647. *Nitration in Sulphuric Acid. Part VII. The Nitronium Ion as Nitrating Agent in 75—85% Sulphuric Acid.*

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As pointed out by Westheimer and Kharasch, the ionisation of nitric acid to form the nitronium ion in a sulphuric acid medium is analogous to the ionisation of a triarylcarbinol indicator. The variations in degree of ionisation, as a function of medium composition, for three triarylcarbinol indicators, are shown to run parallel to one another in 65—90% sulphuric acid. The variations of ionisation also run closely parallel to the variation, with medium composition, of the logarithm of the velocity coefficient for aromatic nitration in the range 75—82% sulphuric acid. The inference is that the nitronium ion is formed in small concentration in 75—85% sulphuric acid solvent, and in sufficient concentration to act as a nitrating agent.

Independent physical evidence for the formation of the nitronium ion from nitric acid dissolved in 75—85% sulphuric acid is lacking (Part VI, preceding paper). Nevertheless, its presence as a nitrating agent may be tested for, and a distinction between the nitronium and nitracidium ions as nitrating agents may be drawn, by an extension of the indicator method, successfully employed by Westheimer and Kharasch (*J. Amer. Chem. Soc.*, 1946, **68**, 1871) to show that the nitronium ion is effective for the nitration of nitrobenzene in 80—90% sulphuric acid.

The Nitracidium Ion as Nitrating Agent.—To form the nitracidium ion, nitric acid must ionise in sulphuric acid in the way shown in equation (1):

$$NO_2{\cdot}OH + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^- \qquad (1)$$

The ionisation is a simple proton uptake by the nitric acid molecule. Consequently, by the reasoning of Hammett and Paul (*ibid.*, 1934, **56**, 830), if the nitracidium ion is the effective reagent in a nitration reaction, in a given range of sulphuric acid–water media, then log k_2 for the nitration should be related to the acidity functions H_0 of the media by a straight line of unit gradient, provided that the extent of ionisation of nitric acid is small.

The Nitronium Ion.—In concentrated sulphuric acid, nitric acid ionises according to equation (2):

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

This form of ionisation is not purely a proton uptake; and Westheimer and Kharasch (*loc. cit.*) have pointed out the analogy between equation (2) and equation (3), which applies to the ionisation of a triarylcarbinol, ROH, in concentrated sulphuric acid (Hantzsch, *Z. physikal. Chem.*, 1908, **61**, 257; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900):

$$ROH + 2H_2SO_4 \rightleftharpoons R^+ + OH_3^+ + 2HSO_4^- \qquad (3)$$

Westheimer and Kharasch went on to prove experimentally that nitration velocity coefficients in 80—90% sulphuric acid run parallel to the ionisation ratio for 4 : 4′ : 4″-trinitrotriphenyl carbinol. By using more strongly basic indicators, we have extended their method to more aqueous media. The underlying theoretical arguments are as follows. They are analogous to those of Hammett and Deyrup, and Hammett and Paul (*ibid.*, 1932, **54**, 2721, 4239; 1934, **56**, 827), for neutral bases acting by simple proton uptake.

The Ionisation of Carbinol Indicators.—Let K_R and K_S be the thermodynamic equilibrium constants, defined in terms of activities, for two carbinol indicators ROH and SOH. If the two carbinols are placed in the same sulphuric acid–water medium, in such small concentration that they do not disturb the activities of the medium constituents, then, independently of the precise form of K,

$$\mathrm{p}K_{\mathrm{R}} - \mathrm{p}K_{\mathrm{S}} = \log\frac{[\mathrm{R}^+]}{[\mathrm{ROH}]} - \log\frac{[\mathrm{S}^+]}{[\mathrm{SOH}]} + \log\left\{\frac{f_{\mathrm{R}^+}}{f_{\mathrm{ROH}}}\cdot\frac{f_{\mathrm{SOH}}}{f_{\mathrm{S}^+}}\right\} \quad . \; . \; . \; . \quad (4)$$

For proton uptake by two simple bases B and C, it has been proved that $f_{\mathrm{BH}^+}/f_{\mathrm{B}} = f_{\mathrm{CH}^+}/f_{\mathrm{C}}$ (Hammett *et al.*, *loc. cit.*; also, Hammett, " Physical Organic Chemistry," New York, 1940, p. 263). If it can be shown, for the carbinol indicators, that, similarly, $f_{\mathrm{R}^+}/f_{\mathrm{ROH}} = f_{\mathrm{S}^+}/f_{\mathrm{SOH}}$, then the term in activity coefficients in equation (4) is zero; and, since $\mathrm{p}K_{\mathrm{R}}$ and $\mathrm{p}K_{\mathrm{S}}$ are thermodynamic constants, independent of medium,

$$\log\frac{[\mathrm{R}^+]}{[\mathrm{ROH}]} - \log\frac{[\mathrm{S}^+]}{[\mathrm{SOH}]} = \text{Const. (independent of medium)} \quad . \; . \; . \; . \quad (5)$$

From the similarity of equations (2) and (3), it would then be plausible to expect equation (6) to be true :

$$\log\frac{[\mathrm{R}^+]}{[\mathrm{ROH}]} - \log\frac{[\mathrm{NO_2}^+]}{[\mathrm{NO_2{\cdot}OH}]} = \text{Const. (independent of medium)} \quad . \; . \; . \; . \quad (6)$$

The validity of equation (5) may be tested, experimentally, by plotting log ($[\mathrm{R}^+]/[\mathrm{ROH}]$) for a series of indicators against the composition of the sulphuric acid–water medium, taking care that the media used for different indicators should overlap in composition. A series of *parallel* lines should result if equation (5) is well founded.

RESULTS.

Westheimer and Kharasch (*loc. cit.*) have already examined the ionisation of 4 : 4′ : 4″-trinitrotriphenylcarbinol in 80—90% sulphuric acid. To shift the range of varying ionisation into more aqueous media, stronger bases are needed. The bases must also be soluble in moderately aqueous sulphuric acid. Both conditions are met by working with triarylcarbinol indicators carrying trimethylammonium groups as substituents, and by introducing them as perchlorates. Ionisation should be complete, in all media, at the ionic centres of the trimethylammonium groups, and the only variation of ionisation should be at the tertiary carbon atom (as in equation 3). We have used the indicators (Table I) 4 : 4′ : 4″-tris(trimethylammonium)-triphenylcarbinyl methyl ether triperchlorate (I) and 4 : 4′-bis(trimethylammonium)triphenylcarbinyl methyl ether diperchlorate (III). The methyl ethers were used owing to convenience in preparation. We have examined one of the corresponding carbinols (II) to make sure that the ionisation of the methyl ether is not anomalous. For comparison, we have also made measurements with Westheimer and Kharasch's indicator (IV).

TABLE I.

	Indicator.	Ionising in :
I	$(\mathrm{ClO_4}^-)_3\{(p\text{-}\mathrm{Me_3}\overset{+}{\mathrm{N}}{\cdot}\mathrm{C_6H_4})_3\mathrm{C{\cdot}OMe}$	78—90% H_2SO_4
II	$(\mathrm{ClO_4}^-)_3\{(p\text{-}\mathrm{Me_3}\overset{+}{\mathrm{N}}{\cdot}\mathrm{C_6H_4})_3\mathrm{C{\cdot}OH}$	78—90% H_2SO_4
III	$(\mathrm{ClO_4}^-)_2\{(p\text{-}\mathrm{Me_3}\overset{+}{\mathrm{N}}{\cdot}\mathrm{C_6H_4})_2\mathrm{CPh{\cdot}OMe}$	66—78% H_2SO_4
IV	$(p\text{-}\mathrm{NO_2{\cdot}C_6H_4})_3\mathrm{C{\cdot}OH}$	80—95% H_2SO_4

The indicators (I) and (II) are related to Crystal-violet and (III) is related to Malachite-green. The perchlorates are colourless crystalline compounds, dissolving in concentrated sulphuric acid to give orange-yellow solutions, similar to those formed by the trinitro-indicator (IV) in the same solvent.

Experimental methods of measurement, and detailed numerical results, for the indicators of Table I are given in the following paper, by Murray and Williams.

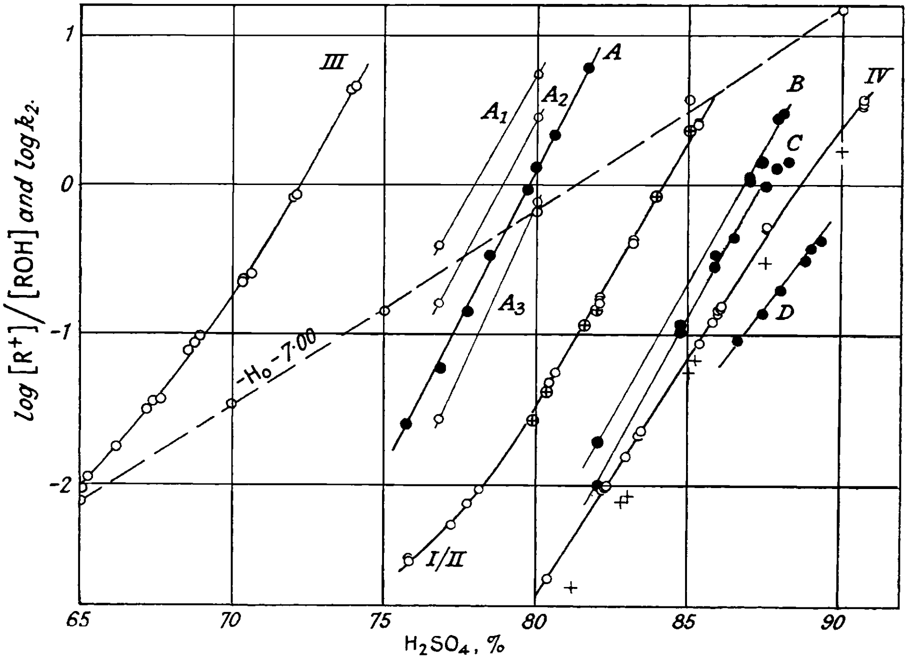
Fig. 1 of the present paper shows the plot of log ($[\mathrm{R}^+]/[\mathrm{ROH}]$) against medium composition for the four indicators. Only values of log ($[\mathrm{R}^+]/[\mathrm{ROH}]$) below +0·7 are plotted, because of the significant experimental errors at higher degrees of ionisation. The plot for each indicator is approximately a straight line; and, as expected, the results (crossed circles) for the carbinol (II) coincide with those for the methyl ether (I). In 80—85% sulphuric acid, the indicators (I) and (IV) both show accurately measurable ionisation; and within this range the lines of variation of log ($[\mathrm{R}^+]/[\mathrm{ROH}]$) for the two indicators are nearly parallel, thus justifying equation (5). This is noteworthy because indicator (I) carries three integral positive charges in addition to (but remote from) the centre of varying ionisation in sulphuric acid, whereas indicator (IV) becomes charged only at the tertiary carbon atom. The slight curvature at the low ionisation end for (I) has little significance. A trace of coloured impurity would produce a similar effect.

The results of Westheimer and Kharasch for indicator (IV) are also shown in the diagram (crosses).* The agreement between these and our own measurements is reasonable in view of the different methods of measurement employed.

The line of indicator (III) is also nearly parallel to those for (I) and (IV). Since the ionisation ranges of (III) and (I) do not overlap, this parallelism signifies only that an acidity function governing the ionisation of carbinol indicators varies almost linearly with medium composition.

The Nitronium Ion as Nitrating Agent.—Since equation (5) is justified for indicators (I) and (IV), it is reasonable to expect equation (6) to be valid.

FIG. 1.



If the rate of nitration of a compound ArH is given by

$$r = k[NO_2^+][ArH] \qquad (7)$$

$$= k[NO_2{\cdot}OH][ArH][NO_2^+]/[NO_2{\cdot}OH]$$

then

$$r \sim k[HNO_3][ArH][NO_2^+]/[NO_2{\cdot}OH] \qquad (8)$$

if the extent of ionisation of nitric acid is *small* and if $[HNO_3]$ denotes the stoicheiometric concentration of total nitric acid.

Experimentally (Part VI),

$$r = k_2[HNO_3][ArH] \qquad (9)$$

in which k_2 varies with medium composition.

From (8) and (9),

$$\log k_2 = \log k + \log([NO_2^+]/[NO_2{\cdot}OH]) \qquad (10)$$

From (10) and (6),

$$\log k_2 = \log k + \log([R^+]/[ROH]) + D \qquad (11)$$

in which D is independent of medium composition.

Provided that k is constant over the medium range examined, the variation of $\log k_2$ with medium composition should run parallel with that of $\log([R^+]/[ROH])$. The velocity coefficient

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* We are indebted to Dr. Westheimer and Professor Kharasch for making available to us figures which were not given explicitly in their paper.

k may be subject to primary kinetic salt effects, but the variation of log k with medium composition should not distort the expected parallelism drastically over the range in question.

In Fig. 1, line A represents log k_2 for the nitration of the p-$C_6H_4Me{\cdot}NMe_3^+$ ion in 75—82% sulphuric acid at 25° (Part VI). The observed parallelism indicates, most probably, that equation (7) is valid, and that the nitronium ion is formed in this medium range in sufficient amount to act as the nitrating agent, even though it is not in sufficient amount to be detected by its Raman spectrum. The lines A_1, A_2, and A_3 refer to nitration at 45°, 35°, and 17·5°, respectively.

The lines B, C, and D of Fig. 1 refer, respectively, to log k_2 for the nitrations of nitrobenzene, the NMe_3Ph^+ ion, and p-chloronitrobenzene in 82—89% sulphuric acid (unpublished experiments by Dr. T. G. Bonner, Mrs. M. E. James, and Miss F. Bowyer; cf. *Nature*, 1949, **163**, 955). The nitronium ion is detectable by its Raman spectrum in these media. Approximate parallelism between log k_2 and log ($[R^+]/[ROH]$) is therefore to be expected (provided that nitric acid is not too extensively ionised), and has been observed previously, for the nitration of nitrobenzene, by Westheimer and Kharasch.

Values of Hammett's acidity function H_0, are also shown in Fig. 1. It is quite evident that there is no parallelism between log k_2 and H_0, so that ionisation of nitric acid to the $H_2NO_3^+$ ion by equation (1) is not a vital factor in nitration, even in 75—85% sulphuric acid media.

The Acidity Function for Carbinol Indicators.—Without specifying the form of K_R or H_R explicitly, equation (12) may be written, to define the acidity function H_R which shall measure the capacity of the medium to ionise a triarylcarbinol indicator:

$$H_R = pK_R - \log([R^+]/[ROH]) \quad . \quad (12)$$

An analogous equation is satisfied by H_0, which measures the capacity of the medium to give a proton to a neutral base (Hammett *et al.*, *loc. cit.*).

So long as nitric acid ionises in the same way as a triarylcarbinol, (13) can be written for (12):

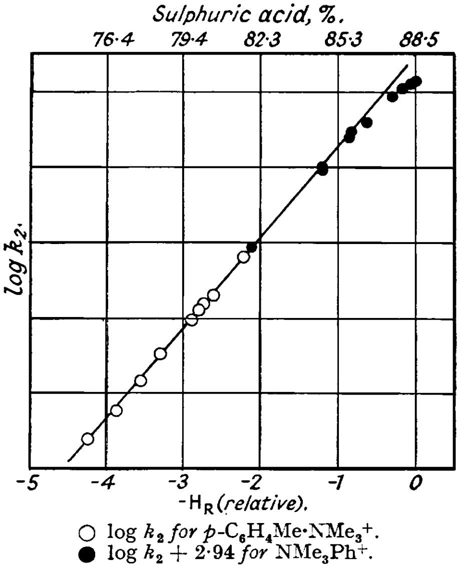
$$H_R = pK_{NO_2{\cdot}OH} - \log([NO_2^+]/[NO_2{\cdot}OH]) \quad . \quad (13)$$

From (13) and (10),

$$\log k_2 = \log k + pK_{NO_2{\cdot}OH} - H_R \quad . \quad (14)$$

in which $K_{NO_2{\cdot}OH}$ is a thermodynamic equilibrium constant for the ionisation of nitric acid, *e.g.*, by equation (2). Being defined in terms of activities, $pK_{NO_2{\cdot}OH}$ is invariant with medium. Provided that k does not vary over the medium range examined, log k_2 should therefore be linear with H_R, and the line connecting the two should have *unit* gradient.

FIG. 2.



Without knowing pK_R for some carbinol indicator ROH, H_R cannot be determined in absolute terms. Nevertheless, values of H_R, relative to an arbitrary zero, may be computed for the range 65—90% sulphuric acid from the results given in the following paper.

The plot of log k_2 for nitration against relative values of H_R is shown in Fig. 2. The values for nitration in 75—82% sulphuric acid are linear with H_R, and the line has gradient 1·20. When produced into the more concentrated sulphuric acid region, the line is found to accommodate, approximately, the points for the nitration of the three compounds nitrated in 82—89% sulphuric acid, if the velocity coefficients for each compound are multiplied by an appropriate constant factor. Values for the nitration of the NMe_3Ph^+ ion are shown in Fig. 2 (black circles). Progressive departure from the linear relation in the more acid media is to be expected, on theoretical grounds.

There is uncertainty about the molecular composition of sulphuric acid–water mixtures containing 65—85% sulphuric acid. Raman spectroscopic results of Woodward and Horner (*Proc. Roy. Soc.*, 1934, *A*, **144**, 129) give HSO_4^- ions as absent and strong in 100% and 90% sulphuric acid respectively. In 75% sulphuric acid H_2SO_4 molecules are only just detectable and the characteristic bands of water begin to show. SO_4^{--} ions just make their appearance in 75% sulphuric acid and increase gradually in concentration with further dilution.

However, other Raman results of Rao (*Indian J. Physics*, 1940, **14**, 143) as re-interpreted by Young and Grinstead (*Ann. New York Acad. Sci.*, 1949, **51**, 765; cf. Redlich, *Chem. Reviews*, 1946, **39**, 333) suggest that molecular H_2SO_4 persists detectably in 25% sulphuric acid and indicate relatively small conversions of water into oxonium and bisulphate ions even in quite concentrated sulphuric acid. Thus, in 91% and in 83% sulphuric acid respectively, H_2SO_4 would be 7·6% and 18·0% ionised. (Complete ionisation of water would correspond to 53% and 100% ionisation of sulphuric acid in these media.)

Against this interpretation and in favour of a more complete conversion of water into oxonium and bisulphate ions are the facts that (*a*) the vapour pressure of water falls to small values for media containing more than 85% sulphuric acid (Greenewalt, *Ind. Eng. Chem.*, 1925, **17**, 522; Vandoni, *Mém. Services chim. de l'État*, 1944, **31**, 87), and (*b*), as pointed out by Brand (*J.*, 1950, 997), the acidity function for 90—99·8% sulphuric acid can be accurately calculated on the supposition that ionisation of the water is complete. Although (as recognised by Brand) this result probably arises from a compensation between minor factors, it suggests that the greater part of the water is ionised in this medium range.

The Influence of the Methyl Group on Nitration Rate.—From the lines *A* and *C* of Fig. 1, the ratio of the nitration velocity coefficients for p-$C_6H_4Me{\cdot}NMe_3^+$ and NMe_3Ph^+ is found to be 870 for 82% sulphuric acid medium. Brand (*J.*, 1950, 1004) has found the analogous ratio for these two compounds in sulphonation to be 360.

The Relative Effects of NO_2 *and* NMe_3^+ *Substituents on Nitration Rate and Degree of Ionisation.*—The ratio $k_2(PhNO_2)/k_2(NMe_3Ph^+)$ for nitration in 97—87% sulphuric acid at 25° is about 1·8 (*Nature, loc. cit.*), and the corresponding ratio in sulphonation is 1·3 at 20°. In these compounds, the substituents influence attack at a *meta*-position (though only to the extent of 80% in sulphonation; cf. Brand, *loc. cit.*). On the other hand, when the same two substituents modify the activating influence of a *p*-methyl group (directing substitution into a position *ortho* to itself), the ratio of speeds in sulphonation is reversed, and $k(p\text{-}C_6H_4Me{\cdot}NO_2)/k(p\text{-}C_6H_4Me{\cdot}NMe_3^+)$ is 0·8. There is evidence (Brand, private communication) that a similar reversal holds for nitration. A contributing factor may be that hyperconjugation from the methyl group to a *p*-nitro-group makes the latter more efficient than the p-NMe_3^+ group in restraining the activating effect of the methyl group in electrophilic substitution.

The effects of these groups on the ionisation of triarylcarbinol indicators are in the same order as their effects on substitution when a *p*-methyl group is also present in the molecule.

Comparison (Fig. 1) of the results for the ionisation of indicators I and IV (Table I) shows that the *p*-nitro-group more effectively restrains ionisation at the tertiary carbon atom than does p-NMe_3^+.

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