190. *Nitration in Sulphuric Acid. Part III. The Influence of Nitric Acid and Other Substances upon the Oleum–Water Titration.*

By John C. D. Brand.

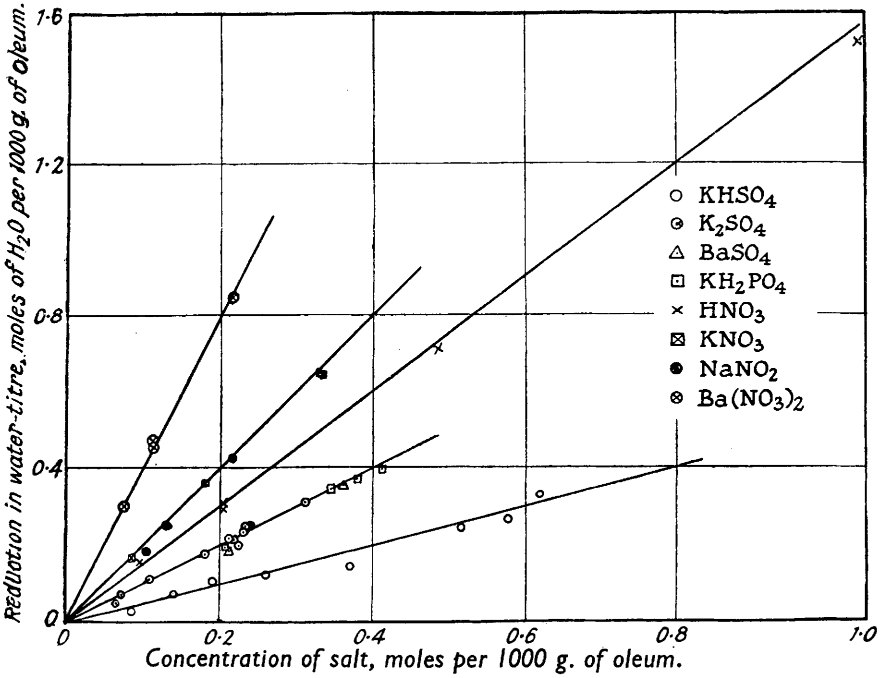
The water titration of oleum (Brand, this vol., p. 585) has been carried out in presence of various added substances. The solutes fall into several groups with respect to their effect in reducing the observed water-titre of the oleum. The reduction in moles of water required per mole of solute added is : (1) for two aromatic trinitro-compounds, none; (2) for potassium hydrogen sulphate, 0·5 mole; (3) for potassium and barium sulphates, 1 mole; (4) for nitric acid, 1·5 moles; (5) for potassium nitrate and sodium nitrite, 2 moles; and (6) for barium nitrate, 4 moles.

These results are shown to be consistent with the reactions $HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ and $HNO_2 + 2H_2SO_4 \longrightarrow NO^+ + H_3O^+ + 2HSO_4^-$. The effect of the bisulphate ion is discussed in terms of the ionic equilibria in the oleum solution.

The liberation of water when nitric acid dissolves in sulphuric acid is shown in a direct and simple manner by experiments based on the fact that sulphur trioxide in excess of the composition H_2SO_4 may be titrated by adding water to oleum until fuming just ceases (Brand, *loc. cit.*); " free " sulphur trioxide is thus determined with an uncertainty of about one part in 100 parts.

For the present purpose, titrations have been made with specimens of oleum to which various amounts of a number of solutes have been added (see Table I). All the substances tested, except the two trinitro-compounds, caused a diminution in the amount of water required for the titration of the oleum; this diminution was proportional to the amount of solute added, and independent of the initial sulphur trioxide concentration in the oleum (although the *total* water-titre necessarily varied with the strength of the oleum used). The two organic compounds had a negligible effect.

The solution for each titration was made up by weight, and the solute concentration expressed as molalities (moles of solute per 1000 g. of solvent oleum). Each titration was calculated in terms of the number of moles of water which must be added, per 1000 g. of solvent, to the solution in order to produce a mixture which does not fume. It is supposed that 1000 g. of oleum, either alone or as solvent, will require the same volume of water for titration provided there is no reaction between oleum and solute in the latter case. As explained, however, addition of a solute usually diminishes the titration of the solvent: the diminution, in moles of water, is compared with the solute concentration in cols. 2 and 1 of Table I. It is found that these two quantities are directly proportional to one another (Table I, cols. 3—4) and, for each substance, the proportionality constant is either integral or half-integral. That this is true is appreciated from the figure, in which the lines are drawn to be of definite slopes (½, 1, 1½, 2, and 4) rather than through the points which group about them.



The results may be summarised as follows: the solutes fall into groups in their effects in reducing the water-titre of oleum, the reduction (in moles of water per mole of solute added) being (1) for the trinitro-compounds, nil; (2) for potassium hydrogen sulphate, 0·5; (3) for potassium and barium sulphates and potassium dihydrogen phosphate, 1·0; (4) for nitric acid, 1·5; (5) for potassium nitrate and sodium nitrite, 2; (6) for barium nitrate, 4.

Discussion of Results.—Diminution of the water-titration means that the addition of solute to an oleum removes some of the " free " sulphur trioxide, presumably by chemical combination with it. The number of moles of water by which the titre of a solution is depressed below that of the pure oleum clearly equals the number of moles of sulphur trioxide which have combined chemically with the solute. The results show that this quantity is in a simple ratio to the solute concentration. It is therefore an experimental fact that, when added to oleum, one mole of bisulphate combines with 0·5 mole of sulphur trioxide. The interpretation of this fact is discussed on p. 882. If this be accepted, the remaining results are consistent if (*a*) one mole of nitric acid or nitrous acid causes the disappearance of 1·5 moles of sulphur trioxide, and (*b*) one mole of orthophosphoric acid removes 0·5 mole of sulphur trioxide. Potassium sulphate dissolves in sulphuric acid as $2KHSO_4$, barium sulphate as $Ba(HSO_4)_2$, potassium nitrate yields $KHSO_4$ and HNO_3, sodium nitrite $NaHSO_4$ and HNO_2, barium nitrate $Ba(HSO_4)_2$ and $2HNO_3$, and potassium dihydrogen phosphate $KHSO_4$ and H_3PO_4. There is no reason to suspect that the inorganic cations present in the solution have any influence upon the water-titre.

TABLE I.

Diminution in Water-titre of Oleum caused by Addition of Solutes.

(a = Moles of solute added to 1000 g. of oleum; b = reduction in water-titre in moles per 1000 g. of oleum.)

Solute.	*a.*	*b.*	*b/a.*	Mean.*	Solute.	*a.*	*b.*	*b/a.*	Mean.*
2 : 4 : 6-Trinitrotoluene	0·135	0·000	0	0	$BaSO_4$	0·214	0·183	0·86	0·96
						0·362	0·367	1·02	
1 : 3 : 5-Trinitrobenzene	0·178	0·033	0·17	0·05	KH_2PO_4	0·208	0·194	0·93	0·97
	0·460	0·006	0·01			0·218	0·211	0·97	
$KHSO_4$	0·087	0·028	0·32	0·48		0·347	0·345	0·99	
	0·141	0·072	0·51			0·385	0·372	0·97	
	0·191	0·106	0·56			0·413	0·400	0·97	
	0·261	0·122	0·47		HNO_3	0·096	0·155	1·61	1·47
	0·372	0·144	0·39			0·205	0·294	1·43	
	0·517	0·245	0·47			0·205	0·311	1·52	
	0·578	0·267	0·46			0·486	0·711	1·46	
	0·621	0·333	0·54			1·042	1·52	1·46	
K_2SO_4	0·065	0·050	0·8	0·99	KNO_3	0·086	0·168	1·95	1·96
	0·073	0·072	0·99			0·182	0·364	2·00	
	0·110	0·111	1·01			0·332	0·651	1·96	
	0·182	0·178	0·98			0·334	0·650	1·95	
	0·213	0·216	1·01		$NaNO_2$	0·105	0·183	1·74	1·94
	0·225	0·200	0·89			0·131	0·250	1·91	
	0·231	0·233	1·01			0·218	0·427	1·96	
	0·235	0·250	1·06		$Ba(NO_3)_2$	0·075	0·300	4·00	4·00
	0·241	0·250	1·04			0·113	0·472	4·18	
	0·313	0·311	0·99			0·114	0·456	4·00	
						0·217	0·849	3·91	

* The mean quotients for each series are calculated by dividing the sum of the figures of col. 2 by the sum of those of col. 1, thus giving increasing weight to the results obtained at higher concentrations.

The inference (*a*) above answers the question about the state adopted by nitric acid in oleum solution. Some of the possible equations representing the supposed behaviour of nitric acid in sulphuric acid are given in Table II, together with the number of moles of sulphur trioxide which should consequently be used up when the solvent is an oleum. The experimental results support equation (5) consistently. If the mixed anhydride in equation (2) is imagined to be ionised, then this equation becomes (5). As mentioned in Parts I and II, there is evidence that nitrogen pentoxide ionises when dissolved in oleum.

TABLE II.

Reaction.	Moles of SO_3 taken up from oleum by 1 mole of HNO_3.
(1) $2HNO_3 = N_2O_5 + H_2O$	0·5
(2) $HNO_3 + H_2SO_4 = NO_2{\cdot}O{\cdot}SO_3H + H_2O$	1·0
(3) $HNO_3 + H_2SO_4 = H_2NO_3^+ + HSO_4^-$	0·5
(4) $HNO_3 + 2H_2SO_4 = H_3NO_3^{++} + 2HSO_4^-$	1·0
(5) $HNO_3 + H_2SO_4 = NO_2^+ + HSO_4^- + H_2O$	1·5

The results with sodium nitrite give an independent demonstration of the conversion of nitrous acid by sulphuric acid into nitrosyl and bisulphate ions (cf. Part I); and it follows from inference (*b*) that orthophosphoric acid dissolves in sulphuric acid to react as follows : $H_3PO_4 + H_2SO_4 = P(OH)_4^+ + HSO_4^-$, requiring in oleum, 0·5 mole of sulphur trioxide per mole of orthophosphoric acid. A phosphacidium perchlorate $[P(OH)_4^+]$ $[ClO_4^-]$ has been prepared by Arlman (*Rec. Trav. chim.*, 1937, **56**, 919). The cryoscopic behaviour of potassium dihydrogen phosphate in sulphuric acid is quite different from that of potassium nitrate (cf. Part I), a much smaller value for the *i* factor being obtained (Hantzsch, *Z. physikal. Chem.*, 1909, **65**, 41), and the effect of orthophosphoric acid upon the rate of decomposition of malic acid in anhydrous sulphuric acid (Dittmar, *J. Amer. Chem. Soc.*, 1930, **52**, 2746) also suggests that each molecule of the acid yields one bisulphate ion in this medium. It is possible that ionisation of nitric acid proceeds through the comparable Hantzsch ion $NO(OH)_2^+$ (whose anion immobilises 0·5 mole of SO_3, cf. Table II) and that this is at once dehydrated to NO_2^+ by the sulphuric acid medium.

The Influence of Bisulphate Ion upon the Water-titration of Oleum.—To interpret the reaction between nitric acid and oleum it was necessary to use, but not to explain, the experimentally observed effect of bisulphate ion upon the water-titration. The end-point of the titration is marked by the cessation of fume. It is assumed that fuming is a property of un-ionised pyrosulphuric acid, a fraction of which dissociates into sulphur trioxide and H_2SO_4 (see Part I; cf. Miles, Niblock, and Wilson, *Trans. Faraday Soc.*, 1940, **36**, 345; Miles, Niblock, and Smith, *ibid.*, 1944, **40**, 281). The solid salts of pyrosulphuric acid have no tendency to lose sulphur trioxide in the cold : it is therefore assumed that the ions $HS_2O_7^-$ and $S_2O_7^{--}$ do not, *of themselves*, give rise to fume.

To explain the influence of bisulphate ions upon the fuming of oleum it is necessary to suppose further that, in sulphuric acid, pyrosulphuric acid is moderately acidic in its first ionisation. The argument is as follows : if pyrosulphuric acid is stronger than sulphuric acid an added bisulphate will be converted into hydrogen pyrosulphate ion by the equilibrium

$$HSO_4^- + H_2S_2O_7 \rightleftharpoons HS_2O_7^- + H_2SO_4 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Were pyrosulphuric acid weak in its behaviour, solvolysis of the ion $HS_2O_7^-$ (equilibrium 6, reading from right to left) would be considerable, always affording sufficient molecular pyrosulphuric acid for fuming to be perceptible, and the titration of the solution would not differ from that of the oleum alone save in the sharpness of the end-point. In practice a diminution is observed. On the other hand, were pyrosulphuric acid to ionise in sulphuric acid as a strong acid, a bisulphate dissolved in a solution containing an excess of pyrosulphuric acid would be transformed quantitatively into acid pyrosulphate, solvolysis of the ion $HS_2O_7^-$ being zero or negligible. This would lead to cessation of fuming when the solution contained one mole of " free " sulphur trioxide per mole of added potassium (or other) hydrogen sulphate, the solutes being present entirely as $HS_2O_7^-$ ions. In fact, the titration is diminished by one-half of this amount, presumably because the acidity of pyrosulphuric acid is between the two extremes chosen for illustration.

The effect of a bisulphate upon the water-titration is summed up by the statement that the addition of $2A$ moles of potassium or another hydrogen sulphate to oleum containing A moles of " free " sulphur trioxide checks the fuming exactly. The result is accounted for if the solution at the end-point contains equal concentrations of $KHSO_4$ and KHS_2O_7 (A moles of each), or if it contains $K_2S_2O_7$ (A moles). The gulf between these two views is smaller than it appears. If the latter view, which accounts immediately for the simple arithmetical ratio encountered, is correct, the second ionisation of pyrosulphuric acid cannot be immoderately weak, permitting the existence of $S_2O_7^{--}$ ions in solutions containing very little or no molecular pyrosulphuric acid. Solvolysis of the ion $S_2O_7^{--}$ (see 7) must be greater proportionately than that of the ion $HS_2O_7^-$,

$$S_2O_7^{--} + H_2SO_4 \rightleftharpoons HS_2O_7^- + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad (7)$$

whose reaction with the solvent (see 6) is small but perceptible. However, molecular pyrosulphuric acid would only be formed from $S_2O_7^{--}$ ions by co-operation of the simultaneous equilibria (6) and (7), which (by the present hypothesis) combine to be unfavourable to its formation, and consequently its concentration would be too minute for fuming to be observed. A solution of potassium hydrogen sulphate ($2A$ moles) in oleum containing an equivalent amount of " free " sulphur trioxide ($2A$ moles) fumes because solvolysis of the KHS_2O_7 produces $H_2S_2O_7$ in one stage. Fuming diminishes on adding water. The addition of A moles of water would convert the KHS_2O_7 ($2A$ moles) approximately into $K_2S_2O_7$ (A moles), reducing the concentration of molecular pyrosulphuric acid to a second order of smallness. Fuming would cease at this point.

The alternative view is that the exactly titrated solution contains an equal concentration of hydrogen sulphate and hydrogen pyrosulphate ions, and its implication is that the second ionisation of pyrosulphuric acid is insignificantly weak. Accordingly, complete solvolysis would befall the ion $S_2O_7^{--}$ in sulphuric acid. This picture differs, therefore, from that offered previously in supposing that equilibrium (7) lies on the right rather than on the left. The accompanying argument interprets the position of the end-point as follows: the fuming of solutions of bisulphate in oleum is supposed to become imperceptible when titration has reduced the concentration of molecular pyrosulphuric acid to a critical concentration C, which should be the same however much bisulphate was dissolved initially, and must be very small. In the final stages of titration pyrosulphuric acid is furnished by adjustment of equilibrium (6); if K be the mass-action constant of this equilibrium, the concentration of molecular pyrosulphuric acid (ignoring changes in the concentration of H_2SO_4) is given by $[H_2S_2O_7] = [HS_2O_7^-]/K[HSO_4^-]$. Provided that K be sufficiently large, this relation accounts for the experimental fact that fuming always ceases ($[H_2S_2O_7] = C$) at the same ratio of the molar concentrations of " free " sulphur trioxide and bisulphate ion, but the interpretation accepts as a coincidence the fact that this ratio is half-integral. It is improbable that the concentration of molecular pyrosulphuric acid left unobserved at the end of a titration could exceed 0·001 molal, and, therefore, because at this point the concentrations of $HS_2O_7^-$ and HSO_4^- ions are equal, the hypotheses of this paragraph yield a figure of $K > 10^3$ for the constant of equilibrium (6). This figure would describe the acidity of pyrosulphuric acid to a better approximation than previous statements.

It will be apparent that the alternative hypotheses which have been discussed reduce to extreme opposite points of view regarding the position of equilibrium in equation (7). An intermediate condition is also possible, the exact solution requiring further data.

EXPERIMENTAL.

Materials.—The purification and titration of oleum are described elsewhere (Brand, *loc. cit.*). The method of preparation of anhydrous nitric acid (99·9% HNO_3) is referred to in Part II. The inorganic salts chosen as solutes were of A.R. purity.

Method.—The strength of the oleum in which the compounds named in Table I were dissolved and titrated varied

TABLE III.

Oleum.		Potassium nitrate.		Water-titration.		Diminution of water-titre, molality.
SO_3, %.	Wt. used, g.	Wt. used, g.	Molality.	Obs., ml.	Molality.	
17·0	23·40	—	—	0·895	2·127	—
	28·94	1·010	0·334	0·770	1·477	0·650
11·4	21·72	—	—	0·554	1·417	—
	25·84	—	—	0·659	1·417	—
	23·19	—	—	0·595	1·425	—
	24·75	0·216	0·086	0·558	1·252	0·168
	25·34	0·468	0·182	0·482	1·056	0·364
	25·28	0·849	0·332	0·350	0·769	0·651

between 5% and 18% of " free " sulphur trioxide. Titrations were made upon samples of 20—50 g., and were reproducible to about 1%. The diminution of titration observed in presence of a solute was subject, therefore, to a greater error than this; the error, moreover, increases with the initial strength of the solvent oleum at a given solute concentration, and, for solutions in a given oleum, rises rapidly with diminishing concentration of substance dissolved. Upon analysis of the results of Table I, it is found that the figures of col. 3 seldom differ by more than the accepted vagary of experiment from the integral or half-integral ratios given in col. 4. Table III contains detailed results of the titration of potassium nitrate in oleum : it is apparent that the lowering of titration produced by this salt does not depend upon the initial strength of the solvent, and that the molar lowering has a value which is double the solute concentration within the error of experiment outlined above.

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