo-4-nitrotoluene*.— 2-Bromo-4-methylanilinium chloride [14] (8.1 g) was added to concentrated sulphuric acid (7 ml) at 0 °C to form a suspension of a white powder. Water (15 ml) was added and at 0 °C sodium nitrite (4 g) in water (13 ml) was added dropwise. The clear solution was passed quickly in portions into a solution of sodium nitrite (50 g) and sodium hydrogen carbonate (22 g) in water (500 ml) at 60 °C through a wide-bore glass tube.[15] After 5 min the black tarry mixture was cooled and extracted with dichloromethane (5 × 25 ml portions). The solvent was removed from the dried ($MgSO_4$) extract under reduced pressure to yield a black oil (7.8 g) which was purified by column chromatography [basic alumina; light petroleum (b.p. 60—80 °C)] to give pale yellow needles (1.9 g) of 3-bromo-4-nitrotoluene, m.p. 35—36 °C.

2,4-*Dibromotoluene*.—*p*-Nitrotoluene (5.6 g) was treated at 0 °C with bromine (2.4 ml) in sulphuric acid (50 ml) in the presence of silver sulphate (6.4 g).[16] After 4 h, the yellow reaction mixture was poured over ice and filtered through a glass sinter. The precipitated 2-bromo-4-nitrotoluene was then separated from the silver bromide by washing the residue on the sinter with dichloromethane. The washings were shaken with sodium metabisulphite solution (2 × 25 ml) and water (2 × 25 ml) and then dried ($MgSO_4$). When the solvent had been removed, a pale yellow solid remained, which was recrystallized from methanol to give pale yellow needles (7.8 g) of 2-bromo-4-nitrotoluene, m.p. 75—76 °C. This material (0.5 g) was reduced with tin (1 g) and concentrated hydrochloric acid (2 ml) at 100 °C to form a clear solution of 3-bromo-4-methylanilinium chloride. The solution was cooled, white platelets were formed and were removed by filtration to form a solid to which was added concentrated sulphuric acid (2 ml) and water (10 ml). At 0 °C, sodium nitrite (0.18 g) in water (3 ml) was slowly added and the clear solution was filtered into another prepared from hydrobromic acid (48%; 5 ml) and copper(I) bromide (2.5 g) and heated on a steam bath for 2 h. The mixture was cooled in ice and extracted with ether (3 × 50 ml). The solvent was removed at the water pump to yield a brown oil, which was purified by column chromatography [basic alumina; light petroleum (b.p. 60—80 °C)] to give 2,4-dibromotoluene (0.15 g) as an oil.

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[14] *Org. Synth.*, Coll. Vol. I, 1944, p. 111.

[15] E. R. Ward, C. D. Johnson, and J. G. Hawkins, *J. Chem. Soc.*, 1960, 894.

[16] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 1950, 573.

3,4-*Dibromotoluene*.—2-Bromo-4-methylanilinium chloride [14] was converted into 3,4-dibromotoluene using a Sandmeyer reaction as for 1,2,4-tribromobenzene. Purification by column chromatography [basic alumina; light petroleum (b.p. 60—80 °C)] gave an oil (yield 41%).

1-*Bromo*-4-*chloro*-3-*nitrobenzene*.— *o*-Chloronitrobenzene (1.6 g) was brominated as for 2,4-dibromotoluene to yield 1-bromo-4-chloro-3-nitrobenzene (1.8 g) as needles, m.p. 70 °C (from MeOH).

1,2-*Dibromo*-3-*nitrobenzene*.—2,3-Dinitroacetanilide [17] was converted into 1,2-dibromo-3-nitrobenzene,[18] m.p. 80—81 °C (from MeOH).

1,2-*Dibromo*-4-*nitrobenzene*.—*p*-Bromonitrobenzene (2.0 g) was brominated as for 2,4-dibromotoluene to yield 1,2-dibromo-4-nitrobenzene (2.3 g) as needles, m.p. 54.5—55 °C (from MeOH).

1,2-*Dibromo*-4-*chlorobenzene*.— 1,2-Dibromo-4-nitrobenzene was reduced with tin and concentrated hydrochloric acid to 3,4-dibromoanilinium chloride as for 2,4-dibromotoluene. This salt (0.62 g) was treated with concentrated sulphuric acid (2 ml) and water (10 ml). At 0 °C sodium nitrite (0.08 g) in water (3 ml) was added. The solution was filtered into another containing copper(I) chloride in concentrated hydrochloric acid (10 ml) and the mixture was heated at 100 °C for 2 h. Cooling, followed by ether extraction (3 × 50 ml) yielded a brown oil, which was purified by column chromatography [basic alumina, light petroleum (b.p. 60—80 °C)] to yield needles (0.2 g) of 1,2-dibromo-4-chlorobenzene, m.p. 35—36 °C.

2,4-*Dibromo*-1-*chlorobenzene*.—2,4-Dibromoaniline (5 g) was converted by a Sandmeyer reaction as for 1,2-dibromo-4-chlorobenzene into 2,4-dibromo-1-chlorobenzene (4.3 g), m.p. 27 °C.

Kinetic Methods.—The methods used have been described in earlier Parts. The wavelengths at which kinetics were followed are given in Table 1.

Product Studies.—The methods used have been described in an earlier paper.[19] Product stabilities in sulphuric acid of low concentration were examined as already described.[19] Details of the g.l.c. procedures used in analysing product mixtures are given in Table 2. The response of the detector to reaction products and to the reference standard was examined and calibration graphs constructed. Areas under peaks were determined with either a Kent Chromologue or a Disc integrator.

1-Bromo-4-chloro-2-nitrobenzene and 1-bromo-4-chloro-3-nitrobenzene were not separable by g.l.c. The mass balance of products from the nitration of *p*-bromochlorobenzene was found by g.l.c., and the ratio of the two isomers by i.r. analysis (Perkin-Elmer 357 instrument). The 1-bromo-4-chloronitrobenzenes were separated from other reaction products by g.l.c. (Pye 105 instrument; 15 ft column of 15% Silicone SE-30 on Chromosorb W, nitrogen flow rate 100 ml min^{-1}, column temperature 192 °C). The i.r. spectrum of their solution in carbon tetrachloride was taken. The relative heights of the peaks at 1 053 and 1 087 cm^{-1} for 1-bromo-4-chloro-3-nitrobenzene, and at 1 048 and 1 098 cm^{-1} for 1-bromo-4-chloro-2-nitrobenzene were used to calculate the isomer ratios.

RESULTS

Kinetics.—Second-order rate constants are listed in Table 1, and rate profiles are plotted in Figure 1. First-order kinetics were not observed for *p*-bromoiodobenzene or *p*-bromofluorobenzene.

Yields of Products.—These are tabulated in Table 3 and plotted in Figures 2—7.

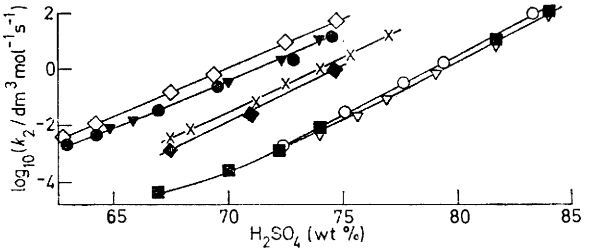

FIGURE 1 Variation of the logarithm of the second-order rate constant for nitration of the substituted halogenobenzenes with the weight percentage of sulphuric acid at 25 °C: ◇, 2-bromo-*m*-xylene; ●, *p*-chlorotoluene; ▼, *p*-bromotoluene; ×, fluorobenzene; ◆, bromobenzene; ○, *o*-dibromobenzene; ▽, *p*-bromochlorobenzene; ■, *p*-dibromobenzene

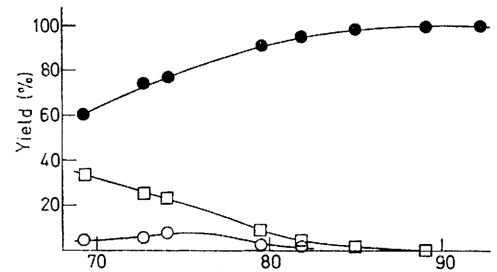

FIGURE 2 Nitration of *p*-dibromobenzene. Yields of products, as a percentage of substrate, plotted against the weight percentage of sulphuric acid: ●, 2,5-dibromonitrobenzene; □, *p*-bromonitrobenzene; ○, 1,2,4-tribromobenzene

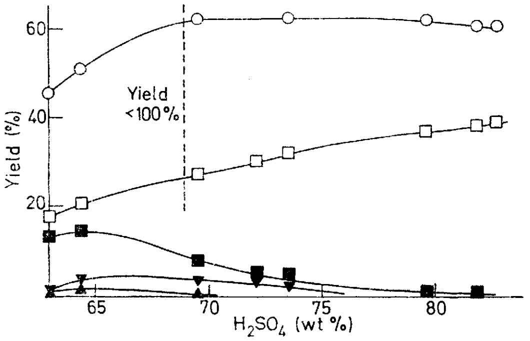

FIGURE 3 Nitration of *p*-bromotoluene. Yields of products, as a percentage of substrate, plotted against the weight percentage of sulphuric acid: ○, 4-bromo-2-nitrotoluene; □, 4-bromo-3-nitrotoluene; ■, *p*-nitrotoluene; ▼, 2,4-dibromotoluene; ▲, 3,4-dibromotoluene

The yields were quantitative over the acidity range covered for each substrate, except for *p*-bromofluorobenzene or those substrates containing at least one methyl group. In Figures 3, 5, and 6 the broken lines indicate the acidities below which yields fell below 100% for nitration of *p*-bromotoluene, *p*-chlorotoluene, and 2-bromo-*m*-xylene, respectively.

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[17] L. H. Welsh, *J. Amer. Chem. Soc.*, 1941, **63**, 3276.

[18] L. Sihlbom, *Acta Chem. Scand.*, 1953, **7**, 1197.

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

Substantial nitrodebromination was observed to occur during the nitration of *p*-dibromobenzene, *p*-bromochlorobenzene, *p*-bromofluorobenzene, and *p*-bromotoluene. From all these substrates nitrodebrominated products, nitrated starting material, and brominated starting material were formed. Results for the nitration of *p*-dibromobenzene support and extend those from earlier work.[13] Presumably the unidentified product mentioned in this account is 1,2,4-tribromobenzene. Small amounts (0.5%) of nitrodebromination were observed during the nitration of *p*-bromoiodobenzene.

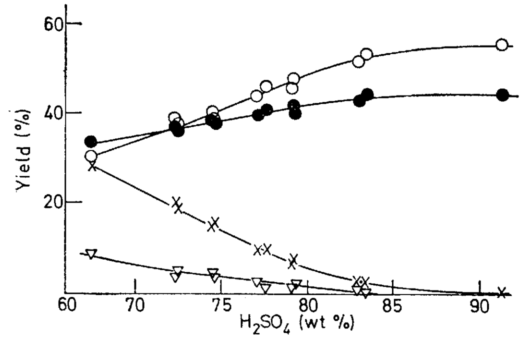

FIGURE 4 Nitration of *p*-bromochlorobenzene. Yields of products, as a percentage of substrate, plotted against the weight percentage of sulphuric acid: ○, 1-bromo-4-chloro-2-nitrobenzene; ●, 1-bromo-4-chloro-3-nitrobenzene; ×, *p*-chloronitrobenzene; ▽, 1-chloro-*x*,4-dibromobenzene

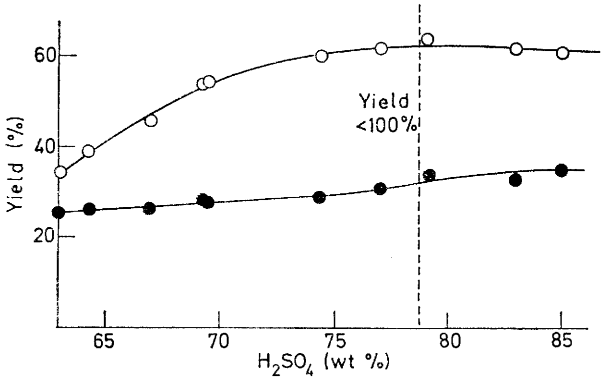

FIGURE 5 Nitration of *p*-chlorotoluene. Yields of products, as a percentage of substrate, plotted against the weight percentage of sulphuric acid: ○, 4-chloro-2-nitrotoluene; ●, 4-chloro-3-nitrotoluene

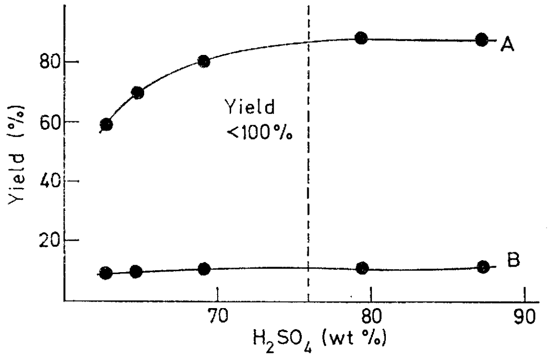

FIGURE 6 Nitration of 2-bromo-*m*-xylene. Yields of products, as a percentage of substrate, plotted against the weight percentage of sulphuric acid: A, 2-bromo-1,3-dimethyl-4-nitrobenzene; B, 2-bromo-1,3-dimethyl-5-nitrobenzene

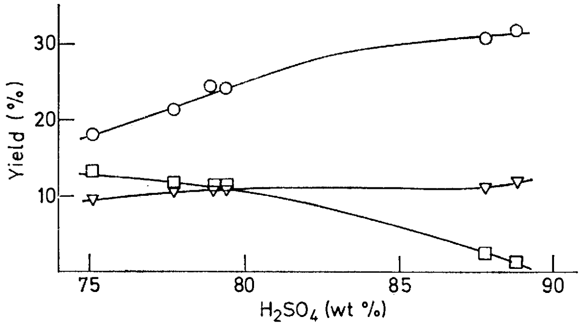

FIGURE 7 Nitration of *p*-bromofluorobenzene. Yields of products, as a percentage of substrate, plotted against the weight percentage of sulphuric acid: ○, 1-bromo-4-fluoro-2-nitrobenzene; ▽. 1-bromo-4-fluoro-3-nitrobenzene; □, *p*-nitrofluorobenzenes

TABLE 1

Second-order rate coefficients for nitration in sulphuric acid at 25.0 ± 0.1 °C[a]

Compound	H_2SO_4 (%)[b]	$[HNO_3]$/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}
o-Dibromobenzene[c]	72.4	1.9×10^{-1}	2.05×10^{-3}
	75.1	1.8×10^{-1}	2.86×10^{-2}
	77.7	2.5×10^{-2}	3.32×10^{-1}
	79.4	5.7×10^{-3}	1.77
	83.3	5.2×10^{-4}	1.01×10^{2}
p-Dibromobenzene[d]	67.1	1.9×10^{-1}	3.98×10^{-5}
	70.0	1.5×10^{-1}	2.60×10^{-4}
	72.2	1.5×10^{-1}	1.35×10^{-3}
	74.0	1.4×10^{-1}	7.35×10^{-3}
	76.9	5.2×10^{-2}	1.05×10^{-1}
	79.1	5.7×10^{-3}	9.07×10^{-1}
	81.7	5.9×10^{-4}	1.17×10
	84.0	4.9×10^{-4}	1.22×10^{2}
p-Bromochlorobenzene[e]	74.0	2.0×10^{-1}	5.53×10^{-3}
	75.6	1.7×10^{-1}	2.15×10^{-2}
	76.9	4.0×10^{-2}	8.11×10^{-2}
	79.1	1.0×10^{-2}	6.59×10^{-1}
	81.7	6.1×10^{-4}	7.60
	84.0	5.3×10^{-4}	8.03×10
2-Bromo-*m*-xylene[c]	62.8	1.9×10^{-1}	3.74×10^{-3}
	64.3	1.5×10^{-1}	1.23×10^{-2}
	67.5	5.0×10^{-2}	1.41×10^{-1}
	69.4	1.5×10^{-2}	6.23×10^{-1}
	72.5	1.3×10^{-3}	9.12
	74.7	5.0×10^{-4}	5.71×10
p-Bromotoluene[d]	64.9	1.9×10^{-1}	7.23×10^{-3}
	65.9	1.6×10^{-1}	1.47×10^{-2}
	67.1	1.5×10^{-1}	4.32×10^{-2}
	69.6	1.5×10^{-2}	2.55×10^{-1}
	70.0	2.1×10^{-2}	3.25×10^{-1}
	72.4	1.8×10^{-3}	2.50
	74.0	5.0×10^{-4}	1.14×10
p-Chlorotoluene[e]	63.0	1.9×10^{-1}	1.96×10^{-3}
	64.3	1.8×10^{-1}	4.49×10^{-3}
	67.0	1.2×10^{-1}	3.38×10^{-2}
	69.6	2.4×10^{-2}	2.40×10^{-1}
	72.9	1.7×10^{-3}	2.24
	74.5	9.9×10^{-4}	1.69×10

[a] [urea] *ca.* 3×10^{-2} mol dm^{-3}; [ArH] *ca.* 5×10^{-5} mol dm^{-3}. [b] ±0.1%. [c] Measurements were made at 320 nm. [d] Measurements were made at 330 nm. [e] Measurements were made at 325 nm.

From bromobenzene very small amounts of a product were formed which might have been nitrobenzene. It appeared to have a retention time in g.l.c. not precisely identical with that of nitrobenzene but our methods were not sensitive enough to settle the point. The *yields* of isomers formed in the nitration of bromobenzene differ slightly (though probably not significantly when experimental error is allowed for) from the *proportions* reported earlier.[13] The small changes with acidity which appear to be indicated by the present results were not noticeable in the earlier work, which covered a smaller range of acidities. No product of nitrodebromination (amounts $<0.2\%$ would have escaped notice) was detected in the nitration of *o*-dibromobenzene or 2-bromo-*m*-xylene.

TABLE 2

G.l.c. analysis data

Aromatic substrate	Product or standard	Column (t/°C) [a]	R_t/s
Bromobenzene	*o*-Bromonitrobenzene	15% Polypropylene glycol (190)	1 193
	m-Bromonitrobenzene		868
	p-Bromonitrobenzene		977
	Nitrobenzene		306
	p-Chloronitrobenzene [b]		585
o-Dibromobenzene	1,2-Dibromo-3-nitrobenzene	2% Polyethylene glycol (175)	676
	1,2-Dibromo-4-nitrobenzene		470
	o-Bromonitrobenzene [c]		204
	p-Chloronitrobenzene [b]		96
p-Dibromobenzene	2,5-Dibromonitrobenzene	15% Silicone SE-30 (161)	890
	p-Bromonitrobenzene		350
	1,2,4-Tribromobenzene		646
	2,4-Dibromonitrobenzene [c]		906
	5-Nitropseudocumene [b]		527
p-Bromochlorobenzene	1-Bromo-4-chloro-2-nitrobenzene	15% Silicone SE-30 (160)	719 [d]
	1-Bromo-4-chloro-3-nitrobenzene		732 [d]
	p-Chloronitrobenzene		277
	2,4-Dibromochlorobenzene		525 [f]
	3,4-Dibromochlorobenzene		
	m-Bromonitrobenzene [b]		412
p-Bromoiodobenzene	*p*-Bromonitrobenzene	15% Silicone SE-30 (165)	360
	p-Iodonitrobenzene		517
	p-Chloronitrobenzene [b]		729
p-Bromofluorobenzene	1-Bromo-4-fluoro-2-nitrobenzene	15% Silicone SE-30 (165)	252
	1-Bromo-4-fluoro-3-nitrobenzene		312
	p-Fluoronitrobenzene		106
	p-Bromonitrobenzene [c]		127
	Dibromofluorobenzenes [e]		183, 189
	Tribromofluorobenzenes [e]		684
	Dibromofluoronitrobenzenes [e]		
	1,2-Dichloro-4-nitrobenzene [b]		433
2-Bromo-*m*-xylene	2-Bromo-1,3-dimethyl-4-nitrobenzene	15% Silicone SE-30 (183)	487
	2-Bromo-1,3-dimethyl-5-nitrobenzene		574
	2-Nitro-*m*-xylene [c]		125
	2,5-Dichloronitrobenzene [b]		339
p-Bromotoluene	4-Bromo-3-nitrotoluene	15% Silicone SE-30 (140)	1 122
	4-Bromo-2-nitrotoluene		910
	p-Nitrotoluene		390
	2,4-Dibromotoluene		598
	3,4-Dibromotoluene		672
	3-Bromo-4-nitrotoluene		1 201
	Nitro-*p*-xylene [b]		494
p-Chlorotoluene	4-Chloro-2-nitrotoluene	15% Silicone SE-30 (153)	449
	4-Chloro-3-nitrotoluene		572
	m-Dinitrobenzene [b]		809
o-Dichlorobenzene	1,2-Dichloro-3-nitrobenzene	15% Polypropylene glycol (196)	949
	1,2-Dichloro-4-nitrobenzene		700
	2,5-Dichloronitrobenzene [b]		439
p-Dichlorobenzene	2,5-Dichloronitrobenzene	15% Silicone SE-30 (152)	498
	Nitromesitylene [b]		388
Fluorobenzene	*o*-Fluoronitrobenzene	2% Polyethylene glycol (122)	502
	m-Fluoronitrobenzene		251
	p-Fluoronitrobenzene		325
	p-Chloronitrobenzene [b]		799

[a] All on Chromosorb W, 6 ft, nitrogen as carrier gas, 40 ml min^{-1}, Pye 104 instrument fitted with a flame ionisation detector. [b] Reference standard. [c] Products which might have been formed in the reaction mixture, but were absent from chromatograms obtained. [d] 1-Bromo-4-chloro-2-nitrobenzene and 1-bromo-4-chloro-3-nitrobenzene were not adequately separated for analytical purposes. See text. [e] See text. [f] 2,4-Dibromochlorobenzene and 3,4-dibromochlorobenzene had the same retention times under the g.l.c. conditions used.

Nitrodechlorination was not observed with *p*-dichlorobenzene, *p*-chlorotoluene, or *o*-dichlorobenzene. Nitrodefluorination was not detected with fluorobenzene or *p*-bromofluorobenzene.

Some of the products formed in the nitrations reacted with sulphuric acid of low concentration (see Table 4). This phenomenon would explain the apparent maxima in the yields of *p*-nitrotoluene (at 64.4% sulphuric acid) formed in the nitration of *p*-bromotoluene, and of 1,2,4-tribromobenzene (at 74.1% sulphuric acid) formed in the nitration of *p*-dibromobenzene. Presumably the same sort of effect manifests itself with dibromotoluenes (formed during the

TABLE 3

Yields of products from the nitration of substituted halogenobenzenes in aqueous sulphuric acid at 25.0 ± 0.1 °C [a]

Compound	H_2SO_4 (%) [b]	Yields of products (%)					Mass balance (%) [d]
		x-Bromonitrobenzene					
		$x = 2$	$x = 3$	$x = 4$	Unidentified product [c]		
Bromobenzene	60.3	37.7	0.8	61.0	0.5		100
	62.8	35.6	1.3	57.7	1.2		96
	63.0	37.2	0.7	61.6	0.5		100
	69.4	38.1	0.7	57.2	0.2		96
	72.4	38.0	0.5	58.9	0.5		98
	74.6	37.2	0.4	57.8	0.2		96
	88.0	39.8	0.5	56.6	0.5		97
			1,2-Dibromo-*x*-nitrobenzene				
			$x = 3$	$x = 4$			
o-Dibromobenzene [e]	71.5		14.5	83.0			98
	75.3		14.5	82.5			97
	78.2		15.1	81.5			97
	82.8		15.4	83.1			99
	92.5		14.1	85.9			100
		2,5-Dibromonitrobenzene [f]	*p*-Bromonitrobenzene [f]	1,2,4-Tribromobenzene			
p-Dibromobenzene	69.3	60.4	33.6	4.9			94
	72.7	74.1	25.9	5.6			100
	74.1	76.6	23.3	7.4			100
	79.6	91.1	8.9	2.2			100
	81.9	95.4	4.2	1.6			99
	85.0	99.0	0.9				99
	89.1	99.8	0.2				100
	92.3	100					100
		1-Bromo-4-chloro-*x*-nitrobenzene [f]		*p*-Chloronitrobenzene [f]	2,4- and 3,4-dibromochlorobenzene		
		$x = 2$	$x = 3$				
p-Bromochlorobenzene	67.5	30.1	33.3	28.3	8.3		92
	72.4	38.6	37.3	20.0	3.6		96
	72.5	37.6	36.3	19.1	4.7		93
	74.6	40.3	39.0	14.8	4.1		94
	74.7	35.9	37.6	15.3	3.5		92
	77.1	43.8	39.6	9.6	2.2		93
	77.7	45.8	40.8	9.7	1.2		96
	79.2	45.6	39.8	6.7	1.5		92
	79.3	48.2	41.9	7.2	1.7		97
	83.0	51.9	43.2	2.8	0.5		98
	83.4	53.2	44.5	2.3	0.1		100
	91.3	53.5	44.3	0.2			100
		1-Bromo-4-fluoro-*x*-nitrobenzene [f]					
		$x = 2$	$x = 3$	*p*-Nitrofluorobenzene			
p-Bromofluorobenzene	75.1	18.0	9.3	13.1			40
	77.7	21.3	10.4	11.3			43
	78.9	24.4	10.9	11.0			46
	79.4	24.2	11.0	10.8			46
	87.8	31.0	11.0	2.4			44
	88.8	32.0	11.9	1.3			45
			2-Bromo-1,3-dimethyl-*x*-nitrobenzene				
			$x = 4$	$x = 5$			
2-Bromo-*m*-xylene [g]	62.8		59.6	9.1			69
	64.7		69.2	9.9			79
	69.1		80.4	10.8			91
	79.4		88.8	11.2			100
	87.3		88.1	11.9			100
		4-Bromo-*x*-nitrotoluene [f]		*p*-Nitrotoluene [f]	2,4-Dibromotoluene	3,4-Dibromotoluene	
		$x = 2$	$x = 3$				
p-Bromotoluene	63.0	45.5	17.7	13.3	0.7	0.7	77.5
	64.4	51.0	20.7	14.2	3.5	1.0	86
	69.5	62.3	27.1	8.0	3.2	0.7	97
	72.1	63.7	30.4	5.0	2.5		99
	73.5	62.4	31.9	4.8	1.9		99
	79.6	62.0	37.1	0.8			100
	81.9	60.8	38.5	0.7			100
	82.7	60.9	39.1				100

TABLE 3 (*Continued*)

Compound	H_2SO_4 (%)[b]	Yields of products (%)			Mass balance (%)[d]
		4-Chloro-*x*-nitrotoluene			
		$x = 2$	$x = 3$		
p-Chlorotoluene	63.0	34.3	25.7		60
	64.3	38.8	26.1		65
	67.0	46.0	26.6		73
	69.4	54.4	28.4		83
	69.6	54.7	28.0		83
	74.5	60.3	28.9		89
	77.1	62.2	31.0		93
	79.2	64.2	34.0		98
	83.0	62.2	33.1		95
	85.0	61.5	35.3		97
		1,2-Dichloro-*x*-nitrobenzene			
		$x = 3$	$x = 4$		
o-Dichlorobenzene	69.6	11.5	87.3		99
	74.6	11.0	89.0		100
	79.2	10.0	90.0		100
	85.0	10.5	89.5		100
	89.0	11.3	83.2		95
		2,5-Dichloronitrobenzene			
p-Dichlorobenzene	69.6	100			100
	72.9	100			100
	74.5	99			99
	79.6	100			100
	85.0	100			100
	89.1	100			100
	92.3	100			100
		x-Fluoronitrobenzene			
		$x = 2$	$x = 3$	$x = 4$	
Fluorobenzene	67.0	11.1	0.1	87.9	99
	71.5	10.5	0.1	82.5	93
	75.3	10.9	0.1	85.0	96

[a] [urea] *ca.* 3 × 10^{-2} mol dm^{-3}; [ArH] *ca.* 5 × 10^{-5} mol dm^{-3}. [b] ±0.1%. [c] This may have been nitrobenzene. See Results section. [d] ±2%. [e] <0.2% *o*-Bromonitrobenzene formed in all runs. [f] Yields corrected for loss of starting material due to bromination. [g] <0.2% 2-Nitro-*m*-xylene formed in all runs.

TABLE 4

Stability of some products of nitration in aqueous sulphuric acid in the light at 25.0 ± 0.1 °C [a,b]

Substrate	Nitration product	H_2SO_4 (%)	Recovery of material (%)
Bromobenzene [c]	*o*-Bromonitrobenzene	63.0	99
	p-Bromonitrobenzene	63.0	95
p-Dibromobenzene [c]	2,5-Dibromonitrobenzene	69.6	100
	p-Bromonitrobenzene	69.6	93
	1,2,4-Tribromobenzene	69.6	89
p-Chlorotoluene [c]	4-Chloro-2-nitrotoluene	63.0	99
	4-Chloro-3-nitrotoluene	63.0	94
p-Bromotoluene [c]	*p*-Nitrotoluene	64.4	78
	4-Bromo-2-nitrotoluene	64.4	100
	4-Bromo-3-nitrotoluene	64.4	91
p-Bromochlorobenzene [c]	1-Bromo-4-chloro-2-nitrobenzene	67.5	100
	1-Bromo-4-chloro-3-nitrobenzene	67.5	100
	p-Chloronitrobenzene	67.5	100
p-Bromofluorobenzene [d]	1-Bromo-4-fluoro-2-nitrobenzene	78.9	100
	1-Bromo-4-fluoro-3-nitrobenzene	78.9	100

[a] [urea] *ca.* 3 × 10^{-2} mol dm^{-3}; [ArH] *ca.* 5 × 10^{-5} mol dm^{-3}. [b] Reaction mixture allowed to stand at 25 °C for the length of time of a nitration experiment under the same conditions. [c] [HNO_3] *ca.* 2 × 10^{-1} mol dm^{-3}. [d] [HNO_3] *ca.* 7.2 × 10^{-3} mol dm^{-3}. [e] ±2%

nitration of *p*-bromotoluene) at low acidities, but the reactivities of these products were not measured. It would seem likely that products arising from bromination of the starting material could be easily nitrated in the media under investigation, as the lack of a deactivating nitro-group in the molecule would make the brominated starting material only very slightly less reactive to electrophilic attack than the actual starting material.

The kinetics of nitration of *p*-bromofluorobenzene with an excess of nitric acid were not first order. It has been observed elsewhere that the nitration of *p*-difluorobenzene and pentafluorobenzene are not simple processes,[20] and complications accompanying the preparative nitration of similar substances have also been noted.[21] Product runs were carried out by calculating lengths of time of reaction based on the rates of nitration of *p*-bromochlorobenzene. Low (but consistent) yields of products were obtained from the

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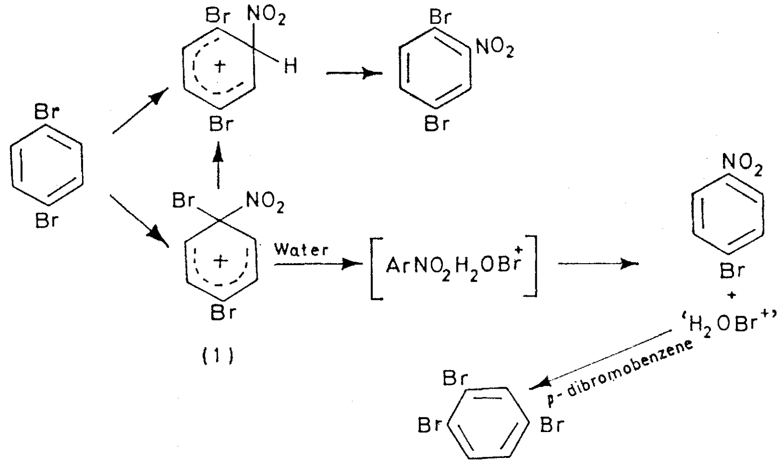
[20] J. G. Hoggett, Ph.D. Thesis, Exeter, 1969, p. 139.

[21] G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort, and R. R. Blough, *J. Amer. Chem. Soc.*, 1951, **73**, 145.

nitration, in a range of acid concentrations, of *p*-bromofluorobenzene; yet no unchanged *p*-bromofluorobenzene was noticeable in the chromatograms of the product mixtures. A total of six products were observable in these chromatograms. 1-Bromo-4-fluoro-2- and -3-nitrobenzene and *p*-fluoronitrobenzene were conclusively identified. Two small, overlapping peaks were observed; the identities of the compounds giving rise to these were not confirmed, but their retention times were such as to suggest (by comparison with the chromatograms obtained from reaction mixtures for the nitration of *p*-bromochlorobenzene, *p*-dibromobenzene, and *p*-bromotoluene) that they were 2,4- and 3,4-dibromofluorobenzenes. The yield of these products varied from 2.3% in 75.1% sulphuric acid to 5.2% in 78.9% sulphuric acid to 0.9% in 88.8% sulphuric acid. A sixth peak (always <0.5%) was identified as a mixture of tribromofluorobenzene(s) and dibromofluoronitrobenzene(s) by analysis of the mass spectrum of a sample obtained by preparative g.l.c. The low yield of products cannot be ascribed to the instability of the 1-bromo-4-fluoronitrobenzenes in such reaction mixtures as experiments revealed that they could be recovered quantitatively from 78.9% sulphuric acid after the length of time of a nitration experiment.



Scheme 1

The kinetics of nitration of *p*-bromoiodobenzene were not first order, and an intense brown colour developed on mixing the aromatic (in sulphuric acid) with the nitric acid and urea (in sulphuric acid). Two product runs were attempted, by making the assumption that *p*-bromoiodobenzene would be nitrated at the same rate as *p*-dibromobenzene. In 74.2% sulphuric acid the major reaction product was *p*-bromonitrobenzene (90% yield); four other peaks were observed in the chromatogram of the products. The reaction was not studied further.

DISCUSSION

The kinetic results (Figure 1) call only for the comment that *p*-bromo- and *p*-chloro-toluene and 2-bromo-*m*-xylene are more reactive than benzene. Their rates of nitration are therefore depressed to some extent by diffusion control, most markedly for 2-bromo-*m*-xylene.

Mechanism of Nitrodebromination.—With any of the substrates the amount of nitrodebromination which may occur depends on the acidity (Figures 2—4 and 7). The variation is such as to suggest that the debromination step is correctly described as the reverse of 'positive bromination' as it has been represented by Ridd and Gilow.[22] The case of *p*-dibromobenzene illustrates the point (Figure 2). In 90% sulphuric acid, 2,5-dibromonitrobenzene is the sole product, whereas in 69% sulphuric acid 34% of nitrodebrominated product is formed. Scheme 1 accounts for the observed features of the nitration. 'H_2OBr^+' represents the species formed in the nitrodebromination reaction. Quantitative evidence for the need for a water molecule to aid the departure of Br^+ comes from the finding that a plot of log [% nitrodebromination/(100 − % nitrodebromination)] against log a_{H_2O} is linear with a slope of 0.92. Evidently not all the 'H_2OBr^+' formed at low acidities reacts with unnitrated *p*-dibromobenzene; nitration competes successfully with bromination under the circumstances. Correction of the observed yield of 1,2,4-tribromobenzene (Figure 2) for the decomposition which occurs at low acidities (Table 4) does not change this conclusion.

In Scheme 1 the *ipso*-Wheland intermediate (W_i) (1) is represented as rearranging to form 2,5-dibromonitrobenzene, so that at any acidity the yield of this product is made up of material arising from this rearrangement and from direct nitration. As the acidity is raised, less and less of W_i (1) is diverted into debromination, and so the aggregate yield of 2,5-dibromonitrobenzene rises (Figure 2). The results do not allow us to say how much of the 2,5-dibromonitrobenzene is formed by direct substitution, but it is clearly $\not>60\%$.

The possibility that (1) loses nitronium ion, to give back *p*-dibromobenzene which is subsequently nitrated, cannot be ruled out, for the symmetry of this substrate precludes our distinguishing between such a process and that of intramolecular rearrangement. That the latter process predominates is made very probable by the behaviour of *p*-bromotoluene and of *p*-bromochlorobenzene.

Migration of the Nitro-group.—In the nitration of *p*-bromotoluene yields of products varied from 76% (in

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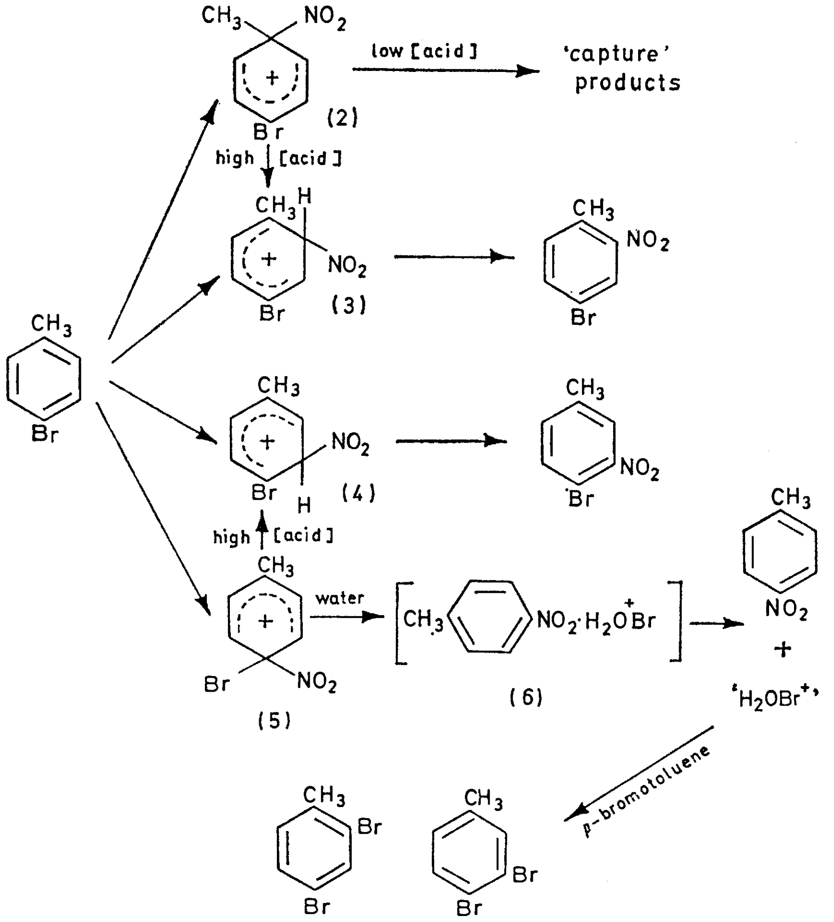
[22] H. M. Gilow and J. H. Ridd, *J.C.S. Perkin II*, 1973, 1321.

63% sulphuric acid) to quantitative (in >72% sulphuric acid) (Figure 3). This variation, and the changes in the amounts of individual products with acidity can be accounted for as shown in Scheme 2. All four Wheland intermediates (2)—(5) are formed. W_i (2) can either be captured by nucleophilic attack of water, or rearrange to (3). W_i (5) can either lose positive bromine with the assistance of water, or rearrange to (4). In each case the relative importance of rearrangement increases with increasing acidity.



SCHEME 2

The results could not be accounted for by supposing that W_i (5) decomposed, as the acidity was raised from 72 to 82% sulphuric acid, to give nitronium ion and *p*-bromotoluene, which was then re-nitrated, for then the yields of both 4-bromo-2- and 4-bromo-3-nitrotoluene would have increased. In fact, the yield of 4-bromo-2-nitrotoluene stays roughly constant over this acidity range, and the increase in the yield of 4-bromo-3-nitrotoluene reflects the decrease in the yield of *p*-nitrotoluene.

We must also remember that, as has been pointed out, *p*-bromotoluene is more reactive than is benzene, and that its nitration must be governed to some degree by diffusion. The return of W_i (5) to its components in the reaction medium is to that degree less likely, and evidently the return to components within the encounter pair [19] does not occur to an appreciable extent.

With *p*-bromochlorobenzene there is no detectable nitrodechlorination, but nitrodebromination occurs to an extent which decreases with increasing acidity (Figure 4). That the accompanying increase in the yield of 1-bromo-4-chloro-2-nitrobenzene is much more marked than that of the 3-nitro-isomer suggests that again migration of the nitro-group in the W_i^{Br} * is predominantly intramolecular, and that regression to starting materials followed by re-nitration is unimportant. In this case, however, there is a small but noticeable change in the yield of the 3-nitro-isomer. This might be due either to the intrusion of an intermolecular component of the rearrangement, or, since overall yields of products are not quite quantitative at low acidities, to nucleophilic capture of W_i^{Cl}, giving unidentified products. This latter possibility is discussed below in connection with the behaviour of *p*-chlorotoluene. Two other factors might be contributing to the observed variation with acidity of the yield of 1-bromo-4-chloro-3-nitrobenzene; they are differential solvent effects on relative positional reactivities (small effects of this kind have been noted in other systems [19]), and experimental error which is larger in this

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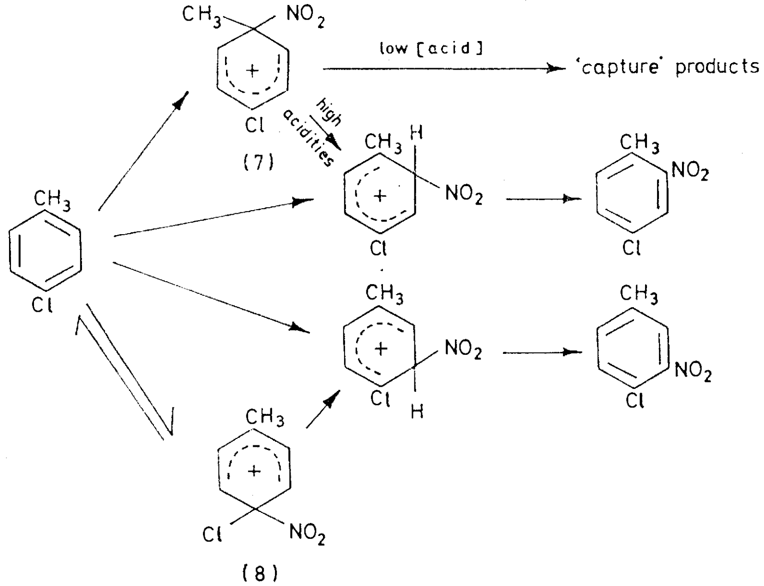
* We use the symbol W_i^X to denote the W_i formed at position C(X).

case because of the method of analysis (see Experimental section).

Nucleophilic capture of W_i*s*.—In the cases so far discussed, nucleophilic capture by water of W_is in which the *ipso*-position carries a bromine atom evidently does not occur to an appreciable extent. Such W_is can behave in three ways; they can rearrange, lose the bromine atom, and possibly revert to their components.

That nitro group migration occurs from methylated *ipso*-positions as in W_i (2), and is in competition with capture by water, has been amply demonstrated.[19,23] The increasing importance of capture at low acidities accounts for the decreasing yield of 4-bromo-2-nitrotoluene in these circumstances (Figure 3). In the nitration of *p*-bromotoluene the reduction in overall mass balance is entirely attributable to the loss in yield of 4-bromo-2-nitrotoluene in sulphuric acid concentrations as low as 64.4%. This demonstrates the absence of ' capture ' affecting W_i (5). Below 64.4% sulphuric acid the further reduction in mass balance is probably due to the decomposition of *p*-nitrotoluene, 4-bromo-3-nitrotoluene, and the dibromotoluenes in dilute sulphuric acid (Table 4).



SCHEME 3

The phenomenon of nucleophilic capture of methylated W_is is well demonstrated in the nitration of *p*-chlorotoluene and 2-bromo-*m*-xylene. In the former case (Figure 5 and Scheme 3) *p*-chloronitrotoluenes are formed quantitatively at high acidities. As the acidity is lowered capture of W_i (7) evidently becomes important and the overall yield decreases because of the decrease in yield of 4-chloro-2-nitrotoluene. Clearly $\not<44\%$ of the 4-chloro-2-nitrotoluene formed at high acidities arises from *ipso*-attack at C-1 followed by migration.

In Scheme 3 we show 4-chloro-3-nitrotoluene arising from direct nitration, and from the formation and rearrangement of W_i (8). In fact, we have no unequivocal evidence for the latter process, nor indeed for the occurrence of *ipso*-attack at a chlorinated carbon atom. Nevertheless, the analogy with brominated positions, the presence in the literature of reactions which appear to be nitrodechlorinations,[24] and of well established instances of *ipso*-nitration (or nitrosation) at C(Cl) [25a] make it likely that W_is such as (8) are formed. In the nitration of *p*-chlorotoluene 75% of the total loss of products at low acidities (Figure 5) is due to loss of 4-chloro-2-nitrotoluene, that is to capture by water of W_i (7), and only 25% to loss by some means of 4-chloro-3-nitrotoluene. Here again, as with *p*-bromochlorobenzene, we might be seeing nucleophilic capture of W_i^{Cl}. However, it is difficult to see why such capture should occur with *p*-bromochlorobenzene and *p*-chlorotoluene, and not with *p*-dichlorobenzene. It is noteworthy that experiments on the acidic decomposition of 1-halogeno-1-nitro-2-oxo-1,2-dihydronaphthalene [25b] indicate the sequence of leaving ability $Br^+ > NO_2^+ > Cl^+$, so that in nitration W_i^{Cl} may well regress to starting materials in preference to losing ' positive chlorine '.

In the case of 2-bromo-*m*-xylene (Figure 6 and Scheme 4), the loss in yield of 2-bromo-1,3-dimethyl-4-nitrobenzene at lower acidities is attributed to capture of W_i (10), which could be formed in two ways, as shown. W_i (9) is not debrominated, and the examples already discussed suggest but do not prove that its major fate must be rearrangement to W_i (10). 2-Bromo-*m*-xylene is the most reactive compound studied (Figure 1), and so even more subject to the influence of diffusion than is *p*-bromo- or *p*-chloro-toluene.

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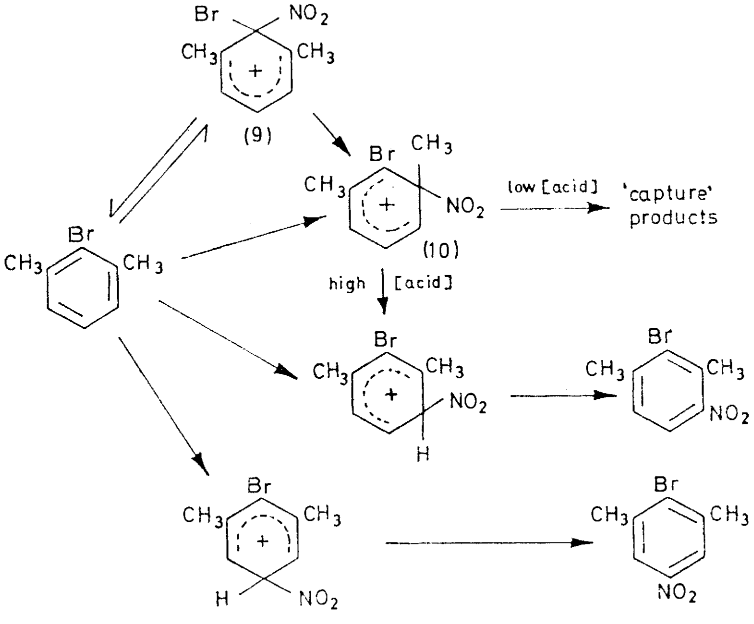
[23] P. C. Myhre, *J. Amer. Chem. Soc.*, 1972, **94**, 7921.

[24] P. W. Robertson and H. V. A. Briscoe, *J. Chem. Soc.*, 1912, **101**, 1964; T. G. Jackson, J. E. Norris, and R. C. Legendre, *J. Org. Chem.*, 1971, **36**, 3638.

[25] (*a*) K. Fries, *Annalen*, 1912, **389**, 305; 1914, **404**, 50; 1927, **454**, 121; 1934, **511**, 213; (*b*) C. L. Perrin, *J. Org. Chem.*, 1971, **36**, 420.

p-Dichlorobenzene is quantitatively nitrated over the range 69.9—92.3% sulphuric acid, and the result permits no conclusion to be drawn about the extent of suspected *ipso*-attack; it might be anything from 0 to 100%.

Orientation of Substituents necessary for Nitrodebromination to occur.—We have demonstrated that nitrodebromination is an important consequence of nitrating bromobenzenes containing activating or mildly deactivating *o* : *p*-directing substituents *para* to the brominated position. Our inability to reach acidities low enough to ensure complete nitrodebromination with *p*-dibromobenzene and *p*-bromotoluene prevents our comparing quantitatively the degree to which *p*-methyl and *p*-bromo facilitate *ipso*-attack, but that it is considerable can be seen by comparing these cases with that of bromobenzene (Table 3).



SCHEME 4

In view of the important role played by *ipso*-attack not only with *p*-xylene but also with *o*-xylene [19] we examined the behaviour of *o*-dibromobenzene. Surprisingly, in the range 71.5—92.5% sulphuric acid only 1,2-dibromo-3- (*ca.* 15%) and 1,2-dibromo-4-nitrobenzene (*ca.* 85%) were formed. In this case, as with 2-bromo-*m*-xylene, there is thus no evidence to reveal the role of *ipso*-attack at C(Br).

Special Cases.—(i) p-*Bromofluorobenzene.* Previous reports [26] on the nitration of this compound suggest that *p*-nitrofluorobenzene, *p*-nitrobromobenzene, dibromofluorobenzenes, and 4-bromo-2,6-dinitrophenol are by-products. In the present work only 1-bromo-4-fluoro-2- and 1-bromo-4-fluoro-3-nitrobenzene, and *p*-fluoronitrobenzene were positively identified (Table 3 and Figure 7), though it is probable that dibromofluorobenzenes, tribromofluorobenzenes, and dibromofluoronitrobenzenes were also formed (see Results section). No nitrodefluorination was detected, and phenols would have been difficult to identify in the circumstances. The low aggregate yields do not result from any obvious diversion of *p*-bromofluorobenzene to other compounds or from further reaction of the main products (Table 4). The fluoro-substituent is dominantly *p*-directing [13] and it would be expected that C(Br) would in this example be very reactive to *ipso*-attack. Perhaps the resulting W_i^{Br}, as well as being able to lose bromine, is capable of reacting in other ways, as for example by nucleophilic displacement of fluorine, to give products not detected by our methods.

(ii) p-*Bromoiodobenzene.* The facile displacement of iodine is probably an instance of nitrode-iodination (rather than nitrosode-iodination). The result, nitrode-iodination with only a trace of nitrodebromination, suggests that the formation of W_i^{Br} is significantly reversible, it being unlikely that 90% of nitronium ion attack occurs at C(I).

Bromine Migration in ipso-*Nitration.*—A conceivable consequence of *ipso*-nitration at C(Br) would be migration of the bromine atom to an adjacent position. The products of such rearrangements were looked for from the nitrations of *p*-dibromobenzene and *p*-bromotoluene, but were not found.

Positional Reactivities in Halogenobenzenes.—The increasing recognition of the importance of *ipso*-attack and the rearrangement of W_is has brought the realisation that current views on substituent effects may need modification. The results reported here do not permit quantitative evaluation of positional reactivities, for in no case is the precise degree of *ipso*-attack known. Further, conventional partial rate factors have no significance in the cases where diffusion control of reaction

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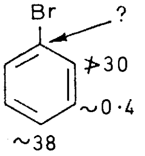
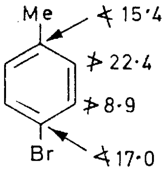
[26] T. van Hove, *Bull. Sci. Acad. Roy. belges*, 1926, **5**, 801; *Bull. Soc. chim. belges*, 1927, **36**, 1, 372; A. F. Holleman, *Rec. Trav. chim.*, 1915, **34**, 204.

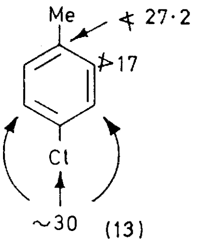
rates is important. Nevertheless, some useful comments can be made.



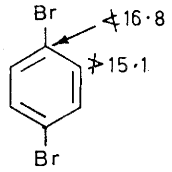
(11)



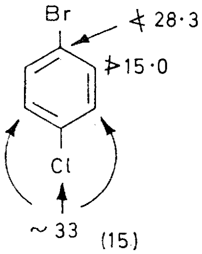
(12)



(13)



(14)



(15)

In (11) we represent the percentages of attack by nitronium ion at the various positions in bromobenzene. The figures are inaccurate because of the unknown (but possibly finite) degree of nitrodebromination, and the figure for the *ortho*-position cannot be corrected for migration of the nitro group. The order of positional reactivities is clearly $p > o \gg m$ ($\approx i$?).

For *p*-bromotoluene an order of positional reactivities (12) can be written C-2 > C–Br ≈ C–Me > C-3. The absence of nitrodechlorination prevents our saying anything about C-3 and C–Cl in *p*-chlorotoluene, but it is seen (13) that C–Me is at least 1.8 times as reactive as C-2.

For *p*-dibromobenzene (14), if the figure of 33.6% nitrodebromination is substantially the extent of *ipso*-attack, the yields combined with the relative rate of *ca.* 0.002 gives partial rate factors for each position of *ca.* 0.03, and the attack of the nitronium ion would be occurring almost equally at the six possible positions. To the extent that the true degree of *ipso*-attack exceeds 33.3%, the C–Br positions would be seen to be more reactive than the C–H positions.

In *p*-bromochlorobenzene (15) C–Br is at least 1.9 times as reactive as the adjacent C–H.

We have stressed the fact that our results throw little light on *ipso*-nitration at C–Cl. It does, nevertheless, probably occur, and accordingly it should be pointed out that an earlier conclusion,[13] that there might be in some cases an activating effect coming from a chloro-substituent (the free position in pentachlorobenzene appearing to be more reactive than one free position in 1,2,4,5-tetrachlorobenzene), is probably wrong. The supposed effect is probably a consequence of *ipso*-attack and migration.

[5/2294 *Received, 24th November,* 1975]