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INORGANIC CHEMISTRY--DIRECT SYNTHESES FROM PURE LIQUID SO_3 AND FROM TRIVALENT AND PENTAVALENT NITROGEN DERIVATIVES

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16. Abstract
From pure liquid SO_3 the authors carried out direct synthesis reactions with N_2O_5, NO_2Cl, NOCl which yielded $N_2O_5 4SO_3$, $3SO_3$, $2SO_3$–$NO_2Cl 2SO_3$–$NOCl 2SO_3$ and $NOClSO_3$, the latter being obtained for the first time in the pure state. In all cases the crystallized product was obtained first by separating the constituents of the mixture and then going through a single viscous liquid phase.

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INORGANIC CHEMISTRY--DIRECT SYNTHESES FROM PURE LIQUID SO_3 AND FROM TRIVALENT AND PENTAVALENT NITROGEN DERIVATIVES*

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Nitryl polysulfates are usually obtained at low /6619** temperature from SO_3 and N_2O_5 in solution in various solvents: nitromethane [1], $POCl_3$ [2], CCl_4 [3], liquid SO_2 [4]. To our knowledge, synthesis in the absence of solvent has never been attempted, or was attempted under such conditions that the formation of polysulfates was impossible [3]. One might think that the authors relied on solvents because of the difficulty of obtaining stable liquid SO_3 and also because the reaction is exothermic.

The fact that we had at our disposal a sure method of preparation and a proven apparatus encouraged us to attempt this synthesis and then generalize it to other nitrogen derivatives.

SO_3 is obtained according to a method specified by J. Bernard [6]: reaction of oleum on P_2O_5, distillation of the raw product and passing over P_2O_5 with the formation of $P_4O_{10}SO_3$. The thermal dissociation of the latter yields pure SO_3, the head fraction of which serves to wash the reactor. This fraction is passed off into an ampule which is removed. The reactor has a ground inlet on the side, connected on the one hand to the apparatus which produces the N_2O_5 and on the other hand to a feed pipe of dry nitrogen. The reactor

*Paper by Bernard Vandorpe and Joseph Heubel, read by Georges Champetier, at the June 14, 1965 meeting of the Academy of Sciences, Paris.

**Numbers in the margin indicate pagination in the foreign text.

remains in place under a current of dry nitrogen and is constantly shielded by columns of P_2O_5 until the completion of the operations. By means of a by-pass system the apparatus can be purged and the head fractions of N_2O_5 can be removed. The latter is produced according to a method described earlier [7] which has been improved so as to produce an hourly yield of about 20 grams of pure product.

In the reactor containing SO_3, N_2O_5 vapor is caused to be given off at ambient temperature which is carried away by the dry nitrogen. A slight increase in temperature is observed which can be compensated for -- without its being absolutely necessary -- by immersing the reactor in cold water. The liquid becomes cloudy and then the constituents of the mixture separate.

The composition of the lower layer remains constant between -30° and +20°. It corresponds approximately to the formula $N_2O_57SO_3$. Following disappearance of the upper layer, the viscosity of the liquid increases sharply, then solid particles form which gradually take over the reactor. When the gas no longer passes easily some pure nitrogen is /662 introduced and the temperature is raised to 60° for about 48 hours in order to remove the excess of SO_3.

The solid obtained sometimes corresponds to the formula $N_2O_54SO_3$, sometimes to $N_2O_53SO_3$. This is explained by the large degree of viscosity of the liquid prior to crystallization. This viscosity promotes the supercooling of $N_2O_34SO_3$, thus the passage of the gas and the concentration of N_2O_5. In fact, one more often obtains $N_2O_53SO_3$ than $N_2O_54SO_3$. In order to be sure of obtaining the latter it is necessary to wait for spontaneous crystallization by supercooling or by feeding which requires a special technique to avoid any traces of water.

The method thus described is limited to the preparation of trisulfates and tetrasulfates, but it never enabled us to obtain directly $N_2O_3 2SO_3$.

$N_2O_5 4SO_3$, ground and subjected to the action of N_2O_5 gas at ambient temperature, fixes the latter and is gradually transformed into $N_2O_3 3SO_3$. $N_2O_5 3SO_3$ submitted to the same treatment does not undergo any significant increase in weight.

By contrast, by grinding $N_2O_5 3SO_3$ or $N_2O_5 4SO_3$ with solid N_2O_5 in a glove box or on a heated plate under a current of dry nitrogen, one can increase the N_2O_5 concentration of the initial product, ending up with the final limit formula $N_2O_5 2, 2SO_3$. This mixture of two polysulfates is stable up to 125°. It is not surprising that one reaches a limit formula without being able to obtain $N_2O_5 2SO_3$, since a solid-solid action is involved without the release of gas. It is possible, on the other hand, to obtain $N_2O_5 2SO_3$ in the pure state by causing N_2O_5 to react on $NO_2Cl 2SO_3$ or $NOClSO_3$, the direct synthesis of which is mentioned below. The reactions seem to proceed as follows:

$$NO_2Cl\,2SO_3 + N_2O_5 \rightarrow N_2O_5\,2SO_3 + NO_2Cl$$

and

$$2NOClSO_3 + 3N_2O_5 \rightarrow 2NO_2Cl + 2N_2O_5 + N_2O_5\,2SO_3$$

With cooled NO_2Cl carried away by an inert gas the reaction on SO_3 occurs with a slight increase in temperature and is analogous to that of N_2O_5: formation of turbidity, followed by separation of the constituents, the lower layer corresponding approximately to the formula $NO_2Cl 5SO_3$, increase in viscosity and crystallization of a solid which, after removal of the excess SO_3 at 60°, corresponds to the formula $NO_2Cl 2SO_3$. The S/N ratio = 2.01; N/Cl = 1.01 as against S/N = 2.16 and N/Cl = 1.075 respectively in the violent reaction of SO_3 on NO_2Cl maintained at -80° [8].

The same type of reaction is found again with NOCl carried away by inert gas: turbidity, separation of the constituents, lower layer corresponding to $NOCl5SO_3$, formation of a solid and obtainment of $NOClSO_3$ after heating the reactor to 70°. This compound is particularly interesting, since it is the only one among the derivatives described which corresponds to S/N = 1. Although having the formula $2SO_3$, NO_2Cl it seems to have been obtained in a very impure form by Weber in 1864 [9]. Since that time attention has no longer been drawn to it, except by Seel [10] who doubts that it exists. /6621

By causing an excess of SO_3 to react on NOCl cooled to -50° one can obtain $NOCl2SO_3$ pointed out by Seel [10] and prepared by Weinreich in solution in liquid SO_2 [4, 11].

Tests in progress with SO_3 and N_2O_3 and NO show that all of these synthesis reactions (gas + liquid SO_3) proceed according to the same plan: the synthesis by means of separation of the constituents in the mixture which in turn, when one of the liquid phases disappears, is followed by an increase in viscosity and then crystallization of a solid. Quantitative transformation from liquid into solid presents a certain degree of experimental difficulty.

These syntheses have the advantage of doing without any solvent, taking place at ambient temperature and easily lending themselves to the preparation of large quantities of product.

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11. Ultimately we hope to be able to specify the composition of the various compounds pointed out. For the time being we are using dualistic formulas.