626. *Nitration in Sulphuric Acid. Part VIII.* Kinetics of Nitration of the Trimethylphenylammonium Ion.*

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The rates of nitration of the trimethylphenylammonium ion (put in as nitrate or methosulphate) have been measured in 100—82% sulphuric acid solutions. The velocity coefficient for nitration has a maximum value in 90·4% sulphuric acid; and, in a given medium, it varies with initial concentration in a qualitatively predictable manner.

The variation of the nitration velocity coefficient in 90—82% sulphuric acid can be correlated with the carbinol acidity function J_0 or directly with results for the extent of ionisation of 4 : 4′ : 4″-trinitrotriphenylcarbinol in the same medium range. The correlation suggests that diminution in the extent of ionisation of nitric acid to nitronium ion is the major factor which causes a 200-fold diminution of the nitration velocity coefficient in this medium range.

The nitration of 2 : 4-dinitrotoluene to 2 : 4 : 6-trinitrotoluene at 60—120° in sulphuric acid–water media (Bennett, Brand, D. M. James, Saunders, and Williams, Part IV, *J.*, 1947, 474) is accompanied by oxidation processes which convert about 40% of the initial nitric acid into nitrous acid at 90°, though without using more than about 3% of the 2 : 4-dinitrotoluene. As shown in Part IV, the nitration reaction can be separated analytically from the simultaneous oxidation, of which the relative extent decreases with falling temperature. Although 2 : 4-dinitrotoluene itself would be nitrated inconveniently slowly at temperatures at which oxidation would be negligible, other compounds can be nitrated at 25° without the complication of a simultaneous oxidation reaction. Detailed experiments have been made with nitrobenzene, *p*-chloronitrobenzene, and the trimethylphenylammonium ion (Bonner, M. E. James, Lowen, and Williams, *Nature*, 1949, **163**, 955). All three compounds are nitrated at an accessible speed at 25° without detectable formation of nitrous acid. The nitration of the trimethylphenylammonium ion has two special features: (*a*) nitration by the nitronium ion is a reaction between two positively charged ions; this circumstance may possibly be expected to give rise to special features in the nitration kinetics; (*b*) the formation of a conjugate acid of the aromatic substance, through proton uptake by the substituent group, is excluded. With some compounds the formation of a conjugate acid may complicate the reaction kinetics in strongly acid media (cf., *e.g.*, Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277), though, in the light of recent measurements of basic strengths of aromatic nitro-compounds in sulphuric acid media (Brand, *J.*, 1950, 997; Gillespie, *ibid.*, p. 2542), it seems unlikely that formation of the actual conjugate acid can affect the nitration results in 99—85% sulphuric acid, for those nitro-compounds which are nitrated *at measurable speeds* in this medium range, since the extent of their ionisation becomes very small in media containing less than 99% sulphuric acid. However, the results for the nitration of 2 : 4-dinitrotoluene in oleum media (Part IV, *loc. cit.*) require correction for salt formation by the aromatic compound.

The nitration of the trimethylphenylammonium ion has been carried out by using, as starting materials, both trimethylphenylammonium nitrate (the reagents then being automatically present in equivalent concentrations, unless additional nitric acid is added) and (in order to vary initial reagent concentrations independently of one another) trimethylphenylammonium methosulphate in combination with nitric acid. The progress of reaction was followed by analysis for residual nitric acid concentration as a function of time.

The trimethylphenylammonium ion is well known to be nitrated (by concentrated nitric acid at 100°) exclusively in the *m*-position (Vorländer and Siebert, *Ber.*, 1919, **52**, 283). The present work shows that, for given initial reactant concentrations in a specified medium, the rate of nitration (in sulphuric acid at 16—35°) is given by the equation

$$-\mathrm{d}[\mathrm{HNO_3}]/\mathrm{d}t = k_2[\mathrm{NMe_3Ph^+}][\mathrm{HNO_3}] \quad \ldots\ldots \quad (1)$$

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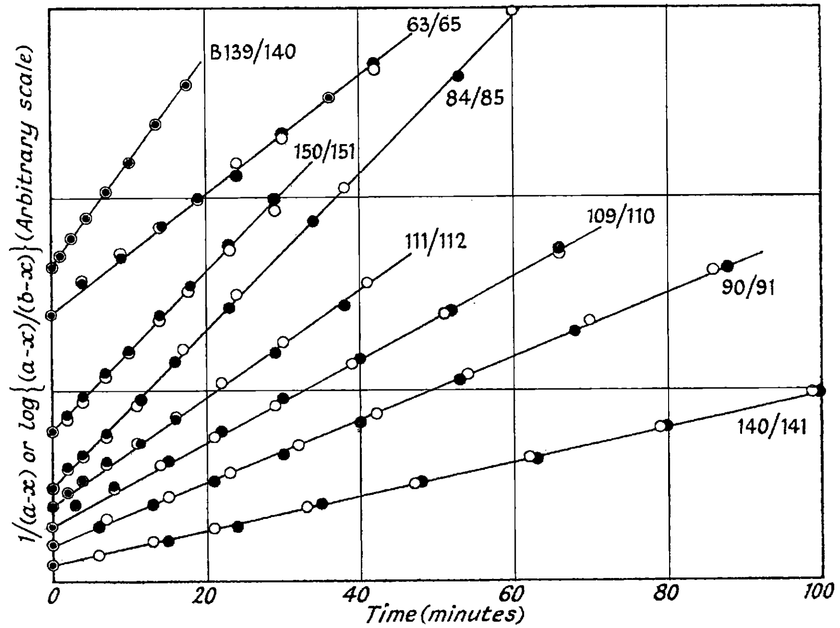
* Part VII, *J.*, 1950, 3318.

in which $[HNO_3]$ represents the stoicheiometric total concentration of nitric acid. The validity of equation (1) is demonstrated in Fig. 1, which shows linear graphs of $1/[HNO_3]$ plotted against time for reactions in which trimethylphenylammonium nitrate was present alone, and linear graphs of $\log\{[HNO_3]/[NMe_3Ph^+]\}$ for reaction mixtures containing unequal reagent concentrations. The results in Fig. 1 are for different initial conditions, which may be read from the tables; and they also show the reproducibility of duplicate experiments.

Influence of Medium Composition.—The results of velocity measurements in different sulphuric acid–water mixtures are shown in Table 1. The general form of the influence of medium composition upon rate of nitration is the same as that observed for the nitration of 2 : 4-dinitrotoluene. At 25°, the nitration of the trimethylphenylammonium ion is fastest in a medium composed of 90·4% of sulphuric acid and 9·6% of water. Nitrobenzene and *p*-chloronitrobenzene have their maximum nitration rate in the same medium at 25° (*Nature, loc. cit.*).

FIG. 1. *Course of individual nitrations.*



Nitration in Media Less Acid than the Optimum.—For nitric acid, $NO_2{\cdot}OH$, ionising according to equation (2)

$$NO_2{\cdot}OH + 2H_2SO_4 \rightleftharpoons NO_2^+ + OH_3^+ + 2HSO_4^- \quad . \quad . \quad . \quad (2)$$

and for a triarylcarbinol indicator, R·OH, ionising according to a similar equation (cf., *e.g.*, Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644), we may write (Lowen, Murray, and Williams, Part VII, *loc. cit.*) :

$$pK_{NO_2\cdot OH} - pK_{R\cdot OH} = \log\frac{[NO_2^+]}{[NO_2{\cdot}OH]} - \log\frac{[R^+]}{[R{\cdot}OH]} + \log\left\{\frac{f_{NO_2^+}}{f_{NO_2\cdot OH}}\cdot\frac{f_{R\cdot OH}}{f_{R^+}}\right\} \quad . \quad (3)$$

in which the K's are thermodynamic equilibrium constants for equilibria of type (2).

If the logarithmic term in activity coefficients in (3) is zero for the medium range considered (see Part VII, *loc. cit.*), then

$$[NO_2^+]/[NO_2{\cdot}OH] = b[R^+]/[R{\cdot}OH] = bR \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which b is independent of medium composition, and $R = [R^+]/[R{\cdot}OH]$.

An acidity function, J_0, for ionisation of type (2), may be defined by equation (5) * (see Part VII, *loc. cit.*) :

$$J_0 = -\mathrm{p}K_{\mathrm{NO_2 \cdot OH}} - \log ([\mathrm{NO_2}^+]/[\mathrm{NO_2 \cdot OH}]) \quad . \quad . \quad . \quad . \quad (5)$$

or by the equivalent definition $J_0 = H_0 + \log a_{\mathrm{H_2O}}$ (Gold and Hawes, *J.*, 1951, 2102), where H_0 is Hammett's acidity function.

Then, if the rate or nitration of an aromatic compound is given experimentally by equation (1), and theoretically by equation (6), equations (7) hold; and, from (5) and (7), equation (8) should represent the variation of the experimental velocity coefficient, k_2, with medium composition.

TABLE 1. *Influence of medium composition upon rate of nitration at* 25°

(Initial concentration of $\mathrm{NMe_3Ph^+\}NO_3^-}$ = 0·0252 ± 0·0002M.)

Medium : H_2SO_4, wt. %	Expt. no.	k_2, min.$^{-1}$	k_2, mean	Medium : H_2SO_4, wt. %	Expt. no.	k_2, min.$^{-1}$	k_2, mean	R *	$(1 + 0·56R)k_2/R$
100	24	0·51	0·51	90·8	82	2·03	2·03		
	23	0·50			83	2·03			
99·6	149	0·531	0·53	90·6	92	2·07	2·07		
	148	0·534			93	2·07			
99·5	123	0·555	0·56	90·3	84	2·06	2·06		
	124	0·555			85	2·06			
98·8	68	0·64	0·64	90·1	101	2·05	2·05	2·63	1·93
98·3	88	0·70	0·71		102	2·05			
	89	0·71		89·4	86	1·91	1·92	1·78	2·17
97·5	91	0·81	0·82		87	1·92			
	90	0·82		88·4	100	1·59	1·60	1·00	2·44
96·6	38	0·93	0·94		99	1·60			
	56	0·95		88·3	103	1·44	1·44	0·871	2·46
95·6	118	1·11	1·12		104	1·44			
	120	1·13		87·9	72	1·27	1·27	0·646	2·68
94·7	117	1·27	1·30	87·5	143	0·98	0·99	0·501	2·52
	119	1·32			142	0·99			
93·8	69	1·46	1·46	86·5	140	0·444	0·446	0·219	2·29
91·9	70	1·86	1·88		141	0·448			
	73	1·90		86·0	74	0·343	0·343	0·148	2·50
91·4	77	1·92	1·94	85·9	162	0·286	0·287	0·132	2·33
	80	1·96			163	0·287			
91·0	94	2·01	2·03	84·7	B110	0·106	0·106	0·0575	1·90
	95	2·05		82·0	B111	0·0101	0·0103	(0·0078) †	(1·33) †
					B112	0·0104			

* For trinitrotriphenylcarbinol.

† In 82·0% sulphuric acid the indicator $(p\text{-X}\cdot\mathrm{C_6H_4})_3\mathrm{C\cdot OH}$ ($\mathrm{X = NO_2}$) is only 0·78% ionised and the colorimetric measurement of its ionisation is liable to error. Calculated from the J_0 function and results for the indicator with $\mathrm{X = NMe_3^+}$ (Murray and Williams, *loc. cit.*), $R = 0·0071$ and $(1 + 0·56R)k_2/R = 1·46$.

$$-\mathrm{d}[\mathrm{HNO_3}]/\mathrm{d}t = k_2^{\circ}[\mathrm{NO_2}^+][\mathrm{ArH}] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$k_2 = k_2^{\circ}[\mathrm{NO_2}^+]/[\mathrm{HNO_3}] = k_2^{\circ}[\mathrm{NO_2}^+]/\{[\mathrm{NO_2}^+] + [\mathrm{NO_2 \cdot OH}]\} \quad . \quad . \quad (7)$$

$$\log k_2 = \log k_2^{\circ} - \mathrm{p}K_{\mathrm{NO_2 \cdot OH}} - J_0 - \log\{1 + [\mathrm{NO_2}^+]/[\mathrm{NO_2 \cdot OH}]\} \quad . \quad . \quad (8)$$

For media in which $[\mathrm{NO_2 \cdot OH}] \gg [\mathrm{NO_2}^+]$, equation (8) reduces to equation (9) :

$$\log k_2 = \log k_2^{\circ} - \mathrm{p}K_{\mathrm{NO_2 \cdot OH}} - J_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Provided that k_2° of equation (6) does not itself vary with medium, equation (9) predicts that $\log k_2$ should be connected with J_0 by a straight line of negative unit gradient.

By this test, equation (9) has been verified in Part VII (*loc. cit.*) for the nitration of the trimethyl-*p*-tolylammonium ion in 76—82% sulphuric acid, whereby the hypothesis of nitration by the $\mathrm{NO_2}^+$ ion has been shown to be preferable to that of a nitrating agent (*e.g.*, $\mathrm{H_2NO_3}^+$) formed from nitric acid by simple proton uptake (cf. Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871). In more acid media, the condition $[\mathrm{NO_2 \cdot OH}] \gg [\mathrm{NO_2}^+]$ no longer holds, equation (9) is invalid, and equation (8) must be used.

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* $K_{\mathrm{NO_2 \cdot OH}}$ is here defined in terms of the ratio $a_{\mathrm{NO_2}^+}/a_{\mathrm{NO_2 \cdot OH}}$ and not of its reciprocal (see Gold and Hawes, *loc. cit.*).

Since the medium range 82—90% sulphuric acid for nitration of the trimethylphenylammonium ion falls within the medium range of variable ionisation of a single indicator, namely 4 : 4′ : 4″-trinitrotriphenylcarbinol (Westheimer and Kharasch, *loc. cit.*; Murray and Williams, *J.*, 1950, 3322; see fifth column of Table 1), it is convenient, instead of (8), to use (10), derived from (7) and (4) :

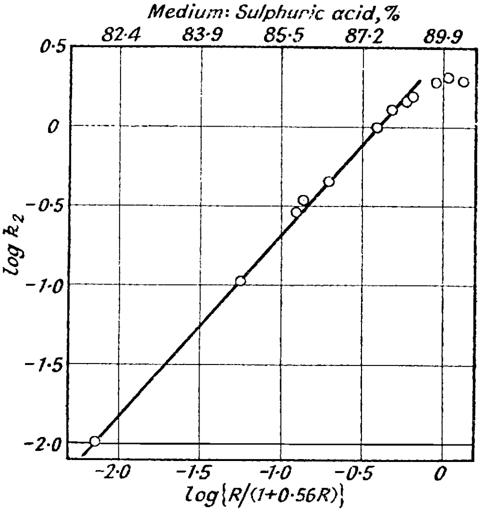
$$\log k_2 = \log k_2{}^{\circ} + \log b + \log\{R/(1 + bR)\} \quad . \quad . \quad . \quad . \quad (10)$$

It has been shown previously (Bonner and Williams, *Chem. and Ind.*, 1951, 820) that, for the medium range 86—89·5% sulphuric acid, the results of Table 1 satisfy the equation derived from (1), (6), and (4) :

$$1/R = k_2{}^{\circ}b/k_2 - b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

with the constants $b = 0{\cdot}56$, $k_2{}^{\circ} = 4{\cdot}3$ (whence the degree of ionisation of nitric acid to the nitronium ion can be estimated). With this value of b, $\log k_2$ is plotted against $\log\{R/(1 + bR)\}$ in Fig 2. The straight line drawn has a gradient of 1·1, which may be compared with the unit gradient demanded by equation (10) if b and $k_2{}^{\circ}$, defined by (4) and (6) respectively, remain sensibly constant over the medium range considered. From Fig. 2, the linear relation appears to hold, within experimental error, for the medium range 82·0—88·4% sulphuric acid, covering a 150-fold variation in k_2 of equation (1). In only slightly more acid media k_2 approaches its maximum value. The linear relation between $\log k_2$ and J_0, predicted by equation (9) when ionisation of nitric acid is small, fails in media more acid than 86% sulphuric acid (Part VII, *loc. cit.*). Otherwise expressed, constancy of b and $k_2{}^{\circ}$ in equation (10) requires that the ratio $(1 + bR)k_2/R$ should be independent of medium. Col. 6 of Table 1 shows how far this expectation is realised for 90—82% sulphuric acid media, in which k_2 changes 200-fold. This more sensitive test indicates that the linear log–log plot in Fig. 2 conceals a small curvature. From carbinol-indicator measurements (Part VII), b is probably constant to within 0·2 log unit over the range 80—85% sulphuric acid. From Fig. 2 and Table 1, it may be provisionally inferred, without excluding the possibility of a change in $k_2{}^{\circ}$ by a small multiple, that diminution of the degree of ionisation of nitric acid to the nitronium ion is the major factor which reduces k_2 by 200-fold in the medium range 90—82% sulphuric acid.

FIG. 2.



Nitration in Media More Acid than the Optimum.—The variation in k_2 over the medium range 100—90% sulphuric acid cannot at present be treated quantitatively (cf. Hughes, Ingold, and Reed, *J.*, 1950, 2400). The absence of an isotope effect in aromatic nitration (Melander, *Nature*, 1949, **163**, 499; *Arkiv Kemi*, 1950, **2**, 211), recently confirmed (unpublished experiments) under the conditions of kinetic experiments for nitrobenzene and deuteronitrobenzene, is evidence against the hypothesis of basic catalysis by bisulphate ion (Part IV, *loc. cit.*).

Influence of Reagent Concentrations.—Increase of initial concentration of either reagent causes increase of anion concentration in the system. From the observed influence of water upon the nitration rate (Table 1), it may therefore be expected that rise of initial reagent concentration should increase or decrease k_2 in media more acid or less acid respectively than the optimum. Table 2 shows that these expectations are realised qualitatively. The effects are barely accessible to experiments with trimethylphenylammonium nitrate, because initial heat effects (see Experimental section) forbid any substantial increase of initial concentration; but they are seen clearly in experiments with the methosulphate. Quantitative aspects will be considered in later papers, together with results for other compounds. In media more aqueous than the optimum for nitration, the addition of various substances to the medium produces an apparent lowering of the (colorimetric) extent of ionisation of a triarylcarbinol indicator and thus (if the effect is real) should affect the extent of ionisation of nitric acid to nitronium ion. The effects of added substances upon the apparent ionisation of an indicator can be correlated with their effects upon speed of nitration (unpublished experiments).

TABLE 2. *Variation of initial reactant concentrations at 25°.*

Medium :	Expt.	Initial concn. (M) of :		k_2,
H_2SO_4, %	no.	NMe_3Ph^+	HNO_3	min.$^{-1}$
100 *	B182	0·0502	0·0301	0·483
	B183	0·0502	0·0301	0·482
	B184	0·300	0·0300	0·728
	B185	0·300	0·0302	0·725
	B186	0·500	0·0300	0·843
	B187	0·500	0·0302	0·873
	B214	2·457	0·0299	0·712
97·4 *	B137	0·0495	0·0298	0·835
	B138	0·0500	0·0303	0·822
	B139	0·1003	0·0305	0·915
	B140	0·1000	0·0305	0·911
	B141	0·200	0·0304	1·00
	B142	0·200	0·0301	1·01
	B143	0·300	0·0303	1·06
	B144	0·300	0·0302	1·08
	B145	0·401	0·0306	1·19
	B146	0·401	0·0304	1·22
96·6 †	38	0·0251	0·0251	0·93
	56	0·0251	0·0251	0·95
	60	0·0253	0·0503	0·99
	64	0·0254	0·0755	0·98
	63	0·0255	0·1004	0·95
	65	0·0251	0·1003	0·95
	58	0·0504	0·0504	1·00
	34	0·0501	0·0501	1·00
88·3 †	103	0·0252	0·0252	1·44
	104	0·0253	0·0253	1·44
	113	0·0252	0·0485	1·42
	114	0·0250	0·0484	1·45
	111	0·0504	0·0504	1·41
	112	0·0504	0·0504	1·39
88·2 *	B170	0·0504	0·0312	1·33
	B180	0·0503	0·0310	1·36
	B168	0·302	0·0312	0·518
	B169	0·302	0·0312	0·510
86·7 *	B162	0·0499	0·0301	0·414
	B164	0·0503	0·0302	0·410
	B163	0·0998	0·0302	0·298

* Expts. with trimethylphenylammonium methosulphate.
† Expts. with trimethylphenylammonium nitrate.

TABLE 3. *Variation of temperature.*

Medium :		Expt.	Initial concn. (M) of :		k_2,
H_2SO_4, %	Temp.	no.	NMe_3Ph^+	HNO_3	min.$^{-1}$
100 *	15°	B250	0·0501	0·0300	0·209
	25	B251	0·0500	0·0300	0·557
	35	B249	0·0503	0·0298	1·25
87·5 †	15·92°	156	0·0254	0·0254	0·479
	15·92	157	0·0252	0·0252	0·481
	24·96	Mean from Table 1			0·985
	35·00	150	0·0254	0·0254	2·01
	35·00	151	0·0252	0·0252	2·05
99·6 †	15·92°	154	0·0252	0·0252	0·225
	15·92	155	0·0252	0·0252	0·227
	19·97	158	0·0253	0·0253	0·346
	19·97	159	0·0252	0·0252	0·344
	24·96	Mean from Table 1			0·533
	29·96	160	0·0254	0·0254	0·821
	29·96	161	0·0252	0·0252	0·821
	35·00	152	0·0252	0·0252	1·21
	35·00	153	0·0252	0·0252	1·21

* Expts. with trimethylphenylammonium methosulphate.
† Expts. with trimethylphenylammonium nitrate.

The effects of adding potassium hydrogen sulphate to reaction mixtures resemble (qualitatively at least) those of change of initial concentration of the aromatic salt.

Influence of Temperature.—Results at different temperatures are shown in Table 3. Over the small temperature range of 20°, the graph of log k_2, plotted against $1/T$, is linear for 87·5% sulphuric acid medium and corresponds to $k_2 = 1{\cdot}05 \times 10^8 \exp.-13{,}390/\boldsymbol{R}T$ litre mole^{-1} sec.$^{-1}$. The results for 99·6% sulphuric acid medium correspond roughly to the equation $k_2 = 1{\cdot}4 \times 10^9 \exp.-15{,}300/\boldsymbol{R}T$ litre mole^{-1} sec.$^{-1}$; but the graph of log k_2 against $1/T$ shows a distinct curvature, giving a maximum range for E of 14·9—16·3 kcal. In 100% sulphuric acid E appears to range from 14·7 ± 0·6 to 16·8 ± 0·6 kcal. at 15—35°.

EXPERIMENTAL

Materials.—Trimethylphenylammonium iodide (made in 96% yield from methyl iodide and dimethylaniline, m. p. after recrystallisation from absolute alcohol 216—218°, decomp.) was converted into the nitrate by the action of aqueous silver nitrate, excess of silver being removed with hydrogen sulphide. The nitrate, obtained by evaporation to dryness, was recrystallised from a solution in the minimum quantity of hot absolute alcohol to which was then added about twelve times the volume of hot dry acetone. The nitrate separated on cooling; m. p. 119—119·5° (Found: C, 54·2; H, 7·1; N, 14·0. Calc. for $C_9H_{14}O_3N_2$: C, 54·5; H, 7·1; N, 14·1%). Vorländer and Siebert (*Ber.*, 1919, **52**, 283) give m. p. 110—115° for the nitrate recrystallised from alcohol–ether.

Trimethylphenylammonium methosulphate was made from dimethylaniline and dimethyl sulphate in dry benzene; it separated out as it was formed, and was recrystallised from a small amount of absolute alcohol. Crystallisation could be accelerated, if desired, by addition of a large volume of dry acetone. It had m. p. 121° (Found: C, 49·1, 49·0; H, 7·2, 7·1; N, 5·5, 5·5; S, 12·8, 12·6. Calc. for $C_{10}H_{17}O_4NS$: C, 48·6; H, 6·9; N, 5·7; S, 13·0%).

Pure nitric acid and other inorganic materials were obtained as described in Part IV (*loc. cit.*).

Nitration Media.—Sulphuric acid–water mixtures were prepared by adding water or redistilled oleum to 98% sulphuric acid. Corresponding media containing nitric acid were obtained by addition of anhydrous nitric acid (freshly distilled from sulphuric acid). Analysis was by alkali titration coupled with ferrous sulphate titration of nitric acid. For example, a medium was found to contain 96·45, 96·56, 96·60, 96·58, mean 96·55%, of sulphuric acid, giving the mol. ratio $H_2O/H_2SO_4 = 0{\cdot}195$. The corresponding nitric acid solution contained total acid 0·01962, 0·01959, 0·01959, 0·01958 equiv./g., and nitric acid 4153, 4145, 4137 × 10^{-7} mole/g., giving mol. ratio $H_2O/H_2SO_4 = 0{\cdot}193$.

Alkali was standardised against 1N-hydrochloric acid, itself standardised gravimetrically or referred to standard potassium iodate or sodium carbonate.

100% Sulphuric acid was prepared by adjusting 98% sulphuric acid to maximum freezing point by the addition of sulphur trioxide.

Velocity Measurements.—Temperature was controlled to ±0·02° and measured on an N.P.L. calibrated thermometer. Most of the velocity measurements were made at 25° (more exactly 24·96°). Solutions were made up to known volumes at thermostat temperature and combined in such a way that the weight of each component of the reaction mixture (including weight of solvent) was always known. The reaction vessel was a three-necked flask carrying a thermometer and a mercury-sealed electric stirrer. Before transference to this vessel, the reagents were pre-mixed in a flask with standard socket neck by addition of the second component from a container with standard cone neck.

When trimethylphenylammonium nitrate was used, 0·245—0·250 g. of the solid salt was added to 50 ml. of medium in the pre-mixing flask, thus starting the nitration. When required, nitric acid was incorporated in the medium to give a higher initial concentration than that provided by the salt alone. With trimethylphenylammonium methosulphate, either 25 ml. of nitric solution were added to 25 ml. of salt solution, or, later, a small volume of more concentrated nitric acid solution was added to 50 ml. of medium containing the aromatic salt and, sometimes, an added inorganic salt or other compound when the effects of these upon nitration rate were to be investigated.

The starting time of the reaction was always taken as the instant at which the reagents came together. Pre-mixing and transfer to the reaction vessel (with stirrer already in operation) required 40—50 seconds with the nitrate and 10—15 seconds with the methosulphate.

The temperature rose by 0·4—0·7° when the solid nitrate salt was added to sulphuric acid; and the temperature of the reaction mixture was observed at one-minute intervals. Normally, the temperature of the reaction mixture came to within 0·05° of that of the thermostat in about 5 minutes and to within 0·02° in about 8 minutes. The total time of observation for a reaction varied from 20 to 240 minutes, being frequently of the order 100 minutes. From the known activation energies, the errors in the velocity coefficients caused by the initial temperature fluctuations were calculated to be not more than 1%. Thermal disturbances were minimised by working with only 0·025M-reagents; and initial errors of all kinds were eliminated as far as possible by evaluating velocity coefficients graphically. Initial temperature rise in the reaction mixture was always much less when it was prepared from the solution of the methosulphate salt.

Analysis of Reaction Mixtures.—5-Ml. samples were extracted at intervals in pipettes calibrated to deliver the reaction media employed with a standard delivery time, including drainage, of 25 sec. (*e.g.*, a pipette delivered 4·92 ± 0·02 ml. for 87·8—100% sulphuric acid). The samples were run into 30 ml. of ice-cold concentrated sulphuric acid, and their nitric acid content was determined by titration against M/20-ferrous sulphate solution in 40% sulphuric acid (preserved under nitrogen), Treadwell and Vontobel's potentiometric method (*Helv. Chim. Acta*, 1937, **20**, 573; cf. Part IV) being used. The titration was carried out under nitrogen, with mechanical stirring. The ferrous sulphate solution was run in from a 10-ml. micro-burette, and the end-point of the titration was marked by a sharp increase of potential of 200—300 mv for the addition of 0·02—0·03 ml. of reagent, provided that the sulphuric acid content at the end of the titration lay between 80 and 95%. This was ensured by adjustment, when necessary. Standardisation of a ferrous sulphate solution against (*a*) potassium nitrate dissolved in 96% sulphuric acid, (*b*) aqueous potassium nitrate, and (*c*) potassium permanganate, gave its concentration as (*a*) 0·0504, (*b*) 0·0508, (*c*) 0·0505N.

Some preliminary experiments were made on the reverse method of running nitrate into excess of standard ferrous sulphate, and observing the potentiometric end-point. The following was a test of the reverse titration: 5-ml. portions of approximately M/5-ferrous sulphate solution in 40% sulphuric acid were run into 40 ml. of concentrated sulphuric acid and titrated by running in M/10-potassium nitrate solution (in 40% sulphuric acid) from the burette to the end-point, which was marked by a drop in potential of about 150 mv, not quite so sharply defined as in the commoner forward titration. Volumes required were: 4·71, 4·70, 4·65, 4·66, 4·76, 4·63, 4·65, 4·68, mean 4·68 ml. From these results, 1 ml. of the potassium nitrate solution was equivalent to 1·07 ml. of ferrous sulphate solution, which may be compared with 1·06 ml. obtained by the forward titration. The reverse titration was not used for velocity measurements.

Absence of Nitrous Acid in Reaction Products.—2-Ml. samples of reaction mixture containing initially 0·025M-trimethylphenylammonium nitrate were run into 10 ml. of approx. N/20-chloramine-T solution, diluted to 100 ml.; and the solutions were titrated, by use of potassium iodide and sodium thiosulphate, with the following results:

(i) Medium: 87·5% sulphuric acid.

Time (min.)	14	23	34	45	60	78
Titre (ml.)	11·71	11·79	11·79	11·76	11·70	11·68

(ii) Medium: 99·6% sulphuric acid.

Time (min.)	15	41	70	92	110
Titre (ml.)	11·76	11·71	11·71	11·75	11·72

The blank titration for 10 ml. of chloramine-T solution after addition of 2 ml. of sulphuric acid, containing no aromatic nitrate, was 11·70 ml. Evidently, no nitrous acid is formed in the reaction.

Results.—Unless otherwise stated, times are given in minutes. One experiment is given in full below.

Expt. 91. Temp. 25·0°. Initial concn. of nitrate salt = 0·0254M. Medium: 97·5% H_2SO_4.

Time, min.	0	6	13	21	30	40	53	68	88
Concn. of HNO_3, M	0·0254	0·0223	0·0199	0·0177	0·0158	0·0139	0·0122	0·01055	0·0091
Change, %	—	12·2	21·8	30·4	37·8	45·1	52·0	58·5	64·5
k_2	—	0·91	0·84	0·82	0·80	0·81	0·81	0·82	0·81

k_2 from linear plot (Fig. 1) = 0·81.

The reproducibility of the velocity measurements may be judged from Fig. 1.

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