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ON THE ACID DISULPHATE (PYROSULPHATE) OF NITROSYLE

Michel Wartel and Joseph Heubel

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# ON THE ACID DISULPHATE (PYROSULPHATE) OF NITROSYLE

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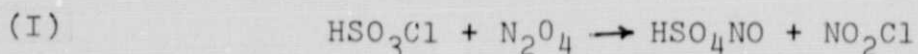
## ABSTRACT

By reacting excess  $\text{NO}_2$  gas with liquid  $\text{HSO}_3\text{Cl}$ , we obtain crystallized  $\text{HS}_2\text{O}_7\text{NO}$ . Stable up to the melting point of about  $105^\circ$ , this reacts with nitrates from about  $25^\circ$  to form  $\text{M}_2\text{S}_2\text{O}_7$ , probably with an acid disulphate intermediary. Excess  $\text{NO}_2$ , whether liquid or gas, reacts with  $\text{HS}_2\text{O}_7\text{NO}$  to five  $(\text{NO})_2\text{S}_2\text{O}_7$ .

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Within the framework of a systematic study of the derivatives of  $\text{SO}_3$  and tri- and pentavalent nitrogen, we have studied the reaction of chlorosulfonic acid and nitrogen dioxide  $\text{NO}_2$ .

A priori we can conceive of a reaction of the type



or even



as this latter compound has recently been prepared in the pure form (ref. 1).

In fact, in 1929 Jones, Price, and Webb (ref. 2) by reacting  $\text{HSO}_3\text{Cl}$  ( $\text{ClSO}_2\text{OH}$  in English) and  $\text{N}_2\text{O}_4$  in stoichiometric proportions, obtained the acid sulphate and the chloride of nitrosyl. This seems to give credence to a reaction of the type (1), where nitrogen has a valence of +3 ( $\text{NOCl}$ ). Lacking specifics about the experimental conditions, and since the presence of nitrosyl chloride could not be explained simply, we have repeated these experiments using a technique applied in other analogous reactions; passing  $\text{N}_2\text{O}_4$  gas through  $\text{HSO}_3\text{Cl}$  at  $0^\circ$  kept in calcination by dry nitrogen under pressure.

We immediately observe hydrogen chloride being liberated, then nitryl chloride, easily characterized by its infrared spectrum. At the same time, some nitrosyl chloride is also formed, which can be explained by

the simultaneous formation of the reducing agent HCl (ref. 3).

The liquid on the calcine becomes more and more viscous, and after a few hours a slight precipitate is formed which accumulates slowly. The excess liquid is for the most part eliminated by filtration. The liquid residue that permeates the crystals is evaporated under vacuum at room temperature and collected at low temperatures. The process

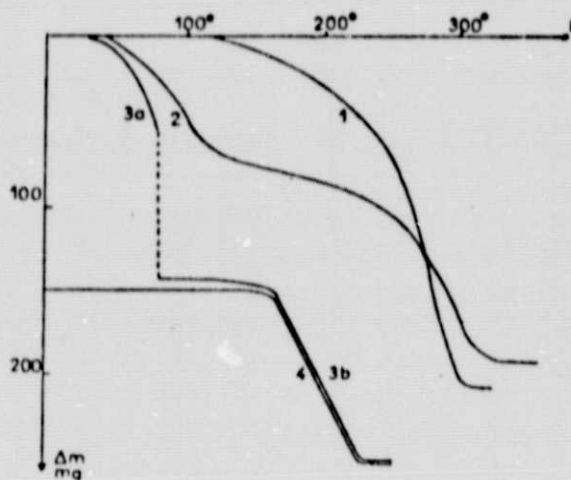
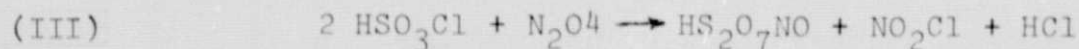


Figure 1

lasts several days. A very hygroscopic white crystalline powder remains that does not "smoke" in air, except for  $\text{Cl}^-$ . It is hydrolysed by a concentrated sodium solution. The concentration depends on the total amount of nitrogen, reducing nitrogen and sulphur, and the acidity.

Despite a slight shortage of nitrogen 3, explained by the violence of the hydrolysis reaction which gives rise to the formation of a small amount of  $\text{NO}_2$  from nitrogen 3, the quantitative analysis and the mass balance are in agreement with the  $\text{HS}_2\text{O}_7\text{NO}$  formula. To our knowledge this compound has never before been prepared. The overall reaction can therefore be written as

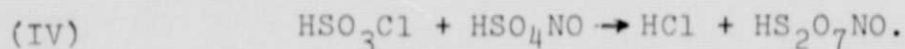


This simple form does not pretend to represent all of the intermediary mechanisms, which, from studies presently underway, seem to be fairly complicated, even more so since  $\text{NO}_2\text{Cl}$  seems to react with  $\text{HSO}_3\text{Cl}$  also.

It is possible that there is an  $\text{HSO}_4\text{NO}$  intermediary. We found some proof of this hypothesis by carrying out a reaction between  $\text{HSO}_3\text{Cl}$  and  $\text{HSO}_4\text{NO}$ . Quantitatively this gives  $\text{HS}_2\text{O}_7\text{NO}$  with the release of HCl as



follows:



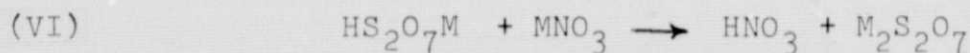
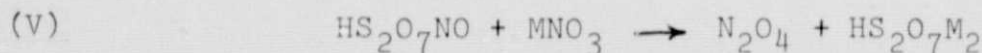
Hence, by assuming the intermediary formation of  $\text{HSO}_4\text{NO}$ , we have a condensation reaction with the elimination of  $\text{HCl}$ . It is perhaps by a reaction of the same type that it is possible to explain the formation of  $\text{NOCl}$  in the reaction of  $\text{SO}_2\text{Cl}_2$  and  $\text{NO}_2$  (ref. 4).

$\text{HS}_2\text{O}_7\text{NO}$  melts at  $105 \pm 2^\circ$  and this melting point was reproducible in several trials even though we could detect a slight decomposition beginning at this temperature. The liquid obtained is viscous and is easy to keep supercooled, especially after several trials. Thermogravimetric analysis with a heating rate of  $100^\circ/\text{hour}$  shows that the decomposition starts around  $115^\circ$  in the dynamic mode (curve 1, in Figure 1). The decomposition accelerates rapidly. All trace of the condensed phase disappears around  $320^\circ$ .

Reacting the acid disulphate of nitrosyl with sodium nitrate, or better yet, with the potassium nitrate-sodium nitrate eutectic, we find that the mass loss and the release of  $\text{NO}_2$  is noticeable from  $25^\circ$ , which shows that the nitrosyl group reacts with the  $\text{NO}_3^-$  ion.

If the nitrate/disulphate ratio in moles is equal to 1 (curve 2) we find that the reaction is followed by the decomposition of excess  $\text{HS}_2\text{O}_7\text{NO}$ . On the other hand, if we use a ratio of 2, we get the metallic disulphate. For this reaction to be complete it is desirable to proceed above an isotherm with thoroughly homogenized mixture (Curve 3a). Therefore the nitrate attacks both the  $\text{NO}$  group and the H-end of the acid, with the formation of  $\text{NO}_2$  on the one hand, and of nitric acid on the other. Both are titrated effectively in the volatile phase.

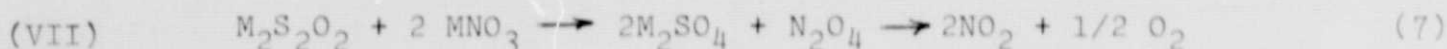
It is possible, and this remains to be proved, that the reaction may proceed two ways:



The second is slower at the temperature at which (5) takes place. Be that as it may, by using the molecular ratio of sodium/disulphate equal to 2, the phase remaining after proceeding along an isotherm at  $85^\circ$  is pure sodium disulphate (x-ray pattern).

Furthermore, by reacting this residue with  $2\text{NO}_3^-$ , using the K eutectic of  $\text{NaNO}_3$ , around  $170^\circ$  we find an abrupt loss of mass which

corresponds to the liberation of  $N_2O_5$  (curve 3b); the nitrate plays the role of an  $O^{4-}$  donor vis-a-vis the disulphate (ref. 5).



On the same graph we show the curve resulting from the reaction of  $Na_2S_2O_7 +$  eutectic  $NaNO_3 + KNO_3$  (curve 4). They overlap.

Therefore, by reacting excess  $N_2O_4$  and  $HSO_3Cl$  we obtain  $HS_2O_7NO$  very probably through an  $HSO_4NO$  intermediary. Other reactions presently being studied at the Laboratory lead to the same product, particularly the reaction of liquid  $SO_3$  and  $HSO_4NO$ . By reacting liquid  $N_2O_4$  and  $HS_2O_7NO$  at  $20^\circ$  for several days, we obtain, after eliminating nitric acid and  $NO_2$ , a crystalline substance whose formula approximates  $(NO)_2S_2O_7$ , obtained effectively by treating the same sulphate by gaseous  $NO_2$  at  $60^\circ$ . We can ask ourselves further whether Jones (ref. 2) hasn't in fact obtained this product which has the same  $S/N/H^+$  ratio as  $HSO_4NO$ .

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