505. *Chemistry of Nitronium Salts. Part I. Isolation of Some Nitronium Salts.*

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The following crystalline nitronium salts have been prepared in a pure state : (1) nitronium perchlorate, $(NO_2^+)(ClO_4^-)$; (2) nitronium hydrogen disulphate, $(NO_2^+)(HS_2O_7^-)$; (3) nitronium disulphate, $(NO_2^+)_2(S_2O_7^{--})$; (4) nitronium trisulphate, $(NO_2^+)_2(S_3O_{10}^{--})$; and (5) nitronium fluorosulphonate, $(NO_2^+)(FSO_3^-)$. The assigned ionic constitutions are spectroscopically established (Millen) in examples (1), (2), (3), and (5), while the constitution of salt (4) is assumed by analogy. (6) Crystalline dinitrogen pentoxide, which is nitronium nitrate, $(NO_2^+)(NO_3^-)$ (Ingold, Millen, and Poole), belongs to the series, its structure having likewise been spectroscopically established (Chédin; Millen). Nitronium polyselenates have been obtained, but only as mixtures. Nitronium hydrogen sulphate probably has temporary existence as a solid, but it could not be prepared in a pure form, because it passed into nitronium hydrogen disulphate. Nitronium chlorosulphonate could not be obtained, because it decomposed to give nitryl chloride, providing a new route to the preparation of that substance.

Hantzsch's work on the preparation of the alleged salts $(H_2NO_3^+)(ClO_4^-)$ and $(H_3NO_3^{++})(ClO_4^-)_2$, from nitric acid and perchloric acid, could not be repeated. The following reactions were elucidated in which nitronium perchlorate is formed :

$$HNO_3 + 2HClO_4 = (NO_2^+)(ClO_4^-) + (H_3O^+)(ClO_4^-)$$

$$N_2O_5 + 3HClO_4 = 2(NO_2^+)(ClO_4^-) + (H_3O^+)(ClO_4^-)$$

$$2N_2O_5 + (H_3O^+)(ClO_4^-) \rightleftharpoons (NO_2^+)(ClO_4^-) + 3HNO_3$$

Nitronium hydrogen disulphate was prepared by treating nitric acid with more than two molecular proportions of sulphur trioxide in nitromethane solution, from which the salt crystallised :

$$HNO_3 + 2SO_3 = (NO_2^+)(HS_2O_7^-)$$

The same salt resulted from all attempts to prepare nitronium hydrogen sulphate, apparently because the ions of this salt interact reversibly,

$$2(NO_2^+)(HSO_4^-) \rightleftharpoons (NO_2^+)(HS_2O_7^-) + HNO_3$$

Normal nitronium disulphate was also produced in the reaction between nitric acid and sulphur trioxide, but it could not thus be obtained free from the hydrogen disulphate. It was prepared in a pure form by treating dinitrogen pentoxide with less than two molecules of sulphur trioxide :

$$N_2O_5 + 2SO_3 = (NO_2^+)_2(S_2O_7^{--})$$

Normal nitronium trisulphate was obtained in a pure state when dinitrogen pentoxide was treated with more than three molecular proportions of sulphur trioxide :

$$N_2O_5 + 3SO_3 = (NO_2^+)_2(S_3O_{10}^{--})$$

No more than three molecules of sulphur trioxide could be induced to enter into reaction with dinitrogen pentoxide. The existence of Pictet and Karl's allegedly stable compound, $N_2O_5,4SO_3$, could not be confirmed.

Nitronium fluorosulphonate was prepared from dinitrogen pentoxide and fluorosulphonic acid. Since dinitrogen pentoxide is nitronium nitrate, this reaction may be regarded as a simple anion exchange :

$$N_2O_5 + F{\cdot}SO_3H = (NO_2^+)(F{\cdot}SO_3^-) + HNO_3$$

The corresponding reaction with chlorosulphonic acid did not yield nitronium chlorosulphonate, apparently because the ions of this salt interact, to give nitryl chloride and nitronium hydrogen disulphate :

$$N_2O_5 + Cl{\cdot}SO_3H = (NO_2^+)(Cl{\cdot}SO_3^-) + HNO_3$$

$$(NO_2^+)(Cl{\cdot}SO_3^-) + HNO_3 = NO_2Cl + (NO_2^+)(HSO_4^-)$$

$$2(NO_2^+)(HSO_4^-) = (NO_2^+)(HS_2O_7^-) + HNO_3$$

Chlorine and dinitrogen tetroxide are formed as by-products :

$$N_2O_5 + Cl{\cdot}SO_3H = N_2O_4 + Cl_2 + H_2SO$$

(1) *Origin and Scope.*

(1.1) *Relation of this Paper to Papers of Other Series.*—After it had been established by kinetic studies (*Nature*, 1946, **158**, 448; *J.*, 1950, 2400) that the nitronium ion, NO_2^+, is formed in nitrating media, and when, also, it had been proved by cryoscopic and spectroscopic investigations (*Nature*, 1946, **158**, 480; *J.*, 1950, 2504 and paper no. 508) that the ion can be produced in considerable concentration in solvents such as nitric and sulphuric acids, it seemed obvious that an investigation into the isolation of nitronium salts would be fruitful.

This work has been undertaken in collaboration with Dr. D. J. Millen. Our part has been to prepare nitronium salts, and to establish their compositions by analysis. His concern has been to prove the presence, or otherwise, of the nitronium ion, and of the anions, in the crystal structures of the compounds, by the method of Raman spectroscopy. His evidence is given in a separate paper (*J.*, 1950, paper no. 509). Geometrically detailed knowledge of the crystal structure of one of the salts is being secured by Prof. E. G. Cox and his collaborators by the method of *X*-ray analysis (cf. *Nature*, 1948, **162**, 159). Dr. R. J. Gillespie has studied the electrolytic properties in solvent sulphuric acid of one of the isolated salts (*J.*, 1950, 2537).

(1.2) *Guiding Principles of this Work.*—A nitronium salt $(NO_2^+)(X^-)$ may be regarded as an ionised form of the mixed anhydride of nitric acid with the acid HX. We know that, if HX is a very weak acid, such as water, or a moderately weak acid such as benzoic acid, the mixed anhydride, NO_2X is completely covalent. According to Ingold, Millen, and Poole (*Nature*, 1946, **158**, 480; *J.*, 1950, paper no. 509), one ionic nitronium salt has long been known: solid dinitrogen pentoxide is nitronium nitrate, $(NO_2^+)(NO_3^-)$; but, as its high volatility shows, this salt very easily passes into a covalent form. Extrapolating from these indications, we expected that stable nitronium salts would be produced only with the anions of acids which are at least as strong as nitric acid. Several nitronium salts with such anions have now been prepared (cf. *Nature*, 1946, **158**, 480). During the work it was discovered that the strength of an acid is not the only factor which is necessary to confer on its anion a stability sufficient to enable it to resist attack by, so that it may form salts with, the nitronium ion. This will be made clear in the sequel (Sections 3.6 and 4.2).

Perchloric acid has hitherto been considered to be the strongest known acid. Accordingly, our first line of approach to this problem was by way of a revision of Hantzsch's work on the interaction of nitric acid and perchloric acid. Although we shall controvert a number of Hantzsch's conclusions, his central conclusion, *viz.*, that nitric acid on treatment with perchloric acid assumes a cationic form, is confirmed.

Gillespie has pointed out (*J.*, 1950, 2537) that disulphuric acid is a stronger acid than perchloric acid, and also that the higher polysulphuric acids are probably stronger acids still (*J.*, 1950, 2516). Hence we have included the study of nitronium salts with anions of these acids in our programme, as well as with some other stable anions, as is mentioned in the Summary.

(2) *The Reaction between Nitric Acid and Perchloric Acid. The Reaction between Dinitrogen Pentoxide and Perchloric Acid. The Preparation of Nitronium Perchlorate.*

(2.1) *Outline of Hantzsch's Investigations.*—Hantzsch claimed to have prepared, from anhydrous nitric acid and perchloric acid, two distinct perchlorates, and to have established their compositions by analysis (*Ber.*, 1925, **58**, 958). He called them at first nitronium perchlorate and nitronium diperchlorate, but later nitracidium perchlorate and hydronitracidium perchlorate, respectively. He regarded them as formed by simple proton transfers, as follows:

$$HNO_3 + HClO_4 = (H_2NO_3^+)(ClO_4^-) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

$$HNO_3 + 2HClO_4 = (H_3NO_3^{++})(ClO_4^-)_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

Hantzsch states (*loc. cit.*) that either salt can be obtained by mixing the component acids in appropriate proportions; and that, by the use of the acids in intermediate proportions, mixtures of the salts are produced, which, by crystallisation from warm nitric acid can be caused to yield the pure monoperchlorate (cf. I), or, by crystallisation from warm perchloric acid, can be completely converted into the diperchlorate (cf. II).

Hantzsch and Berger have given an account of the electrolytic properties of these materials in solution in nitromethane (*Ber.*, 1928, **61**, 1328). They report that the monoperchlorate (cf. I) has a limiting electrical conductivity such as could be expected for a binary electrolyte; and that, during the electrolysis of this salt, nitric acid is transported, as nitracidium ion, towards the cathode. They report also that the diperchlorate (cf. II) has a limiting electrical conductivity appropriate to a ternary electrolyte.

(2.2) *Comment on Hantzsch's Investigation.*—The point of view from which we commenced our revision of Hantzsch's work was that his nitracidium and hydronitracidium perchlorates, the latter especially, were improbable substances. Our assumption was that the reaction between nitric and perchloric acids was likely to proceed analogously to the cryoscopically and spectroscopically established reaction in solution between nitric acid and excess of sulphuric acid. The solid products would in this case be nitronium perchlorate, and the crystalline monohydrate of perchloric acid, which almost certainly has the ionic constitution of hydroxonium perchlorate:

$$HNO_3 + 2HClO_4 = (NO_2^+)(ClO_4^-) + (H_3O^+)(ClO_4^-) \quad . \quad . \quad . \quad . \quad . \quad (III)$$

This hypothesis necessitates the assumption that Hantzsch's analytical samples were mixtures simulating the compositions of compounds other than any of those which they actually contained. Hantzsch did not prove the homogeneity of the samples analysed, *e.g.*, by fractional crystallisation with a change of solvent. He handled his products in the open laboratory, preparing solids for analysis by draining off the excess of acid on porous tile. The removal of adhering acid must often have been very incomplete, and the interaction with atmospheric moisture considerable.

Most of Hantzsch's recorded analyses agree fairly well with the figures he calculates either for nitracidium perchlorate or for hydronitracidium perchlorate. But he remarks on the difficulty experienced in obtaining good analyses, and it can be read into his account that the recorded figures are not all that were obtained. As will be explained, one is forced to assume this in order to reconcile his description with our hypothesis that the reaction under observation is that represented in equation (III).

It is readily possible on the basis of equation (III) to understand analyses agreeing with the formula of hydronitracidium perchlorate. For, if a mixture of nitronium perchlorate and hydroxonium perchlorate, formed in equimolecular quantities according to equation (III), were to undergo no separation during the preparation of the sample for analysis, then the resulting composition would be identical with that of hydronitracidium perchlorate. On the other hand, it is not possible to understand analyses corresponding to nitracidium perchlorate on the basis of equation (III), except by supposing that a mixture, containing one molecular proportion of nitronium perchlorate and one of hydroxonium perchlorate, also happened to contain one molecular proportion of adhering nitric acid. Hantzsch admits that he did not remove the whole of the adhering acid from his samples by pressing them on porous tile; but the amount remaining should not always have amounted to one molecular proportion; and it should not have been so great, because mixtures containing so much acid are semi-solid pastes.

(2.3) *Revision and Extension of Hantzsch's Investigation.*—Guided by these considerations, the study of the reaction between nitric and perchloric acids was undertaken using all-glass apparatus, so designed that preparations, and all filtrations or other transferences, up to, and including, the weighing for analysis, could be accomplished out of contact with the atmosphere. Later, the reaction between dinitrogen pentoxide and perchloric acid was studied, employing the same type of technique. Temperatures have been kept as low as conveniently possible, in order to minimise the thermal decompositions which anhydrous nitric and perchloric acids, and dinitrogen pentoxide, undergo, and thus to reduce the production of contaminants such as nitrosonium perchlorate.

TABLE I.

Analysis of products formed from nitric acid or dinitrogen pentoxide and perchloric acid. (*Expts.* 1—9).

		AEW.*	N, %.	Cl, %.
Required values	$(NO_2^+)(ClO_4^-)$ ...	72·7	9·63	24·4
	$(H_3O^+)(ClO_4^-)$	118·5	0·00	30·0
	$(H_2NO_3^+)(ClO_4^-)$ ...	81·7	8·57	21·7
	$(H_3NO_3^{++})(ClO_4^-)_2$	88·0	5·31	26·9

			Analytical results.				Required for mixtures of $(NO_2^+)(ClO_4^-)$ and $(H_3O^+)(ClO_4^-)$.		
								Calc.	
Expt. no.	Reactants.	Drying time (days).	AEW.*	N, %.	Cl, %.	$NClO_5$, %.	Assumed $NClO_6$, mol. %.	AEW.*	N, %.
1	$2HNO_3 + HClO_4$	6	87·5	$\sim$5·9 †	—	—	50·0	88·0	5·31
2	HNO_3 + excess $HClO_4$, washed with $HClO_4$	2	82·6	6·68	—	0·1	64·7	82·6	6·66
3	$HNO_3 + 2HClO_4$, washed with $MeNO_2$	1	75·9	—	—	—	87·0	75·9	—
4	$N_2O_5 + HClO_4$	2	75·5	8·94	—	—	88·7	75·5	8·72
5	$N_2O_5 + HClO_4$, in $MeNO_2$	1	73·7	9·77	—	0·52	95·8	73·7	9·29
6	N_2O_5 + filtrate from $(HNO_3 + 2HClO_4)$ in $MeNO_2$	4	74·7	9·08	—	0·18	91·7	74·7	8·98
7	Excess N_2O_5 + filtrate from $(HNO_3 + 2HClO_4)$ in $MeNO_2$	8	73·0	9·52	—	0·21	98·8	73·0	9·54
8	Solutions of excess N_2O_5 and of $HClO_4$ in $MeNO_2$ mixed	8	72·8	9·47	24·3	—	99·6	72·8	9·59
9	Hantzsch's preparation of $(H_2NO_3^+)(ClO_4^-)$ repeated	7	74·8	9·06	—	0·12	91·8	74·8	8·95

* AEW = acid equivalent weight. † Approximate result.

A chronological summary of the first series of experiments on these lines will now be given, since this seems the simplest way of presenting the evidence concerning the nature of the reactions. Manipulative details are reserved for description in Section 6, but all analyses are reported in Table I. The three types of analysis which have been performed are the acid equivalent weight, the percentage of nitrogen, determined as ammonia by the use of Devarda's alloy, and the percentage of chlorine, determined by the Carius method. Nitrosonium perchlorate, often present in small amount in the samples, was estimated as nitrous acid in aqueous solution by a standard volumetric method.

Expt. 1. Anhydrous perchloric acid (1 mol.) was transferred by non-ebullient distillation at a low pressure and temperature to a bulb already containing anhydrous nitric acid (2 mols.) in solid form at −80°. The mixture was warmed to −40°, so that the nitric acid melted, and the two acids interacted. The semi-solid product was then vacuum-dried for six days, the temperature being allowed to rise to that of the room as the volatile, liquid material was removed.

Analysis of the dry solid residue (cf. Table I) gave results approximately agreeing with the composition of Hantzsch's hydronitracidium perchlorate $(H_3NO_3^{++})(ClO_4^-)_2$, and therefore also with the composition of the product, $(NO_2^+)(ClO_4^-) + (H_3O^+)(ClO_4^-)$, which should result from the assumed reaction (III), when no opportunity for separation of the components is provided. It is significant that a product of this composition is obtained, not as Hantzsch states to be necessary, by employing initially at least two molecules of perchloric acid to one of nitric acid, but by starting with two molecules of nitric acid to one of perchloric acid. According to Hantzsch, one should in these circumstances, or even if only one molecule of nitric acid is taken to one of perchloric acid, arrive at the monoperchlorate, $(H_2NO_3^+)(ClO_4^-)$. Equation (III) indicates, however, that one would expect to obtain a solid product, which would have the composition of Hantzsch's diperchlorate, but would actually consist of the equimolecular mixture, $(NO_2^+)(ClO_4^-) + (H_3O^+)(ClO_4^-)$, with whatever ratio the nitric and perchloric acids were taken, provided only that, after reaction, only volatile material is removed, no opportunity being allowed for separation of the perchlorates.

Expt. 2. On this occasion the perchloric acid was kept in excess. Anhydrous nitric acid (1 mol.) and perchloric acid (<2 mols.) were mixed by the method used previously, and allowed to react. The solid product, which remained undissolved in the excess of perchloric acid when the mixture had reached the room temperature, was collected on a sintered-glass plate. It was there washed with several further portions of freshly distilled perchloric acid, and finally dried in a vacuum for two days.

This product gave analytical figures (cf. Table I) which agree neither with the requirements of Hantzsch's diperchlorate, nor with those of his monoperchlorate, nor with those of *any* mixture of the two. The figures do, however, correspond to the composition of a mixture of 65 mols. % of nitronium perchlorate and 35 mols. % of hydroxonium perchlorate. According to Hantzsch's view of the reaction, the product should have been pure hydronitracidium perchlorate $(H_3NO_3^{++})(ClO_4^-)_2$, since perchloric acid has been kept in excess. Our interpretation assumes that, as before, the original reaction product was an equimolecular mixture of nitronium perchlorate and hydroxonium perchlorate, but that the filtration and the washing had effected a partial separation by preferentially dissolving out the hydroxonium perchlorate.

Expt. 3. Exploratory tests having shown that hydroxonium perchlorate is readily soluble in nitromethane, an attempt was made to employ this solvent for the separation. The solid product prepared by mixing nitric acid (1 mol.) with perchloric acid (2 mols.) was extracted with successive portions of nitromethane. The first few extracts on cooling to −20° deposited crystals, but the later ones did not; and the residual solid seemed to become less soluble as the extraction was continued. A final residue, amounting to only a small proportion of the solid originally taken for treatment, was dried and analysed. The analysis (Table I) indicated that it contained 87 mols. % of nitronium perchlorate and 13 mols. % of hydroxonium perchlorate.

Expt. 4. Since it appeared that the complete separation of an equimolecular mixture of nitronium and hydroxonium perchlorates by the use of solvents was likely to prove tedious, it was now decided (*a*) to employ dinitrogen pentoxide in place of nitric acid, thereby reducing the proportion of hydroxonium perchlorate initially produced (it can then never be more than 33 mols. %), and (*b*) to decompose as much of that as possible by promoting the second of the following reactions (probably a balanced reaction) by the use of an excess of dinitrogen pentoxide. The expected reactions are as follows, reaction (IV) being analogous to the well-established reaction in solution between dinitrogen pentoxide and excess of solvent sulphuric acid (*J.*, 1950, 2504 and paper no. 508):

$$N_2O_5 + 3HClO_4 = 2(NO_2^+)(ClO_4^-) + (H_3O^+)(ClO_4^-) \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

$$(H_3O^+)(ClO_4^-) + 2N_2O_5 = (NO_2^+)(ClO_4^-) + 3HNO_3 \quad . \quad . \quad . \quad . \quad . \quad (V)$$

Anhydrous perchloric acid was distilled on to an excess of dry dinitrogen pentoxide at −80°. The mixture was brought to room temperature and the volatile material was removed by distillation at low pressure for two days. The residue was vacuum-dried. Analysis of the residue gave results (Table I) agreeing with the composition of a mixture of 89 mols. % of nitronium perchlorate with 11 mols. % of hydroxonium perchlorate.

Expt. 5. This experiment was similar except that nitromethane was used as a solvent for the reaction. Anhydrous perchloric acid was distilled into a solution at −25° of an excess of dinitrogen pentoxide in nitromethane. The mixture was allowed to come to room temperature as the volatile material was distilled away with the nitromethane solvent. The residue, after being vacuum-dried for one day, gave analytical figures (Table I) agreeing with the composition of a mixture containing 96 mols. % of nitronium perchlorate and 4 mols. % of hydroxonium perchlorate.

These results are readily understood on the basis of reactions (IV) and (V), and the expectation that reaction (V) is reversible. For if this is so, reaction (V) cannot be expected to go to completion under the conditions described above, since, on pumping, the residual dinitrogen pentoxide will be removed considerably faster than the nitric acid, the presence of which, coupled with the rapid removal of the dinitrogen pentoxide, will force reaction (V) towards the left.

The obvious counter to this is to remove the dinitrogen pentoxide and nitric acid together by washing with a solvent, which one might so choose that it would wash out also the small amount of remaining hydroxonium perchlorate. This type of principle is employed in the next three experiments, which led to the preparation of pure nitronium perchlorate.

Expt. 6. In the first of them, nitric acid and perchloric acid were brought together in the proportions required by equation (III), in solution in nitromethane, and the formed precipitate was removed by filtration. Then dinitrogen pentoxide was added to the filtrate, in order to convert the hydroxonium perchlorate into nitronium perchlorate, in accordance with equation (V). This led to the formation of another precipitate, which was collected, dried, and analysed. It was thus shown (Table I) to contain 92 mols. % of nitronium perchlorate and 8 mols. % of hydroxonium perchlorate.

Expt. 7. This result proves that, although pure hydroxonium perchlorate is much more soluble in nitromethane than in pure nitronium perchlorate, the former substance has a strong tendency to be co-precipitated with the latter. The obvious reply to this is to have no hydroxonium perchlorate in the solution, *i.e.*, to employ such an excess of dinitrogen pentoxide that reaction (V) is driven completely to the right. Therefore the previous experiment was repeated, but with the use of a considerable excess of dinitrogen pentoxide. The precipitated salt now gave correct analytical figures for nitronium perchlorate (cf. Table I).

Expt. 8. It was realised that the same principles could be applied in a simpler form by using dinitrogen pentoxide throughout as the source of the nitronium ion, instead of nitric acid followed by dinitrogen pentoxide, *i.e.*, by employing reactions (IV) and (V), here summarised in equation (VI), instead of reactions (III) and (V):

$$N_2O_5 + HClO_4 = (NO_2^+)(ClO_4^-) + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (VI)$$

For the reason explained above, it was necessary to use dinitrogen pentoxide in excess of the quantity indicated to be required by equation (VI). Solutions in nitromethane of perchloric acid (1 mol.) and dinitrogen pentoxide (1·7 mols.) were mixed, and the precipitate was filtered off, washed, and dried. This salt gave good analytical figures for nitronium perchlorate (cf. Table I).

These first eight experiments, and the associated analyses, are reported fully because the complete consistency of the analytical data with the chemical interpretation now offered constitutes, as we think, a convincing case for the latter; even though we have isolated, from the product of the reaction of nitric acid, or of dinitrogen pentoxide, with perchloric acid, only one of the two perchlorates which the interpretation assumes to be formed.

The degree of purity of the ***nitronium perchlorate*** obtained in experiments 7 and 8 was not less than 99%. Nitrosonium perchlorate was present as an impurity to the extent of about 0·2%. The method of experiment 8 has been used extensively in this laboratory for the preparation of nitronium perchlorate (for details, see Section 5.2).

Expt. 9. We report one further experiment of this series for the following reason. Our interpretation of the reaction between nitric and perchloric acid identifies Hantzsch's supposed hydronitracidium perchlorate, $(H_3NO_3^{++})(ClO_4^-)_2$, as the equimolecular mixture of nitronium and hydroxonium perchlorates which constitutes the total product of the reaction; but it does not identify his reported nitracidium perchlorate, $(H_2NO_3^+)(ClO_4^-)$; and the possibility of his having obtained this substance had to be taken seriously, because it is shown in accompanying papers that the nitracidium ion * can exist at low concentration in somewhat dehydrating conditions (*J.*, 1950, 2400), and that it also exists, not necessarily in very low concentration, in aqueous conditions (*J.*, 1950, 2441). Therefore we directly repeated the preparation described by Hantzsch of his nitracidium perchlorate.

Hantzsch notes that, when anhydrous nitric and perchloric acids are mixed in equimolecular proportions, the product is not completely solid. This is strange if the nitracidium ion is stable enough to form a solid perchlorate. He states that the product must be recrystallised from nitric acid in order to obtain pure nitracidium perchlorate.

We repeated this experiment as exactly as possible. In agreement with Hantzsch's statement, we found that the product obtained by mixing accurately equimolecular proportions of nitric and perchloric acid was only partly solid (though it could be made to go completely solid by adding a second molecular proportion of perchloric acid). The product obtained by mixing the acids in equimolecular proportions was crystallised from nitric acid, and the crystals were filtered, dried, and analysed, as usual. The resulting figures (Table I) do not agree with those obtained by Hantzsch. They also do not agree with the values required for nitracidium perchlorate, or for hydronitracidium perchlorate, or for *any* mixture of these two compounds. They do agree with values calculated for a mixture of

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* In this paper we adhere for convenience to Hantzsch's name, "nitracidium" for the cation $H_2NO_3^+$, although in the papers cited in the text the same ion is called the "nitric acidium" ion, for the sake of uniformity with the names of other acidium ions, and particularly to avoid confusion with the nitrous acidium ion, $H_2NO_2^+$.

92 mols. % of nitronium perchlorate with 8 mols. % of hydroxonium perchlorate. The production of such a mixture in these circumstances is entirely consistent with the results and discussion given above.

Our inability to isolate nitracidium perchlorate from mixtures of nitric and perchloric acids containing excess of the former accords with the Raman-spectroscopic result (*J.*, 1950, paper no. 506) that the effect of adding only a few units per cent. of perchloric acid to pure nitric acid is to develop the spectra of the nitronium and perchlorate ions.

(2.4) *The Work of Gordon and Spinks.*—By mixing gas streams containing ozone, nitrogen dioxide, and chlorine dioxide, these authors obtained a white crystalline deposit, of the composition $NClO_6$, which with water gave nitric and perchloric acids (*Canadian J. Res.*, 1940, *B*, **18**, 358). They regarded the compound as formed by association of the radical-oxides, nitrogen trioxide and chlorine trioxide, which they assumed to be produced by the action of ozone on the dioxides: $NO_3 + ClO_3 = NClO_6$. For the product they suggested the covalent structure $O_3N{\cdot}O{\cdot}ClO_3$, with the ionic structure as a possible alternative. Though no identifying physical measurements were made, there seems little doubt that their compound is the same as ours.

(2.5) *Properties of Nitronium Perchlorate.*—This salt forms small, colourless, monoclinic crystals. It decomposes, without exploding, above 135°, giving off nitrogen dioxide.

It is readily soluble in absolute nitric acid, and can be crystallised from the cooled solvent. It is less soluble in nitromethane, but can be crystallised from the warm solvent: a saturated solution in nitromethane at room temperature is about 0·08M. It is still less soluble in chloroform and in carbon tetrachloride: a saturated solution in either of these solvents at room temperature is about 0·01M.

The ionic constitution of the crystalline salt follows from Dr. D. J. Millen's investigation of its Raman spectrum, which he found to consist simply of the superposed spectra of the nitronium ion and of the perchlorate ion (cf. *J.*, 1950, paper no. 509).

As Dr. R. J. Gillespie has shown, the salt dissolves in sulphuric acid to form mainly ionised nitronium hydrogen sulphate and non-ionised perchloric acid, just as ammonium perchlorate dissolves to give principally ionised ammonium hydrogen sulphate and non-ionised perchloric acid (*J.*, 1950, 2537).

The salt is rapidly decomposed by water to form nitric and perchloric acids. For this reason, the crystals cannot be exposed to the atmosphere even for a few seconds without acquiring a coating of acid. But the crystals dissolve in excess of water with only a moderate evolution of heat.

Although nitronium perchlorate reacts violently with many organic compounds, causing ignition and explosions under some conditions, it can be employed in solution in nitromethane for the nitration of aromatic compounds. Benzene is thus converted instantly into nitrobenzene, but nitrobenzene is nitrated only slowly. A study of the kinetics of such nitrations will be reported later.

(3) *The Reaction between Nitric Acid and Sulphur Trioxide. The Reaction between Dinitrogen Pentoxide and Sulphur Trioxide. Preparation of Nitronium Hydrogen Disulphate, Nitronium Disulphate, and Nitronium Trisulphate. Stability of Nitronium Hydrogen Sulphate.*

(3.1) *Reported Compounds from Nitric Acid and Sulphur Trioxide.*—The first account of a crystalline product, formed by the interaction of nitric acid with sulphur trioxide, is that of Weber (*J. pr. Chem.*, 1871, **3**, 336), who assigned to his substance the formula $N_2O_5,4SO_3,3H_2O$. Hantzsch suggested (*Ber.*, 1925, **58**, 960) that this compound was nitracidium hydrogen disulphate $(H_2NO_3^+)(HS_2O_7^-)$. However, the existence of a substance of this composition has never been confirmed by later workers, and no such compound has been encountered in the present investigation.

Schultz (U.S.P. 1,047,576/1912) and Caster and O'Callaghan (*Ind. Eng. Chem.*, 1932, **24**, 1146) have examined the same reaction. These authors obtained crystalline products, to which they agree in assigning the formula $N_2O_5,4SO_3,H_2O$. This substance undoubtedly exists; and, as will be noted below, it has the constitution of nitronium hydrogen disulphate, $(NO_2^+)(HS_2O_7^-)$.

The most recently recorded investigation of the reaction between nitric acid and sulphur trioxide is that of Dodé (*Compt. rend.*, 1943, **217**, 153). By dissolving sulphur trioxide in anhydrous nitric acid and cooling the solution to −10°, he obtained crystals of the composition $2N_2O_5,5SO_3,2H_2O$. He noted that this substance had the curious property of liberating nitric acid, and not dinitrogen pentoxide, on heating; and, indeed, that-the crystals appeared to be continuously losing nitric acid at the ordinary temperature, being difficult or impossible to dry, without change of composition, on that account. On being heated to 90° under reduced pressure, the substance melted, gave off nitric acid rapidly. and resolidified. The solid product thus obtained had the composition $N_2O_5,4SO_3,H_2O$. Evidently this was the compound obtained by Schultz, and by Caster and O'Callaghan, *viz.*, nitronium hydrogen disulphate.

A tentative interpretation of these observations is possible on the following lines. It will be pointed out later that nitronium hydrogen sulphate $(NO_2^+)(HSO_4^-)$, although stable in a dilute solution in a solvent in which the separate ions are stable, is not stable in a concentrated form, because it then undergoes a reaction which may be regarded as a dehydration of the anion by the cation, the products being nitronium hydrogen disulphate and nitric acid :

$$2(NO_2^+)(HSO_4^-) = (NO_2^+)(HS_2O_7^-) + HNO_3$$

If we assume that this reaction, although we know it to proceed fairly easily, is not instantaneous, it might be possible by Dodé's procedure to effect a crystallisation of nitronium hydrogen sulphate before it has had time to decompose completely; or, more probably, to crystallise a mixture of nitronium hydrogen sulphate with some of the nitronium hydrogen disulphate formed from it. If this is the nature of Dodé's first substance, one can understand why the crystals should continue to decompose with loss of nitric acid, and why this reaction should be rapidly completed on heating with the production of pure nitronium hydrogen disulphate. If we may suppose that Dodé's crystals, at the time of their analysis, still contained 75 mols. % of undecomposed nitronium hydrogen sulphate, together with 25 mols. % of nitronium hydrogen disulphate, his analytical results would be explained.

(3.2) *Reported Compound from Dinitrogen Pentoxide and Sulphur Trioxide.*—The only previous report of a compound formed from dinitrogen pentoxide and sulphur trioxide appears to be that of Pictet and Karl (*Compt. rend.*, 1907, **145**, 238). They state that a crystalline precipitate of the composition $N_2O_5,4SO_3$ was formed on mixing solutions of dinitrogen pentoxide and of sulphur trioxide in carbon tetrachloride; and that crystals of the same composition were obtained by dissolving dinitrogen pentoxide in liquid sulphur trioxide, and distilling the product, b. p. 218—220°, which, after solidifying, had m. p. 124—125°.

We have not encountered this compound in the course of our study of the interaction of dinitrogen pentoxide and sulphur trioxide, though we describe two substances which are formed from these oxides, but contain lower proportions of sulphur trioxide.

(3.3) *Reaction between Nitric Acid and Sulphur Trioxide.—Preparation of nitronium hydrogen disulphate.* The general experimental methods which had been developed for the study of the reaction between nitric and perchloric acids were applied to the reaction between nitric acid and sulphur trioxide. When the initially pure substances are mixed, much heat is developed, and side reactions due to decomposition of the nitric acid are difficult to avoid. For this reason, the reaction was conducted in solution in nitromethane. The reactants, each in solution in this solvent, were brought together in various ratios, extending over a 5-fold range; and in all cases colourless, crystalline precipitates were produced, which were collected, usually washed with fresh nitromethane, and dried.

The analyses which were carried out were the acid equivalent weight, the percentage of nitrogen determined as the ammonia formed by reduction with Devarda's alloy, and the percentage of sulphur determined as barium sulphate. A record of the conditions applying to the different experiments, and of all the analytical results, is given in Table II.

Referring first to the column of observed acid equivalent weights, it will be noticed that, for the products of all experiments in which the formed precipitate, after being collected on the filter, was washed with fresh nitromethane before drying (Nos. 12 and 14—18), the acid equivalent weights are identical (44·7), whereas for the products of the two experiments in which the washing with fresh nitromethane was omitted (Nos. 11 and 13) the acid equivalent weights had distinctly higher values (45·5, 45·7). In carrying out these experiments it was noticed that the products of all the preparations in which the washing with fresh nitromethane had been given were obtained as dry, freely flowing, granular powders; but the products of the two experiments in which the washing had been omitted appeared sticky, as though they contained a small amount of some adhering liquid, which could not easily be removed by pumping. On account of these observations we assume that the higher equivalent weights of the products of the experiments in which the extra washing was omitted (Nos. 11 and 13) signalise the presence of other substances than those which we wish at present to discuss.

Let us now consider the whole of the analytical data for the remaining experiments (Nos. 12 and 14—18). The products of all these experiments have the same acid equivalent weight,

TABLE II.

Analysis of products formed from nitric acid and sulphur trioxide.

		AEW.*	N, %.	S, %.
Required values	$N_2O_5,4SO_3,3H_2O$ (Weber)	48·2	5·81	26·6
	$N_2O_5,2SO_3,H_2O = (NO_2^+)(HSO_4^-)$	47·7	9·79	22·4
	$2N_2O_5,5SO_3,2H_2O$ (Dodé)	46·6	8·59	24·6
	$N_2O_5,4SO_3,H_2O = (NO_2^+)(HS_2O_7^-)$	44·6	6·27	28·7
	$N_2O_5,2SO_3 = (NO_2^+)_2(S_2O_7^{--})$	44·7	10·45	23·9
	$N_2O_5,3SO_3 = (NO_2^+)_2(S_3O_{10}^{--})$	43·5	8·04	27·6
	$N_2O_5,4SO_3$ (Pictet and Karl)	42·8	6·54	29·9

Expt. no.	Reactants.	Temp.	Drying (days).	$MeNO_2$ † Washing.	Analytical results.		
					AEW.*	N, %.	S, %.
11	$2HNO_3 + SO_3$	−20°	1·5	—	45·7	7·57	—
12	$2HNO_3 + SO_3$	−20	1·5	+	44·8	8·40	—
13	$1{\cdot}33HNO_3 + SO_3$	−20	2·5	—	45·5	7·56	—
14	$HNO_3 + SO_3$	−10	1·0	+	44·8	8·40	—
15	$HNO_3 + SO_3$	−10	5	+	44·7	8·43	—
16	$HNO_3 + SO_3$	+20	4	+	44·9	7·96	—
17	$HNO_3 + 2SO_3$	+20	4	+	44·7	6·45	—
18	$HNO_3 + 2{\cdot}5SO_3$	+20	4	+	44·6	6·26	29·0

* AEW = Acid equivalent weight.

† The symbol + means that the product, precipitated from nitromethane solution, was washed on the filter with fresh nitromethane before being dried; and — means that this washing was not given.

although their nitrogen contents are distributed over a considerable range. This can only mean that the samples consist either of one, or of mixtures of both, of two substances having coincident equivalent weights. In the list at the top of the Table one finds that there are two substances which have a common equivalent weight; and, moreover, that this common value is identical with the value uniformly given by the experiments. The substances concerned are *nitronium hydrogen disulphate*, $(NO_2^+)(HS_2O_7^-)$, and normal *nitronium disulphate* $(NO_2^+)_2(S_2O_7^{--})$, and we assume that they are the components of our substances.

The formation of nitronium hydrogen disulphate may be stoicheiometrically represented as follows:

$$HNO_3 + 2SO_3 = (NO_2^+)(HS_2O_7^-)$$

As is shown by the list of nitrogen determinations given in Table II, one obtains, consistently with this equation, pure nitronium hydrogen disulphate when, and only when, not less than two molecular proportions of sulphur trioxide are taken for one of nitric acid (Expts. No. 17 and 18). Any excess of sulphur trioxide above two molecules (as in Expt. 18) takes no part in the reaction, and is washed out from the products by the nitromethane solvent, as the analytical figures prove.

On the other hand, if nitric acid is supplied in excess of the requirements of the above equation, some of the excess enters into the reaction, and the product consists of a mixture of nitronium hydrogen disulphate and normal nitronium disulphate (Expts. No. 12, 14, 15, and 16). However, even when the nitric acid is furnished in large excess (Expt. 12), we do not obtain the pure normal disulphate, for the reason that this can never be formed from nitric acid and sulphur trioxide, except with the simultaneous production of a protolysing agent, which will bring about a partial reconversion of the normal disulphate into the hydrogen disulphate.

This may be explained for the example in which nitric acid and sulphur trioxide are taken in equimolecular proportions (as in Expts. No. 14, 15, and 16). One then has the correct nitrogen : sulphur ratio for the formation of the normal disulphate. But for every molecule of the normal disulphate produced, one molecule of water must also be formed:

$$2HNO_3 + 2SO_3 = (NO_2^+)_2(S_2O_7^{--}) + H_2O$$

This water is, basically, the protolysing agent. True, it will be immediately converted into other substances, notably sulphuric and disulphuric acids; but this conversion only replaces one proton-donor by another; whether the protolysis of normal nitronium disulphate is a hydrolysis or an acidolysis, its product will be nitronium hydrogen disulphate:

$$(NO_2^+)_2(S_2O_7^{--}) + HB = (NO_2^+)(HS_2O_7^-) + NO_2B$$

When we take nitric acid in substantially larger molecular proportion than the sulphur trioxide (as in Expt. No. 12), we still do not avoid the production of one molecule of water for every molecule of the normal disulphate, in accordance with the above equation. Indeed, we produce the same proportion as before of the basic protolysing agent; and, even though its fate may not now be quite the same in detail, it seems reasonable to expect, as in fact we find (cf. the nitrogen percentages in Table II), a similar amount of protolysis of the normal disulphate.

From the above analysis of the results of Table II, it will be clear that, in order to prepare normal nitronium disulphate in a pure form, it is essential to allow no opportunity for its ready protolysis to the hydrogen disulphate; and therefore it is necessary to conduct the preparation in completely aprotic conditions. This is done in the series of experiments next to be described.

The ionic constitution $(NO_2^+)(HS_2O_7^-)$, of crystalline nitronium hydrogen disulphate has been established by Dr. D. J. Millen (*J.*, 1950, paper no. 509). He has found in the Raman spectrum of the solid substance the characteristic lines of the nitronium and hydrogen disulphate ions; and he has observed no lines foreign to the Raman spectra of these two ions.

Nitronium hydrogen disulphate was obtained from Expts. No. 17 and 18 as a colourless, finely granular precipitate. It had no appreciable vapour pressure at room temperature. In a sealed tube, it melted in the range 100—105°, without obvious decomposition, to a colourless liquid. The precipitated salt recrystallised from warm nitromethane in slender needles, too slender, unfortunately, for *X*-ray analysis by single-crystal methods. Nitronium hydrogen disulphate is extremely hygroscopic, the crystals becoming coated with acid immediately on exposure to the atmosphere. The salt dissolves in water with considerable development of heat, forming a solution of nitric and sulphuric acids. The mixtures of hydrogen disulphate and normal disulphate obtained from Expts. No. 12, 14, 15, and 16 behaved similarly towards water.

(3.4) *Reaction between Dinitrogen Pentoxide and Sulphur Trioxide.—Preparation of nitronium disulphate.* The interaction of these substances was investigated in nitromethane solution. At first the manipulative technique employed was that previously used for the study of the reaction between nitric acid and sulphur trioxide. But for the final experiments of each of two series, a special technique was employed, as will be described below.

Sulphur trioxide is plentifully soluble in nitromethane at temperatures just above the freezing point of the latter, $-29°$; but the solubility of dinitrogen pentoxide in this solvent is somewhat small at such temperatures. The solutions of dinitrogen pentoxide therefore had to be prepared near 0°; and they then had to be used at once, in order to anticipate the thermal decomposition of the pentoxide, the rate of which is appreciable at temperatures above 0°. As soon as the dinitrogen pentoxide had dissolved, its solution was added to the well-cooled solution of sulphur trioxide. Probably the mixing temperature was between $-10°$ and $-5°$. In all cases a colourless, crystalline precipitate was immediately formed, which was filtered off, washed, and dried for some days in a good vacuum.

The proportions in which the reactants were brought together, and all the analytical results, are noted in Table III. Of the experiments of the Series 1, Nos. 19—22 were carried out with our usual technique. The results show that when not more than two molecular proportions of sulphur trioxide are available to react with one of dinitrogen pentoxide, the precipitated product has, at least approximately, the composition of normal nitronium disulphate, $(NO_2)_2(S_2O_7)$. However, these analytical data are not accurate; and we assumed that this is caused by employment of a technique, which, for the preparation of a substance so extremely sensitive to protolysis, was insufficiently rigorous in excluding the entry of traces of acids with the oxides.

Therefore Expt. No. 23 was conducted in an apparatus in which the dinitrogen pentoxide and sulphur trioxide could be sublimed into separate portions of the solvent, and then, by simply tilting the apparatus, the two solutions could be mixed in the space immediately above the filter-plate. This method should give no opportunity for the entry of acids, and in fact the resulting analyses showed that the normal nitronium disulphate had now been produced in a pure form.

The ionic constitution $(NO_2^+)_2(S_2O_7^{--})$, of crystalline nitronium disulphate has been established by Dr. D. J. Millen (*J.*, 1950, paper no. 509), who found the Raman spectrum of the solid substance to contain the characteristic lines of the nitronium and normal disulphate ions but no lines foreign to the Raman spectra of these two ions.

Nitronium disulphate was obtained in these experiments as small, colourless crystals, without appreciable vapour pressure at the ordinary temperature. Heated in a sealed tube, it decomposed between 100° and 150°, and, near the latter temperature, melted, with a rapid evolution of brown fumes. The compound is sparingly soluble in nitromethane. It is extremely hygroscopic, the crystals becoming covered with acid immediately on exposure to the atmosphere. It dissolves in water with a large evolution of heat, forming a solution of nitric and sulphuric acids.

TABLE III.

Analysis of products formed from dinitrogen pentoxide and sulphur trioxide.

		AEW.*	N, %.	S, %.
Required values	$(NO_2^+)(HS_2O_7^-)$	44·6	6·27	28·7
	$N_2O_5,2SO_3 = (NO^+_2)_2(S_2O_7^{--})$	44·7	10·45	23·9
	$N_2O_5,3SO_3 = (NO_2^+)_2(S_3O_{10}^{--})$	43·5	8·04	27·6
	$N_2O_5,4SO_3$ (Pictet and Karl)	42·8	6·54	29·9

	Expt. no.	Reactants.	Analytical results. AEW.*	N, %.	S, %.
Series 1	19	$N_2O_5 + 2SO_3$	44·8	10·28	—
	20	$N_2O_5 + 1{\cdot}6SO_3$	44·7	9·83	—
	21	$N_2O_5 + 2SO_3$	44·8	10·10	—
	22	$N_2O_5 + 1{\cdot}6SO_3$	44·5	9·69	—
	23 †	$N_2O_5 + 1{\cdot}6SO_3$	45·0	10·36	24·2
Series 2	24	$N_2O_5 + 4SO_3$	43·8	7·89	—
	25 †	$N_2O_5 + 4{\cdot}5SO_3$	43·8	8·00	—

* AEW = Acid equivalent weight. † Special acid-excluding apparatus used.

(3.5) *Reaction between Dinitrogen Pentoxide and Excess of Sulphur Trioxide.—Preparation of nitronium trisulphate.* It was recalled in Section 2.2 that Pictet and Karl claimed to have obtained a compound of the composition $N_2O_5,4SO_3$, both as the precipitated product of the interaction of dinitrogen pentoxide and sulphur trioxide in solution in carbon tetrachloride, and also as the distilled product of reaction between the two oxides in the absence of a solvent. The preparation of the substance by a process involving distillation at 220° argues very considerable stability. We have attempted to prepare this substance, with results which are summarised in the experiments of Series 2, as reported in Table III.

Exp. No. 24 was an attempt to prepare the compound by bringing together the two oxides in the correct proportions in solution in nitromethane. The analytical results show that the dinitrogen pentoxide has combined with only three molecular proportions of sulphur trioxide.

The attempt was repeated in Exp. No. 25 with two differences in procedure. First, the proportion of sulphur trioxide taken was increased from 4·0 to 4·5 molecules, per molecule of dinitrogen pentoxide, in order to ensure the availability of more than sufficient sulphur trioxide for the formation of Pictet and Karl's compound. This excess should be much more than sufficient to counteract such tendency as could be possessed by a compound, which survives distillation at 220°, to the loss of part of its sulphur trioxide by dissociation under the conditions of its formation at or below the ordinary temperature. Secondly, a special acid-excluding apparatus was used, similar to that employed for Exp. No. 23, in order to obviate any error due to possible protolysis. As appears from Table III, the result of these precautions was to improve the accuracy with which the analytical figures agree with the formula $N_2O_5,3SO_3$: clearly this represents a definite compound.

The structure of this compound, which we call *nitronium trisulphate*, and formulate $(NO_2^+)_2(S_3O_{10}^{--})$, has not yet been specifically determined; but the formula written has been adopted by analogy with nitronium disulphate, and in the light of our recently acquired knowledge concerning the higher polysulphuric acids (Gillespie, *J.*, 1950, 2516; Millen, *J.*, 1950, paper no. 507).

Nitronium trisulphate was obtained in these experiments as a colourless, minutely crystalline substance. It has no appreciable vapour pressure at the ordinary temperature. On heating in a sealed tube, it softens at 105°, and melts below 150° to a colourless liquid, which at about 200° boils without obvious decomposition, and on cooling sets to a colourless solid. It is sparingly soluble in nitromethane. It is extremely hygroscopic. It dissolves in water with a large development of heat, forming a solution of nitric and sulphuric acids.

(3.6) *Stability of Nitronium Hydrogen Sulphate.*—Even though we know from cryoscopic and spectroscopic investigations (*J.*, 1950, 2504 and paper no. 506) that nitronium hydrogen sulphate, $(NO_2^+)(HSO_4^-)$, can exist, and can even be produced quantitatively in solution in sulphuric acid, we have at no time in the course of the present experiments encountered the substance in crystalline form. As was noted in Section 3.1, Dodé probably obtained it in an impure form. It may be too easily soluble in nitromethane to be crystallised under our conditions. But we think that the main reason why we have not been able to prepare the pure substance is because, in highly concentrated solution, or as solid, indeed, in all condensed forms, the two ions interact fairly rapidly to give the hydrogen disulphate ion and nitric acid :

$$NO_2^+ + 2HSO_4^- = HS_2O_7^- + HNO_3$$

Our procedures of isolation and purification have always been slow enough to allow considerable opportunity for the occurrence of such a reaction; and the tendency of nitronium hydrogen disulphate to be precipitated from nitromethane would encourage such a reaction to proceed to completion. Certainly, nitronium hydrogen disulphate is a main product under all the conditions in which we might expect to obtain nitronium hydrogen sulphate.

As Millen indicates (*J.*, 1950, paper no. 507), this assumed reaction finds spectroscopic support. He notes that, if, to a moderately dilute oleum, as much nitric acid is added as could destroy all the " free " sulphur trioxide (*i.e.*, that which, with sulphuric acid, composes the oleum) according to the equation

$$HNO_3 + SO_3 = NO_2^+ + HSO_4^-$$

then, as the Raman spectrum shows, practically the only dissolved species are, as this equation indicates, the nitronium ion and the hydrogen sulphate ion; but that, if the same experiment is done starting with a highly concentrated oleum, again with an amount of added nitric acid just sufficient to destroy the whole of the " free " sulphur trioxide according to the above equation, then the Raman spectrum shows that comparable amounts of the hydrogen sulphate and hydrogen disulphate ions are present side by side.

In Section 3.1 we described the conversion of nitronium hydrogen sulphate into nitronium hydrogen disulphate as a dehydration of the anion of the former salt by its own cation. Partly in order to cover a case with which we shall meet in Section 4.2, it is convenient to describe the present reaction from a somewhat more general point of view. One may see in it a second limitation to the types of anion with which one may hope to produce crystalline nitronium salts. We noted in Section 1.2 that such anions, in order that they could survive in the presence of nitronium ions, would have to be anions of very strong acids, *i.e.*, they would have to have such a low nucleophilic reactivity as would render them unresponsive towards the high electrophilic reactivity exhibited by the nitronium ion. Now we are reminded that the nitronium ion will even be able to destroy an anion of too low nucleophilic reactivity to participate in direct combination, if it can break off from such an anion a simpler anion of considerably higher nucleophilic reactivity. Evidently that is what is happening in the reaction under discussion : the nitronium ion is extracting from the hydrogen sulphate ion a hydroxide ion, and is combining with the latter to form nitric acid—leaving the sulphur trioxide to combine with another hydrogen sulphate ion.

(4) *The Reaction between Dinitrogen Pentoxide and Fluorosulphonic Acid : Preparation of Nitronium Fluorosulphonate. The Reaction between Dinitrogen Pentoxide and Chlorosulphonic Acid : Formation of Nitryl Chloride.*

(4.1) *Preparation of Nitronium Fluorosulphonate.*—The reaction between dinitrogen pentoxide and fluorosulphonic acid was conducted in solution in nitromethane by the technique already developed for many of the experiments described in Sections 2 and 3. Equimolecular quantities of dinitrogen pentoxide and of fluorosulphonic acid were dissolved in separate portions of nitromethane at −10°, and the solutions were mixed. A crystalline precipitate immediately appeared, which was filtered off, washed, and well dried. The products thus obtained from two such experiments were analysed, with the results shown in Table IV.

These products, when dissolved in water, form fluorosulphonic acid, on the hydrolysis of which to hydrofluoric acid and sulphuric acid the analytical method partly depends. As the errors in the determination of the acid equivalent weight, and of the fluorine content, are rendered appreciable by the low rate of hydrolysis of this substance, a number of control analyses of pure fluorosulphonic acid were made, in order to provide an estimate of the magnitude of the analytical errors. The results of one of these control analyses—a typical one for the standardised procedure employed—are included in Table IV, as an indication of the errors which are discussed in detail in Section 6.3.

TABLE IV.

Analysis of products from dinitrogen pentoxide and fluorosulphonic acid.

Expt. no.	Reactants.		AEW.*	N, %.	F, %.
40	$N_2O_5 + FSO_3H$		36·6	9·6	—
41	$N_2O_5 + FSO_3H$		36·9	9·6	12·8
	Required for $(NO_2^+)(FSO_3^-)$		36·3	9·65	13·1
Control analysis:					
	Fluorosulphonic acid	Found	33·7	—	18·7
		Calc.	33·3	—	19·0

* AEW. = Acid equivalent weight after complete hydrolysis.

From these results it is clear that the precipitated salt is pure nitronium fluorosulphonate, $(NO_2^+)(FSO_3^-)$. Its formation from nitrogen pentoxide and fluorosulphonic acid may be represented by the equation

$$N_2O_5 + F{\cdot}SO_3H = (NO_2^+)(F{\cdot}SO_3^-) + HNO_3$$

As Ingold, Millen, and Poole have pointed out (*Nature*, 1946, **158**, 480), crystalline dinitrogen pentoxide is itself nitronium nitrate, $(NO_2^+)(NO_3^-)$. Hence the equation given above may be taken essentially to represent a simple ionic exchange.

Millen has shown by his study of the Raman spectrum of *nitronium fluorosulphonate* (*J.*, 1950, paper no. 509) that this substance has the ionic constitution by which it is represented in the above-written formulæ.

Nitronium fluorosulphonate was obtained as a colourless, finely crystalline precipitate. It crystallises from nitromethane, in which it is somewhat sparingly soluble, in small needles. It has no appreciable vapour pressure at the ordinary temperature. When heated in a sealed tube, it melts at 200° with slow decomposition to a pale yellow liquid. The salt is very hygroscopic. It dissolves in excess of water with a considerable evolution of heat, forming, as the immediate products, nitric acid and fluorosulphonic acid, and ultimately, of course, nitric, hydrofluoric, and sulphuric acids.

(4.2) *Stability of Nitronium Chlorosulphonate.—Formation of nitryl chloride.* An attempt to prepare nitronium chlorosulphonate, by the analogous reaction

$$N_2O_5 + Cl{\cdot}SO_3H = (NO_2^+)(Cl{\cdot}SO_3^-) + HNO_3$$

using the same type of technique, led to quite different results. They can be understood if one supposes that nitronium chlorosulphonate is unstable, the nitronium ion taking a chloride ion out of the anion, so that nitryl chloride and sulphur trioxide are formed, the latter undergoing such further reactions with nitric acid and dinitrogen pentoxide as have already been described in Section 3. In addition to these main reactions, there are side-reactions of an oxidation–reduction type (reminiscent of the *aqua regia* reaction) leading to nitrogen dioxide, chlorine, and presumably sulphuric acid.

Dinitrogen pentoxide (1·5 mols.) and chlorosulphonic acid (1 mol.) were dissolved in separate portions of nitromethane at −10°, and the solutions were mixed. A white precipitate was quickly formed, which, after some hours, was collected on a filter. Gases were evolved during these operations, and a further supply of gaseous products was obtained by pumping out the filtrate. They were collected by condensation in suitably cooled traps. Nitrogen dioxide and chlorine were easily identified. The main product, nitryl chloride, was identified as described below.

Nitryl chloride has been a much disputed substance, all the earlier claims for its preparation having been subsequently denied. The one adequate and authentic description of its preparation is that of Schumacher and Springer (*Z. anorg. Chem.*, 1929, **182**, 139; *Z. Elektrochem.*, 1929, **36**, 653), who obtained it by the action of 100% ozone on nitrosyl chloride. They found it to be a colourless substance, having m. p. −145° and b. p. −16°, which with water gave nitric and hydrochloric acids, and when heated above 100° decomposed into nitrogen dioxide and chlorine.

Our nitryl chloride was collected, together with some chlorine, as an almost colourless solid in a trap at −180°, less volatile substances, including dinitrogen tetroxide, having been retained in preceding traps at −80°. The scale of the experiment was too small to allow the nitryl chloride to be purified by fractional distillation, but, after a complete distillation, its identity was established, without removing the chlorine, by the following tests. The solid substance melted below −110° to a pale yellow liquid, which boiled below −10°. A portion of the vapour was shaken with a little water: the solution contained chlorine, much nitrate ion and chloride ion, but no nitrite ion. Another portion of the vapour was allowed to enter a tube which had been completely evacuated. When a side-arm attached to this tube was locally heated, it became filled with a dark brown vapour, obviously nitrogen dioxide. No air was present in the tube during this experiment. These tests clearly distinguish the substance from nitrosyl chloride, which forms a deep-red liquid having b. p. −6°, with water gives nitrous acid amongst other products, and on thermal decomposition yields only colourless nitric oxide, besides chlorine.

The crystalline substance which had been collected on the filter was shown by analysis to consist of one or more forms of nitronium disulphate. Its acid equivalent weight was 44·7, which is correct for either the normal disulphate or the hydrogen disulphate. A determination of the nitrogen content would have distinguished between these two possibilities, but this was not done. However, since the substance was produced from chlorosulphonic acid, which is a very strong proton donor, it is practically certain that the main substance which was present was the hydrogen disulphate.

The principal series of decompositions can be approximately represented in the following way:

$$N_2O_5 + Cl{\cdot}SO_3H = (NO_2^+)(Cl{\cdot}SO_3^-) + HNO_3 \quad \ldots\ldots \quad (1)$$

$$(NO_2^+)(Cl{\cdot}SO_3^-) + HNO_3 = NO_2Cl + (NO_2^+)(HSO_4^-) \quad \ldots\ldots \quad (2)$$

$$2(NO_2^+)(HSO_4^-) = (NO_2^+)(HS_2O_7^-) + HNO_3 \quad \ldots\ldots \quad (3)$$

or, collectively,

$$2N_2O_5 + 2Cl{\cdot}SO_3H = 2NO_2Cl + (NO_2^+)(HS_2O_7^-) + HNO_3$$

Stage (1) is essentially an ion exchange, as already discussed for the reaction between dinitrogen pentoxide and fluorosulphonic acid (Section 4.1). Stage (2) represents the extraction by the nitronium ion of the fairly strongly nucleophilic chloride ion from the very weakly nucleophilic chlorosulphonate ion (cf. Section 3.6). This reaction seems to be complete. Stage (3) is the already considered reaction in which the nitronium ion extracts the strongly nucleophilic hydroxide ion from the weakly nucleophilic hydrogen sulphate ion. In some circumstances this is a measurably balanced reaction (cf. Section 3.6), but it will doubtless go to completion in conditions in which the nitronium hydrogen disulphate is precipitated.

The side-reactions of redox type might be roughly expressed by the equation

$$N_2O_5 + 2Cl{\cdot}SO_3H = N_2O_4 + Cl_2 + H_2SO_4$$

Although the necessary development work has not yet been carried out, it is clear that the reactions now described can be made the basis of a method for the preparation of nitryl chloride—a method which has the attraction that it avoids the operation of preparing pure ozone.

(5) *Formation of Nitronium Salts by the Interaction of Dinitrogen Pentoxide with Selenic Acid.*

It has been shown spectroscopically (*J.*, 1950, paper no. 506) that ionised nitronium hydrogen selenate $(NO_2^+)(HSeO_4^-)$ is quite stable in moderately dilute solution in nitric acid and is, indeed, formed quantitatively when selenic acid is dissolved in concentrations up to 12 mols. % in anhydrous nitric acid.

Although we have obtained crystalline nitronium salts derived from selenic acid, we have not yet succeeded in isolating any one such salt of undoubted individuality. The reluctance with which these substances crystallise renders them considerably more difficult to obtain and to purify, than are the analogous nitronium salts derived from sulphuric acid. On the whole, the analytical evidence suggests that a series of difficultly separable nitronium polyselenates exists, possibly of a similar nature to the already discussed series of nitronium polysulphates (Sections 3.3, 3.4, and 3.5).

We may report an experiment which gave a crystalline product. The selenic acid employed was stated to be free from selenious acid, and we could obtain from it no positive test for selenious acid, although, as is commonly known, the available tests for selenious acid in the presence of much selenic acid are not very critical or sensitive. The selenic acid contained 1·4% of water, but the dinitrogen pentoxide with which it was allowed to react was present in excess. Dinitrogen pentoxide (1·5 mols.) and 98·6% selenic acid (1 mol.) were dissolved in separate portions of nitromethane at 0°. The solutions were mixed, and the mixture was kept at −10° for some hours with frequent agitation, while a colourless salt slowly crystallised. This was collected on a filter plate, and vacuum-dried for five days. The acid equivalent weight was 61·6, and the nitrogen content was 5·34%. The solution of the salt in water contained nitric and selenic acids. We could obtain no good evidence that it contained any selenious acid, but, again, the unsatisfactory nature of the available tests has to be borne in mind. Whilst the observed analytical figures do not point to any one substance or mixture uniquely, they could be given by several mixtures of nitronium di- and tri-selenates, or of one or more of them with nitronium hydrogen selenate.

(6) *Experimental Methods.*

(6.1) *Materials.*—The methods which we have used for the preparation or purification of several of the substances required for this work, *viz.*, nitric acid, dinitrogen pentoxide, and perchloric acid, are described in accompanying papers (*J.*, 1950, 2400, 2452, 2467). The obtained nitric acid and dinitrogen pentoxide were very pure, but the perchloric acid (cf. Redlich, Holt, and Bigeleisen, *J. Amer. Chem. Soc.*, 1944, **66**, 15) gave analytical figures corresponding to 100·6% acid, and must therefore have contained a little dissolved dichlorine heptoxide. These three substances were stored at −80°. The methods of purification used for most of the other substances are standard, and need no description. The selenic acid, as obtained by us by the concentration of an aqueous solution (cf. Gilbertson and King, *J. Amer. Chem. Soc.*, 1956, **58**, 180), was not anhydrous: it had m. p. 50—55°, and gave analytical values corresponding only to 98·6% selenic acid. Fluorosulphonic acid was prepared as recommended by Meyer and Schramm (*Z. anorg. Chem.*, 1932, **206**, 24). It had b. p. 162—163°, and appeared to be very pure. Perchloric acid monohydrate (hydroxonium perchlorate), m. p. 50°, was prepared by adding the correct amount of water to perchloric acid pre-cooled to −80°. The drying and purification of nitromethane gave some difficulty: the method finally adopted was to dry it first with calcium chloride, and then with magnesium perchlorate, and then to fractionate it.

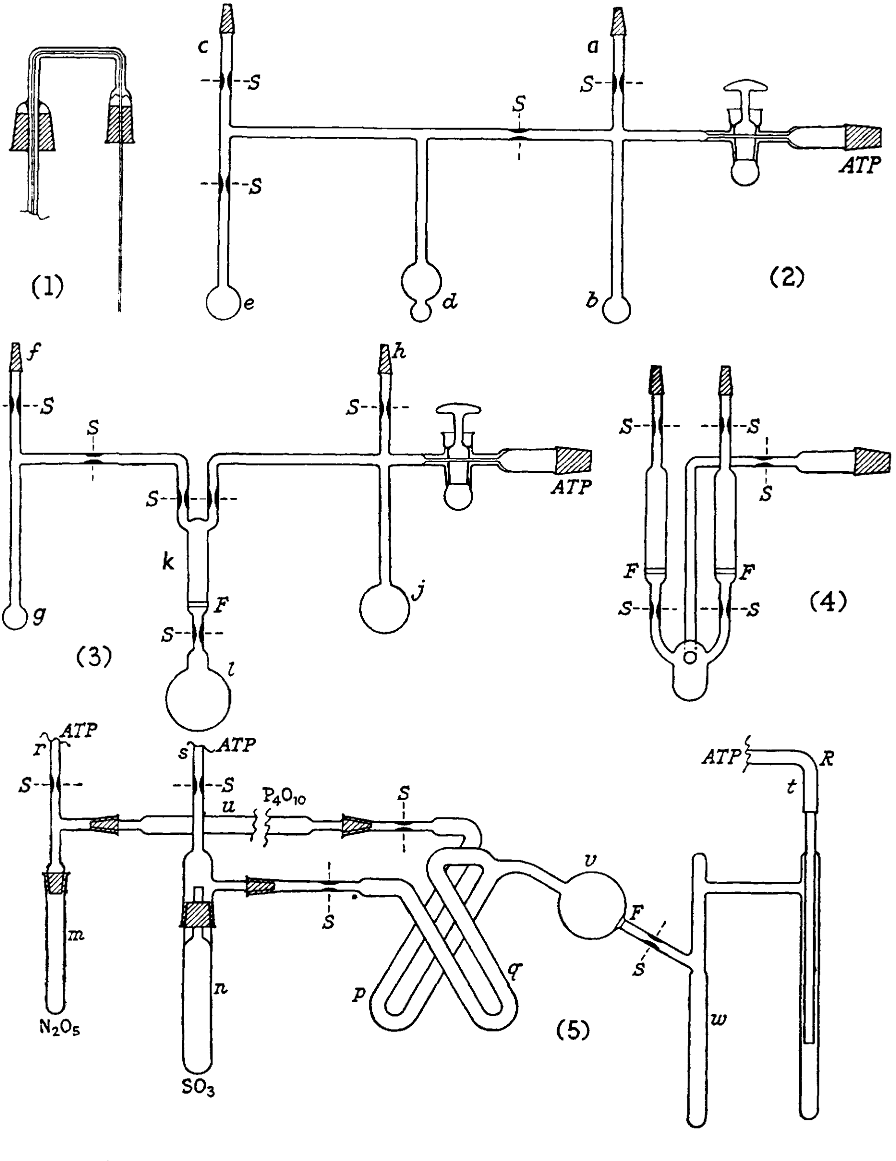
(6.2) *Manipulative Methods.*—Several of the types of apparatus employed are illustrated in Figs. 1—5. Transfers of material from stock were made, when conveniently possible, by non-ebullient distillation at low pressures. When, for liquids or solutions, this was not possible or convenient, any of three other methods of transference was used, each involving a piece of auxilliary apparatus, namely, a capillary funnel, a capillary pipette, and a capillary delivery tube. The last is illustrated in Fig. 1. The funnel worked by gravity, and the pipette by pressure of sulphuric acid in an attached air-reservoir, whilst the delivery tube was brought into operation by the vacuum pump. All ground-glass joints, *e.g.*, those indicated in Fig. 1, were sealed with metaphosphoric acid.

Experiments which did not involve filtration were performed on a simple vacuum line furnished with only bulbs, constrictions *s* for sealing-off, and a single tap, mercury-sealed and lubricated with phosphoric acid, leading to the absorption-tubes, liquid-air trap, and pump *ATP*. An example is illustrated in Fig. 2, which represents the apparatus made for Expt. 5. It was used in the following way. Perchloric acid (*ca.* 1 c.c.) was introduced through joint *a* into bulb *b*, joint *c* being meanwhile closed with a cap sealed on with metaphosphoric acid. Joint *a* was then removed by sealing off at the constriction provided. The apparatus having been evacuated, perchloric acid was transferred by distillation into the double bulb *d*, up to a measured volume given by a mark on the neck between the bulbs. Air was now admitted through the drying tubes to bring the pressure to atmospheric, and then a freshly prepared solution at 0° of dinitrogen pentoxide (3 g.) in nitromethane (15 c.c.) was introduced into bulb *e* through joint *c*. Joint *c* was now removed by sealing off. All the bulbs were now cooled to −80°, while the apparatus was thoroughly pumped out, and the part which contains bulbs *d* and *e* was sealed off from the pump. Bulb *e* was now warmed to −25°, so that the nitromethane melted, and into this solution of dinitrogen pentoxide the perchloric acid was allowed to distil, with occasional gentle shaking. When the transference, and the reaction, were complete, all the volatile material was transferred back into bulb *d* by strongly cooling *d*. The solid reaction product remaining in bulb *e* was dried for one day by maintaining the cooling bath round bulb *d*; and then bulb *e* was sealed off.

As an example of the process of filtration, and of the washing of a precipitate, Expt. 2 may be described. The apparatus made for this experiment is illustrated in Fig. 3. Nitric acid (>1 c.c.) was introduced through joint *f* into bulb *g*, and perchloric acid (*ca.* 12 c.c.) through joint *h* into bulb *j*. The joints *f* and *h* were then sealed off. The bulbs *g* and *j* being strongly cooled, the apparatus was evacuated, and then shut off from the pump by means of the mercury-sealed tap. By cooling to −80° the whole central limb *kl* of the apparatus, up to a point just above the fork, and allowing bulb *g* to become warm, nitric acid could be transferred to the tube *k*, without any of its vapour reaching the perchloric acid in bulb *j*. The nitric acid solidified at the top of tube *k*, but it was caused to melt and run down the tube, and was then resolidified on top of the sintered-glass filter plate *F*. When about 1 c.c. of nitric acid had thus been transferred, the distillation was stopped, and the bulb *g* containing the remainder of the nitric acid was removed by sealing-off. By adjusting the temperature of bulb *j*, about 5 c.c. of perchloric acid were distilled on the layer of solid nitric acid in tube *k*. The nitric acid was allowed to melt, and the two acids to react. Then, by cooling bulb *l* strongly, filtration of the formed precipitate was effected. The remainder of the perchloric acid was then distilled into the tube *k* in three portions, each of which was allowed to mix well with the precipitate before being forced through the filter plate, by reducing the temperature in *l*, and also, if necessary, by admitting a limited amount of dry air through the tap. The bulb *l* being cooled strongly, the apparatus was again completely evacuated; and the precipitate was thus dried in a vacuum for 2 days. It was isolated for analytical purposes by sealing off above and below the tube *k*.

It was found that, in the reactions in which a free acid was used, or could be used, as either reagent, the reaction mixture could, without harm to the product, be allowed to take up the small amount of moisture which is introduced by one transference through air. Thus, in the preparation of nitronium perchlorate from perchloric acid and excess of dinitrogen pentoxide, precautions to exclude every trace of moisture are not essential, and a relatively simple technique will yield a product of purity better than 99%.

FIGS. 1—5.



In such cases, it is mechanically a great convenience to have the apparatus employed for the reaction separate from that used for the filtering, washing, and drying of the reaction product. The separate units of apparatus are then more robust and easily manageable. A filter unit of the seal-off type is illustrated in Fig. 4. It has two filter tubes, between which the reaction product is divided, so that if the contents of one tube are used for analysis there remains in the other a specimen of known composition. A jointed type of filter unit has also been used, which was similar to the unit shown in Fig. 4, except that the four constrictions provided for sealing off were replaced by ground-glass joints, made tight with metaphosphoric acid. Which type of apparatus was used depended on the purpose of the preparation, how long one intended to keep the product, and whether, during a filtration, the solid would easily pass the upper constrictions contained in the seal-off unit.

In illustration of the use of the apparatus shown in Fig. 4, a preparation of nitronium perchlorate by the method of Expt. 8 may be described. Perchloric acid (5 g.) was dissolved in nitromethane (12 c.c.) at −25°. Dinitrogen pentoxide (9 g.) was added to nitromethane (30 c.c.) at −25°, and the mixture was allowed to warm with constant shaking until a clear solution was obtained, which was then immediately mixed with the solution of perchloric acid. The mixture was kept at −20° for 3 hours, in order to allow the crystalline precipitate to become more rapidly filterable, and then it was poured into the filter unit, the upper joints of which were subsequently removed by sealing off. The filtration was effected by operating the pump, while, in order to prevent decomposition, with the formation of nitrosonium perchlorate, the whole apparatus was kept at about −10° by immersion in cooled alcohol up to the tops of the filter tubes. The final drying was done by cooling the filtrate strongly, pumping for several hours to a hard vacuum, and sealing off from the pump. The strong cooling of the filtrate was thereafter continued for several days, before the two filter tubes were removed by sealing off below the filter plates.

As has been indicated in Sections 2.4 and 2.5, the type of technique just described was found to be unsatisfactory for the study of reactions between dinitrogen pentoxide and sulphur trioxide. Hence, for the more critical experiments with these compounds (Expts. No. 23 and 25), the whole apparatus for conducting the reaction and collecting the product was employed as the single unit illustrated in Fig. 5. The method of using such an apparatus will be explained by describing Expt. No. 23.

The well-dried apparatus was assembled as shown. Then the tube *n* was detached and made the receiving end of another apparatus (not shown) by which sulphur trioxide could be transferred from stock by sublimation under reduced pressure. Since very low pressures were not required, the sublimation was conducted with unlubricated joints. This allowed the receiving tube *n* to be fitted with a ground-glass cap and weighed, after it had collected some sulphur trioxide; in the present experiment it was thus found that 2·7 g. of sulphur trioxide had been transferred.

Next, the tube *m* was removed from the apparatus shown in Fig. 5, and attached to another sublimation apparatus (not shown), in which it became the receiver in a transference of dinitrogen pentoxide, by sublimation in a vacuum, through a long tube of phosphoric oxide. The dinitrogen pentoxide was sublimed from a tube, previously charged, by mechanical transference from stock, with the required quantity, 2·3 g., of that substance. In this case a low pressure was used, and all ground-glass joints were made tight with metaphosphoric acid. The charged tube and the receiver being both cooled to −80°, the apparatus was thoroughly evacuated, and then shut off from the pump. The receiving tube *m* being still held at −80°, the temperature of the tube containing the dinitrogen pentoxide was raised to −10°, and there maintained during the sublimation. After 1 hour the whole of the dinitrogen pentoxide had collected, without any sign of decomposition, in the receiving tube *m*.

The U-tube *p* was furnished with 40 c.c., and the U-tube *q* with 30 c.c., of nitromethane. Tubes *m* and *n* were now restored to place, and all ground-glass joints were made good with metaphosphoric acid. Tube *m* and the U-tubes *p* and *q* being cooled to −80°, and tube *n* to −180°, the whole apparatus was evacuated. The three pump connections, *r*, *s*, and *t*, communicated with one another, so that the pressure in the two limbs of either U-tube remained the same during the evacuation. The pump connections *r* and *s* were next removed by sealing off at the constrictions shown. Then the temperature of the tubes *m* and *n* was raised to −10°, in order that their contents should distil into the U-tubes *p* and *q*, on top of the solid nitromethane which occupied the bends of the U-tubes. During this process the dinitrogen pentoxide passed through the long tube of phosphoric oxide *u*, in order to remove any nitric acid that might have arisen from moisture acquired during the last transfer of tube *m* before the apparatus was evacuated. No analogous precaution with respect to the sulphur trioxide was necessary because of the low volatility of sulphuric acid. The empty tubes *m* and *n*, together with the tube of phosphoric oxide *u*, were now removed by sealing off at the two constrictions provided. Next the nitromethane in the U-tubes was melted, at first partly, by pouring alcohol at room temperature over them, the object being to melt first the layer of solid next to the glass, thus obviating breakage by expansion. The U-tubes were then surrounded by baths at −10°, and the whole apparatus was rocked in order to assist the dissolution of the dinitrogen pentoxide and the sulphur trioxide. Through the pump connection *t*, dry air was now admitted slowly until the internal pressure was atmospheric. Then, making use of the flexibility provided by the rubber connexion *t*, the whole apparatus was tilted so that first the solution of dinitrogen pentoxide, and then the solution of sulphur trioxide, ran into the bulb *v*, which meanwhile was kept cool by means of a wrapping of cotton-wool soaked in cold alcohol. A white precipitate was formed immediately. The apparatus was shaken, and then, by operating the pump, the liquid contents of bulb *v* were drawn through the sintered-glass plate, which had been sealed across the opening of the exit tube of *v*. The filtrate in tube *w* was frozen at −180°, and the apparatus was pumped out for many hours. The collected precipitate was then isolated from the filtrate by sealing off at the constriction provided.

(6.3) *Analytical Methods.*—For those analyses which start with the preparation of an aqueous solution, two methods of weighing samples were employed. The samples were usually contained in evacuated sealed filter-tubes, such as form part of the apparatus illustrated in Fig. 4. In the first method, the tube is marked with a file, cleaned, weighed, cracked open, and immersed in water, the parts of the tube being subsequently recovered, washed, dried, and weighed. It was naturally necessary to correct for the absence of air from the tube during the first weighing.

In the cases of the polysulphates, the use of this method was apt to lead to losses by fuming, owing to the large development of heat in the reaction with water. It was found better in these cases, and satisfactory almost always, to cut a filter-vessel open at a narrow extremity, and pour the powdery contents into a tared short tube of the right diameter, standing in a weighing bottle, which could be capped for the weighing. The tube could then be transferred to a stoppered conical flask containing water, which, however, was allowed to reach the analytical sample only while the ground-glass stopper of the flask was being held firmly in position. Substantially the same method was used in weighing samples for the determination of chlorine by the Carius method.

Except in the case of fluorosulphonates, acid equivalent weights were determined by direct titration of the original solution with carbonate-free 0·05N-sodium hydroxide, methyl-red being the indicator.

Attention was paid to the problem of securing accurate nitrogen determinations by reduction with Devarda's alloy. It is known that when the formed ammonia is distilled through an ordinary Kjeldahl trap, the results tend to be high, partly, it is thought, on account of the carrying of alkaline spray by the ammonia, and perhaps partly owing to the presence of nitride as an impurity in the alloy. Donald (*Analyst*, 1936, **61**, 249) has recommended replacing the Kjeldahl trap by a Davisson trap (*Ind. Eng. Chem.*, 1919, **11**, 465). Vandoni and Chazeau (*Mem. Serv. Chim. de l'État*, 1945, **32**, 25) have introduced a new form of trap, and have made other changes in the apparatus. We have tried all three methods. and find that the main difference in the results they produce relates to the magnitudes of blank determinations. Using the quantity of alloy recommended by Donald, we obtained, with the Kjeldahl trap. blank determinations amounting to 1·1—1·2%, with the apparatus of Vandoni and Chazeau, blanks equivalent to 0·8—0·9%, and, with the Davisson trap, blanks corresponding to 0·3—0·4%, of the quantities of nitrate under determination. Therefore our standard procedure involved the use of the Davisson trap, with blank determinations for purposes of correction. Trials with pure sodium nitrate showed that the results obtained in this way were always good to within about 0·3%.

The sulphur in the various nitronium polysulphates was determined as barium sulphate. It is recognised (Allen and Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 588; Adams and Johnston, *ibid.*, 1911, **33**, 829; Fales and Thompson, *Ind. Eng. Chem. Anal. Edn.*, 1939, **11**, 206) that several partly compensating errors affect the determination of sulphates as barium sulphate; but the error of special concern to us is the known, very marked effect of nitrates in producing high weights of barium sulphate. Using solutions of sulphuric and nitric acid in the proportions in which they would be produced when the different nitronium polysulphates react with water, we found that, under the standard conditions of precipitation used throughout, the presence of nitric acid always raised the weight of the precipitated barium sulphate. For instance, when, along with one equivalent of sulphuric acid, one-third of an equivalent of nitric acid was present, the precipitate was too heavy by 0·5%; and the percentage excess weight appeared to be approximately proportional to the number of equivalents of nitric acid initially present with one of sulphuric acid. On this basis one could apply a correction to the estimated sulphur contents of nitronium polysulphates: it would amount to —0·3% for nitronium hydrogen disulphate, —0·8% for normal nitronium disulphate, and —0·5% for nitronium trisulphate. Such corrections have not actually been applied to the sulphur determination recorded in Tables II and III, but it is clear that, if they were applied, the effect would be considerably to improve the agreement of the results with the calculated values.

Comment is necessary on the analysis of nitronium fluorosulphonate. Nitrogen was determined in the usual way. However, the determination of the acid equivalent weight, and of the fluorine content, involved the problem, which was not fully solved, of securing complete hydrolysis of the fluorosulphonic acid without incurring any loss of the formed hydrofluoric acid. This also applied to the determination of the same quantities for fluorosulphonic acid itself; and therefore the analysis of this substance was studied as a control.

Original solutions, prepared from about 1 g. of nitronium fluorosulphonate, or of fluorosulphonic acid, were made up to 500 c.c. The portions taken for the determination of the acid equivalent weight were first neutralised as usual by titration with standard alkali, methyl-red being the indicator. They were then heated on the water-bath, with neutralisation from time to time by continued titration with standard alkali, until the solution no longer became acid on further heating. The period of heating was about two days. It appears from the examples given in Table IV, that the acid equivalent weights of both nitronium fluorosulphonate and fluorosulphonic acid, as estimated in this way, are about 1·5% too high.

The fluorine in nitronium fluorosulphonate, and also in fluorosulphonic acid, was determined, after total hydrolysis, by precipitating lead fluorochloride along with lead sulphate, and then, after dissolving the precipitate in nitric acid, determining the chloride by potentiometric titration with silver nitrate. A portion (25 c.c.) of the original solution of either substance was diluted to 250 c.c. with water, and the diluted solution was heated for 2 days on the water-bath in order to secure hydrolysis. The fluoride was then precipitated following the standard procedure for the determination of fluoride ion as lead fluorochloride. Lead sulphate, although it is precipitated with the lead fluorochloride, is not precipitated completely enough to give to the weight of the total precipitate any simple analytical significance. Therefore the precipitate was collected in a sintered-glass crucible and washed; and the crucible and its contents were warmed with 1·3N-nitric acid (100 c.c.) unti the precipitate had completely dissolved. The solution was then left to cool, and the next day was titrated with 0·012N-silver nitrate. As appears from the examples in Table IV, the results tended to be about 2% low.

Nitrous acid was determined by iodometric measurement of its reducing action on acid permanganate.

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