Electrophilic Aromatic Substitution. Part 19.[1] The Nitration of Some Reactive Aromatic Compounds in Perchloric Acid

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Rate profiles for nitration of *m*-xylene, *p*-xylene, mesitylene, 1,3-dimethoxybenzene, 3,5-dimethylanisole, and (when correction is made for protonation) 3,5-dimethoxytoluene and 1,3,5-trimethoxybenzene in aqueous perchloric acid are all closely similar, and probably reflect the rate of encounter between nitronium ion and aromatic compound in these media. As in sulphuric acid, anisole is nitrated slightly more slowly, and the yields of *o*- and *p*-nitroanisole are markedly acidity dependent. The rate profile for *p*-dichlorobenzene shows that at the highest acidity studied (72% perchloric acid) substantial conversion of nitric acid into nitronium ion has not been achieved.

EVIDENCE has been presented that in a number of aqueous acid media, the rate constants for nitration of increasingly reactive aromatic compounds reach a limit which can reasonably be identified as the rate constant for encounter between the nitronium ion and the aromatic compound.[2] This paper explores further the dependence upon acidity and upon reactivity of this limiting rate in aqueous perchloric acid.[3]

The intrinsically most reactive compounds now studied, 1,3,5-trimethoxybenzene and 3,5-dimethoxytoluene, are extensively ring-protonated at the acidities in question.[4] Our interest was to see if the limit to apparent reactivity could be breached by such highly reactive compounds, which would indicate nitration by an electrophile other than nitronium ion, or if when due allowance were made for protonation, the limiting rate constant were again observed. The problem of sulphonation required the use of perchloric rather than sulphuric acid. We studied for comparison the nitration of 3,5-

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[1] Part 18. R. B. Moodie, K. Schofield, and P. N. Thomas, *J.C.S. Perkin II*, 1977, 1693.

[2] Part 17. R. B. Moodie, K. Schofield, and G. P. Tobin, *J.C.S. Perkin II*, 1977, 1688.

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

[4] A. J. Kresge, Y. Chiang, and L. E. Hakka, *J. Amer. Chem. Soc.*, 1971, **93**, 6167; A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, *ibid.*, p. 6174; A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, *ibid.*, p. 6181.

dimethylanisole, 1,3-dimethoxybenzene, anisole, mesitylene, and *m*-xylene, and, less thoroughly, *p*-xylene, the distribution of substituents being chosen to minimise the consequences of *ipso*-attack.[5]

The medium dependence of isomer ratios in the case of anisole and 3,5-dimethylanisole was of interest for comparison with recent data for the nitration of anisole in sulphuric acid.[6]

In sulphuric acid rates of nitration of deactivated compounds reach a maximum around 88% acid, above which acidity the nitric acid is largely or wholly dissociated at equilibrium to nitronium ion.[7] It was therefore of interest to study rates of nitration in perchloric acid at high acidities to see if a similar maximum could be reached. For this purpose a deactivated compound was needed and we chose *p*-dichlorobenzene.

Kinetic studies on the nitration of 1,3-dimethoxybenzene in sulphuric acid[8] have been carried out previously. The substrate was found to react at the encounter rate. The product was 2,4-dimethoxynitrobenzene, and the kinetics of nitration of this compound, measured at 31 °C, were also studied. Nitration of 1,3,5-trimethoxybenzene in acetic acid at 0 °C has been reported[9] to give the mononitro-compound. There are no references in the literature to the nitration of 3,5-dimethoxytoluene, but both possible mononitro-isomers have been prepared by methylation of the corresponding nitro-orcinols.[10] Both possible mononitro-derivatives of 3,5-dimethylanisole are known, although there is no reference to their being formed by direct nitration.[11]

EXPERIMENTAL

Materials.—Perchloric acid, urea, sulphamic acid, and sulphanilic acid were AnalaR reagents. Concentrations of diluted acids were determined by density measurements or by titration against standardised sodium hydroxide solution. Pure nitric acid was prepared by distillation from sulphuric acid. Mesitylene, b.p. 58 °C at 14 mmHg, *m*-xylene, b.p. 139 °C, *p*-xylene, b.p. 138 °C, anisole, b.p. 155 °C, 1,3-dimethoxybenzene, b.p. 217 °C, and *o*-nitroanisole, b.p. 143 °C at 12 mmHg, were purified by distillation. *p*-Dichlorobenzene, m.p. 52 °C (from ethanol), 1,3,5-trimethoxybenzene, m.p. 50—50.5 °C [from light petroleum (b.p. 60—80 °C)], *m*-nitroanisole, m.p. 38—39 °C [from light petroleum (b.p. 40—60 °C)], *p*-nitroanisole, m.p. 54 °C (from ethanol), and *p*-nitrotoluene, m.p. 54.5 °C (from ethanol), were purified by recrystallisation from the solvent indicated.

3,5-*Dimethoxytoluene*.—This was prepared in 84% yield by methylation of 3,5-dihydroxytoluene with dimethyl sulphate according to the literature method.[12] The crude material was purified by distillation, to yield an oil, b.p. 100—101 °C at 14 mmHg.

3,5-*Dimethoxy*-2-*nitrotoluene*.—Nitric acid (*d* 1.5; 0.21 cm^3) in 57% perchloric acid (50 cm^3) was added at 0 °C to a solution of 3,5-dimethoxytoluene (0.75 g) in 57% perchloric acid (50 cm^3). The solution was stirred for 15 min and the resulting orange suspension was poured over ice. Filtration yielded a yellow solid (0.95 g). Purification by column chromatography [basic alumina; light petroleum (b.p. 60—80 °C)] and crystallisation from methanol gave 3,5-dimethoxy-2-nitrotoluene (0.55 g), m.p. 106 °C (lit.,[10] 106 °C); τ ($CDCl_3$) 3.59 (1 H, d, ArH), 3.63 (1 H, d, ArH), 6.15 (6 H, d, $ArOCH_3$), and 7.71 (3 H, s, $ArCH_3$).

1,3,5-*Trimethoxy*-2-*nitrobenzene*.—Nitric acid (*d* 1.5; 0.22 cm^3) in 57% perchloric acid (50 cm^3) was added at 0 °C to a solution of 1,3,5-trimethoxybenzene (0.78 g) in 57% perchloric acid (50 cm^3). After being stirred for 20 min the yellow solution was quenched in ice-cold water (400 cm^3). Filtration gave a yellow solid (0.90 g) which was recrystallised twice from methanol to give yellow crystals, m.p. 151 °C (lit.,[9] 150—152 °C).

3,5-*Dimethyl*-2- *and* 3,5-*Dimethyl*-4-*nitroanisole*.—Nitric acid (*d* 1.5; 3 cm^3) in glacial acetic acid (10 cm^3) was added dropwise to a stirred solution of 3,5-dimethylanisole (3 g) in acetic acid (40 cm^3). The solution was kept below 17 °C and reaction was allowed to continue for a further 30 min after the addition of nitric acid. The resulting deep blue mixture was quenched in ice-cold water (200 cm^3), and the product extracted with dichloromethane (3 × 30 cm^3). The combined extracts were neutralised and dried (Na_2CO_3, $MgSO_4$) and dichloromethane was removed to yield a dark oil (4.2 g). Examination of this product by g.l.c. (15% SE 30 column; 175 °C; flow rate 40 cm^3 min^{-1}) showed the presence of starting material (<15%) together with two products (R_t 7 min 15 s, 8 min 50 s). This mixture was separated by column chromatography [neutral alumina; light petroleum (b.p. 60—80 °C)]. 3,5-Dimethyl-4-nitroanisole (1.25 g) was eluted first and crystallised from n-pentane giving yellow needles, m.p. 50—51 °C (lit.,[11] 50—

TABLE 1

Gas chromatographic analysis data

Nitration product or standard	Slope of calibration graph [a]	Column [b] (T/°C)	R_t/s
3,5-Dimethyl-4-nitroanisole	1.328	1.25% Polyethylene gycol (147)	296
3,5-Dimethyl-2-nitroanisole			428
m-Nitroanisole [c]			194
2-Nitroanisole	0.913	15% SE–30 (165)	352
3-Nitroanisole			411
4-Nitroanisole			460
4-Nitrotoluene [c]			228
Anisole	0.907	15% SE—30 (135)	126
4-Nitrotoluene [c]			519

[a] Slope converts area ratio of products to reference standard as read from a chromatogram, into a mol ratio. [b] All on Chromosorb W, mesh size 60—80, 6 ft, nitrogen as carrier gas, 40 cm^3 min^{-1}, Pye 104 instrument fitted with a flame ionisation detector. [c] Reference standard.

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TABLE 2

Second-order rate coefficients for nitration in perchloric acid at 25.0 ± 0.1 °C

Compound [a,b]	$HClO_4$ (%) [c]	$[HNO_3]$/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}
1,3,5-Trimethoxybenzene (345 nm) [d]	56.5	1.83×10^{-1}	2.5×10^{-3}
	58.7	1.78×10^{-1}	6.8×10^{-3}
	61.9	1.86×10^{-1}	1.46×10^{-2}
	63.8	1.47×10^{-1}	1.96×10^{-2}
	64.5	1.39×10^{-1}	3.2×10^{-2}
	65.6	8.11×10^{-2}	5.6×10^{-2}
	66.3	1.05×10^{-1}	9.2×10^{-2}
3,5-Dimethoxytoluene (376 nm) [e]	52.7	2.00×10^{-1}	3.6×10^{-3}
	54.3 [d]	2.09×10^{-1}	1.26×10^{-2}
	54.9	1.92×10^{-1}	1.92×10^{-2}
	56.5	1.10×10^{-1}	6.0×10^{-2}
	57.2	2.75×10^{-2}	1.52×10^{-1}
	59.2	1.47×10^{-1}	6.6×10^{-1}
	60.3	1.41×10^{-2}	1.10
	61.3	5.67×10^{-3}	1.45
	62.1	9.84×10^{-3}	1.74
	62.7	1.98×10^{-3}	2.4
	64.4	3.77×10^{-3}	4.5
2-Nitro-1,3,5-trimethoxybenzene (370 nm) [f]	58.7	1.74×10^{-1}	1.56×10^{-3}
	60.5	1.85×10^{-1}	1.26×10^{-2}
	61.9	9.55×10^{-2}	7.9×10^{-2}
	64.5	2.71×10^{-2}	9.2×10^{-1}
3,5-Dimethoxy-2-nitrotoluene (340 nm) [d]	60.1	1.86×10^{-1}	1.86×10^{-3}
	61.2	1.53×10^{-1}	6.8×10^{-2}
3,5-Dimethylanisole (350 nm) [e]	52.7	2.02×10^{-1}	4.9×10^{-3}
	54.7	9.87×10^{-2}	2.7×10^{-2}
	56.2	1.07×10^{-1}	1.16×10^{-1}
	57.5	7.30×10^{-2}	3.7×10^{-1}
	59.2	2.00×10^{-2}	1.55
	59.8	4.99×10^{-3}	2.1
	61.3	3.62×10^{-3}	1.45×10
1,3-Dimethoxybenzene (350 nm) [e]	52.7	2.03×10^{-1}	3.2×10^{-3}
	54.7	1.13×10^{-1}	1.38×10^{-2}
	56.2	1.13×10^{-1}	6.3×10^{-2}
	57.5	7.61×10^{-2}	1.97×10^{-1}
	59.2 [d]	2.00×10^{-2}	6.2×10^{-1}
	59.8	1.96×10^{-2}	1.44
	61.3	3.60×10^{-3}	7.83
Anisole (350 nm) [d]	52.7	1.43×10^{-1}	1.35×10^{-3}
	54.7	1.76×10^{-1}	8.6×10^{-3}
	56.2	1.13×10^{-1}	3.6×10^{-2}
	57.5	7.65×10^{-2}	1.15×10^{-1}
	59.8	4.99×10^{-3}	9.4×10^{-1}
	61.3	3.62×10^{-3}	5.5
m-Xylene (330 nm) [e]	52.7	1.82×10^{-1}	2.5×10^{-3}
	54.7	2.12×10^{-1}	1.59×10^{-2}
	56.2	1.13×10^{-1}	6.9×10^{-2}
	57.5	4.87×10^{-2}	2.0×10^{-1}
	59.2 [d]	2.00×10^{-2}	9.7×10^{-1}
	59.4	1.80×10^{-2}	1.22
	59.8	1.96×10^{-2}	1.81
	6.20	7.55×10^{-4}	2.1×10
p-Xylene (330 nm) [d]	57.5	4.87×10^{-2}	2.6×10^{-1}
	59.4	1.75×10^{-2}	1.46
	61.3	4.49×10^{-3}	1.11×10
Mesitylene (330 nm) [d]	54.3 [e]	2.09×10^{-1}	1.29×10^{-2}
	56.2	1.04×10^{-1}	1.05×10^{-1}
	58.3	3.63×10^{-2}	4.6×10^{-1}
	59.2	1.35×10^{-2}	1.33
p-Dichlorobenzene (325 nm) [d]	64.4	1.83×10^{-1}	5.6×10^{-3}
	65.2	1.82×10^{-1}	1.55×10^{-2}
	66.3	1.75×10^{-1}	6.4×10^{-2}
	68.0	7.75×10^{-2}	5.7×10^{-1}
	70.7	7.68×10^{-4}	2.0×10
	71.8	2.84×10^{-4}	1.02×10^2

[a] [Aromatic] $\simeq 10^{-4}$ mol dm^{-3}. [b] Measurements were made at wavelengths indicated. [c] ±0.1%. [d] Sulphamic acid present in *ca.* 5×10^{-3} mol dm^{-3}. [e] Sulphanilic acid present in *ca.* 2×10^{-2} mol dm^{-3}. [f] Urea present in *ca.* 3×10^{-2} mol dm^{-3}.

52 °C). 3,5-Dimethyl-2-nitroanisole (1.03 g) was crystallised from n-pentane giving pale cream crystals, m.p. 42 °C (lit.,[11] 43 °C).

Kinetic Measurements in Perchloric Acid.—Methods of measuring rates of nitration were similar to those described previously for nitrations in sulphuric acid.[3] For some substrates a stock solution of aromatic in acetic acid or dioxan was prepared. A portion (typically 5 µl of solution containing 3×10^{-5} g of aromatic substrate) was injected directly into the cell containing the nitric acid solution. The cell was shaken to ensure complete mixing and placed in the spectrometer. The reaction was followed in the usual way. This method was found not to give satisfactory results with mesitylene and *p*-xylene, perhaps due to dissolution effects, and therefore with these compounds the more conventional technique of preparing a solution of aromatic compound in perchloric acid prior to mixing with the nitric acid solution was employed.

Product Studies.—Techniques used were similar to those described previously.[1] At acidities where the second-order rate constant for the nitration of the substrate in question was >10 s^{-1} mol^{-1} dm^3, reactions were carried out in a pleated flask with the aromatic in amount equimolar with the nitric acid. Details of reference standards, analytical columns, oven temperatures, and retention times of products used in the analysis by g.l.c. are listed in Table 1.

Protonation of 3,5-*Dimethoxytoluene.*—The spectroscopic method was used. Absorbances were measured on an SP 1800 spectrophotometer with cells of 1 cm path length. The results were analysed as described previously,[1] except that the acidity function H_C was used [13] instead of H_A.

RESULTS

Rates.—The second-order rate constants for nitrations at 25 °C in perchloric acid are listed in Table 2. As previously [6] we have used urea, sulphamic acid, or sulphanilic acid to inhibit nitrosation. Sulphamic acid is known to be more reactive towards nitrosating agents than is urea,[14] but has the disadvantage of low solubility. With mesitylene at the lowest acidity studied, only sulphanilic acid was adequate to ensure first-order kinetics. No appreciable reaction was noted between sulphanilic acid and nitric acid under the conditions of the experiments. Two solutions of nitric acid in 58.3% perchloric acid were prepared, concentrations of nitric acid being identical; sulphanilic acid was then added to both solutions, the first solution being used immediately in a kinetic run with 3,5-dimethoxytoluene, the second allowed to stand for 2 h before a similar run was carried out. Within experimental error the rate constants for both runs were identical.

Because protonation of the substrate reduced the rate of reaction of 1,3,5-trimethoxybenzene and 3,5-dimethoxytoluene, complications arose because of interference due to dinitration. The mononitro-products would not be protonated and their rates of nitration would increase normally with acidity. This problem was overcome by studying the rate of nitration of 1,3,5-trimethoxy-2-nitrobenzene and 3,5-dimethoxy-2-nitrotoluene and finding the isosbestic point in the absorbance changes for both reactions. The nitrations of 1,3,5-trimethoxybenzene and 3,5-dimethoxytoluene were then followed at these wavelengths, so that any absorbance change was due only to the mononitration.

At high acidities (>64% perchloric acid) 1,3,5-trimethoxybenzene was found to be relatively unstable, being hydrolysed to the diether and eventually to phloroglucinol. The kinetics of this reaction have been studied and a possible mechanism suggested.[15] Rate constants for nitration at acidities >64% perchloric acid were obtained using conditions where the rate of nitration was at least eight times the rate of hydrolysis.

TABLE 3

Second-order constants for nitration in perchloric acid at 25 °C before and after correction for protonation

$HClO_4$ (%)	I [a]	k_{2corr}/ dm^3 mol^{-1} s^{-1} [b]
3,5-Dimethoxytoluene		
52.7	52.7	
54.3		
54.9	8.2×10^{-2}	2.1×10^{-2}
56.5	1.86×10^{-2}	7.1×10^{-2}
57.2	2.8×10^{-1}	1.94×10^{-1}
59.2	8.3×10^{-1}	1.20
60.3	1.61	2.9
61.3	2.9	5.7
62.7	7.1	1.95×10
64.4	1.97×10	9.3×10
1,3,5-Trimethoxybenzene		
56.5	3.3×10	8.6×10^{-2}
58.7	1.00×10^{2}	6.8×10^{-1}
61.9	7.8×10^{2}	1.14×10
63.8	2.7×10^{3}	5.2×10
64.5	4.4×10^{-3}	1.43×10^{2}
66.3	1.39×10^{4}	1.28×10^{3}
68.2	5.9×10^{-4}	1.39×10^{4}

[a] Ratio of concentrations of conjugate acid and free base forms of the aromatic substrate. [b] $k_{2corr} = k_2(1 + I)$. This corrected rate constant is that for reaction of nitric acid with the free base form of the aromatic substrate.

TABLE 4

Products of nitration in perchloric acid at 25 °C

Compound	$HClO_4$(%)	Isomer yields (%) [a] *x*-nitro-isomer $x = 2$	$x = 4$	Yield (%)
3,5-Dimethylanisole [b]	47.7	54.5 [c]	45.5 [c]	75.3
	49.9	54.0	46.0	100.0
	52.2	53.6	46.6	100.2
	56.4	52.1	48.3	100.4
	58.3	50.1	48.0	98.1
	60.9	50.0	51.8	101.8
	65.7	45.7	53.2	98.8
		31.9 [d]	68.1 [d]	97.6
Anisole [b]	50.8	59.4	37.6	97.0
	52.2	59.4	38.7	98.1
	54.4	58.7	39.9	98.6
	58.2	58.2	42.1	100.3
	61.0	56.2	44.8	100.9
	65.0	50.3 [c]	49.7 [c]	87.5
	72.7	44.5 [c]	55.5 [c]	96.3

[a] ±2%. [b] Sulphanilic acid $\simeq 10^{-2}$ mol dm^{-3}. [c] Results normalised to quantitative yield. [d] Nitration in acetic anhydride.

Protonation of 3,5-*Dimethoxytoluene in Perchloric Acid.*—The results fitted the equation $\log I = -0.89H_C - 8.69$. These results together with those of Kresge for 1,3,5-trimethoxybenzene [4] were used as before [1] to obtain the corrected rate constants for nitration through the free base (Table 3).

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[15] W. M. Schubert and R. H. Quacchia, *J. Amer. Chem. Soc.*, 1963, **85**, 1284.

Yields of Mononitro-compounds.—The products of the nitration of anisole and 3,5-dimethylanisole in perchloric acid were analysed by g.l.c. and the results are shown in Table 4. The yields were quantitative in most experiments. The nitration of 3,5-dimethylanisole in 48% perchloric acid gave a low yield which may have been due to the starting material being unstable at this acidity over the period of the reaction (5 days). When 3,5-dimethylanisole was nitrated in acetic anhydride, using freshly prepared acetyl nitrate, n.m.r. spectroscopic analysis of the reaction solution showed it to contain only the 2- and 4-mononitro-products, in the ratio 1 : 2.1. No cyclohexadiene adducts or other by-products were observed.

Analysis of the products of the nitration of anisole in high acids showed that some unchanged starting material was present. The amount present was measured (see Table 1 for g.l.c. conditions) and the yields were adjusted accordingly. Except for one experiment, the amount of unchanged anisole found was <6%. At high acidities an unidentified, slow reaction does occur between nitric acid and sulpanilic acid. This might account for the incomplete nitration of anisole in experiments where the initial molar concentration of anisole and nitric acid were equal.

DISCUSSION

The Encounter Rate and the Effect of Protonation.—Figure 1 shows rate profiles for nitration. 1,3,5-Trimethoxybenzene and 3,5-dimethoxytoluene, when correction is made for protonation, have profiles closely similar to those of 1,3-dimethoxybenzene, 3,5-dimethylanisole, mesitylene, and (not shown in Figure 1) *m*- and *p*-xylene. Apparent reactivities are very similar and bear no relation to the intrinsic reactivities which might be deduced from considerations of additivity[16] or basicity.[4] In 60% perchloric acid, rate constants for nitration of the following substrates, relative to that for benzene and corrected where necessary for protonation, are as follows: 1,3-dimethoxybenzene (60), 1,3,5-trimethoxybenzene (74), 3,5-dimethoxytoluene (78), *m*-xylene (84), *p*-xylene (94), mesitylene (94), and 3,5-dimethylanisole (106). A slightly diffuse limiting rate constant is clearly indicated which is probably that for encounter between substrate and nitronium ion, as discussed elsewhere.[2] The barrier is not breached even by 1,3,5-trimethoxybenzene, the extremely high reactivity of which can be judged from the ease with which it is protonated.[4] Even for this compound a less reactive electrophile such as nitric acid or nitric acidium ion is not effective.

The reasons for the small differences amongst the encounter rate constants of these compounds are not clear. However, it is noteworthy that, as for nitration in sulphuric acid,[6] anisole (relative rate 43) is nitrated a little more slowly than are the compounds already mentioned, and that, with the exception of 3,5-dimethylanisole, it is the methoxy-compounds which fall at the lower end of the short spread of reactivities. It seems likely that hydrogen bonding is one of the factors which create that spread.

Isomer Yields.—Figure 2 shows that for anisole these vary with acidity in the same way as in sulphuric acid, and again the explanation may be that anisole is hydrogen-bonded to hydronium ion. The extent to which the encounter pair with the nitronium ion proceeds to Wheland intermediate before or after separation of the partners of this hydrogen bond depends upon acidity.[6] If this explanation is correct it might be expected that an encounter pair formed from a more reactive methoxybenzene would be more likely to proceed to Wheland intermediates before separation of the partners of the hydrogen bond, thus partially or wholly removing the cause of variation of isomer ratios with acidity. 3,5-Dimethylanisole shows a similar but smaller variation of isomer ratios with acidity. It must be borne in mind however that even with toluene[17] isomer ratios show small variations with acidity, and explanations of the

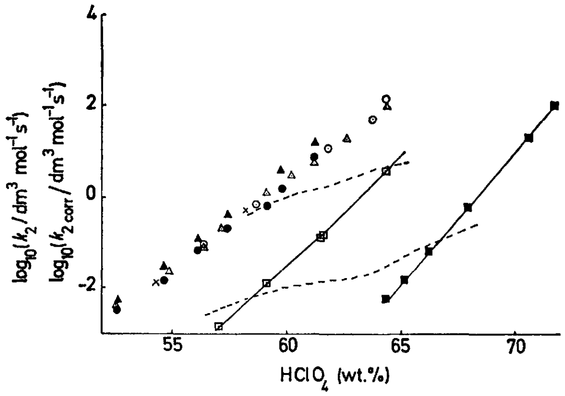

FIGURE 1 Variation with the weight percentage of perchloric acid of the logarithm of the observed second-order rate constant k_2 for nitration at 25 °C of mesitylene (X), 3,5-dimethylanisole (▲), 1,3-dimethoxybenzene (●), benzene (□), *p*-dichlorobenzene (■), 1,3,5-trimethoxylbenzene (lower dashed line), and 3,5-dimethoxytoluene (upper dashed line). The logarithms of the second-order rate constants corrected for protonation, k_{2corr} for 1,3,5-trimethoxybenzene (○) and 3,5-dimethoxytoluene (△) are also shown

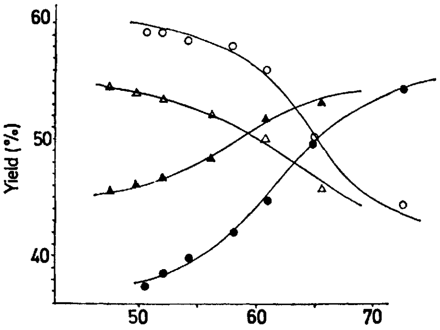

FIGURE 2 Variation with acidity of yields of nitro-products from anisole (*p*-nitroanisole, ●; *o*-nitroanisole, ○), and 3,5-dimethylanisole (3,5-dimethyl-4-nitroanisole, ▲; 3,5-dimethyl-2-nitroanisole, △)

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behaviour of methoxybenzenes in terms of hydrogen bonding are certainly incomplete.

The Rate Profile for p-*Dichlorobenzene*.—Figure 1 shows that no maximum rate of nitration is reached even in 72% perchloric acid. We did not investigate higher acidities because of possible hazard. The rate constant observed in 72% perchloric acid is equivalent to that in 84% sulphuric acid,[18] and about a hundred times smaller than the maximum rate constant observed in the latter medium. This suggestion that the nitronium ion concentration is of the order of one hundredth of the stoicheiometric concentration of nitric acid in 72% perchloric acid.

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