Title
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Publication Date
1963-06-01

UCRL-10876

University of California

Ernest O. Lawrence Radiation Laboratory

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Berkeley, California

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Submitted to Chemistry and Industry

UCRL-10876

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

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June 1963

Four New Methods for Preparing NSCl

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Glemser[1,2] has reported that NSCl may be prepared by the pyrolysis of $(NSCl)_3$. We wish to report four additional methods for preparing NSCl.

(1) When a stream of S_2Cl_2 vapor was passed into a stream of active nitrogen[3], a blue glow was emitted by the mixture, and yellow-brown solids formed on the walls of the reaction tube. A -196° trap immediately following the reaction tube collected (beside the unreacted S_2Cl_2) NSCl, SCl_2, small amounts of $S_3N_2Cl_2$, traces of chlorine, and small amounts of an uncharacterized red-brown solid. The $S_3N_2Cl_2$ probably formed as a result of the reaction

$$S_2Cl_2 + 2\ NSCl \longrightarrow S_3N_2Cl_2 + SCl_2 ,$$

which takes place rapidly in the liquid state.[4] By allowing the trap to stand at room temperature for an hour or so before attempting a separation of the products, it was possible to remove all the NSCl by this reaction. In a typical run, S_2Cl_2 was added at the rate of 0.18 μmoles sec^{-1} to a stream of active nitrogen (P = 5 mm; N/N_2 = 0.014) in which the flow-rate

of atomic nitrogen was 3.02 μmoles sec^{-1}. Sixty-two milligrams of NSCl (calc. from $S_3N_2Cl_2$) formed in a period of 105 minutes, corresponding to a 34% conversion of the S_2Cl_2, based on the equation

$$2\ N + S_2Cl_2 \longrightarrow 2\ NSCl\ .$$

(2) When a suspension of ammonium chloride in excess S_2Cl_2 was refluxed for an extended period, the ammonium chloride eventually was consumed, and a solution of sulfur in S_2Cl_2 remained. Hydrogen chloride, NSCl and S_2Cl_2 were the principal components of the effluent gas. The first two species were probably formed by the reaction

$$NH_4Cl + 2\ S_2Cl_2 \longrightarrow 3\ S + NSCl + 4\ HCl\ .$$

Modifications of this process which permit the isolation of $S_3N_2Cl_2$ are described elsewhere.[6]

(3) When $S_3N_2Cl_2$ was heated <u>in vacuo</u> to 80-100°, NSCl and SCl_2 were evolved and a greenish-black residue of S_3N_2Cl was formed:

$$3\ S_3N_2Cl_2 \longrightarrow 2\ S_3N_2Cl + 2\ NSCl + SCl_2\ .$$

In one experiment, 4.89 g. of $S_3N_2Cl_2$ yieled 2.53 g. of S_3N_2Cl (2.67 g. calc.), 1.36 g. of NSCl (1.61 g. calc.) and 0.74 g. of SCl_2 (0.86 g. calc.).

(4) Meuwsen[5] has reported that, by passing chlorine into a carbon tetrachloride suspension of $S_3N_2Cl_2$, the compound $(NSCL)_3$ may be prepared. He postulated that the intermediate NSCl was involved. Indeed, we have found that NSCl (along with SCl_2 and what is presumably $(NSCl)_3$) is formed by the reaction of chlorine gas on $S_3N_2Cl_2$ at room temperature in the absence of a solvent.

$$S_3N_2Cl_2 + Cl_2 \longrightarrow 2\ NSCl + SCl_2$$

$$3\ NSCL \longrightarrow (NSCl)_3$$

NSCl was identified by its infrared spectrum[1]. In some cases the NSCl was allowed to polymerize to a pale yellow solid (presumably $(NSCl)_3$) which was then analyzed for nitrogen and chlorine. (Calcd. for $(NSCl)_3$: N, 17.18; Cl, 43.49. Found: N, 17.14; Cl, 43.62.) This substance melted in the region 73-77° to a dark green liquid which, upon heating to 110-140°, formed an orange solid which melted at 195-198°. These results differ from those of Schröder and Glemser[7], who reported a melting point of 162.5° for $(SNCl)_3$.

This work was supported by the U.S. Atomic Energy Commission.

References

[1] Glemser, O. & Richert, H., Z. anorg. allgem. Chem., 1961, 307, 313.

[2] Glemser, O. & Perl, H., Naturwiss., 1961, 48, 620.

[3] Prepared by passing dry nitrogen gas at low pressures through a microwave discharge.

[4] Meuwsen[5] has shown that $(NSCl)_3$ reacts with S_2Cl_2 to give $S_3N_2Cl_2$.

[5] Meuwsen, A., Ber., 1932, 65, 1724.

[6] Jolly, W. L., Maguire, K. D. & Rabinovich, D., to be published.

[7] Schröder, H. & Glemser, O., Z. anorg. allgem. Chem., 1959, 298, 78.