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INORGANIC CHEMISTRY--DIRECT SYNTHESSES FROM PURE LIQUID $\text{SO}_3$ AND FROM TRIVALENT AND PENTAVALENT NITROGEN DERIVATIVES

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### Abstract

From pure liquid $\text{SO}_3$ the authors carried out direct synthesis reactions with $\text{N}_2\text{O}_5$, $\text{NO}_2\text{Cl}$, $\text{NOCl}$ which yielded $\text{N}_2\text{O}_5\text{SO}_3$, $3\text{SO}_3$, $2\text{SO}_3-\text{NO}_2\text{Cl}2\text{SO}_3-\text{NOCl}2\text{SO}_3$ and $\text{NOClSO}_3$, 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.

### Translation

Nitryl polysulfates are usually obtained at low temperature from $\text{SO}_3$ and $\text{N}_2\text{O}_5$ in solution in various solvents: nitromethane [1], $\text{POCl}_3$ [2], $\text{CCl}_4$ [3], liquid $\text{SO}_2$ [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 $\text{SO}_3$ 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.

$\text{SO}_3$ is obtained according to a method specified by J. Bernard [6]: reaction of oleum on $\text{P}_2\text{O}_5$, distillation of the raw product and passing over $\text{P}_2\text{O}_5$ with the formation of $\text{P}_4\text{O}_{10}\cdot\text{SO}_3$. The thermal dissociation of the latter yields pure $\text{SO}_3$, 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 $\text{N}_2\text{O}_5$ and on the other hand to a feed pipe of dry nitrogen.
remains in place under a current of dry nitrogen and is constantly shielded by columns of P₂O₅ until the completion of the operations. By means of a by-pass system the apparatus can be purged and the head fractions of N₂O₅ 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 SO₃, N₂O₅ 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 N₂O₅₇SO₃. 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 introduced and the temperature is raised to 60° for about 48 hours in order to remove the excess of SO₃.

The solid obtained sometimes corresponds to the formula N₂O₅₄SO₃, sometimes to N₂O₅₃SO₃. This is explained by the large degree of viscosity of the liquid prior to crystallization. This viscosity promotes the supercooling of N₂O₃₄SO₃, thus the passage of the gas and the concentration of N₂O₅. In fact, one more often obtains N₂O₅₃SO₃ than N₂O₅₄SO₃. 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°C. 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$_2$Cl$_2$SO$_3$ or NOClSO$_3$, the direct synthesis of which is mentioned below. The reactions seem to proceed as follows:

\[
NO_2Cl_2SO_3 + N_2O_5 \rightarrow N_2O_3^3SO_3 + NO_2Cl
\]

and

\[
2NOClSO_3 + 3N_2O_5 \rightarrow 2NO_2Cl + 2N_2O_3 + N_2O_3^2SO_3.
\]

With cooled NO$_2$Cl 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$_2$Cl$_2$SO$_3$, increase in viscosity and crystallization of a solid which, after removal of the excess SO$_3$ at 60°C, corresponds to the formula NO$_2$Cl$_2$SO$_3$. 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$_2$Cl maintained at -80°C [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 NOCl5SO3, formation of a solid and obtainment of NOClSO3 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 2SO3, NO2Cl 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.

By causing an excess of SO3 to react on NOCl cooled to -50° one can obtain NOCl2SO3 pointed out by Seel [10] and prepared by Weinreich in solution in liquid SO2 [4, 11].

Tests in progress with SO3 and N2O3 and NO show that all of these synthesis reactions (gas + liquid SO3) 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.
REFERENCES

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.