203. *Kinetics and Mechanism of Aromatic Nitration. Part X.* Variation of the Rate of Aromatic Nitration in Sulphuric Acid Media with Composition of the Solvent.*

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Rates of nitration at 25° have been measured for (i) the trimethylphenylammonium ion and (ii) its *p*-chloro-derivative in sulphuric acid media containing up to 12% of water and up to 13% of sulphur trioxide, and for (iii) *p*-chloronitrobenzene in sulphuric acid media containing up to 19% of sulphur trioxide. In addition, some measurements were made on the *p*-chlorophenyltrimethylammonium ion at 35° and 45°, and activation energies and non-exponential factors of the Arrhenius equation have been calculated. The results have been interpreted as indicating (*a*) that the protonation of *p*-chloronitrobenzene plays an important part in determining its rate of nitration in oleum media, (*b*) that the formation of a hydrogen-bonded complex between *p*-chloronitrobenzene and sulphuric acid is responsible for part of the observed decrease in its rate of nitration as the medium composition is changed from 90% to 100% sulphuric acid, and (*c*) that the generally observed decrease in nitration rate in passing from 90% to 100% sulphuric acid, and the increase in oleum media with increasing sulphur trioxide concentration may be attributed to a general solvent effect caused by variation in the dielectric constant of solvating power of the medium.

THE variation of the rate of aromatic nitration in sulphuric acid media was first investigated by Martinsen (*Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605), who showed for nitrobenzene that as the concentration of sulphuric acid in a sulphuric acid–water solvent is increased the rate of nitration increases to a maximum at about 90% sulphuric acid and then decreases towards 100% sulphuric acid. Other workers (Klemenc and Scholler, *Z. anorg. Chem.*, 1924, **141**, 231; Lauer and Oda, *J. pr. Chem.*, 1936, **144**, 176; Lantz, *Bull. Soc. chim.*, 1939, **6**, 280; Oda and Ueda, *Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 335; Kharasch and Westheimer, *J. Amer. Chem. Soc.*, 1946, **68**, 871; Bennett, Brand, James, Saunders, and Williams, *J.*, 1947, 474; Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955; Bonner, Bowyer, and Williams, *J.*, 1952, 3274) have confirmed that this behaviour is general for all the compounds investigated. In all cases the maximum rate is in the region of 90% sulphuric acid, although small variations occur with change of compound and temperature (cf. Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277). Aromatic nitration in oleum solvents has been little investigated, but for anthraquinone (Lauer and Oda, *loc. cit.*), nitrobenzene (Martinsen, *loc. cit.*), and 2 : 4-dinitrotoluene (Bennett *et al.*, *loc. cit.*) it has been found that the rate decreases with increasing sulphur trioxide concentration. The only case that has been reported for which the nitration rate is greater in oleum than in 100% sulphuric acid is a single experiment by Klemenc and Scholler (*loc. cit.*) using a disulphonic acid of xylene.

Westheimer and Kharasch (*loc. cit.*), Lowen, Murray, and Williams (*J.*, 1950, 3312), and Bonner, Bowyer, and Williams (*loc. cit.*) have shown that the initial increase in rate with increasing concentration of sulphuric acid in aqueous solvents is due to the increasing conversion of nitric acid into nitronium ion: $HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$. The reason for the decrease in the rate from the maximum to 100% sulphuric acid and its continued decrease in oleum is however not so clear. The theory originally proposed by Bennett *et al.* (*loc. cit.*), which involved the termolecular rate-determining stage, $RH + NO_2^+ + B = RNO_2 + BH^+$, where B is some base, was criticised by Gillespie and Millen (*loc. cit.*) and by Hughes, Ingold, and Reed (Part II, *J.*, 1950, 2400), and was definitely shown to be incorrect by Melander (*Nature*, 1949, **163**, 499; *Arkiv Kemi*, 1950, **2**, 211), who found that tritium is displaced from tritium-substituted toluenes at the same rate as hydrogen is displaced from unsubstituted toluene.

The present work describes a further investigation of the causes of the decrease in the

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* Part IX, *J.*, 1952, 28.

rate of nitration on passing from 90% to 100% sulphuric acid and its continued decrease in oleum. It was recognised at the outset that two main factors would have to be considered: first, that many aromatic compounds, and in fact all those that had previously been used in investigating nitration, have weakly basic properties and undergo protonation or form hydrogen-bonded complexes with sulphuric acid, and secondly, that there would probably be a general solvent effect due to changes in the dielectric constant, ionic strength, or solvating power of the solvent with changes in its composition (Gillespie and Millen, *loc. cit.*; Hughes, Ingold, and Reed, Part II, *loc. cit.*).

In order to eliminate the effect of the basicity of the aromatic compound, two substances were chosen for study, namely, the trimethylphenylammonium ion and its *p*-chloro-derivative, which are incapable of undergoing protonation. The rate of nitration of these substances has been measured in sulphuric acid media containing up to 12% of water and up to 13% of sulphur trioxide. For comparison, a similar study has been made of *p*-chloronitrobenzene in media containing up to 19% of sulphur trioxide in which it is known to undergo protonation.

Measurements on the rate of nitration of *p*-chloronitrobenzene and the trimethylphenylammonium ion in aqueous sulphuric acid solvents have recently been reported by Bonner, James, Lowen, and Williams (*loc. cit.*), and by Bonner, Bowyer, and Williams (*loc. cit.*), and a few measurements on the *p*-chlorophenyltrimethylammonium ion and *p*-chloronitrobenzene in 89·8% sulphuric acid have been made by Brand and Paton (*J.*, 1952, 281). No previous measurements have been made on these compounds in oleum.

EXPERIMENTAL

The two quaternary ammonium ions were used in the form of their nitrates (the hydrogen sulphates are inconveniently hygroscopic). Nitric acid is liberated and nitration commences immediately upon dissolution in the sulphuric acid medium. The rate of reaction was measured by analysing the reaction mixture, at known time intervals, for nitric acid.

Materials.—Trimethylphenylammonium nitrate. The iodide, prepared from dimethylaniline and methyl iodide, was converted into the nitrate in aqueous solution by the action of silver nitrate. Silver iodide was filtered off, and excess of silver precipitated with hydrogen sulphide. The filtrate was evaporated to dryness, and then dissolved in the minimum amount of hot absolute alcohol. Addition of excess of acetone caused white needles of the salt to separate on cooling; m. p. 119·5°.

p-Chlorophenyltrimethylammonium nitrate was prepared similarly and after recrystallisation from hot absolute alcohol had m. p. 195°.

p-*Chloronitrobenzene.* The commercial material was recrystallised several times from absolute alcohol until almost colourless; m. p. 83°.

Nitric acid was prepared as described by Hughes, Ingold, and Reed (*loc. cit.*).

Reaction media. Aqueous media were prepared from "AnalaR" 98% sulphuric acid by addition of water or oleum. Oleum media were prepared by distillation of sulphur trioxide from a commercial oleum into 98% "AnalaR" sulphuric acid. 100% Sulphuric acid was prepared by addition of water to a dilute oleum until the maximum freezing point was reached.

Aqueous media were analysed by titration against standard sodium hydroxide solution, and oleum media by titration with water (Brand, *J.*, 1946, 585).

Rate Measurements.—For the quaternary ammonium nitrates a weighed quantity of the salt was added to a known amount of the medium at thermostat temperature, and after ½ minute's shaking the solution was transferred to a three-necked reaction vessel equipped with a stirrer and immersed in the thermostat. The time of starting the reaction was taken as that when the salt first came into contact with the acid. The initial temperature rise caused by the heat of solution of the salt was minimised by using a low concentration of the salt, namely, 0·025M.

In the case of chloronitrobenzene equal volumes of separate solutions of nitric acid and chloronitrobenzene were made up at thermostat temperature. To start the reaction, the contents of the flask containing the chloronitrobenzene solution were transferred to the reaction vessel, a definite time of draining being allowed. Then the nitric acid solution was added, and the same time of draining allowed. The start of the reaction was taken as 15 seconds after commencing to add the nitric acid solution.

Small portions of the reaction mixture were withdrawn from the reaction flask at suitable time intervals and analysed for nitric acid. The 5-ml. pipette used had a fairly rapid delivery and had been calibrated for delivery of the different media used at the temperature of the thermostat.

Analytical Method.—The determination of nitric acid was carried out by Treadwell and Vontobel's method (*Helv. Chim. Acta,* 1937, **20**, 573; cf. Bennett, Brand, James, Saunders, and Williams, *loc. cit.*).

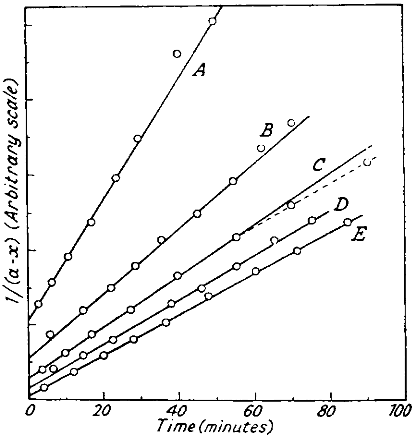
RESULTS AND DISCUSSION

For each of the three compounds the experimental results show that over the whole of the solvent composition range investigated the reaction is of the second order for given initial reactant concentrations, the rate being given by the equation

$$-d[HNO_3]/dt = k_2[ArH][HNO_3]$$

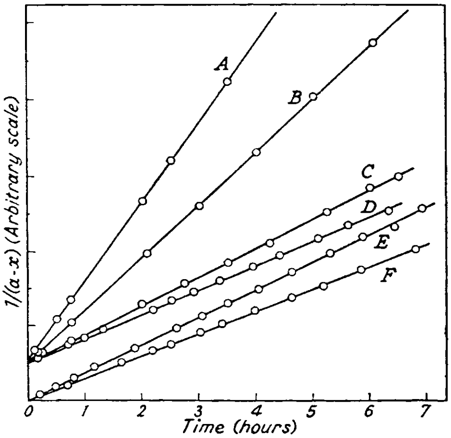
where $[HNO_3]$ is the stoicheiometric concentration of nitric acid. A selection of the results of individual experiments is given in Figs. 1, 2, and 3. In Figs. 1 and 2, $1/[HNO_3]$ is plotted against time for a number of experiments with the two quaternary ammonium ions, and in Fig. 3 log $\{[HNO_3]/[p\text{-}ClC_6H_4{\cdot}NO_2]\}$ is plotted against time for a number of experiments with *p*-chloronitrobenzene. In each case a straight line is obtained, showing that the reaction is of the second order. The mean second-order rate constants, k_2, from duplicate experiments at each solvent composition are listed in Table 1, and the variation of k_2 with the solvent composition is shown graphically in Figs. 4 and 5. The values of k_2 for *p*-chloronitrobenzene and nitrobenzene in 87—97% sulphuric acid, included in Figs. 4 and 5 for comparison, have been obtained from the results of Bonner, James, Lowen, and Williams (*loc. cit.*) and of Bonner, Bowyer, and Williams (*loc. cit.*). The value for nitrobenzene in 100% sulphuric acid is due to Martinsen (*loc. cit.*).

FIG. 1. *Individual nitrations of the trimethylphenylammonium ion.*



A, 93·00% H_2SO_4. *B*, 97·22% H_2SO_4.
C, 6·56% SO_3. *D*, 98·94% H_2SO_4.
E, 2·79% SO_3.

FIG. 2. *Individual nitrations of the* p-*chlorophenyltrimethylammonium ion.*



A, 90·25% H_2SO_4. *B*, 94·65% H_2SO_4.
C, 98·7% H_2SO_4. *D*, 4·21% SO_3.
E, 8·05% SO_3. *F*, 2·87% SO_2.

In the strongest oleum solvents used the nitration was accompanied by a slow sulphonation, particularly with the trimethylphenylammonium ion. The occurrence of sulphonation was apparent from a curvature of the graphs, shown in Figs. 1, 2, and 3, towards the time axis, particularly near the end of the run. No rate constants have been recorded in this paper for runs for which the plots were not linear over the major portion of their length and from which the rate constant was not readily determined. The values of k_2 for the higher oleum concentrations may, however, be too low by several units %.

The variation of the rate of nitration with the solvent composition in sulphuric acid–water solvents for both the trimethylphenylammonium ion and its *p*-chloro-derivative is very similar to the behaviour of all other compounds previously investigated, there being a maximum rate at approximately 90% sulphuric acid. Our values for the trimethylphenylammonium ion agree excellently with those of Bonner, Bowyer, and Williams (*loc. cit.*). The behaviour of the quaternary ammonium ions in oleum solvents, however, differs markedly from that of *p*-chloronitrobenzene and other compounds that have been studied in that the rate increases with increasing concentration, whereas for other compounds it has been generally found to decrease.

The observed decrease in the rate of nitration of the trimethylphenylammonium ion and its *p*-chloro-derivative on change from 90% to 100% sulphuric acid makes it quite clear that the basicity of the aromatic molecule cannot be completely or even largely responsible for this generally observed behaviour; some other factor affecting both basic and non-basic molecules must be responsible. However, the observation that the rate of nitration of *p*-chloronitrobenzene decreases markedly on increasing the sulphur trioxide concentration in an oleum medium, whereas the rate of the quaternary ammonium ions actually increases strongly suggests that in these media the basicity of the chloronitrobenzene is an important factor. A nitro-group is generally considered to deactivate the aromatic nucleus less than a quaternary ammonium group —$\overset{+}{N}R_3$, and hence *p*-chloronitro-

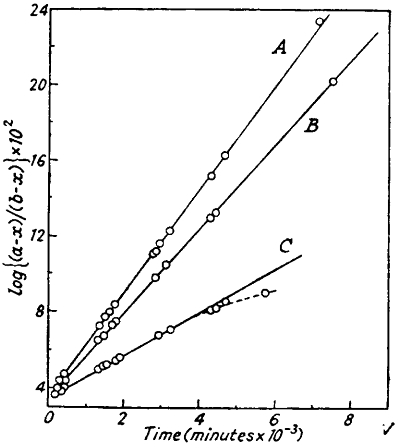
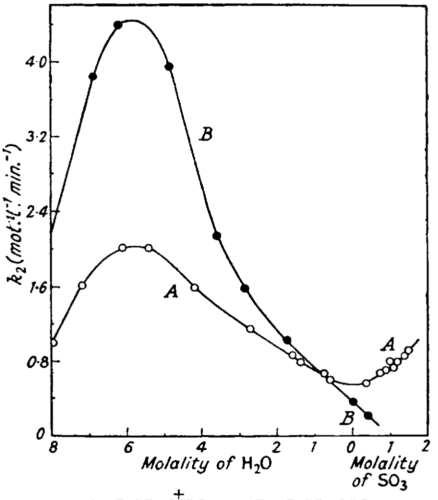


FIG. 3. *Individual nitrations of* p-*chloronitrobenzene.*

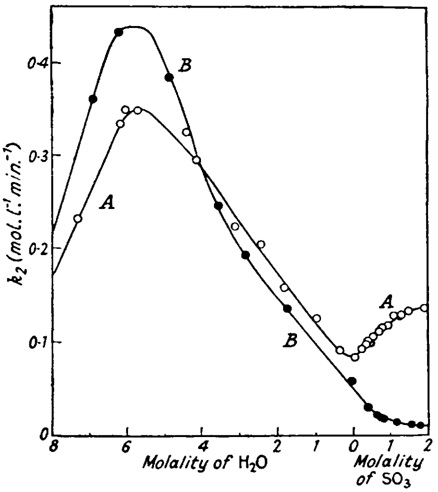
A, 2·8% SO_3.
B, 6·01% SO_3.
C, 12·48% SO_3.

FIG. 4. *Influence of medium composition on the rate of nitration of nitrobenzene and the trimethylphenylammonium ion at* 25°.



A, $C_6H_5{\cdot}\overset{+}{N}Me_3$. *B*, $C_6H_5{\cdot}NO_2$.

FIG. 5. *Influence of medium composition on the rate of nitration of* p-*chloronitrobenzene and the* p-*chlorophenyltrimethylammonium ion at* 25°.



A, p-$ClC_6H_4{\cdot}\overset{+}{N}Me_3$. *B*, p-$ClC_6H_4{\cdot}NO_2$.

TABLE 1. *Influence of medium composition on rates of nitration at 25°.*

(*a*) Trimethylphenylammonium ion (initial concn. of $C_6H_5\cdot\overset{+}{N}Me_3\}NO_3^-$ = 0·0250M).

Medium			Medium			Medium			Medium		
H_2SO_4, %	Molality of H_2O	k_2 *	H_2SO_4, %	Molality of H_2O	k_2 *	SO_3, %	Molality of SO_3	k_2	SO_3, %	Molality of SO_3	k_2
87·45	7·87	0·99	95·34	2·72	1·15	2·79	0·36	0·57	7·96	1·08	0·74
88·55	7·18	1·62	97·22	1·59	0·87	5·50	0·73	0·68	8·65	1·18	0·80
90·13	6·08	2·08	97·59	1·37	0·80	6·56	0·88	0·71	9·92	1·35	0·87
91·11	5·42	2·05	98·88	0·76	0·67	7·48	1·01	0·80	10·33	1·44	0·92
93·00	4·18	1·58	98·94	0·60	0·60						

(*b*) *p*-Chlorophenyltrimethylammonium ion (initial concn. of *p*-$ClC_6H_4\cdot\overset{+}{N}Me_3\}NO_3^-$ = 0·025M).

88·42	7·27	0·231	94·68	3·12	0·223	0·52	0·065	0·084	6·27	0·84	0·116
90·07	6·13	0·333	95·84	2·42	0·205	1·84	0·24	0·093	7·00	0·94	0·119
90·25	6·00	0·348	96·87	1·80	0·159	2·87	0·37	0·098	8·05	1·09	0·123
90·76	5·65	0·348	98·35	0·94	0·126	3·19	0·42	0·102	9·20	1·16	0·130
92·71	4·36	0·324	99·41	0·34	0·092	3·60	0·44	0·101	9·38	1·29	0·130
93·12	4·10	0·295				4·21	0·55	0·107	9·78	1·35	0·131
						5·35	0·71	0·112	10·58	1·48	0·135
						6·21	0·83	0·117	13·10	1·88	0·138

* k_2 is given throughout in the units mol. $l.^{-1}$ $min.^{-1}$.

(*c*) *p*-Chloronitrobenzene (initial concn. of *p*-$ClC_6H_4\cdot NO_2$ and HNO_3 = 0·0240—0·0270M).

Medium					Medium				
SO_3, %	Molality of SO_3	k_2	k_2'	k_2''	SO_3, %	Molality of SO_3	k_2	k_2'	k_2''
0·00	0·00	0·0577	0·065	0·070	6·01	0·80	0·0189	0·091	0·051
2·80	0·36	0·0296	0·083	0·059	8·35	1·14	0·0154	0·108	0·050
3·06	0·40	0·0288	0·086	0·059	10·93	1·54	0·0114	0·113	0·050
4·75	0·62	0·0215	0·084	0·051	12·46	1·78	0·0097	0·115	0·044
5·38	0·71	0·0206	0·088	0·053	14·63	2·14	0·0076	0·119	0·033
5·56	0·73	0·0202	0·090	0·053	19·67	3·06	0·0040	—	0·033

benzene would be expected to be nitrated more rapidly than the *p*-chlorophenyltrimethylammonium ion, and in fact in aqueous sulphuric acid media up to 82% H_2SO_4 it is nitrated more rapidly. However, it can be seen from Fig. 5 that in oleum, for all concentrations of sulphur trioxide, *p*-chloronitrobenzene is nitrated the more slowly. This is in accord with our suggestion that the *p*-chloronitrobenzene is at least partly protonated under these conditions, since the protonated nitro-group might reasonably be expected to be more deactivating than the trimethylammonium group.

It is possible to calculate the rate constants for un-ionised *p*-chloronitrobenzene in oleum media if one knows the degree of ionisation of the *p*-chloronitrobenzene at different solvent compositions, and assumes that the rate of nitration of the protonated molecule is negligible compared with that of the free base. Unfortunately, although there is little doubt that *p*-chloronitrobenzene is ionised in oleum, available information about its degree of ionisation is not very precise. It was first studied spectroscopically by Brand (*J.*, 1950, 997), who obtained a value for pK_a of $-11{\cdot}49$. This value in conjunction with the value of the acidity function H_0 for the solvent, which was also determined spectroscopically by Brand, enables the degree of ionisation of the *p*-chloronitrobenzene to be calculated from the equation $H_0 = pK_a + \log[B]/[BH^+]$. In a recent paper on the ionisation of various aromatic nitro-compounds, Brand, Horning, and Thornley (*J.*, 1952, 1374) used an improved method of obtaining the ionisation ratios from the spectroscopic results, and gave the slightly modified value for *p*-chloronitrobenzene of $pK_a = -11{\cdot}56$, and very considerably modified values of the acidity function H_0. As has been pointed out by Brand, Horning, and Thornley (*loc. cit.*), the basicities of various nitro-compounds determined spectroscopically differ markedly in many cases from the values obtained cryoscopically in 100% sulphuric acid (Gillespie, *J.*, 1950, 2542). We defer to a later paper discussion of the estimates of the basicity of *p*-chloronitrobenzene and its degree of ionisation in oleum media, but here we merely state that, partly because of the better agreement with the cryoscopic results, we consider the earlier estimates of the degree of ionisation of *p*-chloronitrobenzene and other nitro-compounds made by Brand (*loc. cit.*)

to be the more nearly correct. We have in any case calculated the rate constants for un-ionised *p*-chloronitrobenzene, using both sets of spectroscopic data. The values of k_2' calculated from Brand's data (*loc. cit.*) are given in col. 4 of Table 1(*c*), and the values of k_2'' calculated on the basis of Brand, Horning, and Thornley's data (*loc. cit.*) are given in col. 5. Both sets of values are also shown graphically in Fig. 6.

It is at first sight somewhat surprising that the rate constants for un-ionised *p*-chloronitrobenzene should be smaller that those for the *p*-chlorophenyltrimethylammonium ion in all the oleum media investigated, since the nitro-group is generally less deactivating than the trimethylammonium group. This can, however, be adequately accounted for if it is assumed that un-ionised *p*-chloronitrobenzene molecules are not present as " free " molecules but in the form of hydrogen-bonded complexes with sulphuric acid (Gillespie and Millen, *loc. cit.*), since the hydrogen-bonded nitro-group would be expected to be more deactivating than the " free " nitro-group, and it could plausibly be slightly more deactivating than the trimethylammonium group. Support is lent to this explanation by the fact that although, as may be seen in Fig. 4, in 90% sulphuric acid the rate of nitration of *p*-chloronitrobenzene is 1·3 times that of the *p*-chlorophenyltrimethylammonium ion, yet the two rates are equal in approximately 94% sulphuric acid, and at higher concentrations of sulphuric acid *p*-chloronitrobenzene is nitrated the more slowly.

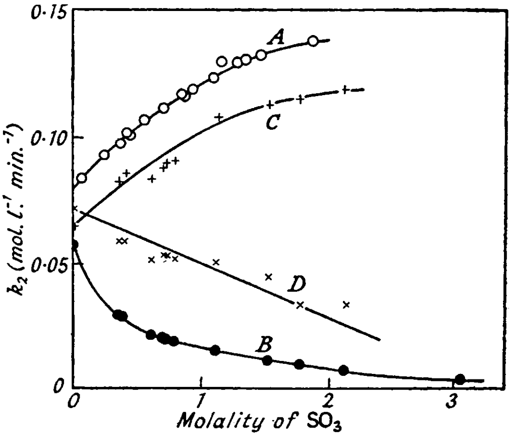


FIG. 6. *The rates of nitration of the* p-*chlorophenyltrimethylammonium ion,* p-*chloronitrobenzene, and un-ionised* p-*chloronitrobenzene in oleum solvents at* 25°.

A, $p\text{-ClC}_6\text{H}_4\cdot\overset{+}{\text{N}}\text{Me}_3$.
B, $p\text{-ClC}_6\text{H}_4\cdot\text{NO}_2$.
C, $k_2'(p\text{-ClC}_6\text{H}_4\cdot\text{NO}_2)$.
D, $k_2''(p\text{-ClC}_6\text{H}_4\cdot\text{NO}_2)$.

Now it is certain from Brand's spectroscopic measurements (*loc. cit.*) that at the solvent composition at which the reversal of rates occurs *p*-chloronitrobenzene is almost completely un-ionised and it cannot therefore be attributed to protonation of the nitro-group. It may, however, be reasonably attributed to an increasing formation of a hydrogen-bonded complex of *p*-chloronitrobenzene with sulphuric acid with increasing sulphuric acid concentration in the medium. If this explanation is correct it follows that all compounds with basic properties should exhibit a more rapid decrease in rate between 90% and 100% sulphuric acid than non-basic compounds, which should all show approximately the same decrease. Table 2 gives the ratios of the rates of nitration of a number of compounds in 95% and in 100% sulphuric acid at 25° calculated from the results of the present work or those of Martinsen (*loc. cit.*) or Lauer and Oda (*loc. cit.*). It may be seen that the value of this ratio is 2·5 for the two non-basic quaternary ammonium ions, and is larger for all the other basic compounds with the single exception of 2 : 4-dinitrophenol. The behaviour of this compound remains unaccounted for and merits further study.

It has been stated (Bonner, James, Lowen, and Williams, *loc. cit.*) that the relative rates of nitration of certain compounds do not vary greatly with medium composition. However, it has already been pointed out (Gillespie and Millen, *loc. cit.*) that this is not generally true, and in view of the above considerations concerning the formation of hydrogen-bonded complexes it would not be expected to be true except perhaps for non-basic compounds. Table 3 gives the values of the rate ratios of three pairs of closely related compounds, and it may be seen that only the ratio of the rates of the two non-basic quaternary ammonium ions remains constant over the whole solvent composition range. The other two ratios decrease on change from 89% to 100% sulphuric acid, which is consistent with the increasing formation of a hydrogen-bonded complex by the basic compound. In oleum media the ratios of the rates of un-ionised *p*-chloronitrobenzene and the *p*-chlorophenyltrimethylammonium ion are constant, suggesting that in these media *p*-chloronitrobenzene is present entirely in the form of a hydrogen-bonded complex with sulphuric acid.

TABLE 2. *Variation of nitration rate with solvent composition at 25°.*

Compound	$\frac{k\ (95\%\ H_2SO_4)}{k\ (100\%\ H_2SO_4)}$	Ref.
Benzoic acid	>18	M
Benzenesulphonic acid	~11	M
Anthraquinone	7	L and O
Nitrobenzene	4·1	Fig. 4, this paper
p-Chloronitrobenzene	3·8	,, 5, ,,
o-Chloronitrobenzene	3·3	M
2 : 4-Dinitroanisole	3·2	M
4 : 6-Dinitro-*m*-xylene	2·9	M
m-Chloronitrobenzene	2·8	M
Trimethylphenylammonium ion	2·5	Fig. 4, this paper
p-Chlorophenyltrimethylammonium ion	2·5	,, 5, ,,
2 : 4-Dinitrophenol	2·2	M

References : M, Martinsen (*loc. cit.*); L and O, Lauer and Oda (*loc. cit.*).

TABLE 3. *Rate ratios at 25°.*

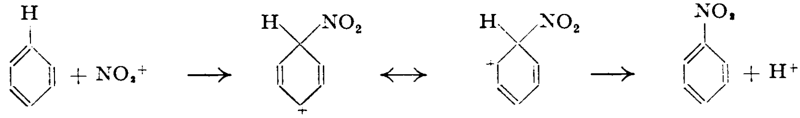
Medium		$\frac{k(ClC_6H_4{\cdot}NO_2)}{k(ClC_6H_4{\cdot}\overset{+}{N}Me_3)}$	$\frac{k(C_6H_5{\cdot}NO_2)}{k(C_6H_5{\cdot}\overset{+}{N}Me_3)}$	$\frac{k(C_6H_5{\cdot}\overset{+}{N}Me_3)}{k(ClC_6H_4{\cdot}\overset{+}{N}Me_3)}$
H_2SO_4, %	Molality of H_2O			
89·0	6·87	1·32	2·1	6·5
90·0	6·17	1·29	2·22	6·0
92·0	4·83	1·15	2·14	5·6
94·0	3·55	0·96	1·55	5·4
96·0	2·32	0·97	1·53	5·6
97·0	1·72	0·88	1·41	5·6
98·0	1·13	0·83	—	5·7
99·0	0·57	0·76	—	5·8
100·0	0·00	0·77 *	1·15 †	6·0
SO_3, %	Molality of SO_3			
2·0	0·256	0·81 *	—	5·9
4·0	0·523	0·77 *	—	5·7
6·0	0·797	0·77 *	—	5·6
8·0	1·084	0·84 *	—	5·6
10·0	1·388	0·83 *	—	6·5
12·0	1·708	0·85 *	—	—

* Calculated from the rate constants k_2' for the un-ionised molecule.

† Calculated from the corrected rate constant for the un-ionised molecule.

Brand and Paton (*J.*, 1952, 281) have recently studied the effect of *p*-substituents on the relative rate of nitration of $C_6H_5{\cdot}NO_2$ and $C_6H_5{\cdot}\overset{+}{N}Me_3$. The relative velocities were mostly measured competitively, and, in order that the rates should in all cases be readily measurable, they used two different temperatures (18° and 25°), and different solvent compositions. The comparison of the results obtained under these different conditions was justified on the grounds that relative rates of nitration are approximately independent of the medium composition and of temperature. The first assumption has been shown above to be incorrect, and there seems to be little experimental evidence for the second. For example, Brand and Paton give the value of 1·1 for the ratio $k(p\text{-}ClC_6H_4{\cdot}NO_2)/k(p\text{-}ClC_6H_4{\cdot}\overset{+}{N}Me_3)$ in 90·7% sulphuric acid and 1·22 in 89·8% sulphuric acid. Reference to the rate ratios listed in Table 3, however, shows that this ratio actually decreases from 1·32 in 89% sulphuric acid to 0·77 in 100% sulphuric acid. Similarly for the ratio $k(C_6H_5{\cdot}NO_2)/k(C_6H_5{\cdot}\overset{+}{N}Me_3)$ Brand and Paton found values of 1·7 and 1·9 in 90·7% sulphuric acid, whereas in Table 3 it may be seen that the ratios decrease from 2·2 in 89·0% sulphuric acid to 1·15 in 100% sulphuric acid. It would seem, therefore, that Brand and Paton's comparisons are not justified and their theoretical interpretation cannot therefore be completely correct. It is essential to measure the rate ratios over a wide solvent composition range, and to take into account the formation of hydrogen-bonded complexes by any compounds containing basic groups such as the nitro-group. Thus, from the data of Table 2 it may safely be concluded that the effect of the introduction of a *p*-chlorine into the trimethylphenylammonium ion is to reduce its rate of nitration six times. On the other hand, it is difficult to estimate the effect of replacing a nitro-group by a trimethylammonium group, since the deactivating influence of the nitro-group is modified by hydrogen bonding to an extent that depends on the composition of the solvent.

The previous considerations have shown that if the effects due to the behaviour of the aromatic compound as a base are eliminated, then the rate of nitration decreases as the concentration of sulphuric acid is increased from 90%, passes through a minimum at 100% sulphuric acid, and then increases with increasing sulphur trioxide concentration in oleum. The behaviour of all the compounds investigated is quite similar, and similar compounds show almost exactly identical behaviour, as is shown, *e.g.*, by the constancy of the ratio of the rates of nitration of the trimethylphenylammonium ion and its *p*-chloro-derivative from a solvent composition of 90% sulphuric acid to 10% sulphur trioxide. It is reasonable therefore to seek an explanation of this dependence of rate on the solvent composition in terms of a general solvent effect. The nitration reaction involves a spreading of the charge, originally concentrated in the nitronium ion, over the aromatic nucleus in the transition state :



and hence, by the general theory of solvent effects, it may be predicted that it will be accelerated by decreasing the dielectric constant of the solvent. Now there are reasons for believing that sulphuric acid has a very high dielectric constant (Gillespie, Hughes, and Ingold, *J.*, 1950, 2473) : a recent somewhat indirect determination made by Brand, James, and Rutherford (*J. Chem. Phys.*, 1952, **20**, 530) has given a value of 110. Because of their tendency to be solvated, ionic solutes may be said to exert a structure-breaking effect on the liquid and hence they would be expected to decrease the dielectric constant. Moreover, the solvent molecules solvating the ions will be bound so tightly as largely to lose the freedom of rotation that they possess in the pure liquid and thus will be unable to orientate in an electric field. For this reason also the addition of an ionic solute to sulphuric acid is likely to decrease its dielectric constant. It is known that electrolytes generally decrease the dielectric constant of water (Collie, Hasted, and Ritson, *ibid.*, 1948, **16**, 1) which is a very similar type of solvent to sulphuric acid, although probably not so highly associated. Thus, although the dielectric constants of sulphuric acid–water mixtures have not yet been determined because of considerable experimental difficulties, it seems reasonable to suppose that addition to sulphuric acid of either water or sulphur trioxide, both of which produce ions, will cause a decrease in the dielectric constant and hence, according to the argument above, an increase in the rate of nitration, as is observed experimentally.

We may alternatively consider the problem of the solvent effect in terms of solvation, assuming that it is due to a variation in the solvating power of the solvent as its composition is changed. Solvation will affect both the energy and the entropy of activation of the reaction. Let us consider the former first. Since the change in the initial state of the reaction is more localised than in the transition state, presumably the solvation of the transition state will be less and hence its energy of solvation smaller. If we can now assume that the solvating power of the solvent is a maximum at the composition of sulphuric acid and decreases as either water or sulphur trioxide is added (Hughes, Ingold, and Reed, Part II, *loc. cit.*), then the energy of activation will decrease accordingly. Changes in the entropy of activation being temporarily ignored, this will lead to a maximum rate of nitration at the composition of sulphuric acid, as is observed experimentally.

For the *p*-chlorotrimethylammonium ion we have measured the rate of nitration at 35° and 45°, in addition to 25°, and at various solvent compositions, and have thus been able to obtain the corresponding energies of activation. The rate constants for 35° and 45°, which are mean values for duplicate runs, and the activation energies calculated from them, and the rates at 25°, are given in Table 4.

TABLE 4. *Variation of the rate of nitration of the* p-*chlorophenyltrimethylammonium ion with temperature* (log $k = Ae^{-E/RT}$).

Medium :	k_2				Medium :	k_2			
H_2SO_4, %	35°	45°	E	$10^{-9}A$	SO_3, %	35°	45°	E	$10^{-9}A$
90·25	0·827	1·92	16·3	4·3	1·8	0·233	0·582	17·5	6·8
94·65	0·580	1·41	17·0	9·3	7·9	0·296	0·676	15·8	0·68
98·70	0·313	0·753	17·4	9·5					

It was found that for each solvent composition used the activation energy plot, *i.e.*, log k_2 against $1/T$, showed a marked curvature, the trend being in the direction of lower energies of activation at higher temperatures. Thus the energies of activation and A factors given in Table 4 are mean values for the temperature range 25—45°. It may be seen from Table 4 that the activation energy actually does pass through a maximum at, or near, the composition H_2SO_4.

Let us now consider the effect of solvation on the entropy of activation. If we assume that 100% sulphuric acid has a maximum solvating power, if solvation causes a decrease in the total entropy of the solution, and if we assume as before that the transition state is less solvated than the reactants, then a maximum entropy of activation and hence a maximum A factor would be expected in the anhydrous acid, and lower values in aqueous sulphuric acid or oleum. The values given in Table 4 for the *p*-chlorophenyltrimethylammonium ion show that in fact the A factor does pass through a maximum at, or near, the composition 100% sulphuric acid.

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