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

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### Inorganic Chemistry — Direct Syntheses from Pure Liquid SO₃ and from Trivalent and Pentavalent Nitrogen Derivatives

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**Supplementary Notes:**

**Abstract:**
From pure liquid SO₃ the authors carried out direct synthesis reactions with N₂O₅, NO₂Cl, NOCl which yielded N₂O₅SO₃, 3SO₃, 2SO₃—NOCl₂SO₃—NOCl₂SO₃ and NOCl₂SO₃, 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.

**Key Words:** Inorganic Chemistry

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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 $\text{P}_4\text{O}_{10}\text{SO}_3$. 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.


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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 N₂O₅₄SO₃,
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 \( \text{N}_2 \text{O}_3 \cdot 2 \text{SO}_3 \).

\( \text{N}_2 \text{O}_5 \cdot 4 \text{SO}_3 \), ground and subjected to the action of \( \text{N}_2 \text{O}_5 \) gas at ambient temperature, fixes the latter and is gradually transformed into \( \text{N}_2 \text{O}_3 \cdot 3 \text{SO}_3 \). \( \text{N}_2 \text{O}_5 \cdot 3 \text{SO}_3 \) submitted to the same treatment does not undergo any significant increase in weight.

By contrast, by grinding \( \text{N}_2 \text{O}_5 \cdot 3 \text{SO}_3 \) or \( \text{N}_2 \text{O}_5 \cdot 4 \text{SO}_3 \) with solid \( \text{N}_2 \text{O}_5 \) in a glove box or on a heated plate under a current of dry nitrogen, one can increase the \( \text{N}_2 \text{O}_5 \) concentration of the initial product, ending up with the final limit formula \( \text{N}_2 \text{O}_5 \cdot 2 \text{SO}_3 \). 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 \( \text{N}_2 \text{O}_5 \cdot 2 \text{SO}_3 \), since a solid-solid action is involved without the release of gas. It is possible, on the other hand, to obtain \( \text{N}_2 \text{O}_5 \cdot 2 \text{SO}_3 \) in the pure state by causing \( \text{N}_2 \text{O}_5 \) to react on \( \text{NO}_2 \text{Cl}_2 \text{SO}_3 \) or \( \text{NOCl}_3 \text{SO}_3 \), the direct synthesis of which is mentioned below. The reactions seem to proceed as follows:

\[
\text{NO}_2 \text{Cl}_2 \text{SO}_3 + \text{N}_2 \text{O}_5 \rightarrow \text{N}_2 \text{O}_5 \cdot 2 \text{SO}_3 + \text{NO}_2 \text{Cl}
\]

and

\[
2 \text{NOCl}_3 \text{SO}_3 + 3 \text{N}_2 \text{O}_5 \rightarrow 2 \text{NO}_2 \text{Cl} + 2 \text{N}_2 \text{O}_5 + \text{N}_2 \text{O}_5 \cdot 2 \text{SO}_3.
\]

With cooled \( \text{NO}_2 \text{Cl} \) carried away by an inert gas the reaction on \( \text{SO}_3 \) occurs with a slight increase in temperature and is analogous to that of \( \text{N}_2 \text{O}_5 \): formation of turbidity, followed by separation of the constituents, the lower layer corresponding approximately to the formula \( \text{NO}_2 \text{Cl}_5 \text{SO}_3 \), increase in viscosity and crystallization of a solid which, after removal of the excess \( \text{SO}_3 \) at 60°, corresponds to the formula \( \text{NO}_2 \text{Cl}_2 \text{SO}_3 \). The \( S/N \) ratio = 2.01; \( N/\text{Cl} = 1.01 \) as against \( S/N = 2.16 \) and \( N/\text{Cl} = 1.075 \) respectively in the violent reaction of \( \text{SO}_3 \) on \( \text{NO}_2 \text{Cl} \) 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 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.