A New Preparation of S₄N₄

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Z. Naturforsch. 35b, 329–331 (1980); received September 17/November 16, 1979

Tetrasulfur Tetranitride Synthesis, Thiazyl Halogenide Decomposition, Metal Reaction, Monothiazyl Chloride Stability, IR Spectra

Pure S₄N₄ is prepared by a new method from reduction of S₂N₃Cl₃ by various metals (Hg, Cu, Sn). Realized either in an inert solvent or directly in gaseous phase the reaction is complete. The stability range of NSCI has been determined by Raman spectrometry.

**A. Action of Metals on S₄N₄Cl₃ in Solution**

During the study of the chlorination of S₄N₄ in CCl₄ by Raman spectrometry, we have shown the existence of the two following equilibria (4):

\[
\begin{align*}
S_4N_4 + Cl_2 & \rightarrow S_4N_4Cl_2 \quad (a) \\
S_4N_4Cl_2 + Cl_2 & \rightarrow S_4N_4Cl_3 + NSCI \quad (b)
\end{align*}
\]

S₄N₄Cl₃ dissolved in an inert solvent is unstable. After 3 days, at room temperature the solution is a mixture containing mainly S₂N₃Cl₃, but also NSCI, S₄N₄Cl₂ and S₄N₄ easily identified by infrared spectroscopy. The same mixture is obtained in half an hour, if the solution of S₂N₃Cl₃ is refluxed. S₄N₄ appears in solution, (a) and (b) equilibria are displaced due to a Cl₂ elimination which is accelerated by refluxing the solution. If we add to it a metal which reduces chlorine, we completely displace the equilibria to the formation of S₄N₄.

Several metals have been studied: Hg, Sn, Cu. These metals are very reactive with chlorine but are inert towards S₄N₄. Mercury, added to a 2·10⁻² M S₄N₄ solution in CCl₄, is immediately covered with a deposit mainly consistuted by Hg₂Cl₂. The solution composition is followed by infrared spectrometry; the mixture is strongly agitated. After 4 h, the spectrum shows only the S₄N₄ bands. After the separation of Hg and Hg₂Cl₂, the solution is evaporated under vacuum. S₄N₄ is recrystallized in CS₂. The yield is about 65%.

Tin and copper lead to similar results, however, the reaction time is much longer. During the contact with the S₂N₃Cl₃ solution, the metals are covered with chloride, which stops the reaction; it is important to add some pure metal.

**B. Action of Metals on S₂N₃Cl₃ in Gaseous Phase**

We have also studied the action of metals on NSCI which has the same N/S ratio than S₄N₄. This
A new preparation of $\text{S}_4\text{N}_4$ gaseous compound is obtained from $\text{S}_3\text{N}_3\text{Cl}_3$ or $\text{S}_4\text{N}_3\text{Cl}$ (5). On heating, these thiazyl chlorides decompose according to:

$$\text{S}_3\text{N}_3\text{Cl}_3 \rightarrow 3 \text{NSCl}$$
$$2 \text{S}_4\text{N}_3\text{Cl} \rightarrow 2 \text{NSCl} + \text{S}_4\text{N}_4 + 2 \text{S}$$

We have studied the first reaction which leads to the formation of NSCl alone.

**B. 1. Stability range of NSCl**

We checked the stability range of NSCl in order to determine the best conditions of the NSCl reaction on metals. The $\text{S}_3\text{N}_3\text{Cl}_3$ decomposition was studied by infrared and Raman spectrometry. The methods used allow to record the spectra directly at the studied temperature.

**B. 1.1. Experimental techniques**

Raman spectrometry: the apparatus is a CODERG PHO spectrophotograph, the scattered light is focused on the cathodic tube of a EM I 955 photomultiplier tube. The laser is a Spectra Physics Model 164 argon ion laser of 1 W, with photon energy of 20,490 cm$^{-1}$ (wave length 4880 Å). We used the following device: the reactor is a cylindrical pyrex tube of 50 cm$^3$, ended by a flat surface. The tube is placed in the axis of an oven constituted by three heating elements separately regulated, which allows to overheat lightly the near part of the spectrograph to avoid deposits on the optic surface of the cell. The laser beam is perpendicular to the axis of the tube. The sample (50 mg) is placed into the tube sealed under vacuum. The temperatures were obtained with a chromel-alumel thermocouple.

Infrared spectrometry: the apparatus is a Perkin Elmer 457 spectrometer. The analysis cell is constituted by a body in stainless steel on which is wound a heating resistance. The windows are made of KBr. The tightness to gas is realized by toric gaskets in viton, which allows to work under vacuum. We measure the temperature with a thermocouple placed alongside the tube in the oven.

**B. 1.11. Results**

We have observed the decomposition of $\text{S}_3\text{N}_3\text{Cl}_3$ from 90 °C with production of NSCl easily identifiable by its three vibrations all visible in Raman (Fig.) and infrared spectrometry:

$$\text{NSCl}$$

<table>
<thead>
<tr>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>$\nu_3$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1321</td>
<td>414</td>
<td>269</td>
</tr>
</tbody>
</table>

Figure. Raman spectrum of NSCl.

By studying the NSCl deposit on CsI window at 15 K, Peake [6] has observed these three vibrations in infrared spectrometry.

$$\nu_1 = 1327 \text{ cm}^{-1}, \ 
u_2 = 403.75 \text{ cm}^{-1}, \ 
u_3 = 267.4 \text{ cm}^{-1}.$$  

The slightly shifted values of the frequencies can be explained by the experimental techniques used.

The range of NSCl is relatively narrow. By increasing the temperature to 120 °C, beside NSCl, we notice the formation of $\text{S}_2\text{Cl}_2$: 92 cm$^{-1}$ (p), 197 cm$^{-1}$ (p) and 456 cm$^{-1}$ (p). The disulfur dichloride results from the decomposition of NSCl according to:

$$2 \text{NSCl} \rightarrow \text{S}_2\text{Cl}_2 + \text{N}_2$$

Above this temperature, only $\text{S}_2\text{Cl}_2$ exists.

We must point out that our infrared spectra are more complex than our Raman ones. As a matter of fact, during the infrared study of the $\text{S}_3\text{N}_3\text{Cl}_3$ decomposition, we cannot avoid the condensation of solid on the windows which are obviously at a lower temperature than the gas. This deposit gives further absorption bands which can be attributed to $\text{S}_3\text{N}_2\text{Cl}_3$, $\text{S}_2\text{N}_2\text{Cl}_2$ and $\text{S}_3\text{N}_3\text{Cl}_2$. The formation of these solid thiazyl chlorides results from the following reactions:

$$3 \text{NSCl} \rightarrow \text{S}_3\text{N}_2\text{Cl}_3$$
$$2 \text{NSCl} \rightarrow \text{S}_2\text{Cl}_2 + \text{N}_2$$
$$\text{S}_2\text{Cl}_2 + 2 \text{NSCl} \rightarrow \text{S}_3\text{N}_2\text{Cl}_2 + \text{SCl}_2$$
$$3 \text{S}_2\text{N}_2\text{Cl}_2 \rightarrow \text{S}_3\text{N}_3\text{Cl}_2 + 2 \text{NSCl} + \text{SCl}_2$$

A small amount of SO$_2$ was also found in the
observed infrared spectrum probably due to the following reaction of NSCl with water vapour:

\[
\text{NSCl} + 2 \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{SO}_2 + \text{HCl}
\]

**B. 2. NSCl-metal reaction**

We studied the action of copper on NSCl.

**B. 2.1. Experimental device**

A reactive tube (\(\varnothing = 40\) mm) is placed on a vacuum rack. In the medium part of this tube is a 10 cm plug of copper turnings previously washed with HNO₃, then dried. The upper part is provided with a glove finger filled with liquid nitrogen. The lower part containing S₃N₃Cl₃ is put in a thermostated bath at 95 °C. To avoid the deposit of S₃N₃Cl₃ on the reactor walls before the zone containing copper, it was necessary to dip the tube deeply in the bath.

**B. 2.11. Results**

When the copper is in contact with NSCl, it gets immediately dark and the glove finger is gradually covered with yellow S₄N₄. After the complete sublimation, we collect pure S₄N₄ on the glove finger; the greater part of S₄N₄ stays on the copper. Then the latter is treated by carbon disulfide; S₄N₄ is soluble and recovered after evaporation of the solution. The insoluble residue, characterized by X-rays is the cuprous chloride.

We have also extracted S₄N₄ from the deposit on copper by sublimation at 100 °C.

To conclude we can schematize the formation of S₄N₄ from S₃N₃Cl₃ and copper by the following reactions:

\[
\text{S}_3\text{N}_3\text{Cl}_3 \rightarrow 3 \text{NSCl (g)}
\]

\[
\text{NSCl + Cu} \rightarrow \text{CuCl} + 1/4 \text{S}_4\text{N}_4
\]

We have tried to follow “in situ” the mechanism of the S₃N₃Cl₃–Cu reaction by infrared spectroscopy by using a heated cell: copper turnings do not influence the recording of infrared spectra. The only gas which appears is NSCl, we have not observed the formation of another gaseous specimen such as SN or S₂N₂.