Anal. Calcd. for $C_{52}H_{48}DCoP_4$: C, 72.8; H, 5.9. Found: C, 72.1; H, 5.65.

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Convenient Methods for Preparing $S_3N_2Cl_2$ and S_4N_3Cl

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When a suspension of ammonium chloride in S_2Cl_2 is refluxed, the principal reaction products are NSCl and HCl.[1]

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

If a sufficiently large amount of ammonium chloride is used, transparent orange crystals of $S_3N_2Cl_2$ soon begin to form in the condenser above the level of the refluxing liquid. When practically all the S_2Cl_2 has been consumed, the $S_3N_2Cl_2$ which has formed in the condenser may be removed. However, if S_4N_3Cl is the desired product, the reaction flask is removed, and a flask containing carbon tetrachloride is attached to the condenser containing the crystals of $S_3N_2Cl_2$. The carbon tetrachloride is boiled so that the refluxing liquid washes the crystals into the flask. During this process the crystals first turn green (S_3N_2Cl) and finally yellow (S_4N_3Cl).

It is believed that the vapors of S_2Cl_2 and NSCl react to form the $S_3N_2Cl_2$.

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

This reaction does not begin immediately upon refluxing the mixture of ammonium chloride and S_2Cl_2 because of the presence of chlorine[2] in the effluent gases. Chlorine is known[1] to react with $S_3N_2Cl_2$ according to the equation

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

However, when the concentration of sulfur in the S_2Cl_2 increases sufficiently to prevent, or almost prevent, the evolution of chlorine,[4] the $S_3N_2Cl_2$ deposition begins. Two types of experiments attest to this interpretation of the delayed deposition of $S_3N_2Cl_2$. First, when relatively small amounts of ammonium chloride are used, no $S_3N_2Cl_2$ is deposited even when the refluxing is continued until the ammonium chloride is completely consumed. (In such cases, the concentration of sulfur never becomes high enough to prevent effectively the evolution of chlorine.) Second, when sulfur is added to the reaction mixture, the time to the first appearance of $S_3N_2Cl_2$ is greatly reduced. Indeed $S_3N_2Cl_2$ is produced when sulfur is added to a reaction mixture that ordinarily does not produce $S_3N_2Cl_2$.

When $S_3N_2Cl_2$ is heated to 80–95° *in vacuo*, greenish black S_3N_2Cl is formed.[1]

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

We believe that this pyrolysis is the best method for preparing S_3N_2Cl. When S_3N_2Cl is heated to 130–150° *in vacuo*, a variety of products, including NSCl and SCl_2, are evolved, and a residue of pure S_4N_3Cl is formed. In view of these facts and the fact that a dark green intermediate is observed during the refluxing of carbon tetrachloride with $S_3N_2Cl_2$, we believe that the over-all conversion of $S_3N_2Cl_2$ to S_4N_3Cl by boiling carbon tetrachloride proceeds *via* S_3N_2Cl. Meuwsen[5] carried out this same conversion, but he stated that the reaction proceeds smoothly only in the presence of S_2Cl_2, and he did not report the intermediate formation of S_3N_2Cl.

Experimental

Preparation of S_4N_3Cl.—NH_4Cl (50 g.) and 25 ml. of S_2Cl_2 were placed in a 500-ml. round-bottomed flask fitted with an air condenser (75 cm. long and 22 mm. in diameter) to the top of which a calcium sulfate drying tube was attached. The mixture was refluxed gently using a heating mantle. The heating was adjusted so that the level of the refluxing S_2Cl_2 was just above the neck of the flask. During approximately 16 hr. of refluxing, orange crystals of $S_3N_2Cl_2$ collected in the air condenser. At the end of this time the heating was stopped and the apparatus was allowed to stand overnight so that most of the liquid adhering to the crystals could drain away. (This liquid contained appreciable amounts of dissolved hydrogen chloride which, if not removed, resulted in a product contaminated with ammonium chloride.) The reaction flask was removed and *immediately* replaced with a similar flask containing 100 ml. of *dry* carbon tetrachloride (freshly distilled from $CaSO_4$). The carbon tetrachloride was then refluxed up into the air condenser over the crystalline deposit. The material first turned dark green and partly bright yellow and fell into the flask. Shaking the assembly or even inserting a long glass rod down the air condenser was sometimes necessary in order to assist the sublimate down into the reflux flask. The carbon tetrachloride was boiled until all the dark material was converted into a bright yellow solid (approximately 4 hr.). The solid S_4N_3Cl was filtered from the carbon tetrachloride while it was still warm; it was washed with dry carbon tetrachloride, and finally dried in a vacuum desiccator; yield 4.5 g.

Anal. Calcd. for S_4N_3Cl: N, 20.38; S, 62.34; Cl, 17.24. Found: N, 21.02; S, 62.09; Cl, 17.58. The infrared spectrum (KBr disk) showed peaks at 8.55, 10.0, and 14.75 μ, and was identical with the infrared spectrum of a sample of S_4N_3Cl prepared in the usual way.[6]

Preparation of $S_3N_2Cl_2$.—The orange $S_3N_2Cl_2$ which formed in

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(1) K. D. Maguire, J. J. Smith, and W. L. Jolly, to be published.

(2) Most of the chlorine probably arises from the decomposition of the S_2Cl_2. When S_2Cl_2 is fractionally distilled at atmospheric pressure, SCl_2 comprises the first fraction. Because SCl_2 is known to decompose appreciably to chlorine,[3] and because in these syntheses the more volatile vapors are being carried away by a stream of hydrogen chloride, it is reasonable to expect chlorine in the initial off-gases.

(3) J. W. George, *Progr. Inorg. Chem.*, **2**, 33 (1960).

(4) Presumably sulfur reduces the concentrations of SCl_2 and Cl_2 in the liquid S_2Cl_2 by shifting the equilibria $S_2Cl_2 = S + SCl_2$ and $S_2Cl_2 = 2S + Cl_2$.

(5) A. Meuwsen, *Ber.*, **65**, 1724 (1932).

(6) M. Goehring, "Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen," Akademie-Verlag, Berlin, 1957, p. 155.

the reaction between S_2Cl_2 and NH_4Cl (described above) could be isolated in a pure state by rapidly removing the reaction flask, closing the open end of the air condenser, and then quickly replacing the drying tube with a connection to the vacuum line. By evacuating the tube and pumping for approximately 30 min. the volatile impurities were removed. The $S_3N_2Cl_2$ was scraped from the inside of the air condenser in a "dry bag" flushed with dry nitrogen. All operations involving $S_3N_2Cl_2$ should be made in a dry atmosphere, since the compound is very sensitive to atmospheric moisture; yield approximately 14 g.

Anal. Calcd. for $S_3N_2Cl_2$: S, 49.29; N, 14.36; Cl, 36.34. Found: S, 49.0; N, 14.27; Cl, 36.64; m.p. (sealed tube) 90–92°. The compound is not stable for prolonged periods even in a dry atmosphere, but may be kept for about 10 days without serious decomposition.

When 5.35 g. of ammonium chloride was refluxed with 35 ml. of S_2Cl_2 for 36 hr. in the manner described above, all the ammonium chloride was consumed and a solution of sulfur in S_2Cl_2 remained. No $S_3N_2Cl_2$ was formed in the air condenser. In a reaction similar to the above, but in which 6.4 g. of elementary sulfur was added to the reactants, crystals of $S_3N_2Cl_2$ began to form after 1.5 hr. of refluxing.

Thermal Decomposition of S_3N_2Cl.—Dark green S_3N_2Cl (1.95 g.) was prepared by thermal decomposition of $S_3N_2Cl_2$. *Anal.* Calcd. for S_3N_2Cl: N, 17.54; Cl, 22.24. Found: N, 17.95; Cl, 21.80. The S_3N_2Cl was thermally decomposed *in vacuo* at 130–150°. The volatile products (0.65 g.) were collected in a −78° trap and were identified by their infrared spectrum as NSCl[7] and SCl_2.[8] By allowing the trap to stand at room temperature overnight the NSCl formed the nonvolatile trimer $(NSCl)_3$ from which 0.145 g. of SCl_2 was readily separated. The solid nonvolatile residue from the pyrolysis was bright yellow S_4N_3Cl (1.03 g.).

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(7) O. Glemser and H. Richert, *Z. anorg. allgem. Chem.*, **307**, 313 (1961).

(8) G. M. Barrow, *J. Phys. Chem.*, **59**, 987 (1955).

CONTRIBUTION FROM THE ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA

Isolation and Storage of Free Radicals on Molecular Sieves. I. The Electron Paramagnetic Resonance Spectrum of Nitrogen Dioxide

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While it has been observed that Linde Molecular Sieves can be used to store numerous materials—amines, organometallic compounds, peroxides, etc.,[1] the use of molecular sieves for the isolation and storage of free radicals has not been reported previously.

Figure 1 is the derivative e.p.r. spectrum of NO_2 adsorbed in or on Linde Molecular Sieve 13X in equilibrium with the gas phase at 750 mm. pressure of $N_2O_4 \rightleftarrows 2NO_2$. The spectrum is seen to consist of three very well defined, slightly overlapping lines. The N^{14} splitting is 56.9 gauss and the over-all width (between points of maximum slope) is 125 gauss. The individual components have widths of about 8–10 gauss, the center line being slightly narrower than the outside peaks. Our measured N^{14} interaction agrees with the isotropic interaction term derived by Atkins, *et al.*,[2] from the spin-resonance spectrum of NO_2 trapped in ice at 77°K. The *g*-value was found to be 2.003, but the influence of the "sieve" on the applied magnetic field has yet to be characterized. From the amplitude of the e.p.r. signal, we estimate the NO_2 concentration in the 13X sieve to be 10^{-5} to 10^{-4} *M*.

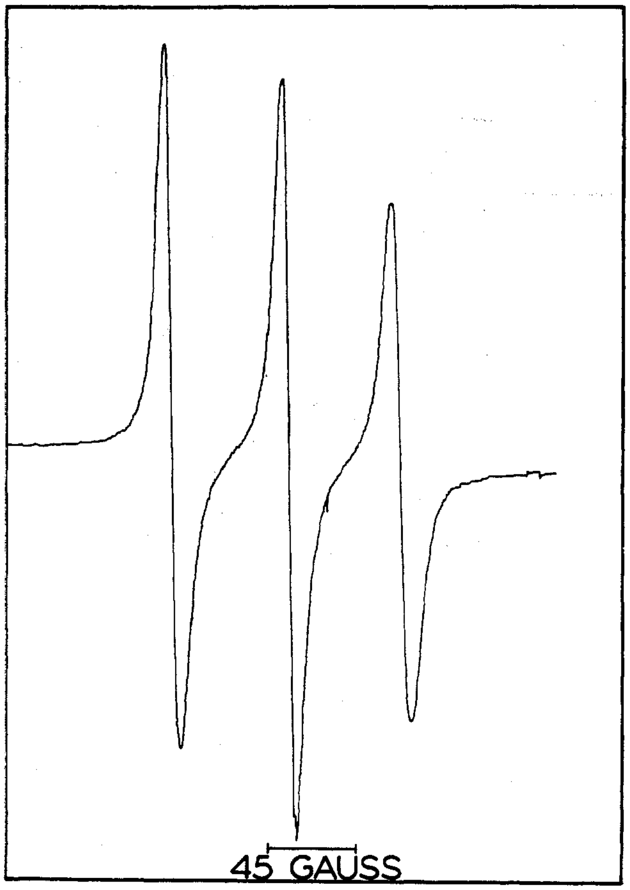

Fig. 1.—Derivative e.p.r. spectrum of NO_2 on Linde Molecular Sieve 13X. Pressure of $N_2O_4 \rightleftarrows 2NO_2$ in the gas phase over the sieve is 750 mm.

By way of comparison, the results of other investigations may be summarized. The e.p.r. spectrum of gaseous NO_2 at 5–10 mm. pressure consists of three overlapping lines, arising from coupling with the N^{14} moment. As the pressure is further decreased and collisional broadening reduced, these lines are split into a large number of components due to interaction with the molecular rotation.[3] At high pressures approaching 1 atm. and in liquid N_2O_4 (NO_2), only a single very broad line is ordinarily obtained.

The broadening of the e.p.r. signal at ordinary gas pressures may be further explained by an extremely rapid radical recombination rate to form the dimer N_2O_4; *i.e.*, the radical has a mean lifetime which is much less than 1 μsec. This effect (uncertainty broad-

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(1) C. K. Hersh, "Molecular Sieves," Reinhold Publishing Co., New York, N. Y., 1961.

(2) P. W. Atkins, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 2873 (1962).

(3) J. G. Castle and R. Beringer, *Phys. Rev.*, **80**, 114 (1950).