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FOUR NEW METHODS FOR PREPARING NSCI

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FOUR NEW METHODS FOR PREPARING NSCI

K. D. Maguire, J. J. Smith and W. L. Jolly

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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 S₂Cl₂ vapor was passed into a stream of active nitrogen³, 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 S₂Cl₂) NSCl, SCl₂, small amounts of S₃N₂Cl₂, traces of chlorine, and small amounts of an uncharacterized red-brown solid. The S₃N₂Cl₂ probably formed as a result of the reaction

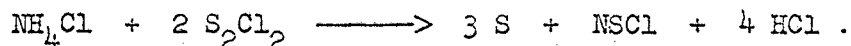


which takes place rapidly in the liquid state.⁴ By allowing the trap to stand at room temperature for an hour or so before attempting a separation of the products, it was possible to remove all the NSCl by this reaction. In a typical run, S₂Cl₂ was added at the rate of 0.18 μmoles sec⁻¹ to a stream of active nitrogen. (P = 5 mm; N/N₂ = 0.014) in which the flow-rate

of atomic nitrogen was $3.02 \mu\text{moles sec}^{-1}$. Sixty-two milligrams of NSCl (calc. from $\text{S}_3\text{N}_2\text{Cl}_2$) formed in a period of 105 minutes, corresponding to a 34% conversion of the S_2Cl_2 , based on the equation

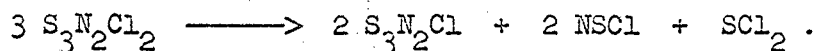


(2) When a suspension of ammonium chloride in excess S_2Cl_2 was refluxed for an extended period, the ammonium chloride eventually was consumed, and a solution of sulfur in S_2Cl_2 remained. Hydrogen chloride, NSCl and S_2Cl_2 were the principal components of the effluent gas. The first two species were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



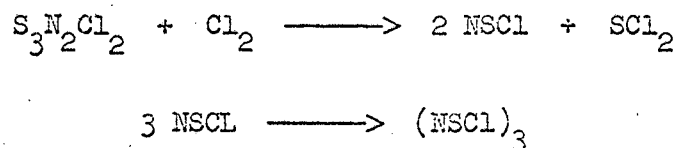
Modifications of this process which permit the isolation of $\text{S}_3\text{N}_2\text{Cl}_2$ are described elsewhere.⁶

(3) When $\text{S}_3\text{N}_2\text{Cl}_2$ was heated in vacuo to $80-100^\circ$, NSCl and SCl_2 were evolved and a greenish-black residue of $\text{S}_3\text{N}_2\text{Cl}$ was formed:



In one experiment, 4.89 g. of $\text{S}_3\text{N}_2\text{Cl}_2$ yielded 2.53 g. of $\text{S}_3\text{N}_2\text{Cl}$ (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) Meuwesen⁵ 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.



NSCl was identified by its infrared spectrum¹. 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 Glemser⁷, 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 Meuwsen⁵ has shown that $(\text{NSCl})_3$ reacts with S_2Cl_2 to give $\text{S}_3\text{N}_2\text{Cl}_2$.
- 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.

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