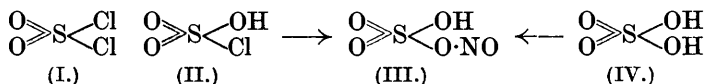


XLVIII.—*Nitrosylsulphuric Acid. Part II.*

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FURTHER evidence for the presence of a hydroxyl group in nitrosylsulphuric acid (III) (compare Part I, J., 1926, 1219) has been obtained by the synthesis of the acid from chlorosulphonic acid and nitrogen tetroxide. An attempt to synthesise the corresponding dinitrosyl sulphate,  $\text{SO}_2(\text{O}\cdot\text{NO})_2$ , from sulphuryl chloride and nitrogen tetroxide was unsuccessful. We were also unable to obtain this substance from silver nitrite and sulphuryl chloride, or by heating nitrosylsulphuric acid under pressure with nitrogen tetroxide.

A comparison of the action of nitrogen tetroxide on some of the substances we have examined is of interest. With (II) and (IV) it



gives (III) as the final product, whereas with (I) it does not react. These facts suggest that the type of reaction under examination occurs only when the transient formation of the substance  $\text{O}_2\text{S}=\text{O}$  is possible, a suggestion for which there is some evidence in the reaction between nitrogen tetroxide and sulphuric acid. The modification in the properties of the second hydroxyl group in sulphuric acid caused by the substitution of the nitroso-group for the other hydrogen atom is remarkable and appears to be parallel to the activity of chlorine in chlorosulphonic acid as compared with its inactivity in sulphuryl chloride, towards nitrogen tetroxide. The facts appear to be difficult of explanation on the octet theory if the sulphur-oxygen double bonds are assumed to be semipolar, but further experimental work is in progress to elucidate this point.

*Nitrosylsulphuric Anhydride.*—Some confusion appears to exist concerning the structure and methods of preparation of this anhydride. From sulphur dioxide and nitrogen tetroxide, Provostaye (*Ann. Chim. Phys.*, 1840, **73**, 362) obtained a substance of empirical formula  $\text{S}_2\text{N}_2\text{O}_9$ , which he regarded as the anhydride, and Rose (*Pogg. Ann.*, 1839, **47**, 605) and Brüning (*Ann. Chem. Pharm.*, 1856, **98**, 377) prepared a substance of similar properties from nitric oxide and sulphur trioxide to which they gave the formula  $2\text{SO}_3\cdot\text{N}_2\text{O}_3$ . On the other hand, Berl (*Z. angew. Chem.*, 1910, **23**, 2250) repeated this work and obtained a product  $4\text{SO}_3\cdot\text{N}_2\text{O}_3$ , but from nitrogen pentoxide and sulphur dioxide he prepared a substance

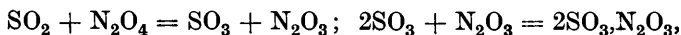
with the properties of the anhydride to which he ascribed the constitution  $S_2O_5(O\cdot NO)_2$ . Also Manchot (*Ber.*, 1926, 59, 2672) further examined Rose and Brüning's method and gave to his product the formula  $2SO_3\cdot NO$ .

We have attempted to prepare the anhydride by the following methods: (a) from liquid sulphur dioxide and nitrogen tetroxide, (b) from sulphur trioxide and nitric oxide, (c) by distillation of nitrosylsulphuric acid with phosphoric oxide, (d) from nitrogen tetroxide and pyrosulphuric acid, (e) from nitrogen tetroxide and pyrosulphuryl chloride.

From (a) we isolated a product of empirical formula  $S_2N_2O_9$ , which was completely decomposed by water into sulphuric and nitrous acids and was soluble in concentrated sulphuric acid without decomposition. On distillation, a hard crystalline *substance* of indefinite melting point was obtained with similar chemical properties but of empirical formula  $5SO_3\cdot 2N_2O_3$ . Methods (b) and (c) both yielded the same product directly, whereas methods (d) and (e) yielded the same initial product as in (a).

Methods (d) and (e) afford evidence that the anhydride has the structure  $O\cdot NO\cdot SO_2\cdot O\cdot SO_2\cdot O\cdot NO$ , which is in agreement with the properties of the substance. We have hitherto obtained no experimental evidence which supports the alternative structure for nitrosylsulphuric acid suggested in Part I (*loc. cit.*). The anhydride is unstable to heat, being partly decomposed on distillation into sulphur trioxide and nitric oxide. The *compound*  $5SO_3\cdot 2N_2O_3$  is formed by the combination of sulphur trioxide with the anhydride and should be represented by the formula  $2\{2SO_3\cdot N_2O_3\}\cdot SO_3$ , there being one molecule of sulphur trioxide to two of the anhydride. In our experiments this substance was produced directly at the ordinary temperature when excess of sulphur trioxide was present (Method b); it is remarkably stable, having no resemblance to the theoretically analogous pyrosulphuric acid. Its chemical properties are similar to those of the anhydride; it is completely decomposed by water into sulphuric and nitrous acids and is soluble in concentrated sulphuric acid.

The reaction between sulphur dioxide and nitrogen tetroxide under pressure at laboratory temperature is represented by the equations



the sole products of the reaction being the anhydride and the green liquid trioxide.

The reaction between sulphur trioxide and nitric oxide has a negative temperature coefficient, for the yield of anhydride at  $100^\circ$  is very small, whereas at  $10^\circ$  it is readily formed with evolution of an

equivalent quantity of sulphur dioxide :  $\text{SO}_3 + 2\text{NO} \rightleftharpoons \text{SO}_2 + \text{N}_2\text{O}_3$ , the anhydride then being formed as before.

The reaction between pyrosulphuric acid and nitrogen tetroxide is analogous to that of sulphuric acid. In the case of pyrosulphuryl chloride we obtained no evidence of the formation of nitroxyl chloride ( $\text{NO}_2\text{Cl}$ ), which might theoretically be expected, nitrosyl chloride being produced.

It is suggested that the ready absorption of sulphur trioxide by the anhydride affords an explanation of the discrepancies in the composition of the anhydride previously found by different workers.

#### EXPERIMENTAL.

Liquid nitrogen tetroxide was purified by the addition of a little fuming nitric acid and phosphoric oxide and subsequently distilled.

*Preparation of Nitrosylsulphuric Acid.*—The liquid tetroxide was slowly added in equimolecular proportion to chlorosulphonic acid in a moisture-free atmosphere. Nitrosyl chloride was vigorously evolved, and the residual crystalline substance was collected on asbestos and dried in a vacuum (Found : N, 10.73 ; S, 25.31. Calc. : N, 11.02 ; S, 25.10%). The methods of analysis of this and subsequent products were those described in Part I (*loc. cit.*), except that the nitrous acid was determined by the modified method of Wilkins and Webb (*J. Soc. Chem. Ind.*, 1926, 45, 304).

*Nitrosylsulphuric Anhydride.*—(a) *Interaction of sulphur dioxide and nitrogen tetroxide.* Equal volumes of liquid sulphur dioxide and nitrogen tetroxide were sealed in a glass tube and kept for 24 hours at 18–20°; the residue then consisted of the green liquid nitrogen trioxide and the crystalline anhydride (Found : N, 11.96, 12.07, 11.97 ; S, 26.53, 26.43, 26.62. Calc. for  $\text{S}_2\text{N}_2\text{O}_9$  : N, 11.87 ; S, 27.14%). On distillation, this substance gave sulphur trioxide and nitric oxide, together with a compound of b. p. 324–326° (Found, in separate preparations : N, 10.46, 10.45, 10.38, 10.39, 10.42 ; S, 28.75, 28.60, 28.78, 28.75, 28.80.  $5\text{SO}_3, 2\text{N}_2\text{O}_3$  requires N, 10.14 ; S, 28.95%).

(b) *Interaction of sulphur trioxide and nitric oxide.* The nitric oxide, prepared by dropping 50% sulphuric acid on a concentrated solution of sodium nitrite and potassium iodide, was purified successively by concentrated sulphuric acid and solid potassium hydroxide. The sulphur trioxide was prepared by warming pyrosulphuric acid. The reaction was first examined by passing the two gases at controlled rates through a long, jacketed, glass tube maintained at temperatures from 10° to 100°. The rate of reaction at the higher temperatures was negligible, and the procedure was modified by leading nitric oxide into sulphur trioxide at 10°. The

gas was rapidly absorbed with evolution of an equivalent volume of sulphur dioxide. At first the excess of sulphur trioxide was removed from the product by gentle warming in a stream of dry air, but it was found that the final product obtained was identical with that resulting from the direct distillation of the impure substance, and the latter procedure was ultimately adopted as being more convenient and giving a purer product [Found, (1) in undistilled product: N, 9.86, 10.05; S, 28.88, 28.76; (2) in distilled product: N, 9.75, 9.97; S, 28.89, 28.80. Calc. for  $S_5N_4O_{21}$ : N, 10.14; S, 28.95%].

(c) *Distillation of nitrosylsulphuric acid with phosphoric oxide.* Dry nitrosylsulphuric acid was heated with an excess of phosphoric oxide at  $180^\circ$  until oxides of nitrogen ceased to be evolved. When the temperature was raised to  $324\text{--}326^\circ$ , an oily product distilled which solidified to a hard, white, crystalline mass (Found: N, 10.51, 10.43, 10.36, 10.38; S, 28.51, 28.77, 28.69, 28.72%).

(d) *Nitrogen tetroxide and pyrosulphuric acid.* Crystalline pyrosulphuric acid and liquid nitrogen tetroxide were mixed in various proportions in a sealed tube and kept at  $15^\circ$  for 2 hours. The residue consisted of the anhydride (Found: S, 26.78, 27.41; N, 11.38, 11.70%) and a mother-liquor containing nitric acid, and on long standing, these interacted, causing partial conversion of the anhydride into nitrosylsulphuric acid.

(e) *Pyrosulphuryl chloride and nitrogen tetroxide.* Nitrogen tetroxide was added slowly with constant shaking to pyrosulphuryl chloride in a moisture-free atmosphere at the ordinary temperature. Nitrosyl chloride was rapidly evolved and crystals of nitrosylsulphuric anhydride separated (Found: S, 26.50, 26.43; N, 11.28, 11.40%). An identical product was obtained by using liquid nitrogen trioxide instead of the tetroxide.

#### *Summary.*

Nitrosylsulphuric acid has been synthesised from chlorosulphonic acid. The reactivity of nitrogen tetroxide with certain substances has been examined and has led to the suggestion of a mechanism for the formation of nitrosylsulphuric acid. The anhydride has been prepared by several methods, two of which throw light on its structure. With sulphur trioxide the anhydride yields a stable complex,  $2(S_2N_2O_9)\cdot SO_3$ .

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