Electrophilic Aromatic Substitution. Part 27.[1] Chemical Selectivities Disguised by Mass Diffusion. Part 6.[2] The Kinetics of Nitration in Aqueous Sulphuric Acid of Durene (1,2,4,5-Tetramethylbenzene), Nitrodurene, and Nitroprehnitene (Nitro-1,2,3,4-tetramethylbenzene). A Comparison of the Rates of Nitration of Methylnitrobenzenes in Aqueous Sulphuric Acid with the Corresponding Rates from Mixing–Disguised Nitrations with Nitronium Hexafluorophosphate in Nitromethane based on a Theoretical Mixing–Reaction Model

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Durene (1,2,4,5-tetramethylbenzene) is nitrated in sulphuric acid at the encounter rate. Nitrations of nitrodurene and nitroprehnitene (nitro-1,2,3,4-tetramethylbenzene) are complicated by the formation of nitrous acid, presumably as a consequence of *ipso*-attack, and subsequent unidentified reactions of this. When an efficient nitrous acid trap is present the complications are removed and the kinetics become straightforward. Although nitrobenzene is 10^8 times less reactive than benzene in nitration, nitroprehnitene and nitrodurene are only 41 and 20 times less reactive than their respective parent hydrocarbons. These reduced relative reactivities are a consequence of the fact that prehnitene and durene react at the encounter rate. The low relative reactivity of durene and 3-nitrodurene leads to the formation of some 3,6-dinitrodurene in the nitration of durene, even under the most favourable circumstances, and if mixing is inefficient the dinitro-compound may be the main product. By measuring the yield of 3-nitrodurene, as it varies with acidity, it is possible to determine the amount formed by direct attack at C-3 as distinct from that formed by *ipso*-attack followed by rearrangement. As a consequence the ratio of positional selectivity between C-3 and C-1 is shown to be 1 : 3.6. Thus, positional selectivity does not disappear. The intrinsic rate constants for nitronium ion nitrations in sulphuric acid of a number of methylnitrobenzenes show an excellent linear correlation with those for nitrations with nitronium hexafluorophosphate in nitromethane deduced by application of a theoretical mixing–reaction model. Differences between the two systems are not large, but appear to be in the direction showing the electrophile in sulphuric acid to be rather more reactive and more selective than that in the organic solvent.

UNDER all the conditions studied before 1952 the nuclear nitration of durene (1,2,4,5-tetramethylbenzene) was reported to produce 3,6-dinitrodurene (and unchanged durene) and no 3-nitrodurene. The early work has been summarised.[3] By nitrating durene with a molar equivalent of nitronium hexafluorophosphate in nitromethane, in the presence of two equivalents of water, Zollinger *et al.*[3] were able to obtain good yields of 3-nitrodurene. In the absence of water 3,6-dinitrodurene was the major product and the ratio of mono- to dinitrodurene depended upon the initial concentrations of the reactants, the method of mixing, and the solvent used. The essential conclusions drawn were that the nitration of durene with nitronium salts is subject to mixing-control and that ' the preferential formation of dinitrodurene under conventional conditions is due to the fact that the reaction occurs at encounter-controlled rate '. A later re-examination [4] of the nitration of durene and pentamethylbenzene with nitronium hexafluorophosphate in organic solvents confirmed that the reactions were subject to mixing-control, and the work, with pentamethylbenzene especially, brought out the importance of *ipso*-attack in these nitrations.[4,5]

Theoretical models for describing and analysing the results of reactions influenced by mass diffusion have been developed by Rys and his co-workers,[2,6a–f] and applied to nitrations of methylbenzenes with nitronium hexafluorophosphate in nitromethane.[6d] This application led to the determination of the relative intrinsic rate coefficients for the nitronium ion nitrations of a series of methylnitrobenzenes. These relative rate coefficients were converted into absolute values by the experimental determination of the rate coefficient for the nitration of nitromesitylene.

Other nitrations of durene relevant to our work were reported by Fischer and his co-workers. From nitration in acetic anhydride, 3-nitrodurene and products formed by *ipso*-attack were found, the former amounting to about half the total.[7a] A second report [7b] of a similar nitration found products formed by >75% of *ipso*-attack and <25% of attack at unsubstituted positions. A third nitration in acetic anhydride–methylene chloride at −55 °C produced no 3-nitrodurene.[7c] This last result was discussed by Perrin as part of the case for his radical–radical cation mechanism of nitration.[8]

The aims of the present work were to determine the rate profile for the nitration of durene in sulphuric acid of a range of concentrations (the expectation being that nitration would occur at the encounter rate) and, with Perrin's work in mind, to determine the positional selectivities for the nitration under these conditions. Further, by determining the rates of nitration of nitrodurene and nitroprehnitene (nitro-1,2,3,4-tetramethylbenzene) we should have results which, together with those for other methylnitrobenzenes, would allow a substantial comparison with the deductions from mixing-disguised nitrations.[6d] In this connection the relative intrinsic rate constants for nitronium salt nitrations of methylnitrobenzenes, determined from reactions influenced by mass diffusion,[6d] have been freshly converted into absolute values by the experimental determination of the rate constant for the nitration of nitro-*p*-xylene from competitive experiments with 4-nitrotoluene under reaction-controlled conditions. The corresponding rate constant for 4-nitrotoluene was evaluated in the same way by competitive experiments with nitrobenzene, for which the rate constant has been determined by direct kinetic measurements.

EXPERIMENTAL

Materials.—Nitromethane was purified as described in previous work.[6d] Nitronium hexafluorophosphate (Ozark-Mahoning, Tulsa, Oklahoma) was dried for at least 15 h under high vacuum over P_2O_5 and stored in a desiccator. The salt contained $<17\%$ of nitrosonium salt, as determined by the method described previously.[6d]

Durene [m.p. 79 °C (from MeOH)], 2,3-dichloronitrobenzene [m.p. 61 °C (from EtOH)], nitrobenzene (b.p. 83 °C at 10 mmHg), 4-nitrotoluene [m.p. 55 °C (from EtOH)], 2-nitrotoluene (b.p. 118 °C at 14 mmHg), nitro-*p*-xylene (b.p. 121 °C at 15 mmHg) and *m*-dinitrobenzene [m.p. 90 °C (from EtOH)] were commercial samples, purified either by crystallisation from the solvent indicated or by fractional distillation. 3-Nitro-*o*-xylene, 2-nitro-*m*-xylene, 4-nitro-*m*-xylene, 5-nitro-*m*-xylene, and 1,3,5-trinitrobenzene were also commercial samples. 2-Nitromesitylene [m.p. 44 °C (from MeOH or EtOH)], 2,4-dinitromesitylene [m.p. 86 °C (from EtOH)] and 2,4-dinitrotoluene [m.p. 71 °C (from EtOH)] were available from previous work.

A literature method,[9] modified in some respects, was used for preparing 3-nitrodurene. Durene (5 g), mercury(II) acetate (11.5 g), methanol (75 ml), and acetic acid (1 ml) were boiled together for 7 days, after which the hot mixture was filtered and allowed to cool. Recrystallisation of the precipitate from methanol gave 3-acetoxymercuridurene (4.5 g), m.p. 159 °C (lit.,[9] 158—159 °C), $\delta(CDCl_3)$ 6.71 (1 H, s, aromatic H), 2.32 (6 H, s), 2.16 (6 H, s), and 2.06 (3 H, s). Acetoxymercuridurene was treated with nitric acid as described in the literature [9] to give crude 3-nitrodurene as a yellow solid. 3-Nitrodurene was purified by column chromatography using neutral alumina and light petroleum (b.p. 40—60 °C)–ethanol. Finally crystallisation from ethanol afforded pure 3-nitrodurene, m.p. 113 °C (lit.,[9] 112—113 °C), $\delta(CDCl_3)$ 6.92 (1 H, s, aromatic H), 2.20 (6 H, s), and 2.08 (6 H, s), *m/e* 179 (34%), 162 (25), 134 (38), 133 (18), 116 (16), and 114 (16). 3,6-Dinitrodurene was prepared by the method of Illuminati and Illuminati.[10a] Repeated crystallisation from ethanol gave a pure product, m.p. 210 °C (lit.,[10a] 210—211 °C), $\delta(CDCl_3)$, 2.28 (s); *m/e* 224 (30%), 207 (150), 161 (30) 133 (45), and 132 (23).

Nitroprehnitene was prepared by nitrating prehnitene with nitronium hexafluorophosphate in a mixture of nitromethane and water. After addition of water (0.18 g) to nitronium hexafluorophosphate (0.96 g) dissolved in nitromethane (5 ml), the solution was allowed to stand for 2 min, before being added to a solution of prehnitene (0.67 g) in nitromethane (20 ml). The reaction was quenched with ammonia gas after 30 min. After filtration the solvent was evaporated, and the residue was purified by thick-layer chromatography using silica gel and 1 : 1 light petroleum (b.p. 60—90 °C)–benzene. Sublimation at 60 °C gave pure nitroprehnitene, m.p. 60 °C, $\delta(CDCl_3)$ 7.42 (1 H, s, aromatic H), 2.36 (3 H, s), 2.31 (3 H, s), 2.27 (3 H, s), and 2.25 (3 H, s).

Dinitroprehnitene was prepared by nitrating prehnitene with nitronium hexafluorophosphate in dry nitromethane. In a dry box nitronium hexafluorophosphate (0.96 g) was dissolved in nitromethane (5 ml). This solution was added to prehnitene (0.67 g) in dry nitromethane (20 ml). The reaction was allowed to proceed for 1 min before being quenched with ammonia gas. After filtration the solvent was evaporated. Two recrystallisations of the residue from ethanol gave pure dinitroprehnitene, m.p. 172 °C, $\delta(CDCl_3)$ 2.33 (6 H, s) and 2.29 (6 H, s).

The purities of all the aromatic compounds were checked by g.l.c.

Solubility Measurements.—The method has been described.[10b] The extinction coefficient of durene in 66.9% H_2SO_4 at 280 nm was 683 $mol^{-1}\ dm^3\ cm^{-1}$. The extinction coefficient of durene in ethanol at 280 nm was found to be similar (651 $mol^{-1}\ dm^3\ cm^{-1}$). The maximum solubility of durene in 66.9% H_2SO_4 was 2.035×10^{-4} mol dm^{-3} at 25 °C. Previously reported [11] values for the maximum solubility at 25 °C of durene in 40, 60, and 70% H_2SO_4 are 1.6×10^{-5}, 2.5×10^{-5}, and 3.6×10^{-5} mol dm^{-3} respectively. As will be seen, the concentration of durene which could be used in kinetic runs was considerably lower than the maximum solubility because of slow dissolution.

Kinetic Measurements in Sulphuric Acid.—The method used for durene, 3-nitrodurene, 2- and 4-nitrotoluene, nitro-*p*-xylene, 3-nitro-*o*-xylene, 2-, 4- and 5-nitro-*m*-xylene, nitroprehnitene, and 2-nitromesitylene has been described.[12] The concentrations of solutions of nitric acid (*ca.* 1×10^{-4}—2×10^{-1} mol dm^{-3}) and of aromatics (*ca.* 1×10^{-5}—1×10^{-4} mol dm^{-3}) were adjusted according to the requirements of the reactions, *e.g.* depending upon the speed of the reaction, amount of absorbance change, and solubility of the aromatic. In some cases, sulphanilic acid (*ca.* 1.5×10^{-2} mol dm^{-3}) was used as a nitrous acid trap in place of urea. U.v. cells (4 cm) were used wherever necessary. In some instances, with durene, the aromatic was taken in excess over the nitric acid. In such cases the concentration of nitric acid was *ca.* 1×10^{-6} mol dm^{-3}. The rate coefficients were calculated as described before but in some cases Guggenheim's method was used and, with 3-nitrodurene, a method described in the literature [13] for determining rate coefficients for an $A \longrightarrow B \longrightarrow C$ reaction was also used.

The rate coefficient for the nitration of 3-nitrodurene in 73.7% H_2SO_4 was determined, and attempts to determine the rate coefficients for nitration of durene in sulphuric acid of various concentrations were made, by measuring the amount of unchanged starting material remaining after different lengths of time and, in the case of 3-nitrodurene, by measuring also the amount of 3,6-dinitrodurene formed during the reaction.

Kinetic Measurements in Nitromethane.—To determine the rate coefficient for the nitration of nitrobenzene in nitromethane the concentrations of the aromatic compound and nitronium hexafluorophosphate (corrected for the true content of NO_2^+) were varied in the ranges 0.08—0.12 and 6×10^{-3}—2.8×10^{-2} mol dm^{-3}, respectively. The absorbance of the reaction mixture at 390 nm was followed using a

Beckman Acta II spectrometer. In addition, samples were removed using a syringe at appropriate time intervals and quenched with aqueous ammonia or with nitromesitylene dissolved in nitromethane. For the g.l.c. analysis a Hewlett–Packard Gas Chromatograph 5880 A, fitted with a flame ionisation detector and attached to a Hewlett–Packard Lab Data system 3352 B, was used. The column was an SP-2100 fused silica capillary column (Carbowax 20M deactivated) of 11 m length and with an inside diameter of 0.20—0.21 mm. The operating temperature for g.l.c. was 130—140 °C. As an internal standard 1,3,5-trinitrobenzene was added before the start of the reaction, after it had been shown that under the conditions used no 1,3,5-trinitrobenzene was formed.

Competitive Experiments in Nitromethane.—To determine the absolute rate constant for the nitration of nitro-*p*-xylene in nitromethane, the reactivity ratios of 4-nitrotoluene to nitrobenzene and of nitro-*p*-xylene to 4-nitrotoluene were determined by competitive experiments under reaction-controlled conditions. The less reactive aromatic compound was used in *ca.* 19—25-fold excess over the more reactive. The product distributions were measured by g.l.c. under conditions similar to those described above. The ratio (r) of the rate coefficient of the more reactive compound to that of the less reactive compound was obtained from the expression $r = \ln(1 - X)/\ln(1 - XP/E_0)$ where X = extent of conversion of the more reactive compound into the corresponding product at time t, *e.g.* $t = \infty$; P = ratio of the concentration of the product from the less reactive substrate to that from the more reactive substrate at time t, *e.g.* $t = \infty$; E_0 = ratio of the concentration of the less reactive to that of the more reactive substrate at the beginning of the reaction. For smaller conversions X, the expression $r = E_0/P$ was used.

Product Analyses.—The methods used for quantitatively analysing the products of nitrations and for determining the stabilities of various aromatics in sulphuric acid were very similar to those described earlier.[12,14] Durene was recovered quantitatively from its solution in 55.2% H_2SO_4 after the time needed for a nitration experiment, and 3-nitrodurene and 3,6-dinitrodurene were similarly recoverable from 61.5 and 83.1% H_2SO_4. 3,6-Dinitrodurene was also recovered quantitatively from 58.9% H_2SO_4, but from this acid only 93% of 3-nitrodurene was recovered.

With durene being nitrated in <75% H_2SO_4 the precise times for which the reactions were carried out were noted. They were of the order of, but not necessarily equal to five half-lives of the first step of nitration of this substrate. The details of this and the methods of calculation of the amounts of 3-nitrodurene formed in the first step of nitration are included in the Results section. At higher acidities where, even with the lowest possible concentration of nitric acid (*ca.* 1×10^{-4} mol dm^{-3}), 10 half-lives of the first step of nitration were equal to only a few seconds, the reactions were allowed to take place for times greater than or roughly equal to 10 half-lives of the second step of nitration. A pleated flask with mechanical stirring was used for the reaction and nitric acid was added last in *ca.* 5—10-fold excess over the aromatic.

RESULTS

Kinetic results are collected in Tables 1a and b.

The Kinetics of Nitration of Durene in Sulphuric Acid.—Early experiments with solutions of durene and nitric acid in sulphuric acid of various concentrations, with either nitric acid or the aromatic in excess and [durene] $>10^{-4}$ mol dm^{-3} encountered difficulties.[15] These arose from the slow dissolution of durene, and were removed for nitrations in <75% H_2SO_4 with [durene] *ca.* 1×10^{-5} mol dm^{-3} and durene in excess over nitric acid. In >75% H_2SO_4 nitration was effected with [durene] *ca.* 3×10^{-5} mol dm^{-3}. Below 71.4% H_2SO_4 and above 76.2% H_2SO_4 reaction velocities were not conveniently measurable in these circumstances.

The Kinetics of Nitration of 3-Nitrodurene and Other Methylnitrobenzenes in Sulphuric Acid.—In kinetic runs with [3-nitrodurene] *ca.* 1×10^{-4} mol dm^{-3} in the presence of urea, and with nitric acid in at least ten-fold excess, the absorbance measured at 250 nm attained a maximum, decreased slowly, and finally became constant. Second-order rate coefficients were estimated over the acidity range 67—76% H_2SO_4 by assuming an approximate ' infinity ', for the maximum in the curve, plotting $-\ln(A_\infty - A_t)$ *versus* t, and calculating the coefficient using the computer-assisted least squares method. The difference between the results of these and similar experiments with durene (*i.e.* kinetics with nitric acid in excess) was that the values of second-order rate coefficients were not greatly changed when the concentration of aromatic was changed to *ca.* 2×10^{-5} mol dm^{-3}, the measurements were taken at a different wavelength (325 nm), and different concentrations of nitric acid were employed in some of these experiments. The g.l.c. analysis of the products of the nitration of 3-nitrodurene in 69.2% H_2SO_4 ([Ar] 1.14×10^{-4} mol dm^{-3}, [HNO_3] 1.65×10^{-2} mol dm^{-3}, [urea] *ca.* 3×10^{-2} mol dm^{-3}) showed that a significant amount of 3-nitrodurene remained after the reaction had gone for 10 half-lives of nitration, the half-life being calculated from the value of the rate coefficient obtained as described above. It was therefore necessary to take into account, in calculating the second-order rate coefficients, the second part of the absorbance *versus* time curves obtained in the nitration of 3-nitrodurene.

A method [13] for calculating the first-order rate coefficients k_{I} and k_{II} from absorbance *versus* time curves for an $A \xrightarrow{k_{\mathrm{I}}} B \xrightarrow{k_{\mathrm{II}}} C$ reaction was applied (full details of the application of the method, and of the checks made to see that the model was appropriate, are given in ref. 15).

A solution of 3,6-dinitrodurene in 70% H_2SO_4, in the presence of urea and excess of nitric acid showed no change of absorbance with time, indicating that the further nitration of 3,6-dinitrodurene was not important in the nitrations of 3-nitrodurene. Also, the low extinction coefficient of 3,6-dinitrodurene makes it evident from the total change in absorbance during the nitration of 3-nitrodurene in 67—76% H_2SO_4 that the nitration of 3-nitrodurene produces other, more strongly absorbing products.

Regarding the second part of the kinetic curves from the nitration of 3-nitrodurene, it was later found that this disappeared if sulphanilic acid, a better nitrous acid trap than urea, was used. The second-order rate coefficient for the nitration of 3-nitrodurene was measured in this way in 70% H_2SO_4 and was found to be in agreement with those obtained as already described (Table 1a and Figure 1).

The rate coefficient for the nitration of 3-nitrodurene was also determined, in 73.7% H_2SO_4 (nitric acid in excess), by measuring the amounts of 3-nitrodurene remaining and of 3,6-dinitrodurene formed as they varied with time. The yields are given in Table 2 and the derived rate coefficient is included in Table 1a and Figure 1.

The nitration of nitroprehnitene in the presence of sul-

TABLE 1

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

	H_2SO_4 (%)	$10^2[HNO_3]$/ mol dm^{-3}	$10^5[Ar]$/ mol dm^{-3}	$k_2$obs./ dm^3 mol^{-1} s^{-1}
Durene [a]	71.4		1.04	16.4
	73.7		1.04	100
	75.5		3.12	400
	76.2		3.12	650
3-Nitrodurene	67.1 [b]	15.6	8.9	530×10^{-4}
	69.2 [b]	2.3	8.9	150×10^{-3}
	70.0 [c]	3.3	2.7	0.32
	71.6 [b]	0.103	8.9	1.03
	73.7 [d]			5.6
	75.5 [b]	6.6×10^{-2}	6.6	20.0
5-Nitroprehnitene [e]	68.1 [f]	14.1		4.9×10^{-2}
	71.5	0.171		0.33
	75.5	8.2×10^{-2}		9.8
4-Nitrotoluene [g,h]	78.9	21		6.5×10^{-3}
3-Nitro-*o*-xylene [g,h]	75.5	19		2.1×10^{-2}
2-Nitro-*m*-xylene [g,h]	75.5	19		7.6×10^{-2}
4-Nitro-*m*-xylene [g,h]	75.5	20		3.6×10^{-2}
5-Nitro-*m*-xylene [g,h]	75.5	19		6.1×10^{-2}
Nitro-*p*-xylene [g,h]	75.5	19		2.1×10^{-2}
2-Nitromesitylene [g,i]	73.7	3.6		0.25

[a] [Urea] *ca.* 3×10^{-2} mol dm^{-3}. Durene in *ca.* ten-fold excess over nitric acid. All measurements at 250 nm. Absorbance range 0.0—0.2 (4 cm cells). [b] Using the A $\longrightarrow$ B $\longrightarrow$ C method (see Results). [Urea] *ca.* 3×10^{-2} mol dm^{-3}. [c] [Sulphanilic acid] *ca.* 1.5×10^{-2} mol dm^{-3}. Measurements at 360 nm. [d] See Table 2. [e] [Sulphanilic acid] *ca.* 1×10^{-2} mol dm^{-3}. Nitric acid in at least ten-fold excess over aromatic. Measurements at 350 nm. [f] The use of urea ([urea] *ca.* 3×10^{-2} mol dm^{-3}) in place of sulphanilic acid gave a similar absorbance *versus* time curve, and a similar value of $k_2$obs. [g] [Urea] *ca.* 3×10^{-2} mol dm^{-3}. [Ar] *ca.* 1×10^{-4} mol dm^{-3}. [h] Measurements at 320 nm. [i] Measurements at 250 nm.

(b) Second-order rate constants for nitration in nitromethane by nitronium hexafluorophosphate at 25.0 ± 0.1 °C

	$k_2$rel. [a]	$k_2$intrinsic/ dm^3 mol^{-1} s^{-1}
Nitrobenzene [b,d]		0.12
4-Nitrotoluene [c]		30
Nitro-*p*-xylene [c]	1	2.1×10^3
2-Nitro-*m*-xylene 4-Nitro-*m*-xylene 5-Nitro-*m*-xylene	3	6.4×10^3
Nitromesitylene	20	4.2×10^4
Nitroisodurene	40	8.5×10^4
Durene	100	2.1×10^5
Prehnitene	300	6.4×10^5

[a] Relative rate constants estimated by a theoretical mixing–reaction model.[6d] [b] $k_2$intrinsic determined directly by kinetic measurements, see text. [c] $k_2$intrinsic determined by competitive experiments, see text. [d] $k_2$intrinsic for the nitration of nitrobenzene with $NO_2^+BF_4^-$ in nitromethane using the same concentrations of reactants is 0.041 dm^3 mol^{-1} s^{-1}.

phanilic acid gave good first-order kinetics. Use of urea instead of sulphanilic acid was also apparently straightforward, giving a rate coefficient close to that obtained using sulphanilic acid. However, when neither sulphanilic acid nor urea were used a good ' infinity ' was not obtained, the rate coefficient calculated by taking an approximate ' infinity ' was about half to one-third of that obtained from experiments in the presence of sulphanilic acid.

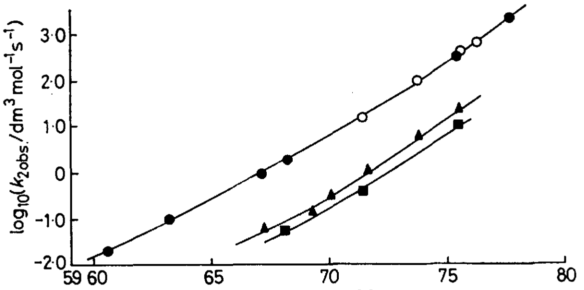


FIGURE 1 Rate profiles for the nitration of mesitylene[16] (●), durene (○), nitrodurene (▲), and nitroprehnitene (■), in sulphuric acid at 25 °C

The nitration of 4-nitroisodurene presented difficulties which were not overcome. The absorption change accompanying the initial reaction was very small, and subsequent reactions complicated the kinetics.

In determining the rate coefficients for the nitrations of the relatively unreactive 4-nitrotoluene, 3-nitro-*o*-xylene, 2-, 4- and 5-nitro-*m*-xylene, nitro-*p*-xylene, and nitromesitylene, higher concentrations of nitric acid at higher acidities of sulphuric acid had to be used. Consequently measurements were made at longer wavelengths where the absorbance due to the nitric acid was relatively smaller. For 2-nitrotoluene, the total change in absorbance during the reaction at these higher wavelengths was very small and the rate coefficient for the nitration of this substrate could not be measured in this way. Other methods were not pursued.

The Kinetics of Nitration of Nitrobenzene in Nitromethane.—No significant difference was detected between values of k_2 determined spectrometrically and those determined by g.l.c. Moreover, no significant change resulted from the introduction of 0.02 mol dm^{-3} of urea to destroy nitrosonium salt present. $o : m : p$-Ratios of 10.0 : 88.2 : 1.8 were determined.

Determination of the Intrinsic Rate Constants for the

TABLE 2

Variation in percentage of unchanged 3-nitrodurene remaining and of 3,6-dinitrodurene formed in the nitration of 3-nitrodurene in 73.7% H_2SO_4 at 25.0 ± 0.1 °C [a]

10^5[Ar]/ mol dm^{-3}	10^4[HNO_3]/ mol dm^{-3}	Reaction time/min	Unchanged 3-nitrodurene remaining (%)	3,6-Dinitrodurene formed (%)
1.36	1.46	14	49.2	24.8
1.36	1.46	28	26.4	38.1
1.36	1.46	42	12.5	45.5
2.08	15.7	14	Nil	51.1 [b]

[a] [Sulphanilic acid] *ca.* 1.5 × 10^{-2} mol dm^{-3}; for $k_2$obs. see Table 1a. [b] *Cf.* Table 4.

TABLE 3

G.l.c. conditions [a]

Substrate	Products and related substances	Response factor [c]	R_t/s	Column (t/°C)
Durene	Durene	1.92	310	15% SE30 [d] (160)
	2,3-Dichloronitrobenzene [b]		900	
Durene–3-nitrodurene	Durene		170	15% SE30 [d] (200)
	2,3-Dichloronitrobenzene [b]		390	
	3-Nitrodurene	1.64	490	
	3,6-Dinitrodurene	1.58	1 080	

[a] Pye 104 instrument fitted with a flame ionisation detector and attached to a Pye Unicam DP88 integrator. [b] Reference standard. [c] Response factor = Area ratio (compound/reference)/Mol ratio (compound/reference). [d] On Chromosorb W, AW–DCMS; 9 ft glass column; nitrogen flow rate 40 ml min^{-1}.

TABLE 4

Yields of products from nitrations in sulphuric acid at 25.0 ± 0.1 °C

Compound	H_2SO_4 (%)	Reaction time (s)	Value used for $k_2$obs. for durene [f]/ dm^3 mol^{-1} s^{-1}	Value used for $k_2$obs. for 3-nitrodurene [g]/ dm^3 mol^{-1} s^{-1}	Number of half-lives (of stage I or stage II of reaction) allowed for reaction to occur	Yield of 3-nitrodurene observed (%)	Yield of 3,6-dinitrodurene observed (%)	3-Nitrodurene formed in the first stage of the reaction (%) Calculated [h]	Calculated [i]	Mean value
Durene [a]	55.2	237 × 60 [b,c]	8.91 × 10^{-4}	3.5 × 10^{-5}	3.7 (I)	10.4	*ca.* 0	12.1		12.1
	57.5	122 × 60 [b,c]	3.16 × 10^{-3}	1.6 × 10^{-4}	6.6 (I)	8.7	*ca.* 0	10.5		10.7
	61.5	23 × 60 [c]	3.16 × 10^{-2}	1.4 × 10^{-3}	5.4 (I)	12.7	*ca.* 0	14.7		14.7
	63.7	20 × 60 [c]	0.112	5.6 × 10^{-3}	3.9 (I)	13.6	*ca.* 0	16.0		16.0
	67.1	33 × 60 [d]	0.89	5 × 10^{-2}	12.5 (I)	18.0	*ca.* 0	27.6		27.6
	70.0	8 × 60 [d]	6.31	0.45	8 (I)	28.3	2.7	39.3	37.4	38.3
	73.7	13 × 60 [d]	89	5.6	12 (I)	37.0	8.0	58.5	52.7	55.6
	75.0 [e]	100	257		10 (I)	*e*	*e*		63.5	63.5
	78.9 [j]	7 × 60 [d]		250	⩾10 (II)	*ca.* 0	69.3		90.2	90.2
	83.5 [j,k]	100 [d]		5 600	⩾10 (II)	*ca.* 0	87.0		93.2	93.2
	86.7 [j,k]	100 [d]		25 000	⩾10 (II)	*ca.* 0	95.2		97.5	97.5
									3,6-Dinitrodurene (%)	
3-Nitrodurene [l,a]	55.2 [b,m]								5.4 [u]	
	58.9 [b,n]								5.0 [u]	
	61.5 [b,o]								9.5	
	63.7								10.5	
	67.1								15.7	
	70.0								29.6	
	73.7								51.1	
	76.2								65.0	
	78.9 [j,p]								76.8	
	81.0 [j,q]								89.0	
	83.1 [j,r,s]								93.4	
	86.7 [j,r,t]								97.6	

[a] [Sulphanilic acid] *ca.* 1.5 × 10^{-2} mol dm^{-3}, [Ar] *ca.* 1 × 10^{-5} mol dm^{-3} unless otherwise stated, nitric acid concentrations in ⩾10-fold excess over the aromatic unless otherwise stated, aromatic added last unless otherwise stated. [b] Reaction carried out in the dark. [c] A small amount of durene remained unchanged in these cases. This was not measured because it was not needed in the calculations. [d] No trace of starting material found in products in these experiments. [e] A number of experiments were performed at this acidity. Aromatic concentration (*ca.* 3 × 10^{-5} mol dm^{-3}) was higher than in experiments at other acidities, the reaction time was shorter and a large amount of durene remained unreacted. In such cases the percentage of starting material remaining unchanged was measured by employing suitable g.l.c. conditions and the yield of 3-nitrodurene was calculated by taking into account this and the yield of 3,6-dinitrodurene observed. [f] Values at <71.4% H_2SO_4 calculated by extrapolation of the rate profile of durene in Figure 1. [g] Values at <67.1% and >75.5% H_2SO_4 calculated by extrapolation of the rate profile of 3-nitrodurene in Figure 1. [h] Calculated from the expression $[B] = fF[A]_0(e^{-Ft} - e^{-Gt})/(G - F)$. See text. [i] Calculated from yield of 3,6-dinitrodurene (this Table). See text. [j] Reaction carried out in a pleated flask, aromatic dissolved first by stirring for about one minute, nitric acid added last. [k] Nitric acid in *ca.* 5-fold excess over the aromatic. [l] [3-Nitrodurene] *ca.* 2 × 10^{-5} mol dm^{-3}. [m] Reaction carried out for about one half-life and yield of 3,6-dinitrodurene calculated by taking into account unchanged 3-nitrodurene remaining, reaction time 23 h. [n] Reaction time 22 h. [o] Reaction time 6 h. [p] Reaction time 4 min. [q] Reaction time 3 min. [r] [Nitric acid] ⩾ [Ar]. [s] Reaction time 10 min. [t] Reaction time 3 min. [u] Yield corrected for incomplete recovery of 3-nitrodurene (see text).

Nitronium Ion Nitrations of a Series of Methylnitrobenzenes in Nitromethane.—Theoretical mixing–reaction models [6a–f] applied to nitrations led to the determination of the relative intrinsic second-order rate constants for the nitration of various methylnitrobenzenes in nitromethane (Table 1b, second column). The rate constant for the nitration of nitro-*p*-xylene was evaluated by competitive experiments (*p*-nitrotoluene–nitrobenzene and nitro-*p*-xylene–*p*-nitrotoluene). Thus, the absolute intrinsic rate constants for the nitration of the other aromatic compounds could be calculated (Tables 1b and 5).

Products of Nitration in Sulphuric Acid.—G.l.c. conditions are given in Table 3 and product yields in Tables 2 and 4 and Figure 2.

It is evident from the rate coefficients for the nitration of durene and 3-nitrodurene (Table 1a) that the nitration of durene cannot be cleanly stopped after the first step of nitration. In any nitration 3,6-dinitrodurene will also be formed, and the yield of 3-nitrodurene will not correspond to the amount of it formed in the first step. The amounts of 3-nitrodurene and of 3,6-dinitrodurene formed will depend upon the length of time for which the reaction is allowed to proceed. This situation is represented by the Scheme (see Discussion section).

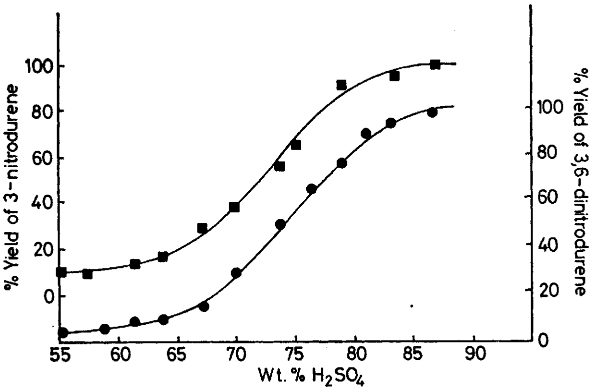
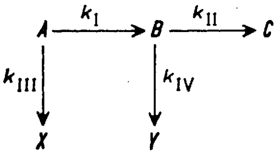


FIGURE 2 Yield of 3-nitrodurene from durene (■), left-hand scale. Yield of 3,6-dinitrodurene from 3-nitrodurene (●), right-hand scale



SCHEME *A* is durene. *B* is 3-nitrodurene formed by both direct and *ipso*-attack. *C* is 3,6-dinitrodurene formed by both direct and *ipso*-attack. *X* are the products of nitrating durene, other than 3-nitrodurene. *Y* are the products of nitrating 3-nitrodurene, other than 3,6-dinitrodurene

It can be shown [15] that during the nitration of durene the concentration of 3-nitrodurene will reach a maximum when the reaction has proceeded for a time of *ca.* $5t_{\frac{1}{2}}$, where $t_{\frac{1}{2}} = \ln 2/(k_{I} + k_{III})$. It can also be shown that $[B] = fF[A]_0(e^{-Ft}-e^{-Gt})/(G-F)$, where $f = k_I/(k_I + k_{III})$, $F = (k_I + k_{III}) = \{k_2\text{obs. for durene}\}[HNO_3]$, and $G = (k_{II} + k_{IV}) = \{k_2\text{obs. for 3-nitrodurene}\}[HNO_3]$. Thus the experimental results permit the calculation of *f*, the proportion of 3-nitrodurene formed in the first step of the nitration of durene. At low acidities, where the yields of 3-nitrodurene are relatively small, the reaction was run for *ca.* 5 half-lives of nitration of durene. At higher acidities the reactions were too fast to allow the accurate estimation of the reaction time. Moreover, owing to extensive dinitration the amount of 3-nitrodurene obtained was very small as compared with the total formed from durene and the conversion of the yield of 3-nitrodurene isolated from the experiment into the true yield of 3-nitrodurene from durene by the use of the expression above was subject to gross error. In such cases the reactions were allowed to proceed for 10 or more half-lives of nitration of 3-nitrodurene and the amount of 3-nitrodurene formed in the first stage of the reaction was calculated by conversion of the amount of 3,6-dinitrodurene obtained into the amount of 3-nitrodurene from which it is formed by use of results from product analyses of the nitration of 3-nitrodurene (Table 4 and Figure 2). At intermediate acidities the reactions were allowed to proceed for *ca.* 10 half-lives of nitration in the first stage and the percentage yield of 3-nitrodurene formed from durene was calculated by both of the above methods. Similar results were obtained by both treatments (Table 4), indicating the correctness of the values used for the second-order rate coefficients for the nitration of durene and 3-nitrodurene.

3-Nitrodurene was the only product from the nitration of durene which we identified and estimated at lower acidities. No other products, other than 3,6-dinitrodurene, were seen in g.l.c. traces from nitrations at higher acidities, but other peaks appeared from runs at lower acidities. The compounds producing these were not identified or estimated.

3,6-Dinitrodurene was the only product from 3-nitrodurene which we identified and estimated. The acidity dependence of the yield of 3,6-dinitrodurene is shown in Figure 2. At higher acidities (>75% H_2SO_4), even when the yield of 3,6-dinitrodurene was not quantitative it was the only product seen in g.l.c. At lower acidities, additional peaks appeared but approximate estimations showed that the aggregate yield of all the products never exceeded *ca.* 40%.

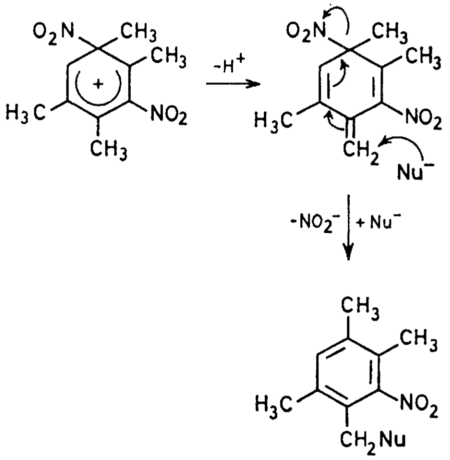
DISCUSSION

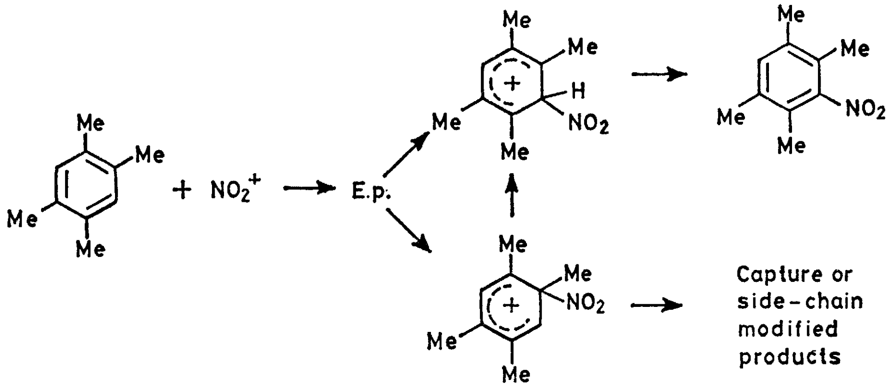
The Kinetics of Nitration of Durene and 3-Nitrodurene.—As suggested by Zollinger *et al.*,[3] and as expected from the behaviour of di- and tri-methylbenzenes,[12,16] durene is nitrated at the encounter rate. The rate coefficients for the nitration of durene and mesitylene fall on the same rate profile (Figure 1).

The kinetics of nitration of 3-nitrodurene are complicated by the changes caused by further reactions involving nitrous acid formed. This is proved by the fact that the complications were removed when an efficient nitrous trap was used. Nitrous acid might originate in the reaction of W_i^{Me} with a nucleophile (Nu^-). With what component of the reacting solution nitrous acid is involved has not been established. Like the nitration of 3-nitrodurene, that of 5-nitroprehnitene is affected by the formation of nitrous acid.

Similar complications would be expected to arise with durene itself reacting under the same conditions, and indeed initial experiments using nitric acid in excess over durene gave complicated kinetics. However, solubility problems could have been responsible for these complications (see Results section) to some degree, and, having discovered more satisfactory behaviour when durene was taken in excess, we did not attempt to disentangle the two possible sources of complication.

Earlier studies of the nitration of durene employed severe conditions (high concentrations of aromatic, nitric acid, and sulphuric acid and sometimes temperatures >25 °C), sometimes heterogeneous, and measures for avoiding nitrosation were not taken. 3-Nitrodurene could not be found as a reaction product in these cases and 3,6-dinitrodurene was the only reaction product. As regards the heterogeneous reactions [10] in which durene dissolved in chloroform was nitrated with mixed acid, the durene which diffused from the organic layer into the acid layer would be nitrated and the resulting 3-nitrodurene would be quickly converted into 3,6-dinitrodurene because passage of durene from the organic layer is much slower than the nitration of durene (Table 1a). In any circumstances, heterogeneous or homogeneous, where high concentrations of nitric acid were used, most of the product would necessarily be 3,6-dinitrodurene. The conditions used did not encourage nucleophilic capture or side-chain modification so that the nuclear-nitrated products were the only products from *ipso*-nitration also.





Since durene reacts at the encounter rate, and 3-nitrodurene only *ca.* 20 times more slowly, reactions carried out with bulk concentrations of nitronium ions would necessarily be subject to mixing control,[17a] as deduced by Zollinger *et al.* for nitrations with nitronium salts in organic solvents.[3,4] When water was added to the nitronium salt solutions the electrophile had to be formed by heterolysis of nitric acid so that the problem of mixing was avoided, and good yields of 3-nitrodurene could be obtained.[3]

The Products of Nitration and Positional Selectivities in the Nitration of Durene and 3-*Nitrodurene.*—Figure 2 shows how the yield of 3-nitrodurene from durene varies with acidity. 3-Nitrodurene is formed by direct attack at C-3 and also by rearrangement of W_i^{Me}. The latter rearrangement has been demonstrated to occur in the acid solvolysis of 1,2,4,5-tetramethyl-4-nitrocyclohexa-2,5-dienyl acetate.[7c] At lower acidities W_i^{Me} is increasingly diverted from rearrangement, and so the yield of 3-nitrodurene decreases from being quantitative at higher acidities to that amount formed by direct attack at C-3. Figure 2 indicates that 12.1% of the initial attack occurs at C-H, and 87.9% at C-Me. Thus, the positional selectivity between C-3 and C-1 is 1 : 3.6.

Perrin [8] argued that if the intermediate preceding the Wheland intermediates in an encounter-controlled nitration were a non-interacting encounter pair (rather than a radical–radical cation pair, [Ar$^{+\bullet}$NO$_2^{\bullet}$], as he believes), intramolecular selectivity between C-1 and C-3 in durene would be lost. The positional selectivities found [12] for C-5 and C-6 in pseudocumene could be understood if the rate constants for the formation of Wheland intermediates in the encounter pair differed by an order of magnitude, but the fourth methyl group in durene would reduce this difference, and rate constants for Wheland intermediate formation at both C-1 and C-3 in durene would be *ca.* 10^{13} s^{-1} (the theoretical limit). Thus, it was argued, in durene the hypothesis of a non-interacting encounter pair would require the disappearance of positional selectivity. In fact, there seemed experimentally to be a large difference in reactivity between C-1 and C-3 in durene, since in nitration in acetic anhydride no 3-nitrodurene was formed [7c] (see Introduction).

Perrin's argument is based on the following assumptions: that C-6 of pseudocumene would be at least 10 times as reactive as C-2 of toluene, and that the rate coefficient for the step leading to the formation of W_0 from the encounter pair in the nitration of toluene is *ca.* 10^{10} s^{-1} (which is equal to the upper limit of the rate coefficient for the reverse step of formation of encounter pair). These assumptions are difficult to evaluate. However, it is interesting to note that using Perrin's source [7b] of partial rate factors for the nitration of toluene, which adopts the values 58.2, 2.8, 35.9, and 3.1 mol % for the degrees of reaction at the *o*-, *m*-, *p*-, and *i*-positions, respectively, then application of Holleman's product rule gives 1 : 2.7 for the ratio of the reactivities of C-3 to C-1 in durene. This is close to the experimental value (1 : 3.6) reported above.

Thus, as previously available evidence suggested,[7b] positional selectivity in durene was expected to persist but to be small, in contradiction to Perrin's argument that with a non-interacting encounter pair it should in this case disappear. Experimentally it is now shown that for nitration in sulphuric acid, as for nitration in acetic anhydride,[7b] positional selectivity *does* persist and *is* small. Like pseudocumene,[12] durene provides no evidence of stabilisation of the encounter pair, which might have manifested itself by producing a large positional selectivity.[17b]

Figure 2 also shows how the yield of 3,6-dinitrodurene formed from 3-nitrodurene varies with acidity. *Ca.* 5.4% of 3,6-dinitrodurene is formed by direct nitration at C-6. The similarity of the two curves in Figure 2 is especially striking. The way in which W_i^{Me} from durene distributes itself between rearrangement and other reactions is clearly very similar to the performance of the W_i^{Me}s from 3-nitrodurene, so that the nitro-group appears to influence the competing processes to similar degrees and in the same directions. Substituent effects on the processes competing for *ipso*-Wheland intermediates will be discussed elsewhere.

TABLE 5

The nitration in sulphuric acid and nitromethane of nitromethylbenzenes

Compound	H_2SO_4 (%)	Reactivity of hydrocarbon relative to that of its mononitro-derivative [e]	$k_2$intrinsic/dm^3 mol^{-1} s^{-1}	
			a	*b*
Nitrobenzene *	80.0	1.07×10^8	0.47	0.12 [c]
4-Nitrotoluene	72.0	7.5×10^5	222	30 [d]
	78.9	7.6×10^5		
2-Nitro-*m*-xylene	75.5	5.3×10^3	5.0×10^4	6.4×10^3
4-Nitro-*m*-xylene	75.5	1.1×10^4	2.4×10^4	
5-Nitro-*m*-xylene	75.5	6.5×10^3	4.1×10^4	
Nitro-*p*-xylene	75.5	1.9×10^4	1.4×10^4	2.1×10^3 [d]
Nitromesitylene	73.7	400	8.9×10^5	4.2×10^4
Nitroprehnitene	75.5	41	6.4×10^6	6.4×10^5
Nitrodurene	75.5	20	1.3×10^7	2.1×10^5

[a] Calculated by reference to 1,4-dichlorobenzene.[18] [b] Except as otherwise indicated, calculated from relative rate constants obtained using nitronium hexafluorophosphate in nitromethane [6d] by use of the value for nitro-*p*-xylene determined by competitive experiments with nitrobenzene. See text. [c] Determined by kinetic measurements. See text. [d] Determined by competitive experiments with nitrobenzene. See text. [e] Rate coefficients for the methylbenzenes come from ref. 16, except that prehnitene has been assumed to react at the same rate as mesitylene.

* F. H. Westheimer and M. S. Kharasch, *J. Am. Chem. Soc.*, 1946, **68**, 1871.

The Relative Reactivities of Methylbenzenes and their Mononitro-derivatives.—The nitro-group is regarded as one which is powerfully deactivating in electrophilic substitutions. Thus in 80% H_2SO_4 benzene is *ca.* 10^8 times more reactive in nitration than is nitrobenzene. The results given in Table 5 illustrate the dramatic influence of diffusion-controlled nitration of the parent methylbenzene upon its apparent reactivity relative to that of its mononitro-derivative. Thus, in 75.5% H_2SO_4 prehnitene is only 40 times, and durene 20 times more reactive than the respective mononitro-derivatives.

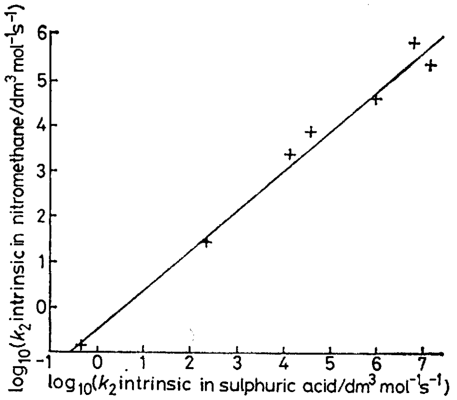


FIGURE 3 Plot of the logarithms of the intrinsic rate constants for nitration in sulphuric acid against those for nitration with $NO_2^+PF_6^-$–$MeNO_2$ (see Table 5). Slope 0.885; intercept −0.523; correlation coefficient 0.994

Comparison of the Rates of Nitration of Methylnitrobenzenes in Aqueous Sulphuric Acid with Results from Mixing-Disguised Reactions.—As shown in Figure 3, an excellent linear correlation exists between the logarithms of the intrinsic rate constants for nitration in sulphuric acid and those for nitronium hexafluorophosphate nitration in nitromethane. Thus, it can be concluded that, to a first approximation, the substituent parameters in the Stock–Brown relationship are equal in both solvents. Of course, such a linear correlation also exists between log($k_2$intrinsic) and the logarithms of the relative rate constants ($k_2$rel) in nitromethane, determined by nitration experiments, which were subject to mixing–disguise.[6d]

The intrinsic rate constants for nitration in sulphuric acid given in Table 5 and used in Figure 3 are calculated from results for 1,4-dichlorobenzene [18] by assuming that the change in the observed second-order rate coefficient with acidity is due only to the increasing degree of ionization of nitric acid with increasing acidity (then from 1,4-dichlorobenzene the ratio of rate coefficients at 90% and x% H_2SO_4 will give $[HNO_3]_{stoich.}/[NO_2^+]$ at x% H_2SO_4). A second calculation of the intrinsic rate constants was based on the relative reactivities of mesitylene and phenyltrimethylammonium ion, and the observed rate coefficient for the ion at 90.1% H_2SO_4.[19] The values so obtained (not given here) are about an order of magnitude smaller than those based on 1,4-dichlorobenzene. Intrinsic rate constants calculated in this way are bound to vary according to the particular comparison made because of the different acidity dependences of rate shown by different substrates.

For each compound studied the intrinsic rate constant for nitration in sulphuric acid, calculated by reference to 1,4-dichlorobenzene, is larger than that for nitration with nitronium hexafluorophosphate in nitromethane (Table 5). That they should differ is not surprising for medium-dependence of the performance of the reagent in nitration is well known.[17c] However, the direction of the difference is interesting since it appears to indicate that the electrophile operating in sulphuric acid is more reactive than that operating in nitronium hexafluorophosphate–nitromethane; the electrophile appears, in fact, to be not only more reactive but more selective. This combination of properties need not be surprising,[20] and, in any case, the differences between the two reagents are not very great. We also note that if phenyltrimethylammonium ion is made the basis of calculation, nitrobenzene appears to be nitrated more slowly in sulphuric acid than by nitronium hexafluorophosphate in nitromethane. Further, the anion appears to exert an influence on nitration with nitronium salts; the second-order rate constant for the nitration of nitrobenzene with nitronium tetrafluoroborate in nitromethane is about three times smaller than that for nitration with nitronium hexafluorophosphate in the same solvent (Table 1b). Olah and Kuhn [21] reported gegenion effects upon isomer proportions. The explanation of these small variations, perhaps to be accounted for in terms of specific solvation, hydrogen-bonding, and ion-pair formation, must await further studies. At this stage the results are impressive evidence for the significance of the theoretical mixing model used.

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