Marked Deviations from the Additivity Principle in the Products of Nitration of Substituted Anilinium Ions

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Product compositions have been determined for the nitration of several substituted anilinium ions activated by a methoxy-group or by two methyl groups. Kinetic studies have been carried out on two compounds with a methoxy-substituent. The results have been shown to deviate markedly from those predicted by the additivity principle but to be understandable on the assumption that the substituents exert independent directing effects which are not necessarily the same as those shown in the corresponding monosubstituted benzenes. In particular, the nitrogen pole appears to deactivate all positions in the ring to a very similar extent and the methoxy-group appears to be much more *ortho*-directing than is observed in the nitration of anisole. These results are shown to accord with other results in the literature and to lead to a reassessment of the apparently anomalous orientation of electrophilic substitution in *meta*-nitroanisole.

PREVIOUS studies on the nitration of the anilinium ion [1] and the phenyltrimethylammonium ion [2] have established that nitrogen poles deactivate *ortho*-positions much more than *meta*- and *para*-positions; this has been ascribed to the electrostatic interactions between the nitrogen pole and the charge on the electrophile in the transition state.[3] A similar explanation has been used to account for the low reactivity of the positions *ortho* to the $\overset{+}{\mathrm{N}}\mathrm{HMe_2}$ group in protodesilylation.[4] Nevertheless, studies of hydrogen isotope exchange in substituted anilinium ions containing activating substituents have given no indication of any additional deactivation of the positions *ortho* to the nitrogen poles.[5] The present work on ions (I)—(IV) was carried out to provide evidence on the cause and extent of this anomaly.

Products.—Consider first the nitration of the monosubstituted benzenes bearing the substituents of compounds (I)—(IV). Nitration of the phenyltrimethylammonium ion is known to give 89% *meta*- and 11%

para-substitution:[2] no *ortho*-substitution was detected. This reaction has been reinvestigated and the amount
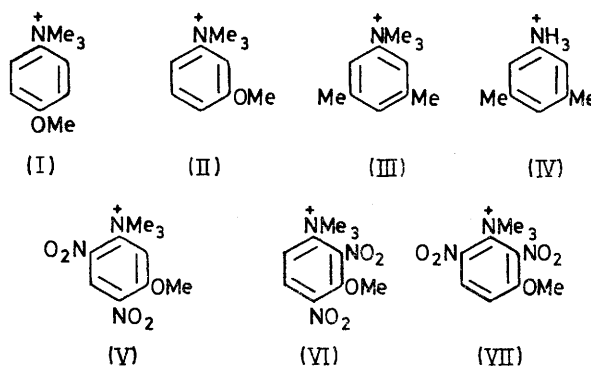
of *ortho*-substitution can now be put at <0·5%. The nitration of the anilinium ion in 82% sulphuric acid gives 5% *ortho*-, 36% *meta*-, and 59% *para*-substitution.[1]

[1] S. R. Hartshorn and J. H. Ridd, *J. Chem. Soc. (B),* 1968, 1063.

[2] A. Gastaminza, T. A. Modro, J. H. Ridd, and J. H. P. Utley, *J. Chem. Soc. (B),* 1968, 534.

[3] A. Gastaminza, J. H. Ridd, and F. Roy, *J. Chem. Soc. (B),* 1969, 684.

[4] C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Chem. Soc. (B),* 1969, 15.

[5] J. R. Blackborow and J. H. Ridd, *Chem. Comm.,* 1967, 132.

The nitration of anisole in aqueous sulphuric acid has been shown [6] to yield 60% *ortho-* and 40% *para-* substitution. The products of nitration of toluene are not very sensitive to the composition of the medium and for the purpose of the present calculations, have been taken as 62% *ortho-*, 3% *meta-*, and 35% *para-*-substitution.[7] From these results and the additivity principle (or Holleman's product rule),[8] the expected orientation of nitration in ions (I)—(IV) can be calculated and the results are given in Table 1. These calculations are based on the upper limit for *ortho-*nitration in the phenyltrimethylammonium ion (0·5%) and so should provide an upper limit for the expected amount of nitration *ortho* to this nitrogen pole.

TABLE 1

Comparison of the observed product compositions (%) for nitration in aqueous sulphuric acid (75% H_2SO_4) with those calculated from the additivity principle (in parentheses). Where two positions are equivalent, the percentage of that isomer is given in one of them and the other is left blank

Substrate	Product composition (%)				
	2	3	4	5	6
4-MeOC6H4$\overset{+}{N}$Me3 (I)		100 (100)			
3-MeOC6H4$\overset{+}{N}$Me3 (II)	24 (2)		76 (95)		(3)
3,5-Me2C6H3$\overset{+}{N}$Me3 (III)	41 (5)		59 (95)		
3,5-Me2C6H3$\overset{+}{N}$H3 (IV)	69 (8·7)		31 (91·3)		

The nitration of the 4-methoxyphenyltrimethyl-ammonium ion (I) would be expected to give effectively complete substitution *ortho* to the methoxy-group and this accords with the n.m.r. spectrum of the reaction product, for only one peak is observed for the $\overset{+}{N}$Me3 group and one for the OMe group. The nitration of the 3-methoxyphenyltrimethylammonium ion (II) would be expected to give *ca.* 95% of the 4-nitro-product (Table 1) but the n.m.r. spectrum of the product from reaction in 75% sulphuric acid indicates the presence of two species in the ratio *ca.* 3 : 1. This ratio depends somewhat on the acidity of the medium (Table 2). The major product has been identified as the 4-nitro-isomer by comparison with an authentic sample. On dinitration,

this isomer gives a product with two aromatic singlets indicating effectively complete conversion into the 4,6-dinitro-product (V). The minor product also analyses correctly for a mono-nitro-derivative but on dinitration does not give (V); instead a more complex n.m.r. spectrum is observed with a pair of quartets in the aromatic region; this accords with a mixture of (VI) and (VII). The minor product has therefore been identified as the 2-nitro-isomer. Unfortunately, attempts to confirm this by an unambiguous synthesis of the 2-nitro-isomer proved unsuccessful.

The absence of the 6-nitro-isomer in the product from the nitration of the ion (II) was unexpected. It is possible but unlikely that the n.m.r. peaks for the $\overset{+}{N}$Me3 and OMe groups of this isomer coincide with those of the 2-nitro-isomer but no evidence for a significant amount of such a third product was obtained in the spectra taken during the separation of the 4- and 2-nitro-isomers or on changing the solvent to [$^2H_4$]-methanol. Alternatively, the 6-nitro-isomer may be the cause of a small unidentified singlet in the region of the $\overset{+}{N}$Me3 groups at *ca.* 7·1 Hz (at 60 MHz) downfield from the peak of the 4-nitro-isomer. If so, the 6-nitro-isomer forms *ca.* 1% of the reaction product. In the following discussion we have assumed that the amount of the 6-nitro-isomer can be ignored but this has not been conclusively established. Fortunately, the conclusions would not be changed by the presence of a few percent of this product.

The n.m.r. spectrum of the reaction mixture from the nitration of the 3,5-dimethylphenyltrimethylammonium

TABLE 2

Variation in the extent of nitration *ortho* to the nitrogen pole (2-substitution) with the acidity of the medium. The remaining product is the 4-nitro-isomer

Substrate									
3-MeOC6H4$\overset{+}{N}$Me3 (II)	H_2SO_4 (%)	64·3	69·0	74·0	75·5	77·2	81·1	84·9	88·9
	2-Isomer (%)	28	26	24	24	23	19	14 *	8 *
3,5-Me2C6H3$\overset{+}{N}$Me3 (III)	H_2SO_4 (%)	72·2	75·6	79·4	83·8	89·4			
	2-Isomer (%)	41	41	40	40	39			
3,5-Me2C6H3$\overset{+}{N}$H3 (IV)	H_2SO_4 (%)	72·2	75·6	79·4	83·8	89·4			
	2-Isomer (%)	69	69	68	68	68			

* Estimated using the dinitro-products (see Experimental section).

ion (III) in 75% sulphuric acid showed two peaks in the region of absorption of the $\overset{+}{N}$Me3 group in the ratio 3 : 2. Comparison with the absorption of the methyl groups showed that the major product was the 4-nitro-isomer. Similar experiments with the 3,5-dimethylanilinium ion (IV) indicated 69% of the 2-nitro-isomer and 31% of the 4-nitro-isomer. In principle, this substrate could undergo some reaction through the neutral molecule but the fact that the product composition is almost independent of acidity (Table 2) shows that this reaction path is not significant.

The above product compositions are compared with those expected from the additivity principle in Table 1.

[6] J. G. Hoggett, R. B. Moodie, and K. Schofield, *Chem. Comm.*, 1969, 605.

[7] G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Amer. Chem. Soc.*, 1962, **84**, 3687.

[8] A. F. Holleman, *Chem. Rev.*, 1925, **1**, 187; *cf.* P. B. D. de la Mare and J. H. Ridd, 'Aromatic Substitution, Nitration and Halogenation,' Butterworths, London, 1959, ch. 6.

Kinetic Studies.—The rate of nitration of the methoxy-phenyltrimethylammonium ions with an excess of nitric acid in aqueous sulphuric acid has been followed from the change in the u.v. spectra of the solutions. As usual, good first-order plots were obtained and the corresponding first-order rate coefficients have been divided by the stoicheiometric concentration of nitric acid to give second-order rate coefficients (k_2). These
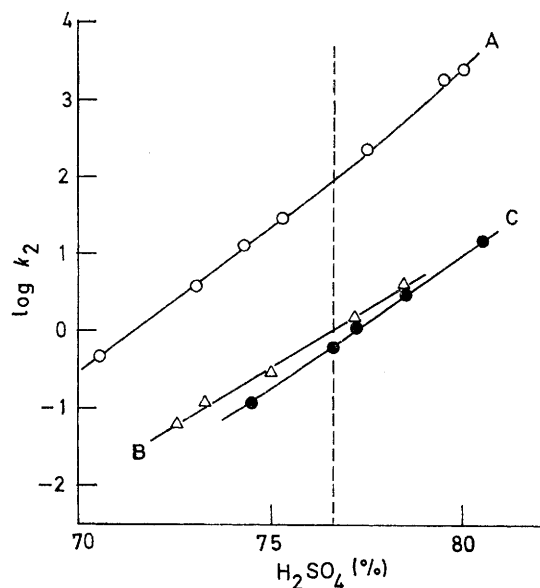

FIGURE 1 The variation of log k_2 with the concentration of sulphuric acid for the nitration of: A C_6H_6; B 4-$MeOC_6H_4\overset{+}{N}Me_3$; C 3-$MeOC_6H_4\overset{+}{N}Me_3$. The results for benzene are taken from ref. 9

second-order rate coefficients are listed in Table 3 and plotted, together with those for benzene,[9] in Figure 1. The slopes of these logarithmic plots for the methoxy-derivatives (3-MeO, slope 0·35; 4-MeO, slope 0·30) are

TABLE 3

Second-order rate coefficients (k_2) for nitration in aqueous sulphuric acid at 30°

3-$MeOC_6H_4\overset{+}{N}Me_3$						
H_2SO_4 (%)	74·58	76·6	77·15	78·5	80·5	76·6
k_2/l mol^{-1} s^{-1}	11·7	57·6	114	287	1460	36·3 *
4-$MeOC_6H_4\overset{+}{N}Me_3$						
H_2SO_4 (%)	72·6	73·3	75·0	77·1	78·5	76·6
k_2/l mol^{-1} s^{-1}	6·36	11·5	28·0	145	377	66·1 *

* At 25°.

less than that for benzene over this region of acidity (slope *ca.* 0·40). In consequence, the rates of nitration of the methoxy-derivatives relative to benzene decrease

† The steric interaction of the $\overset{+}{N}Me_3$ group with nitronium ion is probably similar to that of the CMe_3 group. For nitration in aqueous acetic acid the ratio $f_o : f_p$ is 0·72 for toluene and 0·073 for t-butylbenzene.[10] The difference by a factor of 10 in these ratios is probably attributable mainly to the steric interaction of the nitronium ion with the CMe_3 group. In hydrogen isotope exchange in aqueous sulphuric acid (a reaction not subject to steric hindrance) the ratio $f_o : f_p$ is *ca.* 1 for both toluene and t-butylbenzene.[11]

with acidity: in 76·6% sulphuric acid, these relative rates are 3-MeO, 3·6 × 10^{-3}; 4-MeO, 6·6 × 10^{-3}. These figures, together with the isomer proportions in Table 1, give the partial rate factors shown in Table 4.

TABLE 4

Partial rate factors for nitration in aqueous sulphuric acid at 25°

Substrate	Partial rate factors				
	2	3	4	5	6
4-$MeOC_6H_4\overset{+}{N}Me_3$		2 × 10^{-2}		2 × 10^{-2}	
3-$MeOC_6H_4\overset{+}{N}Me_3$	5 × 10^{-3}		1·7 × 10^{-2}		

The Directing Effect of the Nitrogen Pole.—The comparison of the observed and calculated results in Table 1 shows that the additivity principle provides a very poor guide to the composition of these reaction products, mainly because of the large amount of substitution *ortho* to the nitrogen poles. In analysing these results, it is helpful to look first at the partial rate factors for substitution in the 3-position of ion (I) and in the 2- and 4-positions of ion (II): these positions are all *ortho* to a methoxy-group and are respectively *meta*, *ortho*, and *para* to the $\overset{+}{N}Me_3$ pole. The results in Table 3 show that the reactivities at the positions *meta* and *para* to the nitrogen pole are very similar and are greater than that at the *ortho*-positions by a factor of 3—4. Since this factor is certainly no greater than would be expected from the steric hindrance to nitration *ortho* to a $\overset{+}{N}Me_3$ group,† we conclude that the inductive and field effects of the $\overset{+}{N}Me_3$ group combine to produce very similar deactivation at the *ortho*-, *meta*-, and *para*-positions.

This conclusion accords with the effect of the $\overset{+}{N}H_3$ pole as seen in the nitration of ion (IV). The observed product composition is in marked disagreement with that predicted by the additivity principle (Table 1) but in unexpectedly good agreement with what would be predicted were the nitrogen pole considered to deactivate equally the *ortho*-, *meta*-, and *para*-positions. The predicted product composition would then be: 2-nitro, 69·4%; 4-nitro, 30·6%. The corresponding compound with the $\overset{+}{N}Me_3$ pole [(III)] gives less substitution *ortho* to the pole: the ratio of 2- to 4-substitution is lower than that with the $\overset{+}{N}H_3$ pole by a factor of 3·2. However, as outlined above, such a factor can probably be understood as deriving from the steric interaction of the $\overset{+}{N}Me_3$ group with the nitronium ion.

In considering why the directing effect of the nitrogen pole is absent with these compounds with activating groups, it is worth noting that the absence occurs in both nitration and hydrogen isotope exchange,[5] and for

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

[10] H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature*, 1952, **169**, 291.

[11] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1961, 247; R. Baker, C. Eaborn, and R. Taylor, *ibid.*, p. 4927.

activation by both a methoxy and two methyl groups. The absence of the directing effect is therefore unlikely to derive from any special property of the electrophile or the activating substituent: it seems rather to be a general characteristic of nitrogen poles in these activated systems.

If the low percentage of ortho-attack in the monosubstituted compounds is ascribed to electrostatic interaction between the nitrogen pole and the charge on the electrophile in the transition state, it is difficult to see why the effect should be less in the compounds studied here; indeed the Hammond postulate would suggest the opposite [12] since the presence of the activating substituents should cause the transition state to move towards the initial state and thus lead to an increase in the charge on the electrophile in the transition state. An alternative and more consistent interpretation is to accept that the inductive and field effects of the nitrogen pole deactivate the ortho- and para-positions more than the meta-position and then to assume that the transition states for attack at the ortho- and para-positions are stabilised by hyperconjugative electron donation from the $\overset{+}{N}H_3$ and $\overset{+}{N}Me_3$ groups. There is some evidence from secondary isotope effects [1] and i.r. intensities [13] that the nitrogen poles can act as electron-donating substituents in this way. The results then suggest that such electron donation activates mainly the para-position in the monosubstituted compounds and both the ortho- and para-positions about equally in the activated compounds. This is consistent with the change in the directing effect of the methyl substituent in electrophilic substitution as the transition state changes from one resembling the Wheland intermediate towards one resembling the initial state.[14] On this interpretation, the unexpected decrease in the yield of the ortho-nitro-compound with acidity in the nitration of the 3-methoxyphenyltrimethylammonium ion (Table 2) can be explained in terms of the increased hydrogen bonding of the methoxy-group. Such hydrogen bonding should reduce the activating effect of the methoxy-group (cf. the slopes of the plots in Figure 1) and thus change the reactivity of the system towards that of the monosubstituted compound.

The Directing Effect of the Methoxy-group.—The results for the nitration of the 3-methoxyphenyltrimethylammonium ion indicate that the methoxy-group is much more ortho-directing in this reaction than would be expected from the nitration of anisole (ortho, 60%; para, 40%).[6] This accords with the results of Holleman [15] for the nitration of 3-nitroanisole (VIII). Previous discussions of this product composition [16] have concerned the unexpectedly large amount of substitution between the two substituents, but a comparison with the product composition calculated from the additivity

principle [(IX)] * shows that the ratio of the percentages of substitution in the two positions ortho to the methoxy-group is not anomalous and hence requires no special explanation: the surprising feature is the very small amount of substitution para to the methoxy-group.

(VIII)(observed)   (IX)(calculated)

Product compositions in nitration
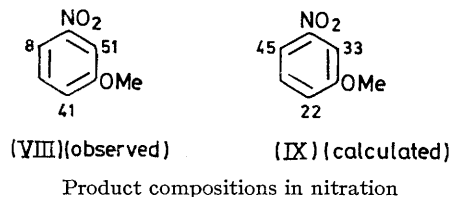
Conclusion.—This work suggests that product compositions in the nitration of a set of benzene derivatives with several substituents may be usefully analysed in terms of the directing effects of the substituents even when these directing effects are not the same as those shown in the monosubstituted compounds. It is reasonable that the directing effect of a group should depend on the overall reactivity of the aromatic system to which it is joined, for this should determine the charge distribution and other characteristics of the transition state. Such changes in the characteristics of the transition state between mono- and di-substituted compounds should be greatest when (as in the above examples) the disubstituted compounds contain a strongly activating and a strongly deactivating group.

EXPERIMENTAL

Materials.—Phenyltrimethylammonium perchlorate was prepared by the reaction of dimethylaniline with methyl sulphate in dry benzene. When the crude methosulphate was added to aqueous sodium perchlorate, phenyltrimethylammonium perchlorate was precipitated, m.p. 178° (from methanol) (Found: C, 46·1; H, 6·0; N, 6·0. Calc. for $C_9H_{14}ClNO_4$: C, 45·9; H, 6·0; N, 6·0%). 3-Methoxyphenyltrimethylammonium perchlorate was prepared in a similar way except that the methylation of the amine (meta-anisidine) was carried out in aqueous sodium hydroxide.[17] The product had m.p. 156—157° (from methanol) (Found: C, 45·2; H, 5·9; N, 5·3. $C_{10}H_{16}ClNO_5$ requires C, 45·2; H, 6·0; N, 5·3%). 4-Methoxyphenyltrimethylammonium perchlorate was prepared in the same way as the 3-methoxy-compound and recrystallised from methanol, m.p. 193—194° (Found: C, 45·1; H, 5·9; N, 5·3%). 3,5-Dimethylphenyltrimethylammonium perchlorate, m.p. 203—204°, was prepared in the same way, starting with 3,5-dimethylaniline. For all the quaternary salts listed above, the extent of methylation was shown to be complete by the n.m.r. spectrum in aqueous sulphuric acid (ca. 90%). Under these conditions the protons of the $\overset{+}{N}Me_3$ pole give rise to a singlet but those of the $\overset{+}{N}Me_2H$ pole to a doublet.

An authentic specimen of 3-methoxy-4-nitrophenyltrimethylammonium perchlorate was prepared by nitration

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* Calculated using the following data for the nitration of nitrobenzene: ortho, 6%; meta, 92%; para, 2%.

[12] G. S. Hammond, J. Amer. Chem. Soc., 1955, 77, 334.

[13] P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, J. Amer. Chem. Soc., 1968, 90, 1767.

[14] G. A. Olah and S. Kobayashi, J. Amer. Chem. Soc., 1971, 93, 6964.

[15] A. F. Holleman, Rec. Trav. chim., 1903, 22, 263.

[16] C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' Cornell Univ. Press, Ithaca, 2nd edn., 1969, p. 319.

[17] P. Groenwoud and R. Robinson, J. Chem. Soc., 1934, 1694.

of 3-dimethylaminoanisole with fuming nitric acid at −5 to +5° to give the known 3-dimethylamino-6-nitroanisole. The product, after recrystallisation from ethanol, had m.p. 121—122° (lit.,[18] 122°). Further methylation with methyl sulphate in benzene followed by treatment of the crude methosulphate with saturated aqueous sodium perchlorate, gave a precipitate of the fully methylated quaternary perchlorate, m.p. 217—219° (from methanol) (Found: C, 38·7; H, 4·8; N, 8·6. $C_{10}H_{15}ClO_7N_2$ requires C, 38·7; H, 4·8; N, 9·0%).

Sulphuric acid and nitric acid were AnalaR reagents and were standardised by titrating a known weight with aqueous sodium hydroxide using phenolphthalein as the indicator.

Product Composition.—The n.m.r. spectrum of the product from the nitration of the phenyltrimethyl-ammonium ion in 98% sulphuric acid shows a single peak in the region of absorption of the $\overset{+}{N}Me_3$ group corresponding to the *meta-* and *para-*nitro derivatives. The *ortho-*compound, if present, would absorb at *ca.* 0·08 p.p.m. to low field [2] of the main peak but a careful search of this region using a Varian HA 100 spectrometer revealed no sign of a peak corresponding to the *ortho-*isomer. The intensity of absorption at this position was less than that of one of the ^{13}C satellites of the main peak and so the amount of *ortho-*substitution must be <0·5%. This work did reveal one additional peak 0·16 p.p.m. to low field of the main product and about equal in area to one ^{13}C satellite: the source of this peak is unknown.
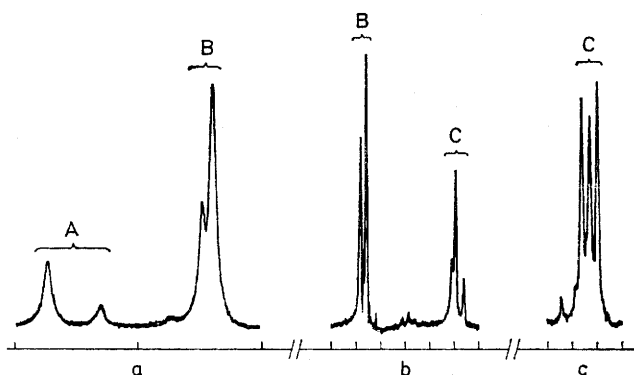

FIGURE 2 N.m.r. spectra (60 MHz) of the methyl protons in the nitration products of: a 3-MeOC$_6$H$_4\overset{+}{N}Me_3$; b 3,5-Me$_2$C$_6$H$_3$-$\overset{+}{N}Me_3$; c 3·5-Me$_2$C$_6$H$_3\overset{+}{N}H_3$. The letters A, B, C refer to peaks from the OMe, $\overset{+}{N}Me_3$, and Me substituents respectively. The scale units are 20 Hz. Solvent 70—80% H$_2$SO$_4$

The n.m.r. spectrum of the nitration product from the 3-methoxyphenyltrimethylammonium perchlorate (Figure 2a) showed two peaks in the OMe region (A) and two peaks in the $\overset{+}{N}Me_3$ region (B). The two products were separated after reaction with 70% nitric acid at room temperature. When the n.m.r. spectrum indicated complete mono-nitration, the excess of nitric acid was removed under reduced pressure. The solid was then extracted with dry methanol: this removed the minor product together with a trace of the major product. Both products analysed correctly for mononitro-derivatives. The major product had m.p. 218—220° (decomp.) (Found: C, 38·7; H, 4·8; N, 8·6%). The minor product had m.p. 156—158° (from

methanol–light petroleum) (Found: C, 38·4; H, 4·8; N, 8·8. $C_{10}H_{15}ClO_7N_2$ requires C, 38·7; H, 4·8; N, 9·0%). The m.p. and n.m.r. spectrum (Figure 3a) of the major product were identical with those of synthetic 3-methoxy-4-nitrophenyltrimethylammonium perchlorate.

Both products were stable in 90% sulphuric acid. On further nitration in this medium, the 4-nitro-isomer was converted into a product giving two sharp aromatic singlets (Figure 3c). This can be *only* the 4,6-dinitro-derivative (V). Under these conditions, the minor product appears to give a mixture of two dinitro-compounds each giving an aromatic quartet (Figure 3d); these have been identified as the 2,4- (VI) and the 2,6-dinitro-derivative (VII). The minor product has therefore been identified as the 2-nitro-derivative and this identification accords
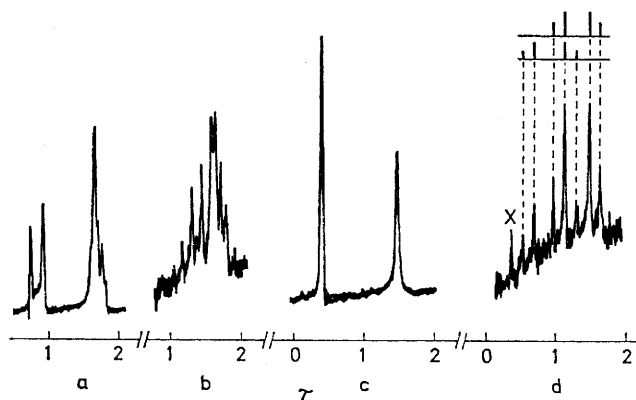

FIGURE 3 N.m.r. spectra (60 MHz) of the aromatic protons in: a 3-MeO-4-NO$_2$C$_6$H$_3\overset{+}{N}Me_3$; b 3-MeO-2-NO$_2$C$_6$H$_3\overset{+}{N}Me_3$; c the nitration product from 3-MeO-4-NO$_2$C$_6$H$_3\overset{+}{N}Me_3$; d the nitration products from 3-MeO-2-$\overset{+}{N}O_2$C$_6$H$_3$NMe$_3$. Solvent 90% H$_2$SO$_4$

with the complex 13 line spectrum of the aromatic protons (Figure 3b) and with the absence of any low field peaks for protons *ortho* to the nitro-group. The additional line X in Figure 3d corresponds to one of the peaks in the 4,6-dinitro-compound and probably derives from a trace of the 4-nitro-isomer present as an impurity. The τ values in these spectra are calculated using toluene as an external standard.

The determination of the isomer ratios in mononitration was carried out by dissolving 3-methoxyphenyltrimethyl-ammonium perchlorate (*ca.* 20 mg) in aqueous sulphuric acid (0·5 ml) in an n.m.r. tube and then adding a 13-fold excess of nitric acid (0·1 ml, 70·3%). The n.m.r. spectrum was recorded before addition of the nitric acid and then at intervals until mononitration was complete. The isomer ratios were determined by cutting out and weighing the peaks for the methoxy-protons (Figure 2aA). At least three separate determinations were made at each acidity. At concentrations of sulphuric acid >82%, the rate of dinitration is sufficiently fast to interfere with this procedure: dinitration was then allowed to proceed to completion and the original isomer proportions were calculated from the areas of the methoxy-peaks in the dinitro-compounds.

Solutions of 3,5-dimethylphenyltrimethylammonium per-

[18] G. W. Amery and J. F. Corbett, *J. Chem. Soc.* (C), 1967, 1053.

chlorate (*ca.* 0·15M) were prepared in concentrations of sulphuric acid from 70 to 95% and the n.m.r. spectra determined. A slight excess of nitric acid (70%) was then added and the n.m.r. spectra redetermined when reaction was complete. A typical result for the methyl protons is shown in Figure 2b: the two peaks for the $\overset{+}{N}Me_3$ protons (B) show that two products are formed and the peaks for the 3,5-Me$_2$ protons (C) show that these methyl groups are identical in the major product. The product ratio was calculated by integrating the peaks for the $\overset{+}{N}Me_3$ protons. The corresponding result for nitration of the 3,5-dimethyl-anilinium ion is shown in Figure 2c: the relative concentrations of the two products are here necessarily calculated from the heights of the 3,5-Me$_2$ peaks. In this region, the 4-nitro-isomer should give a singlet and the 2-nitro-isomer a doublet.

Both these substrates undergo dinitration readily in the presence of an excess of nitric acid but the above spectra were taken before significant dinitration had occurred.

Kinetics.—A solution of the substrate in aqueous sul-phuric acid (2 ml, *ca.* 2 × 10⁻⁴M) was pipetted into a spectrophotometer cell which was then weighed. The cell was allowed to reach thermal equilibrium at 25 or 30° in the spectrophotometer and then reaction was started by injecting *ca.* 0·02 ml of a solution of nitric acid in sulphuric acid followed by rapid and complete mixing. The final concentration of nitric acid was *ca.* 2 × 10⁻³M. The optical density at 325 nm was then measured as a function of time and the rate coefficient calculated in the usual way,[19] taking the infinity reading to be the optical density after 10 half-lives. After complete reaction, the cell was re-weighed and the difference used to calculate the exact amount of nitric acid added to the cell. As usual satis-factory first-order kinetics were obtained but the results proved somewhat less reproducible than in experiments on other substrates. The possibility that this could arise from nitrous acid catalysis was investigated and shown to be false.

[19] T. A. Modrc and J. H. Ridd, *J. Chem. Soc.* (*B*), 1968, 527.