

188. Nitration in Sulphuric Acid. Part I. The Nature of the Nitrating Agent in Nitric-Sulphuric Acid Mixtures.

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A wide range of physical and chemical evidence is reviewed including some new experiments described in the two following papers (Parts II and III) and it is shown that nitric acid is present in mixed acids mainly in the form of the cation NO_2^+ produced according to the equation $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$. The nitronium ion NO_2^+ is identified as the active species upon which the vigorous nitrating action of mixed acid depends.

ACCORDING to Graebe ("Geschichte der organischen Chemie," Berlin, 1920, p. 142), a mixture of nitric and sulphuric acids was first used for nitration in the aromatic nucleus 100 years ago, when Muspratt and Hofmann converted nitrobenzene into dinitrobenzene with the mixed acids (*Mem. Proc. Chem. Soc.*, 1846, **3**, 111; *Annalen*, 1846, **57**, 201). Although this mixture has since come into universal use, particularly as a very powerful reagent for relatively difficult nitrations, the function of the sulphuric acid has not yet been fully explained. The idea that sulphuric acid "absorbs" the water formed during nitration, and so facilitates nitration by a mass-action effect, is excluded by the work of Spindler (*Ber.*, 1883, **16**, 1253), which proved that the retarding influence of water in the nitration of benzene was not due to any chemical action of water on nitrobenzene. Aromatic nitration is not reversible. A more hopeful hypothesis is that sulphuric acid converts nitric acid into an "active form," which is the actual nitrating agent; and the view to be developed in this paper is that the nitrating agent present in mixed acids is the NO_2^+ cation, formed when nitric acid is dissolved in sulphuric acid according to the equation $\text{NO}_2\cdot\text{OH} + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{OH}_3^+ + 2\text{HSO}_4^-$ (cf. Westheimer and Kharasch, *J. Amer. Chem. Soc.*, in the press). This equilibrium is analogous to that proved to be established (Hantzsch, *Z. physikal. Chem.*, 1909, **65**, 41; Hantzsch and Berger, *Z. anorg. Chem.*, 1930, **190**, 321; Angus and Leckie, *Proc. Roy. Soc., A*, 1935, **149**, 327; **150**, 615; *Trans. Faraday Soc.*, 1935, **31**, 958; Klinkenberg, *Rec. Trav. chim.*, 1937, **56**, 749; *Chem. Weekblad*, 1938, **35**, 197) when nitrous acid is dissolved in sulphuric acid, namely, $\text{NO}\cdot\text{OH} + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}^+ + \text{OH}_3^+ + 2\text{HSO}_4^-$.

It may be pointed out that according to this view the water necessarily eliminated in a nitration is in fact released reversibly, but before the actual nitration (itself irreversible) takes place.

The physical and chemical properties of mixtures of nitric acid, sulphuric acid, and water have been studied by numerous workers. Consideration of results from all sources has led to general recognition that the molecular complexon of such mixtures depends primarily upon the molecular proportions of water and sulphuric acid present; for these components interact almost quantitatively to form the ionised hydrate, $[\text{OH}_3]^+[\text{HSO}_4]^-$, regardless of the nitric acid, whose fate is decided by whether water or molecular sulphuric acid remains thereafter in excess. In an equimolecular mixture of water and sulphuric acid, nitric acid is present mainly in the form $\text{NO}_2\cdot\text{OH}$. An excess of water converts the nitric acid into nitrate ion, but an excess of sulphuric acid produces a new "third form," the nature of which is discussed below.

The properties of a dilute solution of nitric acid in sulphuric acid monohydrate and absolute sulphuric acid are summarised and compared in Table I.

In the following discussion it will be necessary to review some of this evidence in detail and it will be shown: (1) that when dissolved in an excess of sulphuric acid, nitric acid is present in an altered form; (2) that it is in fact present as a cation; (3) that this cation is NO_2^+ (the nitronium ion); (4) that the cation NO_2^+ is the active nitrating agent of mixed acids.

1. *Qualitative Evidence that a New Species is present in Mixed Acids.*—a. *Ultra-violet absorption.* The conclusion that a new species derived from nitric acid is present in a mixture of nitric and sulphuric acids was argued by Hantzsch (*Ber.*, 1925, **58**, 941; *Z. physikal. Chem.*, 1930, **149**, 161; v. Halban and Eisenbrand, *ibid.*, 1928, **132**, 433) from the fact that the absorption spectra of ultra-violet light due to the nitrate ion and to the undissociated nitric acid molecule were absent, or much diminished, in solutions of nitric acid in con-

TABLE I.
Solution of nitric acid in :

| Property. | Sulphuric acid mono-hydrate (84.5% w/w). | Absolute sulphuric acid (100% w/w). | References. |
|------------------------------------|---|---|--------------------------------|
| Partial pressure of nitric acid | Maximum | Zero | See Section 1, b and appendix. |
| Ultra-violet absorption | Resembles that of absolute HNO ₃ | Solution is unusually transparent | See Section 1, a. |
| Cryoscopic <i>i</i> factor | 1 | 4 | See Sections 1, d and 3, a. |
| Effect upon conductivity of medium | Small | Large | See Section 2, a. |
| Raman frequencies | Those due to HO·NO ₂ , and 1400 cm. ⁻¹ (weak) | None due to HO·NO ₂ ; 1400 cm. ⁻¹ (intense) | See Sections 1, c, 3, b, 3, e. |

centrated sulphuric acid. In sulphuric acid, therefore, nitric acid must be present in some other form which is transparent in this region of the spectrum.

b. *Vapour pressures of nitric acid over mixed acids.* Vapour-pressure measurements are considered in detail in an appendix to this paper (p. 874). An immediate argument is that the conversion of nitric acid into a less volatile form in concentrated sulphuric acid and in oleum is evident from the fact that these solvents retain dissolved nitric acid at high temperatures. We have found that solutions of 0.00124 mole of nitric acid in 15 ml. each of weak oleum, 98% sulphuric acid, and 85% sulphuric acid, heated to 200° for 5 minutes, lose respectively 1, 10, and 92% of the nitric acid by vaporisation.

c. *Raman spectra.* The Raman spectra of mixtures of nitric acid, sulphuric acid, and water have been studied very comprehensively by Chédin (*Ann. Chim.*, 1937, 8, 243). The outstanding feature is a Raman shift $\Delta\nu = 1400 \text{ cm.}^{-1}$, which can be detected in 100% nitric acid but is stronger in mixed acids having a molar ratio $\text{H}_2\text{SO}_4/\text{H}_2\text{O} > 1$, its intensity increasing with diminishing water or increasing oleum content. This frequency is not due to the nitric acid molecule or to the nitrate ion (or to the normal nitrogen pentoxide molecule) and must represent some new species derived from nitric acid.

d. *Cryoscopy.* Cryoscopic results show that nitric acid dissolves in sulphuric acid with production of several particles per molecule added (see Section 3, a, where references are given).

2. *Evidence for a Cationic Form of Nitric Acid.*—The formation of a nitric acid cation in sulphuric acid solution was proved by the outstanding discoveries of Hantzsch, but additional evidence is now available. The position may be summarised as follows.

a. *Conductivity.* Solutions of nitric acid in absolute sulphuric acid have a high electrical conductivity (e.g., Saposchnikov, *Z. physikal. Chem.*, 1904, 49, 697; 1905, 51, 609; 53, 225; Hantzsch, refs. in para. 3, a; Bergius, *Z. physikal. Chem.*, 1910, 72, 338; Ussanowitsch, *Acta Physicochim. U.R.S.S.*, 1935, 2, 239). Ions must therefore be produced, yet the evidence of the absorption spectrum shows clearly that the NO₃⁻ ion is not present, and Hantzsch took the view that the nitric acid is converted into nitracidium ions according to equations (3) and (4) (see below).

b. *Isolation of salts.* A clear proof that nitric acid can exist as a cation is furnished by the isolation (Hantzsch, 1925, *loc. cit.*; Hantzsch and Berger, *Ber.*, 1928, 61, 1328) of two crystalline salts formed by direct combination of nitric and perchloric acids. Their compositions appeared from analysis to be [H₂NO₃]⁺[ClO₄]⁻ and [H₃NO₃]⁺⁺[ClO₄]₂⁻; and they were found, by conductivity measurements, to be binary and ternary electrolytes, respectively, in nitromethane solution. When these solutions were electrolysed, nitric acid accumulated at the cathode.

c. *Migration to the cathode in electrolysis.* Direct evidence of the presence of a nitric acid cation in sulphuric acid solution by experiments on its migration during electrolysis has hitherto been lacking. We have now found conditions for obtaining this essential demonstration. Experiments on the simultaneous cathode migration of nitric acid and the barium ion in oleum solution show that nitric acid migrates from anode to cathode and that the nitric acid cation has a mobility of 2—4 times that of the barium ion. Migration of nitric acid dissolved in 98.7% sulphuric acid has also been demonstrated, but less conclusively. Details and additional experiments are given in Part II (following paper).

3. *Evidence for the NO₂⁺ Ion.*—Although the Hantzsch cations, H₂NO₃⁺ and H₃NO₃⁺⁺, may exist in concentrated nitric acid, in nitric-perchloric acid mixtures (para. 2, b), and perhaps in mixed acids containing a relatively high proportion of water, it seems probable that in oleum media and in mixed acids containing little water the NO₂⁺ ion is the prevailing form. In order to test this suggestion, it is necessary to reinterpret many of the recorded data and to provide detailed proof of the validity of the equation we propose.

The following five equations represent the various views which have been advocated :

| | No. of particles formed from 1 mol. of HNO ₃ in excess H ₂ SO ₄ . | |
|--|---|---|
| (1) 2HNO ₃ + H ₂ SO ₄ → N ₂ O ₅ + H ₃ O ⁺ + HSO ₄ ⁻ | 3 | (Saposchnikov) |
| (2) HNO ₃ + 2H ₂ SO ₄ → NO ₂ ⁺ ·O·SO ₂ ·OH + H ₃ O ⁺ + HSO ₄ ⁻ | 3 | (Markovnikov) |
| (3) HNO ₃ + H ₂ SO ₄ → H ₂ NO ₃ ⁺ + HSO ₄ ⁻ | 2 | (Hantzsch) |
| (4) HNO ₃ + 2H ₂ SO ₄ → H ₃ NO ₃ ⁺⁺ + 2HSO ₄ ⁻ | 3 | (This paper, and Westheimer and Kharasch, <i>loc. cit.</i>) |
| (5) HNO ₃ + 2H ₂ SO ₄ → NO ₂ ⁺ + 2HSO ₄ ⁻ + H ₃ O ⁺ | 4 | |

It will be seen that Markovnikov's suggestion is identical with our view provided that it is recognised that the mixed anhydride is in fact ionised in sulphuric acid solution.

The idea, represented by equation (1), that nitrogen pentoxide is present in mixed acids was rejected by Hantzsch (*loc. cit.*, 1925) but has nevertheless been advocated by several authors in recent years. A critical examination of the evidence on which this view was based is recorded in the appendix to this paper, but it may be pointed out that, bearing in mind the volatility of nitrogen pentoxide (which is greater than that of nitric acid), the fact that mixtures of nitric acid with concentrated sulphuric acid yield anhydrous 100% nitric acid and not nitrogen pentoxide on distillation, is in itself conclusive.

Evidence giving direct support to equation (5) will now be considered.

a. *Cryoscopic data.* Cryoscopic measurements in sulphuric acid have been made by Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257; **62**, 178, 626; 1908, **65**, 41; 1909, **68**, 204), by Oddo and Scandola (*ibid.*, 1908, **62**, 243), by Robles and Moles (*Anal. Fis. Quim.*, 1934, **32**, 474), by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900), and by Treffers and Hammett (*ibid.*, 1937, **59**, 1708). Hantzsch supposed that nitric acid acts as a base towards the stronger sulphuric acid, according to equations (3) and (4). These equations require that nitric acid dissolved in sulphuric acid should yield 2 and 3 particles per molecule of nitric acid respectively; *i.e.*, the van't Hoff factor *i* should be 2 or 3. On the other hand, our equation (5) requires *i* = 4.

Hantzsch himself deduced *i* = 3, but the most satisfactory of his results for nitric acid were obtained by adding potassium nitrate to a slightly aqueous sulphuric acid; and, allowing for the potassium hydrogen sulphate formed, these gave *i* factors of 3.80, 3.80, and 3.84 for nitric acid. Robles and Moles reported values of 3.26, 2.60, and 2.46; but their observations are subject to a considerable error, pointed out by Hammett, in that absolute 100% sulphuric acid was used as solvent. Correct results are obtained by working with sulphuric acid to which just enough water has been added to repress self-ionisation to a minimum: otherwise the observed depressions may be as low as one-half of the true value.

This question has been carefully re-examined by Hughes and Ingold, who have kindly given us permission to quote their results, as yet unpublished. The measurements were made by following Hammett's procedure. In sulphuric acid (with 0.2 mole % of water), nitric acid gave *i* factors of 3.82 (mean of five additions) and 3.80 (mean of five more), in close agreement with Hantzsch's value and confirming the formation of NO_2^+ .

b. *Raman spectra of mixed acids and related systems.* The Raman spectra of some mixed acids and of possible components are compared in Table II, compiled chiefly from data of Chédin (*loc. cit.*; *Mem. Services chim. de l'État*, 1944, **31**, 113; cf. Médard, *Compt. rend.*, 1934, **199**, 1615). Chédin adopted Saposchnikov's view that nitrogen pentoxide is formed in mixed acids. However, the spectrum of this system is quite different from that of nitrogen pentoxide in inert solvents, and from the infra-red spectrum of gaseous nitrogen pentoxide; Chédin concluded that mixed acid contains nitrogen pentoxide in a "different chemical form," which he first supposed to be a polymer of nitrogen pentoxide, later the association complex $\text{N}_2\text{O}_5 \cdot \text{H}_2\text{SO}_4$. Nitrogen pentoxide dissolved in nitric acid he supposed to exist in a similar (polymerised or solvated) condition, to which in either medium the frequencies $\Delta\nu$ 1050 and 1400 cm^{-1} were allotted.

TABLE II.
Raman Spectrum of Mixed Acid and Related Systems.

| System examined. | Frequencies observed, cm^{-1} . | Notes. |
|---|---|--|
| Nitrate ion | 1050 | |
| Bisulphate ion | 1044 | |
| N_2O_5 in CHCl_3 or CCl_4 | 860 (weak), 1244, 1335 (strong) | } Infra-red absorption at 880 and 1315 cm^{-1} |
| " POCl_3 | 1249, 1337 (strong) | |
| N_2O_5 in nitric acid (<20% w/w N_2O_5) | Lines of $\text{HO}\cdot\text{NO}_2$ molecules + 1050 and 1400 | |
| N_2O_5 in oleum | Lines of oleum medium + 1082 and 1400 | Strong, 1400 sharp |
| Absolute nitric acid | Lines of $\text{HO}\cdot\text{NO}_2$ molecules + 1050, 1120, and 1400 | Sharp, but very weak |
| Anhydrous mixture: | | |
| | 1050 and 1400 | Intense, 1400 sharp |
| 1. $\left\{ \begin{array}{l} 0.20 \text{ HNO}_3 \\ + 0.80 \text{ H}_2\text{SO}_4 \end{array} \right.$ | + lines of $\text{HO}\cdot\text{NO}_2$ + lines of H_2SO_4 | Very weak |
| 2. $\left\{ \begin{array}{l} 0.15 \text{ HNO}_3 \\ + 0.85 \text{ H}_2\text{SO}_4 \end{array} \right.$ | 1050 and 1400 + lines of H_2SO_4 | Intense, 1400 sharp |
| 0.046 HNO_3 -0.482 H_2O -0.472 H_2SO_4 | Lines of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ + lines of $\text{HO}\cdot\text{NO}_2$ + 1400 | Lines of $\text{HO}\cdot\text{NO}_2$ absent Relatively strong; 1400 line very weak |

A much simplified interpretation of the Raman spectrum of concentrated mixed acids proceeds from the assumption that ions of the mixed anhydride, $[\text{NO}_2]^+[\text{HSO}_4]^-$, are present. Before pursuing this in detail we shall point out strong grounds for attributing the 1400 cm^{-1} frequency to the NO_2^+ ion.

An ion NO_2^+ would be iso-electronic with the molecule CO_2 , differing from it only in the nuclear charge of the central atom, which would be +7 instead of +6. It would be expected to adopt the same linear configuration as carbon dioxide, since it is known that four-covalent nitrogen has the same stereochemical disposition of its valencies as carbon; and having the same symmetrical arrangement of two oxygen atoms about a central atom, it should resemble carbon dioxide closely in its modes of vibration. The relationship is somewhat similar to that between NO^+ and N_2 , pointed out by Angus and Leckie (*loc. cit.*).

The sole fundamental vibrational frequency of the carbon dioxide molecule revealed in its Raman spectrum is of about 1320 cm.^{-1} , represented in the Raman spectrum by two lines of comparable intensity, owing to resonance between this frequency and the overtone of another. If NO_2^+ and CO_2 vibrate similarly, only the breathing vibration of NO_2^+ will likewise be active in the Raman spectrum and, since this ion has one extra unit charge on the central nucleus as compared with the carbon dioxide molecule, it is to be expected that the frequency of this vibration will be somewhat higher than that for carbon dioxide. These considerations are consistent with the observed value $\Delta\nu = 1400\text{ cm.}^{-1}$; moreover, the degree of depolarisation (Chédin, *loc. cit.*, found $0.188\text{--}0.20$) confirms that the line must arise from a totally symmetrical vibration, as this view requires. [Compare the pair of frequencies at 1286 and 1388 cm.^{-1} in the Raman spectrum of carbon dioxide which have a degree of depolarisation of 0.18 and 0.14 , respectively (Langseth and Nielsen, *Physical Rev.*, 1934, 46, 1057).]

In the mixed acid, the strong frequency of the bisulphate ion is of 1044 cm.^{-1} , and the coexistence of this pair of lines in anhydrous mixed acid is thus natural. The spectrum of molecular nitric acid is undetected in anhydrous mixtures of nitric and sulphuric acids unless the proportion of the former exceeds about 18 moles %, in harmony with the observation that the partial pressure of nitric acid at 0° is zero up to a similar composition (Vandoni, *Mem. Services chim. de l'État*, 1944, 31, 87). The intensity of the 1400 cm.^{-1} line, and hence the concentration of nitronium ion, diminishes on adding water to the anhydrous acid mixture, and the line vanishes when the mole fraction of water slightly exceeds that of sulphuric acid.

Weak lines at 1050 and 1400 cm.^{-1} are observed in the spectrum of absolute nitric acid. By a coincidence, the frequency of the bisulphate ion is nearly identical with that of the nitrate ion, which is of 1050 cm.^{-1} ; absolute nitric acid evidently contains a proportion of nitronium and nitrate ions. The 1400 line is very weak and corresponds to a low concentration of nitronium ion, which, therefore, may accompany the ion H_2NO_3^+ (and possibly $\text{H}_3\text{NO}_3^{++}$) proposed by Hantzsch (1925, *loc. cit.*) in the absolute acid. Addition of nitrogen pentoxide to nitric acid reinforces the pair of lines at 1050 and 1400 cm.^{-1} , and it was largely on this ground that the frequencies were allotted originally to nitrogen pentoxide (Susz and Briner, *Helv. Chim. Acta*, 1935, 18, 378). There is ample evidence, however, from the vapour pressure, electrical conductivity, and rate of decomposition of this system (Berl and Saenger, *Monatsh.*, 1929, 54, 1042; Eyring and Daniels, *J. Amer. Chem. Soc.*, 1930, 52, 1472, 1486) that the components react with the production of an ionised compound (or compounds) which exists in equilibrium with at most only a few units % of molecular nitrogen pentoxide. With little doubt the lines observed are of nitronium and nitrate ions, which are in direct or indirect equilibrium with nitrogen pentoxide.

c. *Kinetics of nitration.* The general validity of equation (5), and in particular the presence of the bisulphate ions on the right-hand side of this equation, are supported by the fact that its use has enabled us to give a quantitative interpretation of the speeds of nitration, under a wide range of conditions, of 2 : 4-dinitrotoluene and other substances, a full account of which will be given in subsequent papers.

d. *The influence of nitric acid upon the oleum-water titration.* The "free" sulphur trioxide of oleum may be titrated quantitatively with water (yielding sulphuric acid) until the liquid ceases to fume (Brand, this vol., p. 585). The first step in the reaction between nitric and sulphuric acids may be written $\text{HO}\cdot\text{NO}_2 + \text{H}_2\text{SO}_4 = \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$; this suggests that the titration of a solution of nitric acid in oleum should require less water than is needed to titrate the pure oleum. This effect is observed, and is treated in more detail in Part III. Numerically we find that each mole of nitric acid reduces the water titration of oleum by 1.5 moles of water. Moreover, experiment shows that the addition of an inorganic bisulphate to oleum also lowers a subsequent water-titration, but by 0.5 mole of water for each mole of bisulphate (regardless of the nature of the cation). The total effect of nitric acid can be interpreted by using the equation of this paragraph (cf. equation 5); it is made up of a lowering of water-titration of 0.5 mole due to the bisulphate ion, and of 1.0 mole due to the water eliminated between the two acids. The experimental result is incompatible with equations (1)–(4).

e. *The nature of the cognate reaction between nitric acid and pyrosulphuric acid.* Evidence on this point is once again provided by Chédin's data. Addition of nitrogen pentoxide to fuming sulphuric acid leads to the appearance of the 1400 cm.^{-1} frequency together with a line observed between 1076 and 1094 cm.^{-1} . Chemically, it seems likely that nitrogen pentoxide and pyrosulphuric acid will interact to form the ionised mixed anhydride, and therefore that the nitronium ion is formed by reaction thus: $\text{N}_2\text{O}_5 + \text{H}_2\text{S}_2\text{O}_7 = \text{NO}_2^+ + \text{HS}_2\text{O}_7^- + \text{HONO}_2$, $\text{HONO}_2 + 2\text{H}_2\text{S}_2\text{O}_7 = \text{NO}_2^+ + \text{HS}_2\text{O}_7^- + 2\text{H}_2\text{SO}_4$. The frequency of approximately 1085 cm.^{-1} is now therefore allocated, by analogy, to the anion, HS_2O_7^- , which accompanies the nitronium ion in oleum solution.

The spectrum of a solution of nitric acid in oleum resembles in principle that of the solution in absolute sulphuric acid, and possesses two characteristic features: (i) The sole frequency of "nitric acid" in dilute solution is of 1400 cm.^{-1} ; the fraction of nitric acid which must be added before the lines of molecular nitric acid appear, increases with the strength of the oleum. (ii) Progressive addition of nitric acid to oleum weakens the lines of pyrosulphuric acid and strengthens those of sulphuric acid.

The latter observation, which shows that water is eliminated in the reaction between nitric and pyrosulphuric acids, can be used to estimate the number of moles of water liberated per mole of nitric acid dissolved. Consider, for example, the mixtures I and II of 10% and 20% (w/w) of nitric acid, respectively, in an oleum of 60% (w/w; 65 mol. %) "free" sulphur trioxide examined by Chédin (*loc. cit.*). The spectrum of

the oleum medium possesses frequencies due to pyrosulphuric acid and sulphur trioxide only; these are given also by mixture I (together with the 1400 cm^{-1} line), but in mixture II they are much diminished in intensity and are now accompanied by the lines of sulphuric acid. The gross molar composition of these mixtures is as follows in mole fractions:

| | HNO_3 . | SO_3 . | H_2SO_4 . |
|----------|------------------|-----------------|---------------------------|
| I | 0.132 | 0.562 | 0.306 |
| II | 0.256 | 0.482 | 0.262 |

We shall examine the following different views of the process of mixing: (1) that no water is liberated (Hantzsch, 1925, *loc. cit.*), $\text{HNO}_3 + \text{H}_2\text{S}_2\text{O}_7 = \text{H}_2\text{NO}_3^+ + \text{HS}_2\text{O}_7^-$; (2) that 0.5 mole of water is liberated per mole of nitric acid, yielding nitrogen pentoxide; (3) that one mole of water is set free per mole of nitric acid, $\text{HNO}_3 + \text{H}_2\text{S}_2\text{O}_7 = \text{NO}_2^+ + \text{HS}_2\text{O}_7^- + \text{H}_2\text{O}$ (cf. equation 5). The detection of molecular sulphuric acid is incompatible with (1), which cannot account for its formation. Also, (2) is unsatisfactory: the 0.256 mole of nitric acid in II would yield 0.128 mole of water, which would convert 0.256 mole of sulphur trioxide into pyrosulphuric acid. The remaining sulphur trioxide (0.226 mole) would unite with sulphuric acid, of which therefore only 0.036 mole would be free. This amount is quite insufficient to account for the observed strength of the sulphuric acid lines.

On the other hand, (3) requires 0.256 mole of water to be liberated, which would convert 0.482 mole of sulphur trioxide into 0.226 mole of pyrosulphuric acid and 0.030 mole of sulphuric acid. The total quantity of the latter would be therefore 0.292 mole, and in fact this is evident in the Raman spectrum. For mixture I, however, the liberated water would be only 0.132 mole, which would form pyrosulphuric acid with 0.264 mole of sulphur trioxide: the remaining sulphur trioxide (0.298 mole) would leave only 0.008 mole of free sulphuric acid, insufficient to be detected. At the same time, the fact that the Raman spectrum of sulphuric acid is not detected in this mixture excludes the possibility that more than one mole of water is formed per mole of nitric acid. This and similar calculations, which can be made from Chédin's results, provide further clear evidence in favour of the view we advocate.

4. NO_2^+ as the Nitrating Agent in Mixed Acids.—A mixture of nitric acid with sulphuric acid (or oleum) is among the most active nitrating agents known. Benford and Ingold (*J.*, 1938, 929) place sulphuric acid in a class by itself as a "fast" nitration solvent. It is clear that the $\text{NO}_2\cdot\text{OH}$ molecule is not the efficient nitrating agent present in mixed acids: first, because nitric acid is a less effective nitrating agent when alone than when it is mixed with sulphuric acid; and secondly, because, in mixtures of nitric acid, sulphuric acid, and water, molecular nitric acid, $\text{NO}_2\cdot\text{OH}$, is in maximum concentration when the molar ratio $\text{H}_2\text{O}/\text{H}_2\text{SO}_4 \sim 1$, whereas mixed acids with so high a proportion of water to sulphuric acid have lower or zero nitrating power* (the actual speed of nitration varying, of course, with the nature of the substance nitrated). It has been suggested that the actual nitrating agent in mixed acids is a dehydration product of nitric acid; and Markovnikov's idea (*Ber.*, 1899, 32, 1441) that the mixed anhydride $\text{NO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ is the nitrating agent seems particularly plausible. Nitrogen pentoxide has also been proposed (for a recent example, cf., *e.g.*, Titov, *J. Gen. Chem. Russ.*, 1941, 11, 1125) and, in fact, Klemenc and Schöller (*Z. anorg. Chem.*, 1924, 141, 231) found identical velocities for nitration of *m*-xylene-4:6-disulphonic acid, in anhydrous sulphuric acid, by nitric acid and by nitrogen pentoxide, N_2O_5 being counted as 2HNO_3 . But the nitrogen pentoxide molecule, as such, is excluded, because all the evidence goes to show that this molecule is absent in mixed acids. Both the mixed anhydride and nitrogen pentoxide are almost certainly ionised in solution in sulphuric acid, as is shown by the cathode migration on electrolysis of a solution of nitrogen pentoxide in oleum (see following paper). The interpretation of Klemenc and Schöller's result must be that, in sulphuric acid, ionisation of nitrogen pentoxide produces the same nitrating entity as ionisation of nitric acid.

The NO_2^+ ion. We have shown that in mixed acids nitric acid is largely present in the form of the NO_2^+ ion characterised by a strong Raman shift $\Delta\nu = 1400 \text{ cm}^{-1}$. That this is also the nitrating agent in mixed acids may be argued as follows.

From Chédin's results we know approximate values for the limiting acid compositions in which the line 1400 cm^{-1} is just observable. These limiting compositions, shown as line *A* in the figure, may be compared with those which are effective in nitration. Hetherington and Masson (*loc. cit.*) have established that only mixed acids with compositions surpassing certain "threshold" values are capable of nitrating nitrobenzene, when the reaction is performed in the ordinary way, in a two-phase system at 35°. Their limiting compositions are shown as line *B* in the triangular diagram, representing mixed acid compositions in terms of mole fractions. Acid compositions within the triangle to the left of line *B* do not nitrate nitrobenzene; in those to the left of line *A* the concentration of line NO_2^+ ion must fall rapidly to zero. The two lines lie close together, indicating that the NO_2^+ ion is the nitrating agent for nitrobenzene.

According to these views, the function of sulphuric acid in nitrating acid is to furnish a strongly acid medium, towards which nitric acid acts as a base, forming the reactive NO_2^+ ion by equation (5) (p. 870). This will be the most active nitrating agent present, but it is not necessarily required for the nitration of *all*

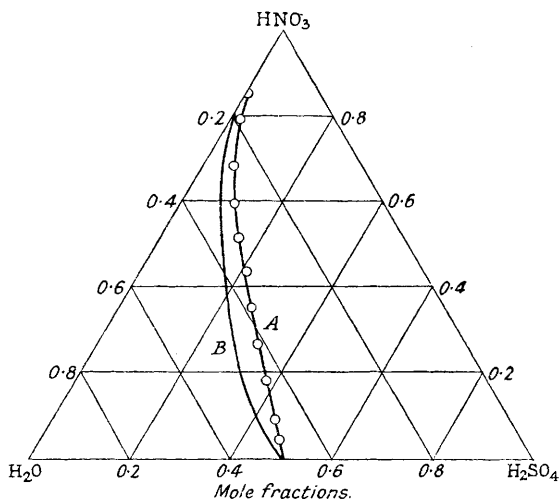
* Cf., *e.g.*, the results of Hetherington and Masson (*J.*, 1933, 105) for nitrobenzene (Fig. 1). In preparative, "two-phase" nitration, increasing solubility of organic matter in the acid phase and also the high proportion of nitric acid generally employed make it advantageous to use nitrating acids with as low a proportion of water as possible. For nitration in homogeneous solution, with a low proportion of nitric acid, the nitration rate is at a maximum in media in which the molar ratio $\text{H}_2\text{O}/\text{H}_2\text{SO}_4 \sim 0.5$ (at 90°). These points will be discussed in later papers.

aromatic compounds. An easily nitrated substance may be nitrated by the $\text{NO}_2\cdot\text{OH}$ molecule. Thus, phenols can be nitrated by dilute aqueous nitric acid, and benzene is nitrated by acid compositions lying to the left of the limiting lines (see figure) (Lewis and Suen, *Ind. Eng. Chem.*, 1940, **32**, 1095). Nor is the action of the Hantzsch ions H_2NO_3^+ and $\text{H}_3\text{NO}_3^{++}$ excluded in all circumstances, if their existence is established.

Under the dehydrating conditions prevailing in mixed acids of low water content, or in oleum media, the NO_2^+ ion seems, however, to be formed; and whatever other possible nitrating agents are present, this may be assumed to be the most active one. This is in accord with the electronic theory of reactions, which postulates that a nitrating agent for the benzene ring is "cationoid," or "electrophilic," and is generally of the form $\text{X}\cdot\text{NO}_2$, where X is an electron-attracting group (Benford and Ingold, *loc. cit.*). The effectiveness will depend upon the degree of electron attraction exerted by X upon the NO_2 group of the nitrating agent, which may thus be the positive end of a partly polarised molecule. It is logical to infer that the most active of all nitrating agents would be the NO_2^+ ion, carrying an integral positive charge.

The idea that a cation derived from nitric acid is the most effective nitrating constituent of mixed acids arises naturally from the electronic theory, but is not in itself new. Von Euler (*Z. angew. Chem.*, 1922, **35**, 580) supposed that sulphuric acid converted nitric acid into the NO_2^+ ion, the active nitrating agent. Walden (*ibid.*, 1924, **37**, 390), quoting a suggestion by Lothar Meyer ("Grundzüge der theoretischen Chemie," Leipzig,

1890, pp. 173, 196), imagined the nitration of benzene by nitric acid as the reaction $\text{C}_6\text{H}_5\cdot\text{H} + \text{HO}^- + \text{NO}_2^+ = \text{H}_2\text{O} + \text{C}_6\text{H}_5\cdot\text{NO}_2$. Brewin and Turner (*J.*, 1928, 334) suggested the ion $\text{N}(\text{OH})_4^+$ as the nitrating agent and, more recently, nitration by a cation has been discussed by Robinson (*J.*, 1941, 238; see also Ri and Eyring, *J. Chem. Physics*, 1940, **8**, 433; Westheimer and Kharasch, *loc. cit.*). Hantzsch's evidence for the existence of nitric acid cations has been used as a basis for suggestions that these are the nitrating agents by Youle (Thesis, Univ. of Sheffield, 1937), by Benford and Ingold (*loc. cit.*), by Lauer and Oda (*J. pr. Chem.*, 1936, **144**, 176), by Lantz (*Bull. Soc. chim.*, 1939, **6**, 302), and particularly by Ussanowitsch (*J. Gen. Chem. Russ.*, 1940, **10**, 219; cf. Williams, *Trans. Faraday Soc.*, 1941, **37**, 746). A quantitative formulation, hitherto lacking, can now be given as a result of kinetic experiments upon the nitration of 2 : 4-dinitrotoluene, nitrobenzene, *p*-chloronitrobenzene, and phenyltrimethylammonium nitrate in sulphuric acid-water mixtures. The hypothesis of exclusive nitration of these compounds by the cation (as against the assumption by Lantz and by Lauer and Oda that the cation nitrates only in anhydrous, or nearly anhydrous sulphuric acid, the $\text{NO}_2\cdot\text{OH}$ molecule being responsible



Raman frequency $\Delta\nu$ 1400 cm^{-1} observed only from line A to right.

Nitration of nitrobenzene proceeds only to right of line B.

for nitration in more aqueous media) not only explains the fundamental function of sulphuric acid as a nitration medium, but also accounts for Martinsen's discovery (*Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605) that nitration is fastest in a medium of 91–92% sulphuric acid and not in anhydrous sulphuric acid or oleum. The effects of nitrous acid and added salts upon nitration speed are accounted for quantitatively. These experiments will be described in later papers.

Appendix : Critical Examination of the Nitrogen Pentoxide Hypothesis.

The idea represented by equation (1) (p. 870), that nitrogen pentoxide is formed in concentrated mixed acid, owes its inception to Saposchnikov (*loc. cit.*) who made the first measurements of vapour pressure of the system. His results agree qualitatively with the more recent determinations by Berl, Address, and Escales (*Kunststoffe*, 1937, **27**, 23) and by Vandoni (*loc. cit.*). The partial pressure of nitric acid is a maximum over mixtures of equal mole fraction of water and sulphuric acid, and declines to zero above solutions having a large excess of water or sulphuric acid owing to immobilisation of the nitric acid as nitrate or nitronium (NO_2^+) ion, respectively.

Progressive addition of sulphuric acid to aqueous nitric acid thus produces first a rise and then a fall of partial pressure of nitric acid. The initial rise was explained correctly by Saposchnikov to result from displacement by the sulphuric acid of molecular nitric acid from its hydrates; he tried, however, to account also for the subsequent fall in partial pressure in terms of the dehydrating property of the sulphuric acid, which here might extract water from the nitric acid itself, leaving nitrogen pentoxide. Saposchnikov used the equation $2\text{HNO}_3 + n\text{H}_2\text{SO}_4 = \text{N}_2\text{O}_5 + \text{H}_2\text{O} + n\text{H}_2\text{SO}_4$, and claimed in support that the vapour of certain acid-rich mixtures contained nitrogen pentoxide. This claim is still quoted as an experimental justification of the nitrogen pentoxide hypothesis, but is mistaken. Distillation of concentrated mixed acid below 30° provides pure, absolute nitric acid (free from any anhydride), and is the method commonly used for its preparation. Above 30° the product is anhydrous nitric acid mixed with some nitrogen dioxide formed by its

thermal decomposition (Pascal and Garnier, *Ann. Chim.*, 1921, **15**, 253; Berl and Samtleben, *Z. angew. Chem.*, 1922, **35**, 201, 206). It is likely that Saposchnikov was misled by this decomposition. He determined vapour pressure by drawing a current of air through the mixed acid at 25°, the volatile product being absorbed in potash, weighed and analysed by a method which estimates both nitric and nitrous acids together. After certain experiments of long duration, the vapour was richer in nitrogen than nitric acid (22.2% of N), and this was attributed to admixture with nitrogen pentoxide (25.9% of N). Retrospectively, there is little doubt that the vapour was in fact that of nitric acid mixed with nitrogen dioxide (30.4% of N), formed by decomposition of the acid during the protracted experiment. Scrutiny of Saposchnikov's results shows that, of 16 acids examined having a higher mole fraction of sulphuric acid than of water, *five*, distributed at random, possessed an abnormal vapour which in *two* cases was richer in nitrogen even than nitrogen pentoxide. The original evidence of the occurrence of nitrogen pentoxide in the vapour of mixed acid is therefore slender; facts which refute its presence are now overwhelming.

Since the nitrogen pentoxide hypothesis was thus based on inconclusive experiments, it may be examined upon its logical merits. The chemistry of nitrogen pentoxide was obscure at the time of Saposchnikov. The compound is more volatile than nitric acid, straightforward dehydration of which would lead to a several-fold increase in total pressure (Russ and Pokorny, *Monatsh.*, 1913, **34**, 1027; Daniels and Bright, *J. Amer. Chem. Soc.*, 1922, **42**, 1131). Thus in the interpretation of their measurements by Berl and others, and by Vandoni, it is assumed that the pentoxide formed within the solution combines there with molecules of the medium. Berl concludes that combination takes place between nitrogen pentoxide and remaining molecular nitric acid: these form an involatile complex, $(\text{HNO}_3)_6 \cdot \text{N}_2\text{O}_5$, whose existence he had assumed earlier to account for the properties of mixtures of nitrogen pentoxide in nitric acid (nitric acid oleum). Vandoni, unable to find evidence for this compound, supposes that the nitrogen pentoxide unites with molecular sulphuric acid to form the complex $\text{N}_2\text{O}_5 \cdot \text{H}_2\text{SO}_4$. Each of these explanations is somewhat formal and mechanical, but that of Vandoni expresses the same idea as our own (namely, that nitric and sulphuric acids interact with the elimination of a molecule of water), and evidence is considered in para. 3, b which sustains the proposal that the ion of nitric acid in mixed acid is also a component of "nitric acid oleum."

Another objection may be raised to the suggestion that concentrated mixed acids contain nitrogen pentoxide, even in small proportion in equilibrium with one or other of the complexes above. Nitric acid dissolved in sulphuric acid is quite stable, whereas it is certain that a solution containing molecules of nitrogen pentoxide would decompose (Lueck, *J. Amer. Chem. Soc.*, 1922, **44**, 757; Eyring and Daniels, *ibid.*, 1930, **52**, 1472, 1486). The exact form of Berl's explanation may thus be discarded, since nitric acid oleum decomposes, more slowly but in the manner of a solution of nitrogen pentoxide in an inert solvent.

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