CLVIII.—*Nitrosylsulphuric Acid. Part I.*

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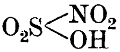
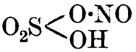
The object of this investigation was to examine the constitution and properties of nitrosylsulphuric acid.

To the substance of the molecular formula HSO_5N have been ascribed two structural formulæ, *viz.*, that of nitrosulphonic acid (I) (Michaelis, *Ber.*, 1874, **7**, 1075; Raschig, *Z. angew. Chem.*, 1905, **18**, 1032) and that of nitrosylsulphuric acid (II) (Tilden, J., 1874, **27**, 630; Lunge, *Ber.*, 1879, **12**, 1058). The evidence for the existence of an acid of the structure (I) is unsatisfactory.

(I.)



$$\mathrm{O_2S}<\begin{matrix}\mathrm{NO_2}\\ \mathrm{OH}\end{matrix}$$



$$\mathrm{O_2S}<\begin{matrix}\mathrm{O{\cdot}NO}\\ \mathrm{OH}\end{matrix}$$

(II.)

We first prepared the acid by several different methods and found that its melting point and crystalline form did not vary with the method used. Fractional crystallisation from sulphuric acid also failed to effect any change. Therefore, whilst the acid may be tautomeric, the existence of non-dynamic isomerides is improbable.

The action of hydrogen chloride on the crystalline acid at the ordinary temperature rapidly led to the formation of nitrosyl chloride and sulphuric acid, the reaction being reversible, as was foreshadowed by the work of Tilden (*loc. cit.*). The presence of the nitroso-group thus indicated was more definitely suggested by the reaction between the acid and benzoyl chloride, which produced *dibenzoylsulphuric acid*, $O_2S(O{\cdot}CO{\cdot}C_6H_5)_2$, whose formation can be satisfactorily explained only on the assumption that nitrosylsulphuric acid contains both a nitroso- and a hydroxyl-group. The mechanism of the reaction would then be as follows. The first stage is the formation of *monobenzoylsulphuric acid* :

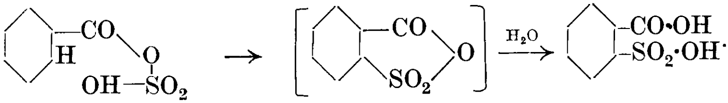
$$OH{\cdot}SO_2{\cdot}O{\cdot}NO + PhCOCl = OH{\cdot}SO_2{\cdot}O{\cdot}COPh + NOCl.$$

Nitrosyl chloride is actually formed as soon as the two substances are mixed and is rapidly liberated at 35—40° without appreciable heat evolution. The monobenzoylsulphuric acid then reacts additively with a further molecule of benzoyl chloride, probably at the carbonyl group of the latter, and a crystalline product is obtained which loses hydrogen chloride on standing, dibenzoylsulphuric acid being formed :

$$PhCOCl + OH{\cdot}SO_2{\cdot}O{\cdot}COPh = PhCCl(OH){\cdot}O{\cdot}SO_2{\cdot}O{\cdot}COPh.$$

Confirmation of this mechanism was obtained by examining the reaction between benzoyl chloride and sulphuric acid. Oppenheim (*Ber.*, 1870, **3**, 736) states that this reaction yields a benzoylsulphuric acid which rapidly changes to *m*-sulphobenzoic acid on standing, and that the latter is formed exclusively if the reaction is carried out at 150°. No mention of an additive product is made and the experimental data are very meagre. We have found that the substance produced at the ordinary temperature is a crystalline additive compound, to which the constitution $PhCCl(OH){\cdot}O{\cdot}SO_2{\cdot}OH$ may most readily be assigned. It loses hydrogen chloride on standing, forming monobenzoylsulphuric acid; this change, however, is inhibited by an atmosphere of hydrogen chloride. The additive compound showed no sign of transformation into sulphobenzoic acid on being kept for 6 months over a dry alkaline absorbent at the ordinary temperature, although during this time the hydrogen chloride was completely eliminated.

At 100°, the highest temperature used in our experiments, conversion of benzoylsulphuric acid into sulphobenzoic acid occurred, but so slowly that the amount formed during our experiments could be neglected in making deductions from the results obtained. The change was a unimolecular one and the product consisted mainly of *o*- and not *m*-sulphobenzoic acid. It is probable that the meta-acid, stated by Oppenheim to be the sole product, is produced by direct sulphonation, and the ortho-acid by intramolecular transformation. The production of the ortho-acid in this way can be satisfactorily explained by assuming intermediate anhydride formation and subsequent rehydration :



We were unable to obtain pure dibenzoylsulphuric acid by the interaction of benzoyl chloride and sulphuric acid.

The action of acetyl chloride on nitrosylsulphuric acid yielded similar evidence of the presence of the nitroso-group. The first product of the reaction appears to be acetylsulphuric acid, but this changes with great rapidity into the isomeric sulphoacetic acid. The evidence for this change lies in the rapid decrease in the amount of free sulphuric acid produced by the decomposition of the product with water, whilst the total sulphur content of the substance remains constant. The change is very much more rapid than that of benzoylsulphuric acid, but we did not investigate it further as it had already been examined by Van Peski (*Rec. trav. chim.*, 1921, **40**, 103) and others.

The action of acetic anhydride on nitrosylsulphuric acid also yielded acetylsulphuric acid. Equimolecular quantities of the two substances without any diluent reacted so violently at the ordinary temperature that the sudden evolution of heat was usually sufficient to shatter the glass container. If the acetic anhydride was in great excess and was kept below 15° during the addition of the nitrosylsulphuric acid, the latter dissolved, and by shaking the solution with silver oxide a substance was obtained to which the constitution $CH_3{\cdot}CO{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO,CH_3{\cdot}CO_2Ag$ is assigned.

By the action of ether on nitrosylsulphuric acid, ethyl nitrite and ethyl hydrogen sulphate were produced :

$$HO{\cdot}SO_2{\cdot}O{\cdot}NO + (C_2H_5)_2O = C_2H_5{\cdot}HSO_4 + C_2H_5{\cdot}O{\cdot}NO.$$

Ethyl hydrogen sulphate and solutions of nitrosylsulphuric acid in sulphuric acid gave no nitroethane, which one would expect to be produced if the acid had the nitrosulphonic structure.

The most important evidence for the nitrosulphonic structure and possible tautomerism of the acid is the work of Biehringer and Borsum (*Ber.*, 1916, **49**, 1402). By treating a sulphuric acid solution of dimethylaniline with solid sodium nitrite they obtained mixtures of *p*-nitro- and *p*-nitroso-dimethylaniline. We decided to repeat their work, for three reasons : (1) The setting up of equilibria involving the two forms of nitrous acid and sulphuric acid was not excluded by their method of experiment. (2) Since they poured a reaction mixture containing an excess of nitrite on ice, direct nitration of unchanged dimethylaniline and secondary oxidation of the nitroso-derivative would be expected. (3) They do not mention the production of sulphur dioxide which would be expected as a by-product from the nitrosulphonic form.

Using a solution of crystalline nitrosylsulphuric acid in sulphuric acid, of concentration equivalent to that used by them, we confirmed the result that both *p*-nitro- and *p*-nitroso-dimethylaniline are produced. We also established the following facts : (1) The percentage yield of the *p*-nitro-derivative increases with the excess of nitrosylsulphuric acid used in the reaction mixture. (2) If an excess of dimethylaniline is used, no oxides of nitrogen are produced by pouring the mixture on ice and no *p*-nitro-derivative is obtained. (3) When an excess of nitrosylsulphuric acid is present and the mixture is poured into absolute alcohol or dry ether, no *p*-nitro-derivative is obtained. Both these solvents rapidly decompose nitrosylsulphuric acid, forming ethyl nitrite and ethyl hydrogen sulphate. (4) When crystalline nitrosylsulphuric acid is added to a solution of dimethylaniline in dilute sulphuric acid (2*N*), in which the former acid is immediately decomposed, both the *p*-nitro- and the *p*-nitroso-derivative are obtained. (5) If a solution of dimethylaniline in concentrated sulphuric acid is added to a dilute solution of nitric acid (10%) or of potassium nitrite (5%), the *p*-nitro-derivative is formed. (6) No sulphur dioxide could be detected in any of the experiments.

All these facts are in accord with the view that the *p*-nitrodimethylaniline is not produced by the action of a presumed nitrosulphonic acid, but is a secondary product obtained by pouring the reaction mixture on ice and is produced either by secondary oxidation of the nitroso-compound or by direct nitration of the dimethylaniline. The results of Biehringer and Borsum do not establish, therefore, in our opinion, the existence of nitrosulphonic acid or the possibility of tautomerism.

Conversion of Nitrosylsulphuric Acid into the Anhydride.

The anhydride of nitrosylsulphuric acid is assumed to have the structure $ON{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO$ and is stated to be formed by the action of nitric oxide on sulphur trioxide, or of sulphur dioxide on well-cooled nitrogen pentoxide (Berl, *Z. angew. Chem.*, 1910, **23**, 2250).

There appears to be no definite experimental evidence for the direct conversion of nitrosylsulphuric acid into the anhydride, a change which would yield important evidence as to structure. We have examined the change by three methods :

(1) By the action of heat alone.

(2) By heating in the presence of dehydrating agents.

(3) By the determination of the solubility of the acid in sulphuric acid.

Action of Heat on Nitrosylsulphuric Acid.—Michaelis and Schumann (*Ber.*, 1874, **7**, 1075) carried out a preliminary investigation on this point and suggested that the decomposition took place according to the scheme :

$$NO_2{\cdot}SO_2{\cdot}O\boxed{H + HO}{\cdot}SO_2{\cdot}NO_2 \rightleftharpoons NO_2{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}NO_2 + H_2O.$$

Their experimental methods, however, were very rough, and no experimental evidence was offered that the final product was the anhydride. They ascribe the nitrosulphonic structure to the acid, but it is improbable that an acid of either the nitro- or the nitroso-structure would undergo a decomposition of the type suggested, in view of the great instability of these groups in the molecule.

Theoretically there is another mode of decomposition :

$$ON{\cdot}O{\cdot}SO_2{\cdot}OH + ON{\cdot}O{\cdot}SO_2{\cdot}OH \rightleftharpoons ON{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}OH + HNO_2.$$

The nitrous acid would then decompose to form nitrogen trioxide and water, which would decompose more nitrosylsulphuric acid. The net result is represented by the equation $3HSO_5N = HS_2O_8N + H_2SO_4 + N_2O_3$. When decomposition is complete, the resulting liquid should yield 15·4% of nitrous acid by decomposition with water. If the reaction proceeds according to the suggestion of Michaelis, however, the percentage of nitrous acid so obtained should be 21·8. (By " percentage of nitrous acid " should be understood the amount of nitrous acid obtained by the complete decomposition of the residue with water, calculated as a percentage of the anhydrous substance.)

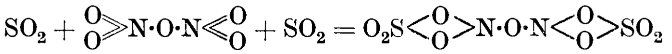
By following the change in the nitrous acid content we found that the decomposition by heat appears to follow the course suggested by Michaelis.

The Action of Dehydrating Agents.—The results obtained by heating the acid in the presence of dehydrating agents (phosphorus pentoxide in particular) were unsatisfactory. We were unable to detect the anhydride in the distillate : nitrosylsulphuric acid, the main product obtained, was probably formed by the recombination of sulphur trioxide, water, and nitrogen peroxide in the receiver. Dehydration of nitrosylsulphuric acid was also attempted by making a saturated solution in 98% sulphuric acid at 50°. The solution, after being heated for several hours at 100°, was cooled to 16° and found to be supersaturated. A crystal of nitrosylsulphuric acid induced crystallisation, the product being the unchanged acid. Further experiments showed that nitrosylsulphuric acid appears to be capable of existence in saturated solution in sulphuric acid even at 300°. This is remarkable in view of the ease with which water is lost on heating the acid alone.

The Solubility of Nitrosylsulphuric Acid in Sulphuric Acid.—The method previously described for the attempted isolation of the anhydride would yield positive results only if the anhydride (if formed) were relatively less soluble in sulphuric acid than nitrosylsulphuric acid. We therefore examined the solubility of nitrosylsulphuric acid at 0°, 20·9°, 37·3°, and 49·6° in various concentrations of sulphuric acid. The curves expressing the relationship between the solubility of nitrosylsulphuric acid and the concentration of sulphuric acid all showed a marked increase in the solubility coefficient when the concentration of sulphuric acid reached 73%. Schlesinger and Salathe (*J. Amer. Chem. Soc.*, 1923, **45**, 1863) have investigated the absorption spectra of a series of 0·1*N*-solutions of nitrosylsulphuric acid in sulphuric acid of different concentrations. If the concentration of sulphuric acid is plotted against the frequency for a given value of the logarithm of the thickness in their results, the curves so obtained are similar to ours and show a change of slope at a concentration of 78% H_2SO_4.

The shape of our curves is not incompatible with the conclusion that anhydride formation takes place.

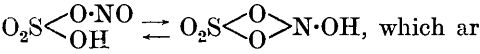
From some points of view, an alternative structure $O_2S{<}\substack{O\\O}{>}N{\cdot}OH$ seems to merit consideration. (1) An acid of this type would lose water on heating to give an anhydride of the structure (III), a change which is parallel to the conversion of nitric acid into nitrogen pentoxide. (2) It offers an explanation of the great difficulty of replacing both the hydroxyl groups of sulphuric acid by the nitroso-group. (3) The structure is in accord with the methods of synthesis of the acid. (4) The behaviour of the acid on reduction is more in accord with this structure than with the nitroso-structure. (5) The synthesis of the anhydride from sulphur dioxide and nitrogen pentoxide (Berl, *loc. cit.*) is readily explicable in terms of the above formula :



$$SO_2 + \substack{O\\O}{\gg}N{\cdot}O{\cdot}N{\ll}\substack{O\\O} + SO_2 = O_2S{<}\substack{O\\O}{>}N{\cdot}O{\cdot}N{<}\substack{O\\O}{>}SO_2 \qquad \text{(III.)}$$

and so is the production of the anhydride from nitrogen tetroxide and sulphur dioxide (Provostaye, *Ann. Chim. Phys.*, 1840, **73**, 362), in which reaction nitrogen trioxide is a by-product :

$$SO_2 + \substack{O\\O}{\gg}N{\cdot}O{\cdot}N{:}O + O{:}N{\cdot}O{\cdot}N{\ll}\substack{O\\O} + SO_2 = \text{(III)} + N_2O_3.$$

It is possible that nitrosylsulphuric acid exists in two tautomeric forms,  $O_2S{<}\begin{matrix}O\cdot NO\\ OH\end{matrix} \rightleftharpoons O_2S{<}\begin{matrix}O\\ O\end{matrix}{>}N\cdot OH$, which are in equilibrium in sulphuric acid solution and in the molten state.

EXPERIMENTAL.

Preparation of Nitrosylsulphuric Acid.—(1) By the addition of dry liquid nitrogen tetroxide to concentrated sulphuric acid at 15—18°. The separation of crystals and the removal of excess of tetroxide were facilitated by blowing dry air through the mass. (2) As above, but using gaseous nitrogen tetroxide. (3) By passing sulphur dioxide, dried by sulphuric acid, into pure nitric acid (94·5% HNO_3) at 25°. (4) By leading nitrosyl chloride, generated by heating aqua regia, into concentrated sulphuric acid.

The crystals in each case were rapidly drained by a pump and dried on a porous plate over sulphuric acid. All the products consisted of rhombic prisms (m. p. 73·5°). Tilden (*loc. cit.*) obtained by the last method of preparation a product of m. p. 85—87°, but we have not been able to repeat his work.

The Action of Benzoyl Chloride.—A mixture of 1 g.-mol. of nitrosylsulphuric acid with 2·4 g.-mols. of benzoyl chloride was heated for 30 minutes on the water-bath, moisture being excluded. After 12 hours, yellowish-brown, rhombic crystals separated. These were filtered off rapidly on asbestos, washed with dry carbon tetrachloride, and dried on a porous plate over phosphorus pentoxide. The product was very hygroscopic. It had no odour of benzoyl chloride, and on treatment with water it was completely decomposed into sulphuric, benzoic, and hydrochloric acids. Ethyl alcohol was readily converted by it into ethyl benzoate. It was insoluble in all common organic solvents and reacted readily with substances containing a hydroxyl group and with ether and acetone. No evidence of the presence of an acid with a sulphonic group could be obtained. The product was analysed as follows: A weighed sample was warmed with excess of water until completely dissolved. The total acidity was then determined by sodium hydroxide and phenolphthalein, and the sulphuric acid as barium sulphate. Hydrochloric acid was estimated by silver nitrate and ammonium thiocyanate. As an approximate check on the results the benzoic acid was estimated in several samples by removing the sulphuric acid with baryta, slightly acidifying the solution with hydrochloric acid, extracting with ether, and weighing the dried product. The hydrochloric acid content of the samples varied with the time which elapsed before analysis and, in order to make apparent the composition of the acidic residue, the analyses are expressed in terms of hydrochloric acid-free substance. For convenience of expression also, the acidities obtained after aqueous decomposition are expressed as percentages of the anhydrous substance. The same device is used also for the theoretical values, which are those calculated for $(PhCO{\cdot}O)_2SO_2,HCl$.

				Calc. for HCl-free product.			
Sample.	% Total acidity, as H_2SO_4.	% H_2SO_4.	% HCl.	% Total acidity, as H_2SO_4.	% H_2SO_4.	% $PhCO_2H$.	Remarks.
1	71·55	28·66	10·60	64·18	32·06	—	Dried in an atmosphere of HCl.
2	66·00	31·01	3·00	63·89	31·97	—	Analysed after 3 weeks.
3	69·01	29·75	7·30	63·89	32·09	76·73	Analysed after 24 hours.
Theory	71·53	28·61	10·66	64·05	32·02	79·73	

The hydrochloric acid content does not exceed one molecule, and sample 1, dried in hydrochloric acid vapour, approximates closely to the theoretical value. It might be expected that a substance of the nitrosulphonic structure under the conditions of our experiments would yield sulphur dioxide as a decomposition product. 2·4 G.-mols. of benzoyl chloride were heated on the water-bath with 1 g.-mol. of nitrosylsulphuric acid, and the evolved gases drawn through potassium dichromate solution. The amount of sulphur thus found as sulphur dioxide is shown as a percentage of the total sulphur.

Time (hours)	2	4	6	8	10	12
% S as SO_2	0·49	0·44	0·26	0·19	0·10	0·02

The results indicate that about 1·5% of the total sulphur is evolved as sulphur dioxide on continued heating at 100°. Although the rate of evolution decreases with time, it is considered that the sulphur dioxide is formed by reduction of sulphuric acid and is not due to the presence of the nitrosulphonic form of the acid, since benzoyl chloride and sulphuric acid yield a similar result (*q.v.*).

Action of Sulphuric Acid on Benzoyl Chloride.—The first method used was to mix benzoyl chloride (1 or 2 mols.) with concentrated sulphuric acid. The manner of mixing made a great difference to the purity of the product and to the hydrogen chloride content. If the sulphuric acid was added to the benzoyl chloride, the solution became deep green and most of the chlorine was evolved as hydrogen chloride. If the reverse process was adopted, the coloration was much less and the evolution of hydrogen chloride was very small at the ordinary temperature. Preparations were made in this way, using sulphuric acid varying in concentration from 96 to 100% at temperatures from 0—40°. The products were treated and analysed as previously described for nitrosylsulphuric acid.

Mode of addition.		Temp.	% Total acidity, as H_2SO_4.	% H_2SO_4.	% HCl.
2 g.-mol. PhCOCl to 1 g.-mol. H_2SO_4.	(1)	30°	76·50	37·55	12·75
	(1A) *	17	67·52	38·29	3·64
	(2)	32	70·11	35·80	10·13
	(3)	30	69·80	36·50	12·91
1 g.-mol. H_2SO_4 to 2 g.-mols. PhCOCl.	(1)	29	77·66	35·65	14·27
	(2)	30	77·87	35·32	14·47
	(3) †	28	73·30	34·54	9·85
	(4)	0	80·21	38·27	15·30
	(5)	0	79·41	37·43	15·16
	(6)	0	80·63	38·77	14·70
1 g.-mol. H_2SO_4 to 1 g.-mol. PhCOCl.	(1)	0	77·30	43·90	8·19
	(2)	0	76·40	45·08	7·01
Theory for $PhCO\cdot O\cdot SO_2\cdot OH,HCl$			82·18	41·09	15·34

* After 48 hours over lime. † After keeping 48 hours.

The last two preparations, when calculated to hydrochloric acid-free product, gave total acidity = 72·24, 72·06% H_2SO_4, and sulphuric acid = 47·82, 48·48%, respectively, whereas the values theoretically required are 72·77 and 48·51%.

The repetition of the exact experimental conditions used in the case of nitrosylsulphuric acid yielded products which appeared to be mixtures of mono- and di-benzoylsulphuric acids or of the mono-acid and sulphobenzoic acid. Preparations carried out at 16° and 30° gave similar products. At 0°, however, the products were very near in composition to the mono-acid.

In view of the difficulty of purifying the products, the method of preparation was further improved by dissolving the benzoyl chloride in excess of dry carbon tetrachloride, adding the 98% sulphuric acid gradually with continuous shaking, and keeping the mixture for 30 minutes, with exclusion of moisture. In this way, it is immaterial whether 1, 2, or 3 molecular proportions of benzoyl chloride are used and the temperature can also be varied between 0—35° without affecting the purity of the product : the yield is theoretical. Analyses of typical products were as follows :

	% Total acidity as H_2SO_4.	% H_2SO_4.	% HCl.
1	78·40	44·02	9·20
2	78·88	43·64	10·00
3	78·78	43·31	10·04

The total sulphur content of the products was determined by usion, and the fact that the figure so obtained was identical with hat for the percentage of sulphuric acid obtained by decomposing he substance with water was taken to indicate the absence of sulphobenzoic acid from the products. This estimation was carried out as follows. To 1 g. of the substance contained in a platinum dish about 5 g. of moistened sodium peroxide were added and the mixture was stirred with a platinum rod. The product was intimately mixed with 30—40 g. of a mixture of 1 part of potassium nitrate and 2 parts of fusion mixture. The top of the mass was then covered with 15—20 g. of fusion mixture, and the whole heated gently until fusion was complete. If signs of charring appeared, the determination was repeated. The method was much quicker than a Carius estimation and better than the Eshka method for the substances under analysis. The method is given in detail, as duplicates showed it to be quite satisfactory.

Transformation of Benzoylsulphuric Acid into Sulphobenzoic Acid.—Determinations were made of the total sulphur content of a number of products by fusion, and of the sulphuric acid produced by decomposition with water. The samples were prepared using equimolecular proportions of sulphuric acid and benzoyl chloride at 0°, 16°, and 120°. The results were as follows :

	1.	2.	3.
Sulphuric acid by water treatment (H_2SO_4 %)	42·31	43·30	37·40
Total sulphur (by fusion) as H_2SO_4 %	42·16	43·16	37·43

This evidence for the absence of sulphobenzoic acid is conclusive unless the latter is completely decomposed by treatment with warm water. No satisfactory information could be found in the literature on this point and therefore we determined the velocity of transformation of benzoylsulphuric acid into sulphobenzoic acid at 100°, the highest temperature used in our experiments. 70 G. of monobenzoylsulphuric acid were heated, in a constant-temperature bath at 100°, in a flask fitted with a moisture trap. The gases were drawn off continuously through potassium dichromate and the sulphur dioxide content was estimated. Samples of the residue in the flask were drawn off at intervals and the sulphuric acid produced by decomposition with water was estimated. At the conclusion of the heating the total sulphur content of the residue was determined by the fusion method previously described.

Time (hours).	% H_2SO_4 obtained.	k.	% Total S lost as SO_2.
0	43·20	—	—
10	36·67	0·01639	0·26
15	33·83	0·01630	0·25
20	31·14	0·01637	0·23
25	28·75	0·01628	0·22

Total sulphur content of the residue after 25 hours = 42·10% as H_2SO_4. k is calculated on the basis of a unimolecular reaction.

Isolation of Sulphobenzoic Acid [With R. PEPPERELL].—The above material which had been heated for 25 hours at 100° was warmed with 500 c.c of water and concentrated to 250 c.c. The precipitated benzoic acid was filtered off and the sulphuric acid precipitated with baryta and filtered off. This filtrate was concentrated to 100 c.c., and the excess of barium exactly precipitated with sulphuric acid. The barium sulphate and any further benzoic acid were removed and the filtrate was evaporated to small bulk and extracted with ether until no further benzoic acid could be obtained. The residue on final concentration on the water-bath solidified to an amorphous hygroscopic mass which was dried by heating to 105° (Found: S, 16·1. Theory for $CO_2H{\cdot}C_6H_4{\cdot}SO_3H$: S, 15·8%). The substance did not melt sharply, but was completely molten at 135°. The anhydride (m. p. 129—130°) was prepared by refluxing with acetyl chloride for 2 hours and extraction with benzene. The acid also condensed readily with resorcinol in presence of zinc chloride to give a phthalein. The product was hence *o*-sulphobenzoic acid, but the original substance contained some meta-acid also.

Action of Acetyl Chloride.—25 G. of nitrosylsulphuric acid were added slowly to 35 g. of acetyl chloride dissolved in 100 c.c. of carbon tetrachloride, and the mixture was warmed to 30—35° to start the reaction. A vigorous evolution of nitrosyl chloride occurred, the temperature rising to 60—70°, and a yellow, viscous, non-crystallisable oil separated. This was washed repeatedly with carbon tetrachloride and ligroin and analysed as rapidly as possible by methods similar to those used in the case of the corresponding benzoyl derivative (Total acidity, as H_2SO_4, 101·9; H_2SO_4, 68·4. $CH_3{\cdot}CO{\cdot}O{\cdot}SO_3H$ requires 105·0 and 70·0%, respectively). The substance was completely decomposed by water into acetic and sulphuric acids.

The product was heated under reflux in carbon tetrachloride for 30 minutes and the percentage of sulphuric acid obtained by decomposition with water was reduced to 54·32% from 68·40%. After another hour's refluxing, it was further reduced to 27·58%, the total sulphur content remaining constant.

Action of Acetic Anhydride.—(1) 10 G. of acetic anhydride were dissolved in 200 c.c. of carbon tetrachloride and 12 g. of nitrosylsulphuric acid were added. On refluxing for 30 minutes a yellow oil separated, from which the last traces of solvent were removed in a vacuum. (2) 5 G. of nitrosylsulphuric acid were dissolved in 200 c.c. of acetic anhydride, the mixture being kept cool, and the solution was shaken with 5 g. of dry silver oxide. The silver oxide was rapidly converted into a gelatinous suspension, which was filtered off in a vacuum, washed with acetic anhydride, and dried over sulphuric acid. The product was amorphous and hygroscopic and on treatment with water gave no oxides of nitrogen. The resulting solution gave no precipitate with barium nitrate. Liebermann's reaction showed the presence of nitrite or a nitroso-group in the substance. The salt contained sulphur, nitrogen, and silver, in addition to carbon, hydrogen, and oxygen (Ag, by heating, 31·5; by conversion to AgCl, 32·0. S, estimated as $BaSO_4$, 9·4. $CH_3 \cdot CO \cdot O \cdot SO_2 \cdot O \cdot NO, CH_3 \cdot CO_2Ag$ requires Ag, 32·1; S, 9·5%).

Action of Nitrosylsulphuric Acid on Dimethylaniline.—(1) To a solution of 35 g. of dimethylaniline in 40 c.c. of concentrated sulphuric acid a solution of 70 g. of nitrosylsulphuric acid in 30 c.c. of sulphuric acid was added, at 10—15°. By following the experimental procedure of Biehringer and Borsum (*loc. cit.*) there were obtained: *p*-nitrodimethylaniline, 63%; *p*-nitrosodimethylaniline, 37%. (2) The above experiment was repeated using half the amount of nitrosylsulphuric acid (*i.e.*, an excess of dimethylaniline). No nitro-derivative was obtained but only the nitroso-derivative. (3) Quantities as in Expt. (1) were used and the mixture was dropped slowly into absolute alcohol at 0°. No nitro-derivative was obtained. By pouring the product into 300 c.c. of dry ether a mixture of the sulphates of dimethylaniline and *p*-nitrosodimethylaniline was obtained. Some nitric oxide was evolved on first mixing the reactants, but no sulphur dioxide could be detected at any stage of the reaction.

Action of Heat on Nitrosylsulphuric Acid.—(1) 30 G. of the crystalline acid were heated for 30 minutes at 350° in a wide glass tube fitted with a moisture trap; nitrogen trioxide was rapidly evolved during the first 15 minutes. A pale yellow, very viscous oil remained (Found: HNO_2, 19·3%).

(2) 50 G. of nitrosylsulphuric acid were heated under similar conditions at 300° for 9 hours. The residual oil was analysed as before (Found: HNO_2, 20·2%).

At both these temperatures sulphur trioxide was evolved owing to the decomposition of the product, and this fact may explain the poor agreement with the value required by the suggestion of Michaelis. On attempting to carry out the decomposition at temperatures low enough to ensure that no sulphur trioxide was produced, it was found that the rate of decomposition was so slow that several weeks would be required for complete decomposition.

(3) 50 G. of the acid were heated in a constant-temperature bath at 150°. Samples were withdrawn at intervals and analysed as before.

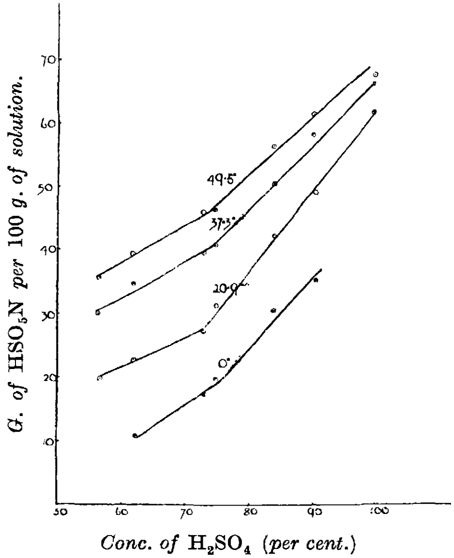
Time (hrs.) ...	0	0·75	11·3	16·5	26·3	39·0	46·8	59·3	137·0
% HNO_2........	35·9	32·8	30·7	30·2	29·7	29·0	28·1	27·5	25·8

(Theoretical value for anhydride, 21·8% HNO_2.)

Similar determinations were carried out at 115° and 130° and in each case the early rapid evolution of nitrogen trioxide was observed. The slowness of decomposition of nitrosylsulphuric acid at the lower temperatures is undoubtedly due to the stabilising influence of sulphuric acid, which is a secondary product of the reaction. The decomposition of the acid begins at 73°, when it begins to melt.

The general conclusion to be drawn from the results is that the mode of decomposition suggested by Michaelis is in accord with the experimental facts. It must be pointed out, however, that (1) sulphuric acid is produced by the decomposition and tends to prevent further loss of nitrogen trioxide on heating, and (2) water escapes from the reaction zone in the early part of the heating; consequently the nitrous acid content of the residue would be expected to exceed the theoretical value.

FIG. 1.



Solubility of Nitrosylsulphuric Acid in Sulphuric Acid.—The general method of solubility determinations was adopted, the nitrosylsulphuric acid in excess being agitated with sulphuric acid of known concentration contained in thin glass tubes in a thermostat. Each tube was protected against the ingress of moisture by running the stirrer through a glass tube sealed with petroleum jelly. The sulphuric acid used was of concentrations 56·7, 62·1, 73·1, 74·9, 84·1, 90·4, and 99·8%.

After 3 hours, a sample was filtered through glass wool into a weighing bottle containing sulphuric acid and, after weighing, the contents were made up to 100 c.c. with sulphuric acid, the nitrous acid then being estimated by a method specially devised for this work. At the higher temperatures and with the lower concentrations of sulphuric acid, some of the solutions contained free nitrous acid (*i.e.*, not combined as nitrosylsulphuric acid). In order to determine the amount of the latter acid actually present, this free nitrous acid was removed by rapid blowing with air followed by immersion in the thermostat for 15 minutes. The sample was then taken in the usual way. The results here given are also shown graphically in the figure.

Conc. of H_2SO_4 (%).	56·7	62·1	73·1	74·9	84·1	90·4	99·8	Temp.
Solubility of nitrosylsulphuric acid as per 100 g. of solution.	—	11·9	17·3	19·7	30·5	35·1	—	0·0°
	19·3	22·6	27·0	31·4	42·4	49·2	62·0	20·9
	29·9	34·3	39·4	40·8	50·2	58·5	66·1	37·3
	35·6	39·3	46·0	46·2	56·5	61·6	67·8	49·6

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