Electrophilic Aromatic Substitution. Part 22.[1] The Nitration of Some Reactive Aromatics in Methanesulphonic Acid, and the Question of Positional Selectivity in Encounter Rate Nitrations of Substituted Naphthalenes and 1,2-Diphenylethanes

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Nitrations in aqueous methanesulphonic acid are shown by the steep acidity dependence of the rate constants, the identification of a kinetic form zeroth-order in the concentration of the aromatic, and the existence of a limiting rate constant identified as the encounter rate constant, most probably to involve the nitronium ion.

2-Methyl-, 2-methoxy-, and 2-methoxy-6-methyl-naphthalene react at the encounter rate. In the last compound the ratio of reactivities of C-1 and C-5 is 6.5 : 1 (smaller than that reported by other workers because of the suppression of nitrosation). Comparison amongst the three compounds suggests that in the nitration of 2-methoxy-6-methylnaphthalene the rate-controlling step is the irreversible formation of an encounter pair which is sufficiently long-lived and mobile to allow selection between positions of differing reactivities in the following product-controlling step of σ-complex formation. The case resembles that of the nitration of 1,2,4-trimethylbenzene reported earlier.

Mesitylene, 3,5-dimethoxytoluene, and 1-(3,5-dimethoxyphenyl)-2-(3,5-dimethylphenyl)ethane react at the encounter rate (with the two methoxylated compounds account has to be taken of the effect upon their performances of ring protonation). In the unprotonated diarylethane the ratio of reactivities (1.8) of the methoxylated and and the methylated rings is very close to the ratio of reactivities (1.4—1.5) of the mononuclear compounds. The small selectivity between the two rings in the unprotonated diarylethane shows that the compound is nitrated by the formation of two non-interconverting encounter pairs, formation of which is both rate- and (so far as intranuclear behaviour is concerned) product-determining.

Although 1-(3,5-dichlorophenyl)-2-(3,5-dimethylphenyl)ethane also reacts at the encounter rate (being nitrated only in the methylated ring), comparison with the previously mentioned diarylethane shows that a statistical factor (not exactly 2 because of the slightly differing efficiencies of the two rings in the dimethoxylated compound in forming productive ion pairs) has to be taken into account in comparing the two compounds.

The behaviour of these various compounds in no way requires the assumption of bonding forces between electrophile and aromatic in the encounter pair, but the performance of 1-(3,5-dimethoxyphenyl)-2-(3,5-dimethylphenyl)-ethane could be very easily understood if the two encounter pairs were π-complexes, or involved some other kind of stabilisation.

1,2,4-TRIMETHYLBENZENE is nitrated at the encounter rate in aqueous sulphuric acid, but positional selectivity between C-5 and C-6 is maintained.[2] Here we explore the extent to which selectivity is retained between positions which are activated but more widely separated than in the case mentioned. Ring-substituted 1,2-diphenylethanes and naphthalenes were chosen for this purpose. The low solubility of the aromatics in aqueous sulphuric acid led us to investigate methanesulphonic acid as a medium for nitration. The only previous study concerns the nitration of nitrobenzene in the pure acid.[3] For our investigations of much more reactive substrates, 80—92% $MeSO_3H$ was suitable.

It was necessary to establish the level of reactivity at which the rate constant for nitration becomes limited by encounter. The result has already been mentioned [4] and the details are given here. Rate limitation by the earlier step of nitronium ion formation [4,5] was discussed in the previous paper in this series.[1] In the present work, either concentrations of the aromatic compound were low enough for deviations from first-order dependence upon these concentrations to be negligible, so that true second-order rate constants were obtained directly, or concentrations of the aromatic compound were greater than those of nitric acid, and the true second-order rate constant was calculated by using equation (5) of ref. 1.

The products of nitration of 2-methyl-,[6] 2-methoxy-,[7] 2,5-dimethyl,[8,9] and 2-methoxy-6-methyl-naphthalene [9] have been reported. 2-Methyl- and 2-methoxy-naphthalene have been studied under various conditions. Rate constants relative to that for naphthalene established by the competition method showed wide variations, and it is not unlikely that nitration *via* nitrosation (a reaction to which naphthalene and its activated derivatives have been shown to be sensitive [10,11]) was a complicating factor. The 1-nitro-product was predominant under all the conditions studied, which makes it likely that this is the preferred orientation whether or not nitration proceeds *via* nitrosation. 2,6-Dimethylnaphthalene [8,9] gave predominantly the 1-nitro-product when nitrated either in acetic anhydride or in acetic acid. The three products from the nitration in aqueous acetic acid of 2-methoxy-6-methylnaphthalene were [9] the 1-, 5-, and 8-nitro compounds formed in the ratio 27 : 1 : 3. Again the conditions used make it very likely that nitration occurred *via* nitrosation. The very high partial rate factors reinforce this conclusion, for in direct nitration such high rate constants would indicate a reaction occurring faster than diffusion would allow.

EXPERIMENTAL

Materials.—Methanesulphonic acid was purified by repeated vacuum fractional distillation (140—141 °C at 0.1 mmHg) through a 6 in fractionating column, packed with

glass helices. The purified acid was odourless and showed no absorbance >0.1 at wavelengths >210 nm. Titration indicated a purity of not less than 99.8%. Dilute aqueous solutions of methanesulphonic acid were prepared by weighing, and the concentrations of some of the diluted acids were checked by titration.

Nitric acid, chlorobenzene, benzene, toluene, the xylenes, trimethylbenzenes, and naphthalene were purified as described previously.[2,4,11] Urea and sulphanilic acid were used without further purification.

Recrystallisation of commercial samples from 95% ethanol gave 2-methyl- and 2-methoxy-naphthalene, m.p. 33—34 °C and 71—72 °C, respectively. 2,6-Dimethyl- (m.p. 108—109 °C) and 2,6-dimethoxy-naphthalene (m.p. 152 °C) were obtained by vacuum sublimation and crystallisation from 95% ethanol of commercial samples. 2,6-Dimethoxy-1-nitronaphthalene, prepared by the method of Chakravarti and Pasupati,[12] had m.p. 185—188 °C (lit.[12] m.p. 189 °C).

2-Methoxy-6-methyl-1-nitro- and -8-nitro-naphthalene were prepared by nitrating [9] 2-methoxy-6-methylnaphthalene (m.p. 77 °C; lit.,[13] m.p. 78—79 °C). The product was chromatographed on neutral alumina in carbon tetrachloride. The mixture of mono-nitro isomers obtained was then repeatedly sublimed. This gave 2-methoxy-6-methyl-1-nitronaphthalene (m.p. 104—105 °C, lit.,[9] 106—107 °C); ^{1}H n.m.r. spectrum ($CDCl_3$), δ 7.68 (d, 1 H, H-4), 7.48 (d, 1 H, H-8), 7.41 (d, 1 H, H-5), 7.26 (q, 1 H, H-7), 7.12 (d, 1 H, H-3), 3.85 (s, 3 H, OCH_3), 2.37 (s, 3 H, CH_3); ^{13}C n.m.r. spectrum ($CDCl_3$), δ(^{13}C), p.p.m. from $SiMe_4$ 147.9 (C-2), 134.8 (C-6), 131.4 (C-4 or C-7), 131.3 (C-4 or C-7), 128.4 (C-1), 126.9 (C-5), 120.2 (C-8), 113.0 (C-3), 57.0 (OCH_3), and 21.3 (CH_3). A sample consisting predominantly of the 8-nitro-isomer was also obtained. This was applied, in carbon tetrachloride containing 10% of chloroform, to a chromatographic plate (8 in × 8 in; 40 g of silica gel activated at 200 °C for 2 h). The upper band was removed and left in dichloromethane. Filtration and removal of the solvent gave impure 2-methoxy-6-methyl-8-nitronaphthalene (containing *ca.* 85% of the 8-, 10% of the 1-, and 5% of the 5-nitro-isomer). The signals for the 8-isomer in the ^{1}H n.m.r. spectrum ($CDCl_3$) were: δ 7.97 (d, 1 H, H-7), 7.80 (d, 1 H, H-1), 7.62 (d, 1 H, H-5), 7.58 (d, 1 H, H-4), 7.07 (q, 1 H, H-3), 3.83 (s, 3 H, OCH_3), and 2.43 (s, 3 H, CH_3); ^{13}C n.m.r. spectrum ($CDCl_3$), δ(^{13}C), p.p.m. from $SiMe_4$ 159.9 (C-2), 134.0 (C-5), 129.5 (C-4 or C-7), 126.8 (C-4 or C-7), 120.0 (C-3), 101.3 (C-1), 55.4 (OCH_3), and 20.9 (CH_3).

3,5-Dimethoxy-4-nitrotoluene and 3,5-dimethoxy-2-nitrotoluene. Nitric acid (*d* 1.5; 0.21 ml) in methanesulphonic acid (12 ml) and water (2 ml) was added at 0 °C to a solution of 3,5-dimethoxytoluene (0.75 g) and urea (0.2 g) in methanesulphonic acid (18 ml) and water (3 ml). After 30 min the orange suspension was poured onto ice. Filtration yielded a yellow solid (0.95 g) which was crystallized from methanol and dried. Chromatography on basic alumina (light petroleum, b.p. 60—80 °C) yielded 3,5-dimethoxy-2-nitrotoluene (0.55 g) which recrystallized from methanol as pale yellow needles, m.p. 106 °C (Found: C, 54.7; H, 5.6; N, 6.8. Calc. for $C_9H_{11}NO_2$: C, 54.8; H, 5.6; N, 7.1%); ^{1}H n.m.r. spectrum ($CDCl_3$), δ 6.41 (d, 1 H, Ar-H), 6.37 (d, 1 H, Ar-H), 3.85 (d, 6 H, $OCH_3)_2$), and 2.29 (s, 3 H, CH_3). The remaining fractions from the chromatography were combined and pure 3,5-dimethoxy-4-nitrotoluene (0.1 g) was obtained by preparative gas chromatography (Pye 105 instrument, 15% Silicone SE-30 on Chromosorb W, N_2 flow rate 80 ml min^{-1}, oven temperature 195 °C). Recrystallization (MeOH) gave pale yellow needles, m.p. 147.5 °C (Found: C, 54.5; H, 5.6; N, 6.8); ^{1}H n.m.r. spectrum ($CDCl_3$), δ 6.45 (s, 2 H, Ar-H), 3.84 (s, 6 H, $(OCH_3)_2$), and 2.35 (s, 3 H, CH_3).

1-(3,5-Dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane. 3,5-Dimethylbenzyl bromide [14] (5.0 g) in xylene (20 ml) was mixed with triphenylphosphine (11.1 g) in xylene (30 ml). After the mixture had been boiled for 2 h, the precipitated phosphonium salt was collected, washed with xylene, and dried *in vacuo* at 60 °C for 1 h. The phosphonium salt (11.2 g) was a white powder, m.p. 300—303 °C (decomp.).

A solution of the phosphonium bromide (12.1 g) in pure ethanol (200 ml) was rapidly added, dropwise, to a solution of sodium (0.58 g) in ethanol (70 ml) in a vessel protected against atmospheric moisture. To this well stirred mixture was added a solution of 3,5-dimethoxybenzaldehyde (4.0 g) in ethanol (75 ml) and the mixture was boiled for 24 h. The solvent was evaporated and the residue was digested with light petroleum (b.p. 60—80 °C, 150 ml). Triphenylphosphine oxide was filtered off. The soluble material was chromatographed on neutral alumina in 1 : 1 benzene–light petroleum (b.p. 60—80 °C). Fractions which contained 3,5-dimethoxy-3′,5′-dimethylstilbene were combined to yield a colourless oil (5.2 g). The oil (5.0 g) was hydrogenated at atmospheric pressure, over 5% Pd on C. Removal of the catalyst (filtration through Kieselguhr) and the solvent gave a brown oil. This was crystallized from light petroleum (b.p. 40—60 °C) to give white crystals (1.4 g; m.p. 36—37.5 °C) of 1-(3,5-*dimethoxyphenyl*)-2-(3′,5′-*dimethylphenyl*)*ethane* (Found: C, 79.8; H, 8.2. $C_{18}H_{22}O_2$ requires C, 79.9; H, 8.2%); ^{1}H n.m.r. spectrum δ 6.86 (s, 3 H, H-2′, H-4′, and H-6′), 6.38 (s, 3 H, H-2, H-4, and H-6), 3.79 (s, 6 H, $(OCH_3)_2$), 2.84 (s, 4 H, $-CH_2-CH_2-$), and 2.31 [s, 6 H, $(CH_3)_2$]; mass spectrum, *m/e* 270, 255, 151, 119, and 91; i.r. (Nujol) 1 600 cm^{-1} and 860 cm^{-1}.

1-(3,5-Dichlorophenyl)-2-(3′,5′-dimethylphenyl)ethane. This was prepared similarly from 3,5-dichlorobenzaldehyde. 3,5-Dichloro-3′,5′-dimethylstilbene (white prisms, m.p. 116—117 °C) {^{1}H n.m.r. spectrum ($CDCl_3$), δ 7.21 (d, 1 H, H-4), 7.90 (q, 2 H, H-2 and H-6), 7.00 (d, 2 H, $-CH=CH-$), 6.84 (d, 3 H, H-2′, H-4′ and H-6′), and 2.25 [s, 6 H, $(CH_3)_2$]} gave on hydrogenation, and crystallisation of the product from light petroleum (b.p. 40—60 °C) white prisms of 1-(3,5-*dichlorophenyl*)-2-(3′,5′-*dimethylphenyl*)*ethane*, m.p. 85—86 °C (Found: C, 68.4; H, 5.7. $C_{16}H_{16}Cl_2$ requires C, 68.8; H, 5.7%); ^{1}H n.m.r. spectrum ($CDCl_3$), δ 7.09 (s, 1 H, H-4), 6.95 (s, 2 H, H-2 and H-6), 6.75 (s, 1 H, H-4′), 6.68 (s, 2 H, H-2′ and H-6′), 2.74 (s, 4 H, CH_2-CH_2), and 2.21 [s, 6 H, $(CH_3)_2$].

1-(3,5-Dimethoxy-2-nitrophenyl)-2-(3′,5′-dimethylphenyl)-ethane. Solutions of the substrate (0.63 g) in acetic anhydride (25 ml) and of nitric acid (0.14 g) in acetic anhydride (25 ml) were prepared and kept at room temperature for 20 min. The solutions were mixed and the whole was kept at 25 °C overnight. The solution was then poured onto ice and the mixture was stirred to hydrolyse acetic anhydride, neutralised with sodium hydrogen carbonate solution and extracted with dichloromethane (5 × 25 ml). The solvent was removed from the dried ($MgSO_4$) extract to yield a yellow oil (0.75 g) which was chromatographed on basic alumina (80 g) in light petroleum (b.p. 60—80 °C). Elution with chloroform in light petroleum (b.p. 60—80 °C) gave starting material (40 mg) in the 5% chloroform frac-

tions, a mixture of starting material and the 2-nitro-product (130 mg) in the 10% chloroform fractions, and a mixture of all four mononitro-isomers in the remaining fractions. The mixture of starting material and 2-nitro-compound was applied to a chromatographic plate (8 in × 8 in, 40 g of silica gel activated at 150 °C for 2 h) in chloroform (20%) and light petroleum (b.p. 60—80 °C). A yellow band was removed from the plate and set aside in dichloromethane. Filtration, and removal of the solvent under reduced pressure, and recrystallisation of the product (80 mg) from methanol gave pale yellow needles of 1-(3,5-*dimethoxy*-2-*nitrophenyl*)-2-(3′,5′-*dimethylphenyl*)*ethane*, m.p. 71—72 °C; ^{1}H n.m.r. spectrum ($CDCl_3$), δ 6.80 (s, 3 H, H-2′, H-4′ and H-6′), 6.36 (d, 1 H, H-4 or H-6), 6.22 (d, 1 H, H-4 or H-6), 3.77 [d, 6 H, $(OCH_3)_2$], 2.78 (s, 4 H, CH_2–CH_2), and 2.26 [s, 6 H $(CH_3)_2$]; mass spectrum, *m/e* 315, 270, 151, and 119.

1-(3,5-*Dimethoxyphenyl*)-2-(3′,5′-*dimethyl*-2′-*nitrophenyl*)-*ethane and* 1-(3,5-*dimethoxyphenyl*)-2-(3′,5′-*dimethyl*-4′-*nitrophenyl*)*ethane*. To a solution of the substrate (0.21 g) in 100% methanesulphonic acid (5 ml) at 0 °C was added a solution of nitric acid (0.05 g) in 100% methanesulphonic acid (5.0 ml). The reaction mixture was stirred for 3—4 min and then poured onto ice. The solution was extracted with dichloromethane. From the dried ($MgSO_4$) extracts, a brown oil (0.23 g) was obtained, which contained almost equal amounts of the 2′- and 4′-nitro-isomers; ^{1}H n.m.r. spectrum ($CDCl_3$), δ 6.90 (s, 2 H, H-4′ and H-6′), 6.30 (s, 3 H, H-2′, H-4′, and H-6′), 3.73 [s, 6 H, $(OCH_3)_2$], 2.80 (d, 4 H, CH_2–CH_2), and 2.26 [d, 6 H, $(CH_3)_2$]; mass spectrum, *m/e* 315, 285, 270, 151, and 119. Attempts to separate the isomers by crystallization, or by chromatography (column chromatography on basic alumina, thin layer chromatography, preparative gas chromatography) failed.

Nitration of 1-(3,5-*Dichlorophenyl*)-2-(3′,5′-*dimethylphenyl*)-*ethane*.—Solutions of the substrate (0.61 g) in acetic anhydride (25 ml) and of nitric acid (0.14 g) in acetic anhydride (25 ml) were kept at room temperature for 20 min and then mixed. After being kept overnight at 25 °C the mixture was poured onto ice. Neutralisation with sodium carbonate, extraction of the product with dichloromethane (6 × 25 ml), drying ($MgSO_4$) of the extract, and removal of the solvent gave a white solid (0.7 g). This was chromatographed on basic alumina (80 g) in light petroleum (b.p. 60—80 °C). The first fraction contained the starting material. Further elution with 5% chloroform in light petroleum (b.p. 60—80 °C) gave a fraction containing the 2′-nitro-compound. Further elution with 10% chloroform in light petroleum (b.p. 60—80 °C) gave a fraction containing the 4′-nitro-compound. The fractions were recrystallised separately from light petroleum (b.p. 60—80 °C). 1-(3,5-*Dichlorophenyl*)-2-(3′,5′-*dimethyl*-2′-*nitrophenyl*)*ethane* gave fluffy crystals (0.32 g), m.p. 98—99 °C (Found: C, 59.0; H, 4.6; N, 4.2. $C_{16}H_{15}Cl_2NO_2$ requires C, 59.2; H, 4.6; N, 4.3%); ^{1}H n.m.r. spectrum ($CDCl_3$), δ 7.08 (t, 1 H, H-4), 6.93 (d, 2 H, H-2 and H-6), 6.86 (s, 1 H, H-6′), 6.73 (s, 1 H, H-4′), 2.74 (s, 4 H, CH_2–CH_2), 2.23 [d, 6 H, $(CH_3)_2$]. 1-(3,5-*Dichlorophenyl*)-2-(3′,5′-*dimethyl*-4′-*nitrophenyl*)-*ethane* gave small needles (0.19 g), m.p. 121—122 °C (Found: C, 59.0; H, 4.7; N, 4.2%); ^{1}H n.m.r. spectrum ($CDCl_3$), δ 7.13 (t, 1 H, H-4), 6.97 (d, 2 H, H-2 or H-6), 6.81 (s, 2 H, H-2′ and H-6′), 2.78 (s, 4 H, CH_2–CH_2), and 2.22 [s, 6 H, $(CH_3)_2$].

Kinetic Measurements in Methanesulphonic Acid.—The following run is typical. Nitric acid (0.040 g) was weighed into 84% methanesulphonic acid (20.0 ml) at 25 °C, and an aliquot (0.080 ml) was transferred to a 20 ml graduated flask containing urea (0.04 g), and this was made up to the mark with more methanesulphonic acid solution. The mixture was thermostatted at 25 °C. An aliquot (20.0 μl) of a solution of the substrate in acetic acid was syringed into the reaction mixture. After being mixed, the solution was rapidly transferred to a silica cell in the thermostatted cell compartment (25.0 °C) of an SP 1800 spectrophotometer and the change of absorbance with time, at a selected wavelength, close to the maximum in the u.v. spectrum of the products, was measured.

Viscosities.—Measurements were made with a Cannon–Ubbelhode viscometer at 25.0 °C. The velocity constant was 0.84 $m^2 s^{-1}$.

RESULTS

Kinetics.—Second-order rate constants for nitration, k_2, are given in Table 1. Except for 1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane, conditions were such that $k_2[AR] < 5k_1$ (k_1 is the first-order rate constant for conversion of nitric acid into nitronium ion determined previously [1]) to ensure that departures from a first-order dependence upon concentration of the aromatic compound were insignificant. Aromatic concentrations greater than that of nitric acid were used for 1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane to minimise problems which might have arise from dinitration. Some of the runs with 3,5-dimethoxytoluene and with mesitylene were similar. Values of k_2 were then deduced from the observed first-order rate constant by using equation (5) of ref. 1.

Equimolar concentrations of nitric acid and aromatic were used for 2,6-dimethyl- and 2-methoxy-6-methylnaphthalene, and the rate constants were obtained by fitting the results to the second-order rate equation by a computer technique. Calculations showed that, if the rate constants for the second nitrations of these substrates were not greater than that for nitration of 1-nitro-2,6-dimethoxynaphthalene (Table 1), dinitration would not be significant. A brown coloration of the solution at the top of the cuvette used for u.v. spectrophotometric studies of the kinetics of nitration of 2-methoxy-6-methylnaphthalene was noted. It is not certain whether this influenced the observed kinetics. Sulphanilic acid, previously found to be particularly effective as a nitrous acid trap,[15] was added in the studies of the nitration of naphthalene and its derivatives. With the other substrates either sulphanilic acid or urea was used (Table 1). Attempts to study the kinetics of nitration of 2,6-dimethoxynaphthalene were unsuccessful; it was judged that in this case nitration *via* nitrosation was occurring even in the presence of sulphanilic acid.

Competition Experiments.—The nitrations involved mixtures of 3,5-dimethoxytoluene and mesitylene (molar ratios 1 : 1 to 1 : 3), the concentration of each being more than ten times that of nitric acid ($[HNO_3] = 10^{-4}$ mol dm^{-3}) in 84.4% $MeSO_3H$ containing urea (0.03 mol dm^{-3}). Product analysis by g.l.c. (see below) gave the ratio of mononitro products. When divided by the molar ratio of starting aromatic compounds and further by the fraction of 3,5-dimethoxytoluene unprotonated at this acidity (0.94), this analysis gave the reactivity of unprotonated 3,5-dimethoxytoluene relative to that of mesitylene as 1.48 (±0.08) (mean of 6 determinations). This is in satisfactory agreement with the ratio [1.38 (±0.10)] of values of k_2s

for this acidity from smooth curves through the results reported in Table 1.

Products.—See Table 2 for these. The conditions used for g.l.c. analysis are in Table 3. In the study of 2-methoxy-6-methylnaphthalene, the mass balance was assessed by n.m.r. spectroscopy. The ^1H n.m.r. integration of the total methoxy signal, including that of unchanged starting material, was compared with that of the methyl protons of the internal standard, *NN*-dimethyl-*p*-nitroaniline. Yields assessed in this way were quantitative within the considerable error of the method. The presence of three mononitro-derivatives in the products was revealed by g.l.c.; two of the products were identified as the 1- and the 8-nitro-compounds. The third, whose presence was also shown in the g.l.c. record of the impure sample of the 8-nitro-compound prepared (see Experimental section) was taken to be the 5-nitro-compound in the light of the work of Clark and Fairweather.[9] A smaller fourth peak with larger retention time indicated the formation of some dinitro-product, but this was estimated to be less than 5% of the total yield of nitro-compounds.

TABLE 1

Second-order rate constants for nitration in methanesulphuric acid at 25.0 (±0.1) °C

$MeSO_3H$ (%)	$10^3[HNO_3]$/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1} (±5%)
	Chlorobenzene [a]	
87.9	410	1.45×10^{-4}
88.0	310	1.34×10^{-4}
	Benzene [a]	
84.2	490	2.4×10^{-4}
88.0	430	3.1×10^{-3}
90.3	300	1.72×10^{-2}
	Toluene [a]	
83.6	80	3.8×10^{-3}
84.2	17	6.2×10^{-3}
86.5	6—70 [b]	2.8×10^{-2}
86.8	79	3.0×10^{-2}
87.3	3.8	7.1×10^{-2}
88.0	25	9.02×10^{-2}
88.6	77	1.65×10^{-1}
89.6	2.8	3.2×10^{-1}
89.8	38	3.6×10^{-1}
90.8	34	1.01
91.5	1.6	1.59
91.7	14.1	1.44
91.8	4.7	1.27
	o-Xylene [a]	
87.4	27	4.3×10^{-1}
	m-Xylene [a]	
84.2	15	6.1×10^{-2}
88.0	8.2	6.5×10^{-1}
90.3	7.2	3.2
	2-Methylnaphthalene [c]	
81.8	111	8.4×10^{-3}
83.6	110	2.8×10^{-2}
87.1	6.9	2.8×10^{-1}
89.3	1.7	1.27
89.4	2.0	1.60
90.5	2.3	3.3
90.7	2.3	3.6
91.6	3.2	7.9
	2,6-Dimethylnaphthalene [c]	
82.9	0.37	2.9×10^{-2}
85.6	0.126	2.2×10^{-1}
87.6	0.38	5.5×10^{-1}
90.1	0.13	2.8
	2-Methoxynaphthalene [c]	
83.6	4.8	3.8×10^{-2}
85.1	13.0	1.28×10^{-1}
86.5	3.0	2.6×10^{-1}
87.3	6.2	4.2×10^{-1}
88.6	3.7	1.59
	2-Methoxy-6-methylnaphthalene [c]	
81.4	0.16	3.5×10^{-2}
82.9	0.37	6.2×10^{-2}
83.6	0.17	1.90×10^{-1}
83.6	0.12	1.50×10^{-1}
84.5	0.10	2.1×10^{-1}
85.6	0.13	4.0×10^{-1}
86.3	0.15	5.7×10^{-1}
86.5	0.17	4.5×10^{-1}
88.6	0.14	1.43
	p-Xylene [a]	
87.4	19	3.3×10^{-1}
	1,2,4-Trimethylbenzene [a]	
87.4	31	4.5×10^{-1}
	1,3,5-Trimethylbenzene	
81.8	111	2.4×10^{-2}
83.6	110	7.0×10^{-2}
84.4 [a]	200 [c]	9.7×10^{-2}
84.9 [a]	200 [c]	1.55×10^{-1}
87.1	6.9	6.3×10^{-1}
87.5	4.8	8.8×10^{-1}
	3,5-Dimethoxytoluene [c,e]	
84.1 [a]	200 [d]	1.23×10^{-1}
84.5	49	1.51×10^{-1}
	Naphthalene [c]	
81.4	76	2.9×10^{-3}
83.6	93	1.01×10^{-2}
85.1	13	2.1×10^{-2}
86.2	77	5.8×10^{-2}
86.5	188	7.6×10^{-2}
86.5	3.0	9.4×10^{-2}
86.8	2.6	8.8×10^{-2}
87.3	122	1.23×10^{-1}
88.6	77	4.0×10^{-1}
89.0	95	3.9×10^{-1}
89.3	1.8	4.5×10^{-1}
90.5	2.3	1.45
90.7	2.3	1.43
91.5	1.6	3.48
	2,6-Dimethoxy-1-nitronaphthalene [c]	
86.5	188	4.4×10^{-2}
89.3	61	3.9×10^{-1}
90.5	2.3	6.7×10^{-1}
	1-(3,5-Dichlorophenyl)-2-(3′,5′-dimethylphenyl)ethane [c]	
81.8	85	1.15×10^{-2}
84.7	84	7.03×10^{-2}
85.7	43	1.34×10^{-1}
86.1	41	1.67×10^{-1}
86.5	37	2.2×10^{-1}
88.5	36	8.8×10^{-1}
89.8	38	2.1
	1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane [a]	
82.8 [b]	1.06 [d]	4.9×10^{-2}
83.8	1.00 [d]	9.9×10^{-2}
85.0	0.67 [d]	2.2×10^{-1}
86.8 [b]	0.99 [d]	8.4×10^{-1}
87.5	1.00 [d]	1.53
88.5	1.00 [d]	1.95
88.8	1.02 [d]	2.30
89.0	1.01 [d]	4.00
90.0	1.09 [d]	4.31

[a] 0.03 mol dm^{-3} of urea added. [b] Mean of three runs. [c] 0.016 mol dm^{-3} of sulphanilic acid added. [d] These represent 10^3[AR]/mol dm^{-3}, not $10^3[HNO_3]$/mol dm^{-3}. $[HNO_3] < 0.1$ [AR]. [e] Rate constants are for reactions of the free base, after correction for partial protonation.

TABLE 2

Products of nitration

Compound	$MeSO_3H$ (%)	Yields of isomers (%)				Mass balance (%)
Mesitylene		Nitromesitylene				
	83.2	99				99
	84.4	100				100
	84.8	100				100
3,5-Dimethoxytoluene		3,5-Dimethoxy-*x*-nitrotoluene				
		$x = 2$	$x = 4$			
	83.2	84	16			100
	84.4	85	15			100
	84.8	84	14			98
1-(3,5-Dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane		1-(3,5-Dimethoxy-*x*-nitrophenyl)-2-(3′,5′-dimethylphenyl)ethane or 1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethyl-*x*-nitrophenyl)ethane				
		$x = 2$	$x = 4$	$x = 2'$	$x = 4'$	
	83.2	54	9	23	14	100
	84.3	54.7 (±1.0) [a]	7.0 (±0.8) [a]	24.4 (±0.6) [a]	13.9 (±0.7) [a]	100
	85.0	50	8	24	13	94
	88.5	47	9	24	15	95
	88.8	49	5	27	19	99
	88.9	49	7	27	17	100
	91.8	34	2	43	22	100
	99.0	9	0	53	38	100
	100.0	3	0	57	40	100
1-(3,5-Dichlorophenyl)-2-(3′,5′-dimethylphenyl)ethane		1-(3,5-Dichlorophenyl)-2-(3′,5′-dimethyl-*x*-nitrophenyl)ethane				
				$x = 2$	$x = 4'$	
	89.6			57	40	97
	92.0			55	41	100 [b]
2-Methoxy-6-methylnaphthalene		2-Methoxy-6-methyl-*x*-nitronaphthalene [c]				
		$x = 1$	$x = 5$	$x = 8$		
	80.6 [d]	72	17	12		98
	84.5 [e]	71	16	12		126
	86.3 [e]	73	16	11		103
	86.8 [d]	70	18	13		97
	88.8 [d]	71	19	10		103
	90.4 [e]	76	13	11		101
	90.8 [d]	68	20	12		106

[a] Mean of 9 separate determinations. Errors are standard deviations. [b] After allowance for 4% of unchanged starting material in the product. [c] Isomer proportions rather than yields are reported because of the inaccuracy of the mass balance. [d] $[AR] = [HNO_3] = 1.4 \times 10^{-2}$ mol dm^{-3}. [e] $[AR] = 2[HNO_3] = 1.4 \times 10^{-2}$ mol dm^{-3}.

TABLE 3

Gas chromatography conditions

Compound	Product or standard	Slope of calibration graph	Column [a] (temperature)	Retention time/s
Mesitylene	Nitromesitylene	0.979	A (172 °C)	319
	1,2,4-trimethyl-5-nitrobenzene [b]			540
3,5-Dimethoxytoluene	-2-nitro	1.297	A (172 °C)	1 258
	-4-nitro	1.297		1 589
	1,2,4-trimethyl-5-nitrobenzene [b]			540
1-(3,5-Dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane	-2-nitro	0.475	B (191 °C)	1 708
	-4-nitro	0.475 [c]		2 068
	-2′-nitro	0.475 [c]		2 380
	-4′-nitro	0.475 [c]		3 642
	2-methyl-3-nitroacetanilide [b]			828
1-(3,5-Dichlorophenyl)-2-(3′,5′-dimethylphenyl)ethane	-2′-nitro	0.667	C (180 °C)	305
	-4′-nitro	0.667		544
	1-nitro-2-methoxy-6-methylnaphthalene [b]			
2-Methoxy-6-methylnaphthalene	-1-nitro	— [d]	C (155 °C)	666
	-5-nitro	— [d]		444
	-8-nitro	— [d]		513

[a] All with Pye 104 instrument fitted with flame ionisation detector, with nitrogen as carrier gas (40 cm^3 min^{-1}). Column A: 15% Silicone SE–30 on Chromasorb W. Column B: 1.25% Polyethylene glycol on Chromasorb W. Column C: 0.03% Polyethylene glycol on glass beads. [b] Reference standard. [c] Assumed the same as for the 2-nitro-product. [d] Assumed the same for the three isomers. Relative areas only determined.

With the other substrates, the concentrations of aromatic compounds used were at least ten times that of nitric acid (1.5×10^{-4} mol dm^{-3}), and overall yields were based on the starting nitric acid. Of the four mononitro-products that can be formed from 1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane, only the 2-nitro-compound was isolated and characterised. A mixture of the 2′- and 4′-nitro-compounds was also available which allowed two more peaks in the g.l.c. record of the products to be identified, the larger being assigned to the 2′-nitro-compound. The

fourth peak from the products was therefore that of the 4-nitro-compound. The ratio of the 2- to the 4-nitro-compound is closely similar to that found in the nitration of 3,5-dimethoxytoluene, which supports this identification. The yields of the products of nitration in 84.3% $MeSO_3H$ were measured in nine independent experiments which made possible an assessment of the error of the method (Table 2).

Ionisation Ratios.—The acidity, with respect to the acidity function H_R, of aqueous methanesulphonic acid was assessed by using *p*-phenylbenzhydrol as indicator. For comparison similar measurements were made for aqueous sulphuric acid. Results are given in Table 4. For sulphuric acid, rectilinear relationships between log I and both H_R and H'_R were observed and the following equations were derived by weighted least squares.[16] (I is the ratio of the cationic to the neutral form). The acidity function H'_R

$$\log I = -0.96\ H_R - 10.21$$
$$\log I = -1.23\ H'_R - 11.72$$

is held [17] to be appropriate to the ionisation of benzhydrols. In our case, perhaps because *p*-phenylbenzhydrol has three benzene rings, correlation with H_R, the acidity function for triarylmethanols,[18] gave a slope closer to unity. This makes it likely that the variations of log I with acidity in methanesulphonic acid (Table 4) can be taken as a guide to the variation of H_R.

TABLE 4

Ionisation ratios (I) [a]

p-Phenylbenzhydrol

H_2SO_4 (%)	log I	$MeSO_3H$ (%)	log I
64.1	−0.62	84.1	−1.08
65.0	−0.37	84.9	−0.94
65.8	−0.16	85.9	−0.75
66.5	0.02	86.9	−0.47
67.5	0.22	88.0	−0.23
68.8	0.59	88.7	−0.08
70.3	0.73	89.7	0.16
		92.0	0.71

1-(3,5-Dimethoxyphenyl)-2-(3,5-dimethylphenyl)ethane

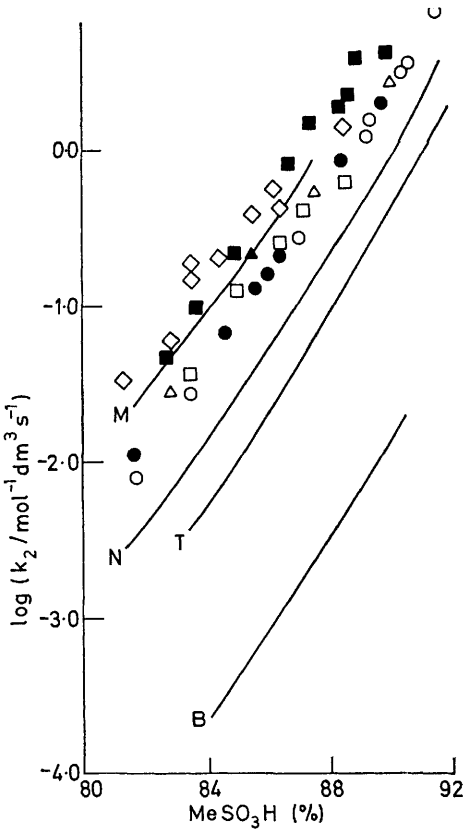
$MeSO_3H$ (%)	log I
84.3	−1.10
87.3	−0.69
89.1	−0.20
91.0	0.06
92.2	0.53
94.4	0.87
95.8	1.09

[a] I is the ratio of the concentration of the conjugate acid or carbonium ion to that of the free base species.

The ionisation ratios of 1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane in aqueous methanesulphonic acid are also given in Table 4. The ionisation of 3,5-dimethoxytoluene was determined similarly in only one acid, 84.5% $MeSO_3H$, in which medium it was found that log $I = -1.17$.

Solubilities of Aromatic Compounds in Aqueous Methanesulphonic Acid.—These are given in Table 5. The solubility of 1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethylphenyl) ethane was not measured, but a Beer's law test showed linear correlation of absorbance with concentration up to at least 1.1×10^{-3} mol dm^{-3} in 84.4% $MeSO_3H$. This and the results in Table 5 show that kinetic, product, and competition experiments were carried out under homogeneous conditions.

Viscosities.—In the indicated media, our measured values



Variation with the weight percentage of methanesulphonic acid of the logarithm of the second-order rate constant k_2 for nitration at 25 °C of benzene (line B), toluene (line T), naphthalene (line N), mesitylene (line M), 2-methylnaphthalene (open circles), 2,6-dimethylnaphthalene (open triangles), 2-methoxynaphthalene (open squares), 2-methyl-6-methoxynaphthalene (open diamonds), 1-(3,5-dichlorophenyl)-2-(3′,5′-dimethylphenyl)ethane (full circles), and 1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane (full squares)

of (viscosity/10^{-3} Pa s) are: 79.8% $MeSO_3H$ (18.8), 83.5% $MeSO_3H$ (18.4), 87.7% $MeSO_3H$ (17.8), and 91.9% $MeSO_3H$ (16.4). In deriving these dynamic viscosities from the measured kinematic viscosities, use was made of densities obtained from ref. 19. A viscosity of 15.51×10^{-3} Pa s has previously been reported for the pure acid.[20]

TABLE 5

Solubilities of aromatics in aqueous methanesulphonic acid

	$MeSO_3H$ (%)	Solubility/mol dm^{-3}
Benzene		
	60.0	0.033
	70.0	0.060
	80.1	0.106
	86.0	0.169
	87.0	0.179
	88.0	0.182
	89.1	0.196
	90.0	0.21
	92.0	0.24
	98.0	0.43
2-Methoxy-6-methylnaphthalene		
	86.5	0.017
Mesitylene		
	84.4	0.026
3,5-Dimethoxytoluene		
	84.4	0.220

DISCUSSION

The Mechanism of Nitration in Aqueous Methanesulphonic Acid.—This is very similar to the process in sulphuric or perchloric acid. Thus, (a) log k_2 increases more rapidly with acidity than does $-H_R$, (b) reaction of, for instance, mesitylene proceeds at a similar rate at a given value of H_R in each of the three acids, (c) deviations from first-order towards zeroth-order dependence of rate on aromatic concentration can be observed,[1] and (d) there is a limit to observable reactivity as discussed below. The last two features particularly argue for the operation of the nitronium ion mechanism in this acid.

The Encounter Limit.—Rate profiles are given in the Figure. Table 6 compares rate constants in 88% $MeSO_3H$. Where the results (Table 1) were for slightly different acidities use was made of the average slope, $d(\log k_2)/d(\%\ MeSO_3H) = 0.27$, to derive values of k_2 at the common acidity. All the compounds more reactive than toluene or naphthalene are seen to have values of k_2 in 88% $MeSO_3H$ between 0.5 and 1.75 $dm^3\ mol^{-1}\ s^{-1}$. The rate profiles show that this similarity extends over a range of acidity. Reasons have been presented [4] for the conclusion that this indicates the onset of diffusion-controlled reactions between aromatic and nitronium ion. The levels of reactivity in various media at which the limit is observed have been compared.[4] (The ratio of reactivities of mesitylene and benzene in 88% $MeSO_3H$ is wrongly given as 550 in ref. 4; in fact it is 390.) The rather diffuse nature of the encounter limit probably reflects differences in diffusion coefficients, and in efficiencies of the encounter process in producing productive encounter pairs.

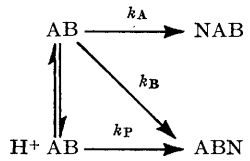
TABLE 6

Second-order rate constants for nitration in 88% $MeSO_3H$ at 25 °C

Substrate	k_2/$mol^{-1}\ dm^3\ s^{-1}$
Chlorobenzene	1.34×10^{-4}
Benzene	3.1×10^{-3}
Toluene	9.0×10^{-2}
Naphthalene	0.23
p-Xylene	0.50
o-Xylene	0.65
m-Xylene	0.65
1,2,4-Trimethylbenzene	0.66
1,3,5-Trimethylbenzene	1.20
Anisole	0.63
2-Methylnaphthalene	0.55
2-Methoxynaphthalene	0.79
2,6-Dimethylnaphthalene	0.91
2-Methoxy-6-methylnaphthalene	1.14
CB [a]	0.60
AB [b]	1.75
3,5-Dimethoxytoluene [b]	1.74

[a] 1-(3,5-Dichlorophenyl)-2-(3′,5′-dimethylphenyl)ethane. [b] 1-(3,5-Dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane [c] This refers to the unprotonated substrate and assumes that the reactivity relative to 1,3,5-trimethylbenzene is the same as in 84.5% $MeSO_3H$.

Selectivity between Rings in 1-(3,5-*Dimethoxyphenyl*)-2-(3′,5′-*dimethylphenyl*)*ethane.*—In what follows, this compound is called AB. Ring A is that with methoxy-substituents, ring B that with methyl substituents, and NAB and ABN refer to the products of mononitration of the A and B rings respectively. The selectivity within rings (the ratio of 2- to 4-nitro- and of 2′- to 4′-nitro-products) is not discussed. The decrease with increasing acidity of the fraction f of nitration occurring in ring A (Table 2) is clearly associated with protonation of that ring to give H^+AB (Scheme 1).



SCHEME 1

If the ratio of reactivities of H^+AB and AB is r, and the fraction of nitration of AB occurring in ring B is x, then from Scheme 1 it is apparent that

$$f = k_A/(k_A + k_B + k_P I) = \text{Yield of NAB/Yield of (ABN + NAB)},$$
$$r = k_P/(k_A + k_B),$$
$$x = k_B/(k_A + k_B).$$

It is readily shown that

$$f = (1 - x) - rfI.$$

A plot of f against fI gave $r = 0.34$, $x = 0.36$. The ratio of the reactivities of ring B in AB to that of ring B in H^+AB ($k_B/k_P = r/x$) is therefore close to unity, showing that protonation of the A ring does not significantly affect the reactivity of ring B. In the unprotonated species AB, the ratio of the reactivities of rings A and B [$k_A/k_B = (1 - x)/x$] is 1.8. This is similar to the ratio of the reactivities of 1.4 or 1.5 to 1 of the two molecules which can be regarded as the two 'halves' of AB, 3,5-dimethoxytoluene and mesitylene. If encounter between nitronium ion and AB were to give one encounter pair within which repeated collisions of the randomly orientated partners could occur, much greater selectivity would have been expected. It seems therefore that encounters of nitronium ions with ring A of AB and with ring B of AB should be regarded as separate events, leading to different non-interconverting encounter pairs. This suggests that 1-(3,5-dichlorophenyl)-2-(3′,5′-dimethylphenyl)ethane, now called CB, which resembles AB in shape and size and presumably diffusion coefficient but has only one reactive ring, should react more slowly than AB and by a predictable amount. In fact k_2^{CB}, the observed second-order rate constant for nitration of CB (Table 1) should be closely similar to k_P, the rate constant for reaction of H^+AB (Scheme 1), in which ring A is deactivated by protonation.

The observed second-order rate constant for nitration of AB, k_2^{AB} (Table 1) contains contributions from AB and H^+AB. It follows from Scheme 1 that

$$k_2^{AB} = (k_A + k_B)\left(\frac{1}{1+I}\right) + k_P\left(\frac{I}{1+I}\right)$$

and if $k_2^{CB} = k_P$

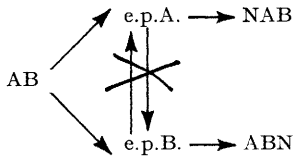
$$\frac{k_2^{AB}}{k_2^{CB}} = \frac{1}{r}\left(\frac{1}{1+I}\right) + \left(\frac{I}{1+I}\right) \qquad (3)$$

A smooth curve was drawn through the plot of log k_2^{AB} *versus* $\%MeSO_3H$, and values interpolated at the acidities at which k_2^{CB} was studied. This led to the observed ratio of reactivities [l.h.s. of equation (3)] which is compared in Table 7 with the calculated ratio of reactivities [r.h.s. of equation (3)]. The agreement, almost within experimental error, is most satisfactory. Scheme 2 therefore describes the nitration of unprotonated AB; e.p.A and e.p.B represent encounter pairs of nitronium ion with ring A and ring B respectively which do not have time either to revert to AB and nitronium ions or to be interconverted, before forming σ-complexes and thence nitro-products.

TABLE 7

Observed and calculated ratio of second-order rate constants for nitration of AB and CB (see text)

$MeSO_3H$ (%)	81.8	84.7	85.7	86.1	86.5	88.5	89.8
Calculated	2.9	2.8	2.7	2.6	2.6	2.4	2.2
Observed	2.4	2.8	2.8	2.9	2.9	2.7	2.3



SCHEME 2

This conclusion would receive a simple explanation if there were attractive interaction within e.p.A and e.p.B, of the type provided by π-complexing,[21] or electron transfer.[22] The results however do not prove the existence of such interaction.

Selectivity between Positions in 2-Methoxy-6-methylnaphthalene.—Loss of selectivity between rings in AB contrasts with retention of selectivity between C-5 and C-6 in 1,2,4-trimethylbenzene.[2] 2-Methoxy-6-methylnaphthalene provides an intermediate case, with regard to the distance between the positions undergoing nitration. The kinetic results (Table 1) show that 2-methyl- and 2-methoxy-naphthalene are nitrated at the encounter rate. The predominant product of nitration for both is the 1-nitro-compound, as discussed in the introduction. C-1 and C-5 in 2-methoxy-6-methylnaphthalene are probably therefore sufficiently activated to allow 2-methoxy-6-methylnaphthalene to react upon encounter. The selectivity that we observe between these positions, 6.5 to 1, is much less than previously reported (we believe this is because we have taken steps to avoid nitration *via* nitrosation) but is still significant. It suggests a situation more like that of 1,2,4-trimethylbenzene, than that of diphenylethane AB. The encounter process between nitronium ion and 2-methoxy-6-methylnaphthalene is therefore best viewed as one in which nitronium ion and aromatic form irreversibly one encounter pair (or indistinguishably several rapidly interconverting encounter pairs) in which there is sufficient mobility and longevity for selection between positions of different intrinsic reactivity to occur.

An alternative but less satisfactory view would be that provided by Scheme 2, with A and B now representing the two rings of 2-methoxy-6-methylnaphthalene. Selection between C-5 and C-8 would still occur (though these are of similar intrinsic reactivity), but there would be no selection between C-1 and (C-5 + C-8). In this model, the ratio of the reactivities of the two rings (2.6) differs from unity because of different efficiencies of the two rings in forming encounter pairs. However, the ratio of the reactivity of 2-methoxynaphthalene to that of 2-methylnaphthalene (in both of which reaction occurs almost entirely in the substituted ring) is only 1.4. The former description therefore seems preferable.

We consider therefore that in 2-methoxy-6-methylnaphthalene the rate-controlling step is encounter-pair formation, and the product-controlling step is the subsequent conversion of the encounter pair into the various σ complexes. In 1-(3,5-dimethoxyphenyl)-2-(3′,5′-dimethylphenyl)ethane on the other hand, two different encounter pairs can be formed in the rate-controlling step and the same step also controls product distribution between the two rings. (The subsequent step of σ-complex formation probably controls product distribution within each ring.) There is a statistical factor [23] to be applied when comparing the reactivities of the two diarylethanes AB and CB, though both reactions are encounter controlled and differences in diffusion coefficients are likely to be small. The statistical factor is not exactly two because the A and B rings are not equally efficient in forming productive encounter pairs.

[8/1110 *Received*, 14*th June*, 1978]

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