Electrophilic Aromatic Substitution. Part 31.[1] The Kinetics and Products of Nitration of Naphthalene, Biphenyl, and Some Reactive Monocyclic Aromatic Substrates in Aqueous Phosphoric Acid containing Nitric Acid or Propyl Nitrate

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Rate coefficients for nitration of naphthalene, 1- and 2-nitronaphthalene, biphenyl, 2-, 3-, and 4-nitrobiphenyl, anisole, and 2- and 4-nitroanisole in 90—97% H_3PO_4, and of biphenyl and 2- and 4-nitrobiphenyl in 69—72% H_2SO_4, have been measured. With results previously reported, these confirm that aromatics more reactive than benzene are nitrated in H_3PO_4 at the rate of encounter of aromatic and nitronium ion. This rate is slightly higher for the bicyclic than for the monocyclic compounds. Rate coefficients for solvolysis of propyl nitrate in H_3PO_4 are closely similar to those for nitronium ion formation from nitric acid, suggesting that these reactions have similar mechanisms. Kinetics and products of nitration of naphthalene with propyl nitrate in place of nitric acid, show that propyl nitrate is first solvolysed, followed by normal nitronium ion nitration of naphthalene. Product yields following nitration in 94—97% H_3PO_4 of benzene, toluene, anisole, chlorobenzene, naphthalene, and biphenyl, and for nitration in 69—72% H_2SO_4 of biphenyl are reported. Isomer ratios from nitration in phosphoric acid of toluene, anisole, naphthalene, and biphenyl reveal a marked preference for nitration at the site remote from the substituent, when comparison is made with nitration in sulphuric acid of comparable acidity. This is not the case for chlorobenzene, the least reactive of the substrates studied. It is suggested that viscosity can affect rates of translation within encounter pairs, so that unhindered positions of highly reactive substrates are relatively favoured in the more viscous solvent.

We have reported previously[2] on the kinetics of aromatic nitration in 92—98% H_3PO_4. The steep dependence of rate on acidity, the change in kinetic form from first towards zeroth order in aromatic with increasing concentration of aromatic, and (under conditions where reaction is first order in aromatic) the close similarity of rate coefficients for several reactive aromatic compounds, led us to conclude that the mechanism is analogous to that for nitration in sulphuric and other strong acids[3] (Scheme).

In this mechanism, nitronium ion is formed from nitric acid in a step which is acid catalysed and at high concentration of sufficiently reactive aromatic, rate-limiting. With low concentrations of aromatic either the second (diffusion) or third (Wheland intermediate formation) step is rate limiting, depending on the reactivity of the aromatic compound.

Probably because of the high viscosity of phosphoric acid, the level of aromatic reactivity at which diffusion control sets in is lower than for any other medium so far investigated;[2,4] all substances with reactivities equal to or greater than that of benzene are nitrated at the encounter rate in >95% H_3PO_4.

There are two reasons for this further investigation of nitration in phosphoric acid. Firstly the nitrations of naphthalene and biphenyl (compounds which are more reactive than benzene but in other media insufficiently reactive to react at the limiting rate) should be diffusion controlled, making possible a comparison of diffusion limited rate constants for mono- and bi-cyclic compounds. Secondly, isomer proportions for a variety of substrates were of interest because there have been reports of unusual product distributions arising from nitrations in these and related media, leaving some room for doubt about whether nitration is, as concluded above, a normal nitronium ion reaction.

Nitration of toluene (in other media known[5] to give *ortho*/*para* ratios in the range 1.4—2.2) in media containing P_2O_5 or H_3PO_4 has been reported to give *ortho*/*para* ratios of 0.5—1.2.[6,7] Particularly low ratios (0.49—0.76) have been observed using alkyl nitrates rather than nitric acid in the presence of polyphosphoric acid.[6]

$$\mathrm{HNO_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO_2}^+ \underset{k_s}{\overset{k_d[\mathrm{AR}]}{\rightleftharpoons}} (\text{e.p.}) \xrightarrow{\Sigma k_r'} \text{Products}$$

Scheme.

In most of these studies,[6,7] the overall yields were either less than quantitative or not reported, which lessens their significance. We were concerned to establish relative and total yields under the conditions of our kinetic experiments, bearing in mind the potentially serious problem (in this medium in which rates of mononitration are levelled by diffusion) of dinitration. The surprising results with alkyl nitrates[6] led us also to study solvolysis of, and nitration with, propyl nitrate in phosphoric acid.

Experimental

Materials.—Phosphoric acid was an AnalaR reagent, and contained *ca.* 10% of water which was partially removed as described.[2] Concentrations were determined by density measurements. Pure nitric acid was prepared by distillation of fuming nitric acid from concentrated sulphuric acid under vacuum. Acetic acid, urea, and hydrazinium hydrogensulphate were AnalaR reagents. Sulphanilic acid (B.D.H.) was recrystallised from aqueous solution.

AnalaR benzene was used without further purification. Toluene (b.p. 110 °C) was twice redistilled from the technical grade material. Anisole (b.p. 155 °C), chlorobenzene (b.p. 132 °C), nitrobenzene (b.p. 87 °C at 17 mmHg), *o*-nitrotoluene (b.p. 92 °C at 17 mmHg), and *m*-nitrotoluene (b.p. 100 °C at 18 mmHg) were commercial samples redistilled before use. *o*- and *p*-nitroanisole were available from previous work and were used without further purification.

Naphthalene (m.p. 80 °C; EtOH), 1-nitronaphthalene (m.p. 61 °C; EtOH), 2-nitronaphthalene (m.p. 79 °C; EtOH), biphenyl (m.p. 71 °C; aq.EtOH), 2-nitrobiphenyl (m.p. 37 °C; EtOH), 3-nitrobiphenyl (m.p. 61 °C; aq.EtOH), 4-nitrobiphenyl (m.p. 114 °C; EtOH), *o*-chloronitrobenzene (m.p. 34 °C; petroleum), *m*-chloronitrobenzene (m.p. 44 °C; petroleum), *p*-chloronitrobenzene (m.p. 83 °C; petroleum), and *p*-nitrotoluene (m.p. 54 °C; EtOH) were commercial materials recrystallised before use. The purity of all nitro-compounds was confirmed by g.c. analysis.

Propyl nitrate (b.p. 51 °C at 100 mmHg) was a commercial material distilled before use [n_D^{20} 1.3975, n_D^{20} (lit.) 1.3973].

Solubility Measurements.—The solubilities of anisole, naphthalene, chlorobenzene, and biphenyl in 90% H_3PO_4 and of toluene in 94.7% H_3PO_4 and of biphenyl in 72.2% H_2SO_4 were measured as follows. Aromatic (*ca.* 1 g) was shaken with the mineral acid (*ca.* 30 cm^3) for 30 min. The mixture was centrifuged and concentrations of aromatic in the acid layer estimated from absorbance measurements. Solubilities of anisole, naphthalene, and biphenyl in 90% H_3PO_4, of toluene in 94.7% H_3PO_4, and of biphenyl in 72.2% H_2SO_4, were 8×10^{-2}, 1×10^{-4}, 2×10^{-5}, 7×10^{-3}, and 1×10^{-5} mol dm^{-3}, respectively. The solubility of chlorobenzene in 90% H_3PO_4 was estimated to be at least 1×10^{-4} mol dm^{-3} from this and previous [2] work.

It was not possible to determine the solubility of propyl nitrate in 90% H_3PO_4 because of the rapid decomposition of the substrate in the medium. In kinetic and product studies, concentrations used were at least ten times smaller than that at which a slight persistent turbidity was observed.

Stabilities of Aromatics.—Reactants and products were dissolved in the appropriate acid solution. Stabilities (in the absence of nitric acid) for the length of time of the corresponding product run were investigated spectrophotometrically. Biphenyl was sulphonated very slowly in 72% H_2SO_4; the extent of this was insufficient to interfere with the product runs. Apart from this all solutions were stable, unless exposed to laboratory lighting. When so exposed, the mono- and di-nitrobiphenyls, *m*-nitrotoluene, and to a lesser extent *o*-nitrotoluene, underwent photochemical decomposition. Accordingly, where necessary in kinetic and product runs, vessels were wrapped in tin-foil.

Kinetic Measurements.—These were spectrophotometric. For biphenyl, cells of 10 cm pathlength were used. For other substrates, cells of 1 or 4 cm pathlength were used. Wavelengths for observation of nitrations of naphthalene and biphenyl were chosen to minimise interference from the subsequent nitration of the mononitro-products. The isosbestic points between 2-nitrobiphenyl and its mixture of dinitro-derivatives, and between 4-nitrobiphenyl and its mixture of dinitro-derivatives, were (fortuitously) coincident. This wavelength was therefore chosen. 1-Nitronaphthalene and its dinitro-derivatives, and 2-nitronaphthalene and its dinitro-derivatives, did not share an isosbestic point, so wavelengths close to that for the former (major) isomer where absorbance changes from dinitration of the two isomers were both small and compensatory, were chosen. First-order rate coefficients were calculated by microcomputer, the absorbance–time data being provided either manually or directly *via* an interface between the Pye Unicam SP 1800 spectrophotometer and the Commodore Pet microcomputer. Absorbance measurements continued for at least three half-lives. The program gave simultaneous least-squares fitting values of the first-order rate coefficient and the initial and final absorbances. Reactions were accurately first order (aromatic concentrations being too small for zeroth-order kinetics [2] to interfere), and there was close agreement between fitted and observed final absorbances except in some runs with naphthalene for the reasons described above. The concentration of nitric acid was at least ten times greater than that of aromatic, and second-order rate coefficients were deduced by dividing first-order rate coefficients by the concentration of nitric acid.

Kinetics of Acidolysis of Propyl Nitrate in Phosphoric Acid.—A solution of propyl nitrate (1.0 g) in acetic acid (25 ml) was prepared. In the initial kinetic runs a portion (20 µl) of this solution was injected into phosphoric acid (*ca.* 3 ml) in a u.v. cell maintained at 25 °C. The cell was thoroughly agitated to ensure that thorough mixing occurred. The change in the u.v. absorbance with time at 266 nm was followed. In further kinetic runs essentially the same procedure was adopted except that a portion of the acetic acid solution of propyl nitrate was injected into phosphoric acid containing hydrazinium hydrogensulphate (4×10^{-3} mol dm^{-3}). First-order rate coefficients were calculated as before.

Kinetics of Nitration of Naphthalene in Phosphoric Acid using Propyl Nitrate.-Reference and sample cells for these runs contained sulphanilic acid, acetic acid, and propyl nitrate. The sample cell also contained naphthalene. The last substance added to the sample cell, at zero time, was the propyl nitrate. The wavelength was chosen to minimise interference from dinitration as described above. Second-order rate coefficients were calculated by dividing the observed first-order rate coefficients by the stoicheiometric concentration of propyl nitrate.

Products from Mononitration of Naphthalene and Biphenyl.—For these compounds dinitration proceeds to a significant extent during the progress of mononitration, so the following procedure was used. The spectra of the mixtures of dinitro-products formed from the nitration of 1- and 2-nitronaphthalenes and 2- and 4-nitrobiphenyls were first separately determined. No attempt was made to analyse these mixtures. Naphthalene and biphenyl were then nitrated in the presence of excess of nitric acid for a time sufficient for dinitration to become complete. The final spectra in each case were intermediate between those of the products of nitration of the two corresponding mononitro-isomers, and showed that quantitative prior mononitration had occurred. Isomer proportions were deduced by the method of Dewar and Urch,[8] using a weighted least-squares procedure. The same procedure was used to analyse the products of nitration of naphthalene in phosphoric acid using propyl nitrate.

Isomer proportions for mononitration of naphthalene were also measured by g.c. Rate coefficients for dinitration of 1- and 2-nitronaphthalenes are closely similar, so that dinitration does not remove one isomer preferentially. After a time for nitration calculated to be that (*ca.* three half-lives for mononitration) at which the concentration of mononitro-compounds would be at a maximum, the acid solution (100 cm^3) was poured onto ice-water, and isomer proportions were deduced by g.c. [Pye 104 intrument, flame ionisation detector (250 °C), L.D.C. 308 computing integrator, 2 m 15% SE-30 on Chromasorb W, 80–100 mesh, carrier gas N_2, flow rate 40 cm^3 min^{-1}, column temperature 188 °C, retention times of 1-nitronaphthalene and 2-nitronaphthalene, 905 and 1052 s respectively, relative response factor 1.285]. Relative yields only were determined.

Results

Kinetics of Nitration.—Second-order rate coefficients for nitration k_2 are in Tables 1 and 2. Naphthalene is known [9] readily to undergo nitrous acid catalysed nitration; this was prevented by addition of a nitrous trap, sulphanilic acid. In the absence of the latter, reaction was extremely rapid and

Table 1. Second-order rate coefficients for nitration in phosphoric acid at 25.0 ± 0.1 °C [a]

Compound	H_3PO_4(%) [b]	$[HNO_3]$/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}
Naphthalene [c]	89.9 [d]	5.35×10^{-2}	4.8×10^{-2}
	90.8 [f,g]	3.32×10^{-2}	9.4×10^{-2}
	90.8 [f]	3.57×10^{-2}	9.4×10^{-2}
	90.8 [f,g]	3.63×10^{-2}	9.2×10^{-2}
	93.9 [i]	2.72×10^{-3}	5.9×10^{-1}
	95.1 [d]	1.36×10^{-3}	1.35
	96.0 [d]	5.33×10^{-4}	2.5
	96.3 [d]	1.12×10^{-3}	2.9
	89.9 [d]	(1.04×10^{-3}) [e]	4.2×10^{-2}
		(1.89×10^{-3}) [e]	3.9×10^{-2}
		(2.12×10^{-3}) [e]	4.3×10^{-2}
		(5.78×10^{-4}) [e]	3.9×10^{-2}
	96.3 [d]	(5.15×10^{-4}) [e]	2.5
		(3.08×10^{-4}) [e]	2.6
Biphenyl [j,k]	89.8	2.81×10^{-2}	5.0×10^{-2}
	90.6	1.74×10^{-2}	8.3×10^{-2}
	92.0	7.59×10^{-3}	1.62×10^{-1}
	93.9	1.42×10^{-3}	5.4×10^{-1}
	94.6	1.32×10^{-3}	9.1×10^{-1}
	95.5	8.06×10^{-4}	1.59
1-Nitronaphthalene [l,m]	89.9	5.86×10^{-2}	3.6×10^{-3}
	91.8	7.15×10^{-2}	9.8×10^{-3}
	95.7	1.58×10^{-2}	2.7×10^{-1}
2-Nitronaphthalene [l,n]	89.9	6.54×10^{-2}	3.8×10^{-3}
	91.8	8.38×10^{-2}	1.00×10^{-2}
	95.7	9.19×10^{-3}	2.6×10^{-1}
2-Nitrobiphenyl [o]	89.9	4.59×10^{-2}	9.2×10^{-3}
	95.5	1.23×10^{-3}	6.0×10^{-1}
3-Nitrobiphenyl [o]	89.9	4.59×10^{-2}	1.15×10^{-2}
	95.5	1.23×10^{-3}	5.1×10^{-1}
4-Nitrobiphenyl [o]	89.9	4.59×10^{-2}	8.8×10^{-3}
	95.5	1.23×10^{-3}	4.4×10^{-1}
Anisole [l,p]	96.5	4.02×10^{-4}	1.86
2-Nitroanisole [l,q]	96.5	4.20×10^{-2}	9.0×10^{-3}
4-Nitroanisole [l,p]	96.5	4.20×10^{-2}	3.9×10^{-3}

[a] [Sulphanilic acid] *ca.* 5×10^{-3} mol dm^{-1} unless otherwise stated, 1 cm cells used unless otherwise stated. [b] ±0.1%. [c] 4 cm cells used, [Ar] 2×10^{-5} mol dm^{-3}. [d] Measurement at 380.5 nm. [e] Propyl nitrate, used in place of nitric acid, and added last to the reaction mixture. [f] Measurement at 376 nm. [g] [Sulphanilic acid] *ca.* 10^{-3} mol dm^{-3}. [h] [Sulphanilic acid] *ca.* 2.5×10^{-2} mol dm^{-3}. [i] Measurement at 378 nm. [j] Measurement at 375 nm. [k] 10 cm cells used, [Ar] *ca.* 10^{-5} mol dm^{-3}. [l] [Ar] *ca.* 10^{-4} mol dm^{-3}. [m] Measurement at 310 nm. [n] Measurement at 290 nm. [o] [Ar] *ca.* 5×10^{-5} mol dm^{-3}, measurement at 306 nm. [p] Measurement at 300 nm. [q] Measurement at 302 nm.

deviated from a first-order form. In its presence, reaction was slower, accurately first-order, and the rate was independent of the concentration of sulphanilic acid, showing that the nitrous acid catalysed reaction had been effectively prevented.

Kinetics of Solvolysis of Propyl Nitrate.—Because of the viscosity of the solvent, considerable shaking of the cell was required at the start of the reaction and the initial part of the kinetic trace was ignored to allow for the disappearance of the air bubbles so introduced. In the preliminary runs in the absence of a nitrous trap, the absorbance decrease indicated a first-order reaction but this was superceded after varying intervals of time in different runs by a rapid increase in absorbance giving eventually an intense absorption maximum at 270 nm. The absorption increase could be prevented by the addition of hydrazinium hydrogensulphate, in the presence of which the absorbance decrease was kinetically first order. Despite the rather small absorbance change, first-order rate coefficients could be deduced and are in Table 3.

Table 2. Second-order rate coefficients for nitration in sulphuric acid at 25 ± 0.1 °C [a]

Compound	H_2SO_4 (%) [b]	$[HNO_3]$/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}
Biphenyl [c]	69.0	1.15×10^{-3}	1.43
	72.2	1.70×10^{-4}	21
2-Nitrobiphenyl [d,e]	69.0	1.46×10^{-2}	2.3×10^{-2}
	72.2	1.96×10^{-2}	4.0×10^{-1}
4-Nitrobiphenyl [d]	69.0 [e]	1.46×10^{-2}	3.2×10^{-2}
	72.2 [f]	1.96×10^{-2}	5.0×10^{-1}

[a] [Sulphanilic acid] *ca.* 5×10^{-3} mol dm^{-3}, 1 cm cells used unless otherwise stated. [b] ±0.1%. [c] 10 cm cells used, [Ar] *ca.* 7.5×10^{-6} mol dm^{-3}, measurement at 370 nm. [d] [Ar] *ca.* 5×10^{-5} mol dm^{-3}. [e] Measurement at 290 nm. [f] Measurement at 280 nm.

Table 3. First-order rate coefficients for the solvolysis of propyl nitrate in phosphoric acid at 25 ± 0.1 °C [a]

H_3PO_4 (%) [b]	k_{obs}/s^{-1}	Absorbance change
89.9	8.2×10^{-4}	0.12—0.06
	8.1×10^{-4}	0.13—0.07
93.3	2.9×10^{-3}	0.12—0.07
	2.6×10^{-3}	0.13–0.07
96.3	7.8×10^{-3}	0.10—0.07
	8.4×10^{-3}	0.10—0.07

[a] [Hydrazinium hydrogensulphate] *ca.* 4×10^{-3} mol dm^{-3}, [propyl nitrate] *ca.* 3×10^{-3} mol dm^{-3}, 1 cm cells used, measurements made at 266 nm. [b] ±0.1%.

Kinetics of Nitration of Naphthalene in Phosphoric Acid using Propyl Nitrate.—Again considerable shaking was necessary and the initial part of the absorbance trace was lost. Satisfactory first-order kinetics were observed, but values of k_2 were rather more scattered (±5%) than when nitric acid was used. Results are in Table 1.

Products of Nitration.—These are in Table 4. The yield of nitrobenzene was quantitative when benzene was in excess and yields based on nitric acid, but not when nitric acid was in excess and yields based on benzene. The deficiency is therefore due to loss of benzene. We attribute this to its partial evaporation into the enclosed air space above the solution during the mixing period. (When the enclosed air space was reduced, mixing times with these viscous media were unacceptably long.) The yields of chloronitrobenzenes from chlorobenzene were also less than quantitative, perhaps for the same reason. Toluene and anisole were nitrated with aromatic in excess of nitric acid, and the other substrates are relatively involatile; for these, yields are seen to be quantitative (Table 4).

Discussion

Rate Profiles for Nitration.—We have recently provided evidence[2] that aromatic compounds more reactive than benzene, at low concentrations as here, are nitrated in concentrated phosphoric acid at the rate of diffusion together of aromatic and nitronium ion, and thus react at closely similar rates. Rate profiles (90—97% H_3PO_4) for all such compounds so far studied are in Figure 1.[10] The lower line is a mean drawn through the points for all the monocyclic compounds. Factors which may contribute to deviations from this line (always

Table 4. Products of nitration in phosphoric acid at 25 ± 0.1 °C[a]

Compound	H_3PO_4 (%)[b]	Isomer yields (%)[c]			Total yield (%)[c]
Benzene		Nitrobenzene			
	94.1[d,f]	100.0			100.0
	95.4[e]	85.0			85.0
	96.5[d,f]	100.0			100.0
Toluene[d,f]		Nitrotoluene			
		o	*m*	*p*	
	94.7	50.8	1.2	45.2	97.2
	96.4	50.4	2.3	46.0	98.7
	97.0	50.0	2.5	46.7	99.2
Chlorobenzene[e]		Chloronitrobenzene			
		o	*m*	*p*	
	97.0	36.2	0.2	58.3	94.7
Anisole[d,k]		Nitroanisole			
		o	*p*		
	94.7[f]	39.6	60.4		100
	94.7[g]	40.2	61.8		102
	96.5[f]	37.7	62.3		100
Biphenyl[e,h,i]		Nitrobiphenyl[m]			
		2-	4-		
	94.6	54.8	45.2		100
Naphthalene[e,i]		Nitronaphthalene			
		1-	2-		
	95.2[l]	84.1	15.9		100
	95.2[l,n]	86,8	13.2		100
	95.2	(85.2)[p]	(14.7)[p]		

[a] [Ar] *ca.* 10^{-4} mol dm^{-3}, nitric acid in at least ten-fold excess over the aromatic, measurements made using 1 cm cells, all unless otherwise stated. [b] ±0.1%. [c] ±2.5%. [d] [Ar] *ca.* 10^{-3}—3×10^{-3} mol dm^{-3}, aromatic in at least ten-fold excess over nitric acid. [e] [Sulphanilic acid] *ca.* 5×10^{-3} mol dm^{-3}. [f] [Hydrazinium hydrogensulphate] *ca.* 2×10^{-3} mol dm^{-3}. [g] [Urea] *ca.* 3×10^{-2} mol dm^{-3}. [h] Measurements made using 10 cm cells. [Ar] *ca.* 5×10^{-6}—10^{-5} mol dm^{-3}. [i] [Ar] *ca.* 5—8 × 10^{-5} mol dm^{-3}. [k] Correction made to u.v. spectrum of reaction solution to take account of unreacted starting material. [l] Analysis based upon spectra of dinitro-products (see text). [m] 3-Nitrobiphenyl was not detected (<1%) by g.c. method. [n] Propyl nitrate used in place of nitric acid. [p] Relative isomer proportions only, determined by g.c.

<0.13 in log k_2) are differences in diffusion coefficients, the possibility that for some of the compounds ($k_s/\Sigma k_r'$) (Scheme) is not negligible compared with unity (reactions not *entirely* encounter controlled), and experimental error.

The two bicyclic compounds, naphthalene and biphenyl, react slightly but detectably more quickly. (The vertical distance between the two lines in Figure 1 is 0.22 in log k_2.) It seems unlikely that the difference is due to the intrusion of another mechanism. Care was taken to exclude nitrous acid catalysed nitration[9] (see Results section). This and the fact that the two compounds share the *same* line and that this line runs parallel to that for the monocyclic compounds, strongly suggests that these also are undergoing encounter-controlled nitration by nitronium ion. The two bicyclic compounds react slightly more quickly probably because their molecules provide a bigger target for the nitronium ion to hit.

In 68% H_2SO_4, naphthalene and biphenyl react more slowly than, say, mesitylene.[11] In the less viscous solvent, they are insufficiently reactive to react upon encounter.

Kinetics of Solvolysis of Propyl Nitrate.—The rate coefficients obtained (Table 3), are closely comparable to rate coefficients for the formation of nitronium ion from nitric acid in the same media[2] (Figure 2). These observations make it likely that the solvolyses of nitric acid and alkyl nitrates occur by a similar mechanism.

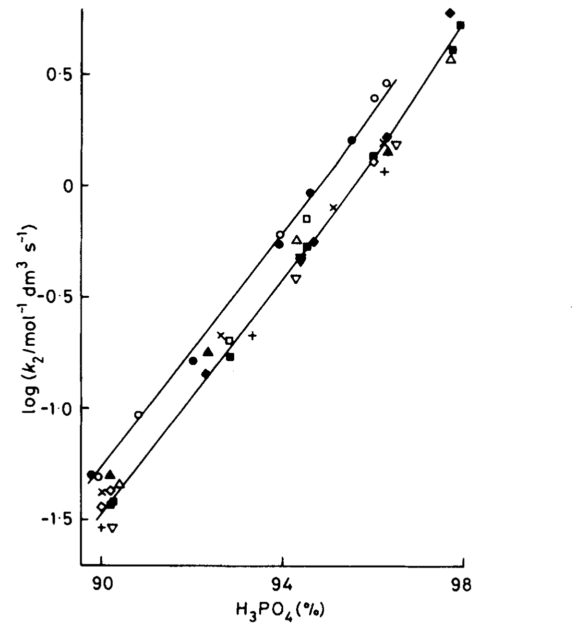

Figure 1. Rate profiles for nitration in phosphoric acid: ○, naphthalene; ●, biphenyl; □, phenol; ■, anisole; △, 2-methylanisole; ▲, *o*-xylene; ▽, pseudocumene; ▼, *p*-xylene; ◇, mesitylene; ◆, toluene; ×, 4-methylanisole; +, 4-methylphenol

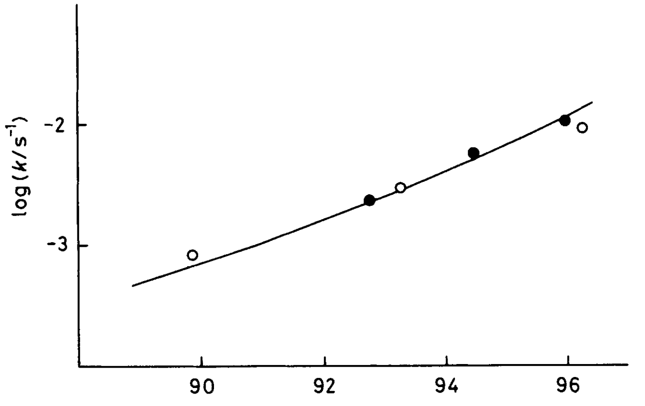

Figure 2. Rate profiles for solvolysis of propyl nitrate (○) and for formation of nitronium ion from nitric acid (●)

$$RONO_2 + H^+ \longrightarrow ROH + NO_2^+$$
$$HNO_3 + H^+ \longrightarrow H_2O + NO_2^+$$

A similar comparison can be made between rate coefficients for solvolysis of ethyl nitrate[12] and for nitronium ion formation from nitric acid[13] in aqueous sulphuric acid.

Kinetics and Products of Nitration of Naphthalene using Propyl Nitrate in Place of Nitric Acid.—Observed first-order rate coefficients for the nitration were considerably slower than for solvolysis of propyl nitrate. Thus solvolysis of propyl nitrate to give nitronium ion and thence nitric acid, followed by normal nitronium ion nitration, rather than nitration by propyl nitrate or its conjugate acid, must be occurring. In accord with this conclusion, second-order rate coefficients, obtained by dividing the observed first-order rate coefficients by the concentration of propyl nitrate, are similar to (though a little lower than) those for nitration by nitric acid (Table 1). The imperfect agreement may be attributed to the fact that the solvolysis is not complete before nitration starts. The product ratio was the same within experimental error, whether propyl nitrate or nitric acid was used (Table 4).

We conclude that alkyl nitrate nitrations in strong acid normally involve the nitronium ion, and we are unable to explain or substantiate claims of unusual product distributions obtained in this way.

Isomer Ratios.—Results for each compound are first discussed, and comparisons made in each case with results for other nitration media, particularly aqueous sulphuric acid of comparable acidity (a medium as similar as possible, except with regard to viscosity).* General conclusions follow.

Toluene. The *o*/*p* ratios of 1.12—1.07 (Table 4) are low (see Introduction). In aqueous sulphuric acid of comparable acidity the ratio is *ca.* 1.7.[14]

Chlorobenzene. The *o*/*p* ratio of 0.62 (Table 4) is slightly higher than that for sulphuric acid or comparable acidity,[15] but the difference is within the combined experimental errors. Results for other media are more diverse.[3]

Anisole. The *o*/*p* ratio falls from 0.66 in 94.7% H_3PO_4 to 0.60 in 96.5% H_3PO_4 (Table 4). These values are markedly lower than those for sulphuric acid of comparable acidity [16] (1.22 and 1.14). The significance of the comparison in this case is however diminished by the fact that the marked medium dependence of the *o*/*p* ratio in sulphuric acid has been attributed to hydrogen-bonding,[1,6] the relative importance of which in the two media cannot be estimated independently.

Biphenyl. The *o*/*p* ratio for nitration in 94.6% H_2PO_4 is 1.2 (Table 4). In this case useful comparison with results for sulphuric acid reported in the literature was not possible, because reported values vary very widely,[17–19] ranging from 0.5 to 3.7. Possible reasons for these disparities include heterogeneity, incursion of nitrous acid catalysed nitration, dinitration, and photochemical decomposition of nitroisomers. Nitrous acid catalysed nitration has been shown to give rise to low values.[18] Where high values have been observed, yields have been less than quantitative [19,28] and may be partly due to the incursion of some dinitration [*o*-nitrobiphenyl is nitrated less quickly than *p*-nitrobiphenyl (Table 2)]. Another cause of high ratios could be photochemical decomposition, to which *p*-nitrobiphenyl is more sensitive than *o*-nitrobiphenyl. We have therefore redetermined isomer proportions in aqueous sulphuric acid, using methods designed to eliminate as far as possible all these unwanted complications. The *o*/*p* ratio is 2.6 in 69% H_2SO_4 and 2.3 in 72.2% H_2SO_4 (Table 5). These results confirm that there is a greater than statistical preference for *o*-nitration. The point of present interest here however is that the *o*/*p* ratio is much lower in phosphoric acid than in sulphuric acid of comparable acidity.

Naphthalene. The 1 : 2 ratio of 5.3 (by u.v.) or 5.8 (by g.c.) (these results agree within experimental error) is substantially lower than for a wide range of other media.[20] A ratio of 10.0 has been reported [11] for 67% H_2SO_4.

Table 5. Products of nitration of biphenyl in sulphuric acid at 25 ± 0.1 °C [a]

	Isomer yields (%) [b] Nitrobiphenyl		
H_2SO_4 (%) [b]	2-	4-	Total yield (%) [c]
69.0	72.9	27.1	100.0
72.2	68.2	28.9	97.1

[a] [Sulphanilic acid] *ca.* 5 × 10^{-3} mol dm^{-3}, [Ar] *ca.* 5—7.5 × 10^{-6} mol dm^{-3}, nitric acid in at least ten-fold excess over the aromatic, aromatic added last, measurements made using 10 cm cells. Analysis based on spectra of dinitro products (see text). [b] ±0.1%. [c] ±2.5%.

General Conclusions.—These unusual product distributions point at first sight to the operation either of a different electrophile, or of a nitronium ion modified by solvation [6] in this medium. However consideration of all the results make it difficult to accept this view. A different electrophile would be either more or less selective, but the results are not consistent in this respect. There is apparently greater selectivity between *o*- and *p*-positions of toluene and anisole, but less between *o*- and *p*-positions in chlorobenzene and 1- and 2-positions in naphthalene. In the case of biphenyl, the *ortho*-position is favoured in sulphuric acid and the *para*-position in phosphoric acid. A nitronium ion modified by bulky solvation would lead to more substitution at the site remote from the substituent. This is in fact observed in the cases of toluene, anisole, naphthalene, and biphenyl, but significantly, not in the case of chlorobenzene.

Chlorobenzene is the only one of these substrates which is not nitrated at the encounter rate, and this suggests an alternative explanation. It is that the high viscosity of the phosphoric acid media affects not only rates of diffusion apart of the partners in the encounter pair, but rates of translation of the partners within the encounter pair. Similar conclusions have been drawn regarding product distributions in the nitramine rearrangement.[21] Initial encounter is more likely near to sites remote from the substituent, and with sufficiently reactive aromatics in sufficiently viscous solutions, reaction at such sites competes favourably with translation of the nitronium ion to sites closer to the substituent. On this view chlorobenzene is seen as insufficiently reactive for the effect to manifest itself.

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* Here and below, comparable acidities are considered to be those in which second-order rate coefficients for nitration of chlorobenzene are approximately equal. The range 94—97% H_3PO_4 is thus comparable to 72—74% of H_2SO_4.

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