646. *Nitration in Sulphuric Acid. Part VI. Nitration of the Trimethyl-*p*-tolylammonium Ion in 75—85% Sulphuric Acid.*

By Gwyn Williams and Ailsa M. Lowen.

Compounds containing an activated aromatic nucleus may be rapidly nitrated by nitric acid–sulphuric acid–water mixtures, containing more than 50 moles % of water, in which the nitronium ion has not been detected spectroscopically. In order to examine a compound of this kind, rates of nitration of the trimethyl-*p*-tolylammonium ion (structurally analogous to *p*-nitrotoluene) have been measured in 75—82% H_2SO_4 between 17·5° and 45°. At 25°, the rate of nitration rises very rapidly in media stronger than 80% H_2SO_4 and approaches zero asymptotically at about 75% H_2SO_4. Vapour-pressure evidence indicates that the $NO_2{\cdot}OH$ molecule is unlikely to be the nitrating agent. A decision between the $H_2NO_3^+$ and NO_2^+ ions as nitrating agents is considered in Part VII (following paper).

The nitrating activity of a mixture of nitric and sulphuric acids depends on the water content of the mixture. Hetherington and Masson (*J.*, 1933, 105) have shown that, under ordinary preparative conditions in a two-phase system at 35°, nitrobenzene is only nitrated at an appreciable rate by acids containing less than 50 moles % of water. For very small nitric acid content, the limiting condition corresponds to an equimolar medium of water and sulphuric acid (84·5% H_2SO_4). For higher nitric acid contents, Hetherington and Masson established a boundary of limiting nitrating compositions, on the aqueous side of which nitrobenzene is not nitrated. Analogous results have been found for the two-phase nitration of 2 : 4-dinitrotoluene (DNT) to 2 : 4 : 6-trinitrotoluene (TNT) at 90° (Bennett, Brand, D. M. James, Saunders, and Williams, Part V, *J.*, 1947, 1185; *idem*, with Dine, Fysh, McClelland, and Wiseman, *J. Soc. Chem. Ind.*, 1947, **66**, 288). With mixtures containing 2—15% nitric acid the yields in two-phase batch nitrations fall towards zero as the mole ratio H_2O/H_2SO_4 rises to unity. In kinetic experiments, carried out with small concentrations of reagents dissolved in sulphuric acid–water mixtures of different compositions, the rate of nitration of dinitrotoluene at 90° falls sharply towards small values as the mole ratio H_2O/H_2SO_4 for the medium rises towards unity (Part IV, *J.*, 1947, 474); and the same is true for the nitration of nitrobenzene, *p*-chloronitrobenzene, and the trimethylphenylammonium ion at 25° (Bonner, M. E. James, Lowen, and Williams, *Nature*, 1949, **163**, 955). The accepted interpretation of these facts is that the above-mentioned substances are only nitrated by the nitronium (NO_2^+) ion, one argument being (Bennett, Brand, and Williams, Part I, *J.*, 1946, 869) that Hetherington and Masson's line of limiting nitrating acid compositions which fail to nitrate nitrobenzene nearly coincides with a locus of acid compositions (Chédin, *Ann. Chim.*, 1937, **8**, 243) in which the Raman line characteristic of the nitronium ion is just detectable.

On the other hand, benzene (Lewis and Suen, *Ind. Eng. Chem.*, 1940, **32**, 1095) and toluene (McKinley and White, *Trans. Amer. Inst. Chem. Eng.*, 1944, **40**, 143) can be nitrated in a two-phase system by nitrating acids whose compositions lie outside Hetherington and Masson's boundary; and the nitration of mono- to di-nitrotoluene is often conducted with similar nitrating acids. The experiments shown in Table I have been carried out to illustrate this point. The initial acid composition for Experiment 3 lies approximately on the boundary; yet the compound is completely nitrated.

It is clear, therefore, that benzene, toluene, and *p*-nitrotoluene can be nitrated by acids in which the nitronium ion has not yet been detected spectroscopically. The entity which nitrates these compounds under the usual conditions is therefore not known.* It may be the neutral nitric acid molecule $NO_2{\cdot}OH$, or the nitracidium ion $H_2NO_3^+$ (Halberstadt, Hughes, and Ingold, *Nature*, 1946, **158**, 514), or it may be the nitronium ion present in very small concentration.

TABLE I.

Nitration of 25 *g.* (0·18 *mole*) *of* p-*nitrotoluene by* 0·22 *mole of* HNO_3 *in mixed acids of varying composition.*

Nitration no.	1.		2.		3.	
	Wt. %	Mole fraction	Wt. %	Mole fraction	Wt. %	Mole fraction
H_2SO_4	81·6	0·602	77·6	0·501	72·0	0·402
HNO_3	11·7	0·133	11·6	0·116	11·5	0·100
H_2O	6·7	0·265	10·8	0·388	16·4	0·497
Mole H_2O/H_2SO_4 ratio, initial	0·44		0·77		1·24	
Mole H_2O/H_2SO_4 ratio, final, calc.	0·62		0·95		1·44	
Yield (%) of $(NO_2)_2C_6H_3{\cdot}CH_3$	92·8% *		98·3%		99·6%	

* The slightly lower yield in experiment 1 is fortuitous.

Kinetics of Nitration in 75—85% *Sulphuric Acid.*—Hammett has pointed out (" Physical Organic Chemistry," New York, 1940, p. 277) that kinetic data for reactions are lacking in sulphuric acid–water media in a range intermediate between fairly concentrated sulphuric acid and dilute aqueous acid. No kinetic results for nitration are available for media in the range 75—85% sulphuric acid. The choice of a compound for investigation in this range presents some difficulty, though guidance is furnished by the results of Martinsen (*Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605). To be suitable a compound must not only have a measurable nitration velocity in this range of media; but it must also be soluble enough to permit reasonable variation of its concentration. Many substances show a solubility minimum in this range of sulphuric acid–water mixtures (Hammett and Chapman, *J. Amer. Chem. Soc.*, 1934, **56**, 1282). We have examined a number of compounds. *p*-Nitrotoluene, the most obvious choice, has a suitable nitration velocity but limited solubility. Benzoic acid, phenylacetic acid, and sodium benzenesulphonate are rather rapidly nitrated, and also have rather unfavourable solubilities. Benzenesulphonic acid is nitrated at a suitable speed in 80% sulphuric acid and presents no solubility difficulty; but its extreme deliquescence makes it unattractive. Toluene-*p*-sulphonic acid is nitrated much too rapidly. (That benzenesulphonic acid can be nitrated rapidly in 80% sulphuric acid, and nitrobenzene only very slowly, is an illustration of the much weaker deactivating influence of the SO_3H group on substitution, compared with the NO_2 group.) The most suitable compound was found to be the trimethyl-*p*-tolylammonium ion which may be introduced as its nitrate or as its methyl sulphate (the more desirable hydrogen sulphate is too hygroscopic). The quaternary ammonium salt presents no solubility difficulty and is nitrated at a convenient rate in the media in question. It is structurally related to the trimethylphenylammonium ion in the same way as *p*-nitrotoluene is related to nitrobenzene. The NMe_3Ph^+ ion is not nitrated at all in 80% sulphuric acid at 25°. The kinetics of its nitration in 85—100% sulphuric acid have been worked out (unpublished experiments of Dr. T. G. Bonner; cf. *Nature*, 1949, *loc. cit.*).

Nitration of the Trimethyl-p-*tolylammonium Ion.*—This ion (present as nitrate) was nitrated, with nitric acid, by Vorländer and Siebert (*Ber.*, 1919, **52**, 304). The only nitration product isolated contained the nitro-group in the *ortho*-position to the methyl group. In 0·1M-concentration (with 0·1M-nitric acid) in sulphuric acid media the $p\text{-}C_6H_4Me{\cdot}NMe_3^+$ ion is (*a*) completely nitrated in less than 1·75 minute at 0° in 98% sulphuric acid, (*b*) not nitrated in 18 hours at 5° in 70% sulphuric acid, and (*c*) not nitrated in 24 hours at room temperature in 65% sulphuric acid. The ion is nitrated at a measurable speed in 76—82% sulphuric acid at 25°. No nitrous acid is formed during the reaction at 25°, indicating that the nitration of this ion at 25° is not accompanied by oxidation.

For fixed initial conditions, the rate of nitration in a given experiment is given by the equation

$$-\mathrm{d}[HNO_3]/\mathrm{d}t = k_2[p\text{-}C_6H_4Me{\cdot}NMe_3^+][HNO_3] \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

in which $[HNO_3]$ is the stoicheiometric concentration of total nitric acid. Results, justifying

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* Westheimer and Kharasch (*J. Amer. Chem. Soc.*, 1946, **68**, 1871; cf. Part VII, following paper) have made it very probable that the nitronium ion is responsible for a slow nitration of nitrobenzene in 80% sulphuric acid. But the reagent which nitrates more active aromatic molecules at a speed one thousand times greater in the same medium, and which is also effective in more aqueous media, still needs to be identified.

FIG. 1.

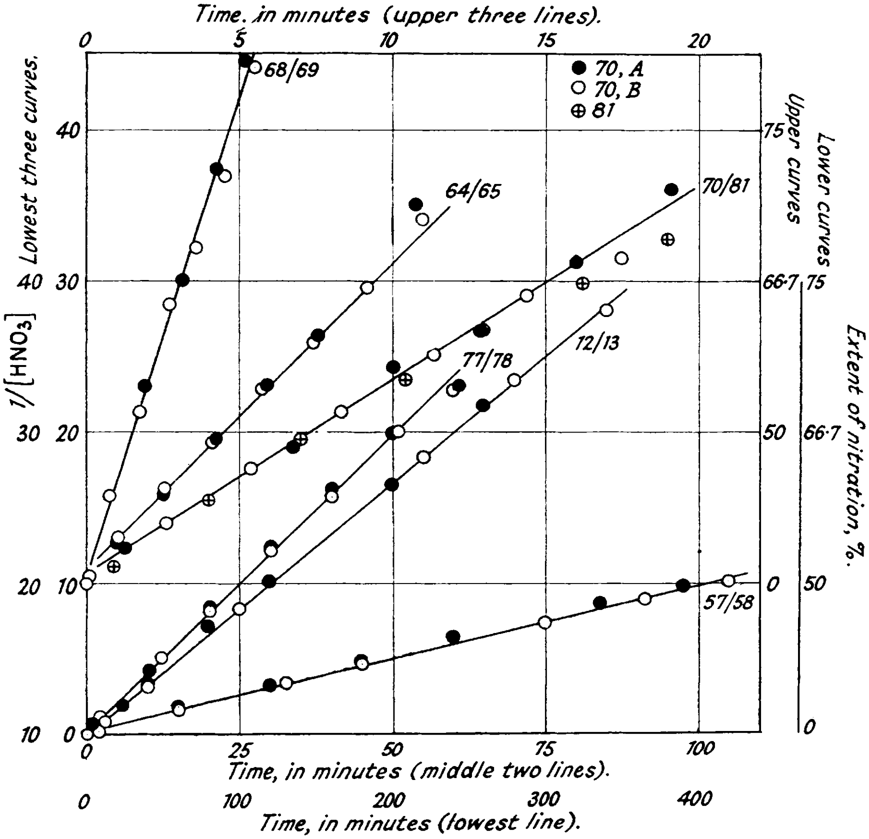
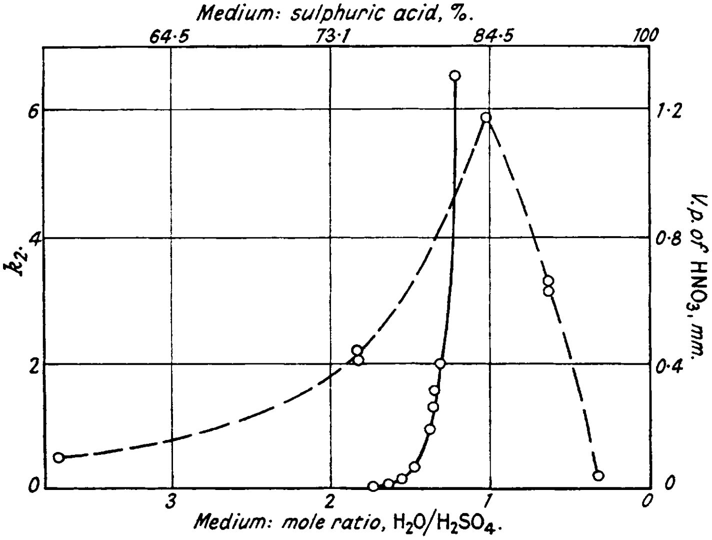

Time, in minutes (upper three lines).
0
5
10
15
20
● 70, A
○ 70, B
⊕ 81
68/69
64/65
70/81
77/78
72/13
57/58
1/[HNO3]
Lowest three curves.
40
30
20
10
Upper curves
Lower curves
75
66·7
50
0
Extent of nitration, %.
25
50
75
100
Time, in minutes (middle two lines).
0
100
200
300
400
Time, in minutes (lowest line).

FIG. 2.


Medium: sulphuric acid, %.
64·5
73·1
84·5
100
k_2.
6
4
2
0
V.p. of HNO3, mm.
1·2
0·8
0·4
0
3
2
1
0
Medium: mole ratio, H2O/H2SO4.

equation (1), are given in Fig. 1, in which $1/[HNO_3]$ is shown to be linear with time for a number of representative experiments. The rate of nitration may be measured by analysing the reaction mixture, at known time intervals, for nitric acid. Two analytical methods have been used; they give closely concordant results (see Table II and, particularly, Fig. 1, expt. 70). In most of the experiments, the reaction mixture has been made up by dissolving trimethyl-*p*-tolylammonium nitrate in the sulphuric acid medium, whereby the reagents are automatically introduced in equimolar proportions, and nitration starts immediately. We have obtained concordant results by mixing solutions of trimethyl-*p*-tolylammonium methyl sulphate and nitric acid (*e.g.*, see expts. 70 and 81 in Fig. 1). The conversion of the nitrate ion into the nitrating agent is therefore not a rate-determining step in the media employed.

TABLE II.

Temp. 25°.

Medium.						
H_2SO_4, %.	Mol. ratio H_2O/H_2SO_4.	Expt. no.	Initial concn. of ion nitrate, M.	Analyt. method.	k_2.	k_2 (mean) l. mole^{-1} min.$^{-1}$.
81·68 (*Q*)	1·220	68	0·1010	B	6·5	6·5
		69	0·1011	B	6·5	
80·58 (*P*)	1·311	64	0·1012	B	1·90	1·99
		65	0·1011	B	2·07	
80·13 (*G*)	1·350	5	0·1013	A	1·48	1·56
		6	0·1013	A	1·61	
		9	0·1013	A	1·59	
		22	0·1014	A	1·55	
80·05 (*M*)	1·355	40	0·1011	A	1·58	1·55
		46	0·1011	A	1·54	
		47	0·1011	A	1·53	
80·02 (*N*)	1·359	55	0·1011	A	1·3	1·29
		66	0·1011	B	1·27	
		67	0·1012	B	1·27	
		70	0·1012	A, B	1·28	
		71	0·1009	A, B	1·33	
		81 *	ion 0·1011 HNO_3 0·1014	B	1·27	
79·71 (*L*)	1·384	16	0·1011	A	0·931	0·938
		17	0·1010	A	0·944	
78·57 (*J*)	1·482	12	0·1010	A	0·334	0·337
		13	0·1010	A	0·333	
		41	0·1011	A	0·35	
		42	0·1011	A	0·337	
		79 *	ion 0·13 HNO_3 0·10	B	0·331	
77·75 (*K*)	1·557	18	0·1011	A	0·151	0·146
		19	0·1012	A	0·151	
		60	0·1011	B	0·141	
		61	0·1011	B	0·140	
76·83 (*O*)	1·640	62	0·1011	B	0·0593	0·0599
		63	0·1011	B	0·0604	
75·78 (*H*)	1·738	57	0·1009	B	0·0250	0·0244
		58	0·1010	B	0·0238	

* Quaternary ion introduced as methyl sulphate.

Influence of Medium Composition.—The coefficients k_2 of equation (1) are constant only for fixed initial concentrations of reactants in a specific medium. Only results for the influence of changing medium composition on k_2 are given in this paper; they are contained in Table II.

In Fig. 2 the influence of medium composition on nitration rate is compared with its influence on the vapour pressure of nitric acid over solutions of nitric acid in sulphuric acid–water mixtures. The broken line in Fig. 2 represents the vapour pressure measurements of Vandoni (*Mém. Services chim. de l'État*, 1944, **31**, 83, 87) for a fixed content of nitric acid (4·85% w/w) dissolved in media composed of water and sulphuric acid in varying molecular proportions. The partial pressure of nitric acid is always a maximum over mixtures of equal mole fraction of water and sulphuric acid (*e.g.*, compare Berl, Andress, and Escales, *Kunstoffe*, 1937, **27**, 23). From Fig. 2 it may be inferred (*a*) that the rate of nitration varies very rapidly with medium composition in a region in which the vapour pressure of nitric acid changes slowly, and (*b*) that nitration becomes very slow in media over which nitric acid still exerts a vapour pressure equal to 40% of the maximum value. If the vapour pressure can be taken as a measure of the concentration of un-ionised nitric acid in the solution, then it is unlikely that the $NO_2{\cdot}OH$ molecule can be the agent which nitrates the $p\text{-}C_6H_4Me{\cdot}NMe_3^+$ ion in 75—82% sulphuric acid media.

Influence of Temperature.—Results at different temperatures are shown in Table III; and a pair of experiments at 45° (77/78) is included in Fig. 1. The results correspond to the Arrhenius equations (2) and (3) :

Medium : 80·02% H_2SO_4,

$$k_2 = 2{\cdot}3 \times 10^8\ e^{-13,660/RT}\ \text{l.mole}^{-1}\text{sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Medium : 76·83% H_2SO_4,

$$k_2 = 8{\cdot}3 \times 10^9\ e^{-17,620/RT}\ \text{l.mole}^{-1}\text{sec}^{-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

TABLE III.

	Medium.				
Temp.	H_2SO_4, %.	Mol. ratio H_2O/H_2SO_4.	Expt. no.	Initial concn. ion nitrate, M.	k_2, l.mole^{-1}min.$^{-1}$.
35·0°	80·02 (*N*)	1·359	72	0·1010	2·85
35·0			73	0·1010	2·84
25·0			Mean from Table I		1·29
17·5			75/76	0·101	0·75
45·0	76·83 (*O*)	1·640	77	0·1010	0·384
45·0			78	0·1008	0·394
35·0			74	0·1009	0·159
25·0			Mean from Table I		0·0599

EXPERIMENTAL.

*Materials.—Trimethyl-*p*-tolylammonium nitrate.* Trimethyl-*p*-tolylammonium iodide prepared from dimethyl-*p*-toluidine and methyl iodide was converted in aqueous solution into the nitrate by the action of silver nitrate. Silver iodide was filtered off and excess of silver was removed with hydrogen sulphide. After evaporation of the filtrate, the crude quaternary nitrate crystallised out in a vacuum desiccator. The salt was recrystallised from warm ethyl alcohol and ether, and had m. p. 130—131° (Found for two samples : C, 56·4, 56·5; H, 7·5, 7·6; N, 12·8, 13·2. Calc. for $C_{10}H_{16}O_3N_2$: C, 56·6; H, 7·6; N, 13·2%). The salt is slightly hygroscopic but can be handled without elaborate precautions.

Trimethyl-p-tolylammonium picrate (Found : C, 50·8; H, 4·9; N, 14·6. Calc. for $C_{16}H_{18}O_7N_4$: C, 50·8; H, 4·8; N, 14·8%) had m. p. 195—196° (cf. Vorländer and Siebert, *loc. cit.*, m. p. 195—197°; Groenewoud and Robinson, *J.*, 1934, 1692, m. p. 193—198°).

Trimethyl-*p*-tolylammonium methyl sulphate (cf. Brand, *J.*, 1950, 997) was prepared from dimethyl-*p*-toluidine (12 g.) and methyl sulphate (11·2 g.) in benzene (25 ml.). The crystalline product separated either at once on heating or after about 40 minutes. Further heating is detrimental. The crude product was purified either by recrystallisation from a large volume of acetone or by precipitation with ether from a solution in methyl alcohol; the salt had m. p. (in open capillary) 142—143° (some decomp.) (Found : C, 51·2; H, 7·0; N, 5·2; S, 12·0. Calc. for $C_{11}H_{19}O_4NS$: C, 50·5; H, 7·3; N, 5·4; S, 12·2%). The substance is not tiresomely hygroscopic, contrary to the statement of Ullmann (*Annalen*, 1903, **327**, 111), whose product was possibly an impure quaternary sulphate or hydrogen sulphate. The methyl sulphate decomposes somewhat at about 80° with formation of free SO_4''; but it can be preserved unchanged for two months if kept cold in a desiccator.

An attempt was made to prepare trimethyl-*p*-tolylammonium sulphate; but the substance was intolerably hygroscopic.

Reaction Media.—Sulphuric acid–water media were analysed by means of potassium iodide and potassium iodate. As shown in Fig. 1, the rate of nitration is very sensitive to medium composition. The limit of accuracy in determining medium composition is illustrated by the following figures.

%H_2SO_4: Medium *Q* : 81·67, 81·70. Medium *P* : 80·54, 80·63. Medium *G* : 80·11, 80·11; after 1 month, 80·16, 80·07; after 3 months, 80·20, 80·12. Medium *K* : 77·73, 77·78; after 7 months, 77·90. Medium *H* : 75·76, 75·80; after 8 months, 75·84.

When required, solutions of nitric acid were prepared by adding pure nitric acid to the medium in question. They were analysed for nitric acid by the methods described below.

Velocity Measurements.—Reaction was started by dissolving a known weight of trimethyl-*p*-tolylammonium nitrate in a known amount of medium at thermostat temperature. Dissolution of the salt was immediate, but any uncertainty about zero time for the reaction was eliminated by graphical computation of k_2 from lines such as those in Fig. 1. 5-ml. Pipette samples were withdrawn for analysis and run into ice-cold quenching liquid—30 ml. of correctly adjusted aqueous sulphuric acid for analysis by method A, or 10—15 ml. of water for method B.

The heat of solution of the solid salt caused an initial temperature rise in the solution of as much as 1° in 82% sulphuric acid medium, falling to 0·1° or zero in 78% medium. The maximum error in k_2, due to this cause, amounts to 1—1·5% at the beginning of the reaction. Dilution of the medium by the water formed during complete nitration—with 0·1M-reagents—might lower k_2 by some 3% in those media in which nitration is at its most sensitive to water content. Sampling was not generally continued much beyond 65% nitration.

Volatility of Nitric Acid.—When dissolved in 75—85% sulphuric acid, nitric acid is probably present mainly in un-ionised form. To test for possible loss of nitric acid vapour during a nitration experiment, 0·0958M-nitric acid in 76·83% sulphuric acid was held at 45° (conditions of expts. 77/78, Table II), and was given the same sampling treatment as a normal reaction mixture. After 4 hours the nitric acid concentration fell to 0·0941M., *i.e.* by 1·8%. This was not a serious loss and could be expected to be less at 25°. There was no loss of nitric acid from a 0·1M-solution in 80% sulphuric acid, kept at 25° for 25 minutes.

Absence of Oxidation Reaction.—During the nitration of di- to tri-nitrotoluene at 90°, some dinitrotoluene is oxidised, with formation of nitrous acid. To test for a similar oxidation during nitration of the p-$C_6H_4Me{\cdot}NMe_3^+$ ion, samples of a reaction mixture in 80% sulphuric acid were analysed for nitrous acid, using chloramine-T, potassium iodide, and thiosulphate, with the following results:

Blank chloramine-T titre, ml.: 11·69, 11·65, 11·71, 11·73. Mean 11·70.

Titres (ml.) after treatment of chloramine-T with 2-ml. samples of reaction mixture: after 10 minutes' nitration, 11·79; after 25 minutes, 11·72.

Thus, no nitrous acid is formed during the nitration of the trimethyl-*p*-tolylammonium ion at 25°.

Analytical Methods.—For analysis, nitration must be stopped at a definite time in a sample of reaction mixture; and the analytical problem is then to estimate nitric acid in a solution containing a readily nitrated organic compound. The excellent method (Treadwell and Vontobel, *Helv. Chim. Acta*, 1937, **20**, 573; cf. Bennett, Brand, James, Saunders, and Williams, Part IV, *loc. cit.*) of electrometric titration of nitric acid with ferrous sulphate at 0° cannot be used, because this titration is carried out in a concentrated sulphuric acid medium, in which the aromatic compounds discussed in this paper are nitrated even more rapidly than in the original reaction mixture. We have tried to use the titration in reverse by running a sample of reaction mixture into an excess of ferrous sulphate solution and back-titrating with standard nitrate solution, but the end-point is not sharp because of further nitration of the aromatic compound as soon as the end of the titration is reached. Successful results have been obtained with two analytical methods.

Method A. This is a modification of the Treadwell–Vontobel method, devised by Mr. W. W. Jones, M.Sc., of the Explosives Research and Development Establishment, Ministry of Supply. The titration is carried out in 65% sulphuric acid solution at 50°, the organic compound not being nitrated in this medium. The sample of reaction mixture is run into 30 ml. of ice-cold aqueous sulphuric acid, adjusted to make the final medium 65% sulphuric acid. The solution is titrated with a standard solution of ferrous sulphate in 40% sulphuric acid to an electrometric end-point. We found that the first drop of ferrous sulphate added was often slow to react with the nitrate. A small crystal of pure ferric chloride, added at the beginning of the titration, removed this difficulty. The following are drawbacks of the method: (*a*) the potential jump at the end-point is only of the order of 50 mv. instead of the 200—300 mv. observed in the titration in highly concentrated sulphuric acid; (*b*) air must be excluded during the titration by bubbling a stream of carbon dioxide through the solution; since nitric acid is present mainly in the undissociated form, there is danger of some loss of nitric acid by volatilisation if the carbon dioxide stream is too fast; (*c*) the platinum electrode immersed in the solution is subject to capricious misbehaviour which does not yield to cleaning of the electrode; a bad electrode gives sloping and indefinite end-points.

Under the most favourable conditions the method has given good results: *e.g.*, 4·98 ml. of 0·0981N-potassium nitrate solution required 4·16, 4·15, 4·13, 4·18, 4·17 ml. of ferrous sulphate solution. Hence, $FeSO_4$, found = 0·2402M.; calc. = 0·2406M.

Titration in 70% sulphuric acid medium at 50—60° gave sharper, but less consistent, end-points.

Method B. This was a slight modification of the method of Kolthoff, Sandell, and Moskovitz (*J. Amer. Chem. Soc.*, 1933, **55**, 1454). Nitric acid in concentrated hydrochloric acid solution is reduced to nitric oxide by excess of standard ferrous sulphate solution at the boiling point in the absence of air, with ammonium molybdate as catalyst. Excess of ferrous sulphate is titrated with potassium dichromate.

In operation, nitration was stopped abruptly and definitively by running the sample of reaction mixture into 10—15 ml. of water. At least 50% excess of ferrous sulphate solution was added, followed by 70 ml. of concentrated hydrochloric acid and 4—5 g. of sodium hydrogen carbonate to expel air. The solution was boiled for 2 minutes to expel oxygen, and 3 ml. of a 1% solution of ammonium molybdate were added. The reaction was completed by 10 minutes' boiling. After cooling, the excess of ferrous sulphate was determined by titration with standard potassium dichromate to the electrometric "dead stop" end-point of Foulk and Bowden (*J. Amer. Chem. Soc.*, 1926, **48**, 2045), observed by having a potential difference of 15 mv. across two similar bright platinum wire electrodes dipping into the solution. At the equivalence point, when all ferrous ion had been oxidised, polarisation occurred and flow of current ceased. The end-point could be judged to 0·01 ml.

The following is an example of the titration:

(*a*) Approx. M/4-ferrous sulphate required: 10·99, 11·03, 10·95, 10·99 ml. of approx. N/10-potassium dichromate solutions. Hence, 4·99 ml. of ferrous sulphate solution are equivalent to 11·01 ml. of potassium dichromate solution. (Buffering of solutions for this titration showed no advantage.)

(*b*) 4·98 ml. of 0·0737M-potassium nitrate solution in 40% H_2SO_4, after treatment with 7·98 ml. of the ferrous sulphate solution, required : 7·23, 7·33, 7·21, 7·26, 7·30 ml. of the potassium dichromate. Hence, $FeSO_4$ = 0·2353M. Another standardisation, with 0·0987M-KNO_3 gave $FeSO_4$ = 0·2355M.

Titration by method *B* of an aqueous solution of trimethyl-*p*-tolylammonium nitrate with the standardised ferrous sulphate gave 0·4704 g.-ion of nitrate per 100 g. of salt (calc. 0·4713 g.-ion/100 g.).

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ROYAL HOLLOWAY COLLEGE (UNIVERSITY OF LONDON),
ENGLEFIELD GREEN, SURREY.

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