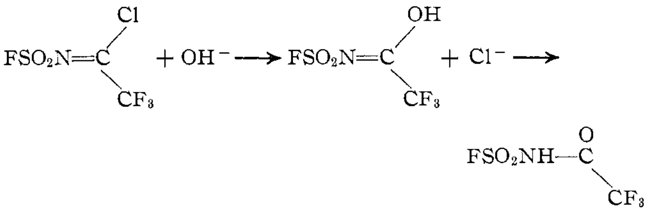


The ^{19}F nuclear magnetic resonance measurements of the FSO_2 group in all of the compounds are essentially nonvarying. The fluorine resonances compare favorably with other fluorosulfonyl compounds, *e.g.*, FSO_2NSO[13] (−59.2 ppm) and $FSO_2N{=}S{=}NSO_2F$[14] (−58.5 ppm).

In $FSO_2N{=}CCF_3N(C_2H_5)_2$ interaction occurs between the fluorine in the fluorosulfonyl group and the fluorines bonded to the CF_3 group but no such interaction is observed in the NH_2 or $N(CH_3)_2$ compounds. With $FSO_2N{=}CCF_3N(CH_3)_2$ coupling between the CF_3 fluorines and the protons occurs but no F–H coupling occurs in the NH_2 or $N(C_2H_5)_2$ compounds. The substitution of a chlorine atom by an NH_2 group causes the fluorine in the FSO_2 group to shift to higher field (Cl, −55.2 ppm; NH_2, −51.6 ppm).

Acknowledgments.—We wish to thank Professor Dr. O. Glemser for helpful discussion. Financial support by the Verband der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[13] H. W. Roesky, *Angew. Chem.*, **79**, 724 (1967).

[14] H. W. Roesky and D. P. Babb, *ibid.*, **81**, 494 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, AND THE
INORGANIC MATERIALS RESEARCH DIVISION, LAWRENCE RADIATION LABORATORY, BERKELEY, CALIFORNIA 94720

The Sublimation of Trithiazyl Trichloride and the Equilibrium between Trithiazyl Trichloride and Thiazyl Chloride

BY R. LYLE PATTON AND WILLIAM L. JOLLY

Received November 12, 1969

The pressure of NSCl vapor in equilibrium with solid $S_3N_3Cl_3$ was measured in a static system in the temperature interval 31–60° and can be represented by the equation $\log P_{NSCl}(\text{mm}) = 12.321 - 3360/T$. From this we calculate $\Delta H° = 46.2 \pm 1.5$ kcal mol^{-1} and $\Delta S° = 129.6 \pm 4.8$ cal deg^{-1} mol^{-1} for the reaction $S_3N_3Cl_3(s) \rightarrow 3NSCl(g)$. The pressure of $S_3N_3Cl_3$ vapor in equilibrium with solid $S_3N_3Cl_3$ was measured by a gas-flow saturation method in the temperature interval 35–50° and can be represented by the equation $\log P_{S_3N_3Cl_3}(\text{mm}) = 14.270 - 5316/T$. From this we calculate $\Delta H° = 24.3 \pm 1.5$ kcal mol^{-1} and $\Delta S° = 52.1 \pm 4.6$ cal deg^{-1} mol^{-1} for the reaction $S_3N_3Cl_3(s) \rightarrow S_3N_3Cl_3(g)$. Combination of the above data yields $\Delta H°$ and $\Delta S°$ for the gaseous trimerization reaction.

Introduction

Compounds containing sulfur–nitrogen bonds are a fascinating class of substances which are poorly understood.[1–4] Very few of the reactions or structures of these compounds can be reliably predicted. We believe that a good start toward the systemization of sulfur–nitrogen chemistry can be achieved by collecting appropriate thermodynamic data. However, practically no thermodynamic data are available for sulfur–nitrogen compounds. Apparently no equilibrium measurements of reactions involving sulfur–nitrogen compounds have been made. Of the cyclic compounds, S_4N_4 is the only one whose heat of formation has been determined.[5,6] Heats of formation and bond energies of a few noncyclic NS compounds have been determined by mass spectrometry,[7] and, recently, some thermodynamic functions of NSCl were calculated from its infrared spectrum.[8]

In this paper we report the results of our study of the equilibria between solid $S_3N_3Cl_3$ (trithiazyl trichloride) and the vapor species $S_3N_3Cl_3$ and NSCl. The data yield the thermodynamic functions for the trimerization of NSCl to form the six-membered ring compound $S_3N_3Cl_3$.

Experimental Section

General Methods.—The moisture sensitivity of the materials required their manipulation in a vacuum line or in a polyethylene glove bag flushed with dry nitrogen or argon. Glass stopcocks and joints were lubricated with Kel-F No. 90 grease (3M Co.), which is inert to the materials handled but which tends to absorb some of them. When grease was intolerable, either Delmar-Urry 0–4-mm stopcocks or Fischer–Porter needle valve stopcocks with Teflon plugs and Viton O rings were used.

The identity and purity of solids were determined by infrared spectrometry with Perkin-Elmer Infracord spectrometers and by melting point determinations in argon-filled, sealed capillaries.

---

[1] M. Becke-Goehring, *Angew. Chem.*, **73**, 589 (1961).

[2] O. Glemser, *Angew. Chem. Intern. Ed. Engl.*, **2**, 530 (1963).

[3] M. Becke-Goehring and E. Fluck in "Developments in Inorganic Nitrogen Chemistry,' Vol. 1, C. B. Colburn, Ed., Elsevier Publishing Co., Amsterdam, 1966, Chapter III, pp 150–240.

[4] W. L. Jolly in "The Chemistry of Sulfides," A. V. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968, pp 3–7.

[5] M. Berthelot and P. Vieille, *Ann. Chim. Phys.*, **27**, 202 (1882).

[6] C. K. Barker, A. W. Cordes, and J. L. Margrave, *J. Phys. Chem.*, **69**, 334 (1965).

[7] O. Glemser, A. Müller, D. Bohler, and B. Krebs, *Z. Anorg. Allgem. Chem.*, **357**, 184 (1968).

[8] A. Müller, G. Nagarajan, O. Glemser, S. F. Cyvin, and J. Wegener, *Spectrochim. Acta*, **23A**, 2683 (1967).

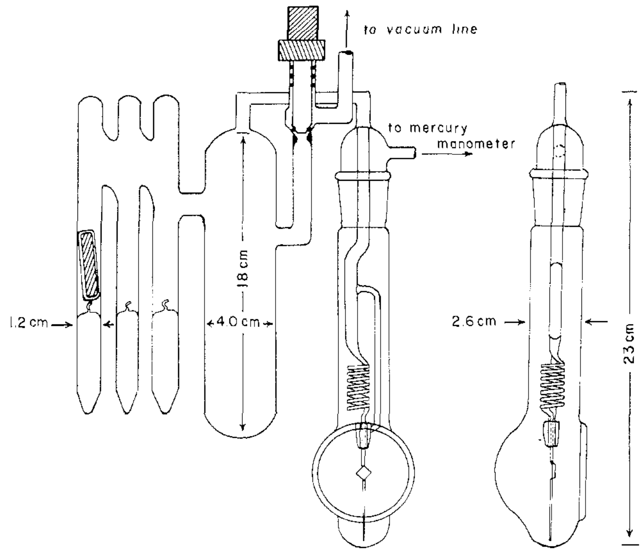


Figure 1.—Glass spiral manometer and sample chamber used to determine equilibrium NSCl pressures.

Volatile materials were identified and checked for purity by infrared spectrometry (both vapors and condensate), by mass spectrometry with a Consolidated Engineering Corp. mass spectrometer (Model 21-620), by vapor pressure measurements, and by molecular weight determinations.

Frequent pressure measurements of gaseous systems containing species that react rapidly with mercury, such as Cl_2, S_2Cl_2, SCl_2, and NSCl, necessitated the use of a glass spiral differential manometer (distributed by Electronic Space Products, Inc., Los Angeles, Calif.) depicted in Figure 1 with the attached sample chamber. With this apparatus the sample chamber pressure could be determined to ±0.2 mm. The manometer had the desirable property that the sample volume did not change with pressure and that the manometer, including the sample chamber, could be completely immersed in a constant-temperature bath. The bath was constructed of a cylindrical glass jar (8-in. i.d. × 17-in. height) surrounded by several inches of vermiculite insulation in a box with a cardboard tube inserted through a hole in its side to allow the light beam to reach the mirror. The bath temperature (both oil and water were used as bath liquids) was controlled to within ±0.05°, as read with a total-immersion mercury-in-glass thermometer with 0.1° graduations. In a system check, 113.4 mm of helium at 28.7° was transferred into the sample chamber of 156.9-cm³ volume; pressure readings taken at 12 temperatures up to 140° showed a maximum deviation of 0.15 mm from the values predicted from the perfect gas law. Introduction of materials into the sample chamber was accomplished either by transfer from the vacuum line through a Delmar–Urry O ring valve or by sealing the materials into break-seal-equipped tubes and glassblowing them onto the chamber; the break-seals could then be opened by magnetic manipulation of a breaker to open the sample to the chamber even when the apparatus was in the bath.

Carbon tetrachloride was refluxed for 6–10 hr over P_2O_5, distilled, and stored under an inert gas. Chlorine (Matheson) and S_2Cl_2 (Eastman Kodak Co.) were purified, when necessary, by vacuum-line fractional condensation. Tetrasulfur tetranitride was prepared and purified using the method of Villena-Blanco and Jolly,[9] and S_4N_3Cl, $S_3N_2Cl_2$, and S_3N_2Cl were identified by comparing their infrared absorptions, appearance, and thermal properties with those of known samples prepared by the method of Jolly and Maguire.[10]

Preparation and Preliminary Investigations of $S_3N_3Cl_3$.—Trithiazyl trichloride was prepared once by the chlorination of S_4N_4[11] and thereafter by the chlorination of $S_3N_2Cl_2$.[10] The crude product from the chlorination of S_4N_4 melted (with decomposition) at 77–78° (lit.[11] mp 162.5°); the crude product from the chlorination of $S_3N_2Cl_2$ exhibited decomposition points ranging from 76 to 82° (lit.[10] dec pt: crude, 75°; recrystallized from CCl_4, 91°). Samples prepared by both methods exhibited the same infrared absorptions (including the strongest band at 1015 cm^{-1}, reported to be characteristic of $S_3N_3Cl_3$ by Glemser and Richert[12]) and dissolved in CCl_4 to give yellow solutions which turned a vivid mint green above 55° but which returned to yellow when cooled. The melting points of $S_3N_3Cl_3$ recrystallized from hot CCl_4 ranged from 73 to 93°, although all samples melted in a 1–2° range. The samples crystallized from solutions that had not been hot enough to produce the green color were high melting, and the samples from solutions heated above 60° were low melting. We suggest that the 162.5° melting point reported by Schröder and Glemser[11] corresponds to the melting or decomposition of a solid decomposition product of $S_3N_3Cl_3$. Our results indicate that the "melting–decomposition" of $S_3N_3Cl_3$ is catalyzed by small amounts of impurities which can be minimized by treatment with chlorine.

When the recrystallization solution was heated to 65° and maintained at that temperature while a stream of chlorine was bubbled through the stirred solution, the green color immediately disappeared, leaving the original yellow color. The crystalline $S_3N_3Cl_3$ obtained by cooling such a solution consistently melted between 95 and 98°. This higher melting material exhibited the same infrared absorptions as material recrystallized without passage of chlorine and was used in the vapor pressure studies.

When a 100-mg sample of $S_3N_3Cl_3$ in a 100-ml bulb closed with a Delmar–Urry stopcock was held at 80° for 2 hr, it completely vaporized to a green gas. When cooled quickly, the gas condensed to a green liquid which soon completely solidified to yellow crystals of $S_3N_3Cl_3$ (identified by its infrared spectrum). A similar sample was vaporized at 80°, and the bulb was allowed to cool very slowly to 20°. No liquid phase was visible as the green gas slowly disappeared and yellow crystals grew on the walls. Infrared spectrometry showed the residual vapor to contain NSCl,[12] S_2Cl_2,[13] and SCl_2[13] and the solid to contain principally $S_3N_3Cl_3$ with a small amount of $S_3N_2Cl_2$. The latter compound presumably formed in the reaction $S_2Cl_2 + 2NSCl \rightarrow S_3N_2Cl_2 + SCl_2$. The S_2Cl_2 arose from decomposition of the NSCl vapor to S_2Cl_2 and N_2, of which the latter was detected by Toepler pumping.

In a continuously evacuated sublimator $S_3N_3Cl_3$ sublimed very slowly at 55°, giving yellow $S_3N_3Cl_3$ on a water-cooled cold finger and only traces of NSCl condensate in a subsequent cold trap. However, when ~40 mm of nitrogen or helium was present during sublimation in a closed system at 70–80° to a −196° finger, a yellow-white film and, later, white-to-purple crystals collected. This deposit could be almost entirely vaporized when warmed to 20° under vacuum and was shown to consist principally of NSCl and less than 5% $S_3N_3Cl_3$. However in the presence of nitrogen or helium at 50°, only $S_3N_3Cl_3$ sublimed to the −196° cold finger. A sample of $S_3N_3Cl_3$ was sublimed through a 9-in. long, 22° inlet to a mass spectrometer (Consolidated Engineering Corp. Model 21-103C) ionization chamber at 200° using 70-eV electrons. Although the parent $S_3N_3Cl_3^+$ peak was not detected, an $S_3N_3^+$ peak 47% as high as the largest peak ($S_2N_2^+$) was found, indicating the probable presence of intact $S_3N_3Cl_3$ molecules in the vapor. The mass spectral data are presented in Table I. Presumably the $S_4N_4^+$ and $S_4N_2^+$ pdaks are due to intermolecular or ion–molecule reactions in the hot ionization chamber of the mass spectrometer.

Measurement of the Equilibrium $S_3N_3Cl_3(s) \rightleftharpoons 3NSCl(g)$.—The equilibrium pressure of NSCl(g) over $S_3N_3Cl_3(s)$ was deter-

---

[9] M. Villena-Blanco and W. L. Jolly, *Inorg. Syn.*, **9**, 98 (1967).

[10] W. L. Jolly and K. D. Maguire, *ibid.*, **9**, 102 (1967).

[11] H. Schröder and O. Glemser, *Z. Anorg. Allgem. Chem.*, **298**, 78 (1959).

[12] O. Glemser and H. Richert, *ibid.*, **307**, 313 (1961).

[13] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963.

TABLE I

MASS SPECTRAL DATA FOR $S_3N_3Cl_3$

Species	Rel abund	Species	Rel abund	Species	Rel abund
$S_4N_4^+$	1	$NSCl^+$	9	Cl^+	46
$S_4N_2^+$	86	NS_2^+	7	S^+, O_2^+	79
$S_3N_3^+$	47	SCl^+	2	N_2^+	88
$S_3N_2^+$	5	N_2Cl^+	9	Cl^{2+}	5
$SNCl_2^+$	22	S_2^+	6	H_2O^+	57
S_3N^+	7			OH^+	14
S_2Cl^+	3	NS^+	98	O^+	15
$S_2N_2^+$	100	HCl^+	94		

mined at various temperatures in the glass spiral manometer apparatus. Runs were started by glassblowing onto the manometer a break-seal-equipped tube of $S_3N_3Cl_3$ (which had been finely ground in a drybag and weighed), raising the thermostated bath into place while evacuating the manometer, recording the null point with both sides evacuated, and opening the $S_3N_3Cl_3$ into the sample chamber.

Small amounts of nitrogen gas were evolved in all the runs and were determined after each pressure equilibration by cooling the system to −196° and Toepler pumping the nitrogen. The following reactions are the conceivable sources of nitrogen

$$^2/_3S_3N_3Cl_3(s) \longrightarrow N_2(g) + S_2Cl_2(g)$$

$$^2/_3S_3N_3Cl_3(s) \longrightarrow N_2(g) + S(s) + SCl_2(g)$$

$$^4/_3S_3N_3Cl_3(s) \longrightarrow N_2(g) + S_3N_2Cl_2(s) + SCl_2(g)$$

In each of these reactions the total amount of evolved gas is twice the amount of evolved nitrogen. Therefore the observed pressures were corrected for volatile decomposition products by subtracting a pressure corresponding to twice the evolved nitrogen.[14]

In some runs, the $S_3N_3Cl_3$ was initially treated with chlorine and then briefly evacuated in order to eliminate the solid products of the above reactions. Chlorine reacts with these solid products as in

$$Cl_2(g) + S(s) \longrightarrow SCl_2(g)$$

$$3S_3N_2Cl_2(s) + 3Cl_2(g) \longrightarrow 2S_3N_3Cl_3(s) + 3SCl_2(g)$$

In some runs, known amounts of chlorine were added to the system and allowed to remain there during the measurements. Inasmuch as the reactions of chlorine involve no change in the amount of gaseous materials, the pressures in the latter runs were corrected for the presence of chlorine and its gaseous reaction products by subtracting a pressure corresponding to the initial added chlorine.

Pressure *vs.* time plots always gave sigmoidal curves; that is, the NSCl pressure at first rose very slowly, then rose rapidly, and finally asymptotically approached equilibrium. The duration of the induction period was unpredictable; however it was increased, and the initial rate of pressure rise was greatly reduced, by the addition of chlorine to the system. At each temperature setting the pressure was followed until no change in pressure was detected during several hours (this was the case at temperatures below 50°) or until a final, constant, low rate of pressure rise was established (this was the case at temperatures above 50°). The experimental data for eight different preparations of $S_3N_3Cl_3$ are given in Table II.

We are convinced that the tabulated P_{NSCl} values truly correspond to the pressures of NSCl vapor (as opposed to $S_3N_3Cl_3$ vapor) for two reasons. First, as will be shown in the next section, the measured vapor pressures of $S_3N_3Cl_3(g)$ in this temperature range are more than 4 orders of magnitude smaller than the P_{NSCl} values. Second, two molecular weight determinations were made by completely vaporizing weighed $S_3N_3Cl_3$ samples in the glass spiral manometer apparatus. The molecular weights found were 81.9 at 45° and 82.0 at 50°; the theoretical value for NSCl is 81.5.

TABLE II

RESULTS OF STATIC NSCl PRESSURE MEASUREMENTS

Temp, °C	P, mm	P_{N_2}, mm	ΣP_{N_2} (prev runs), mm	P_{Cl_2}, mm	P_{NSCl},[a] mm	P_{NSCl} (calcd),[b] mm
31.0	20.47	0.01	1.26		19.2	18.9
35.4	29.25	0.04	1.24		27.9	27.2
40.3	41.1	0.1	0.92		40.0	40.3
45.1	59.5	0.23	1.04		58.0	58.3
47.2	69.8	0.3			69.2	68.4
49.4	85.0	1.9			81.2	80.7
49.55	85.3	1.65			82.0	81.7
49.9	84.65	0.55			83.55	83.8
49.9	85.16	0.57	0.55		83.45	83.8
49.9	93.4	3.2		2.8	84.2	83.8
49.9	102.0	6.6		5.35	83.5	83.8
52.1	100.7	1.65			97.4	98.4
57.5	267.7	29.2		62.6	141.7	145.2
60.0	261.0	25.7		36.4	173.2	173.0
60.0	273.5	18.85		59.6	176.2	173.0

[a] $P_{NSCl} = P - 2P_{N_2} - \Sigma P_{N_2}$(prev runs) $- P_{Cl_2}$. [b] Equation 1.

Measurement of the Sublimation Pressure of $S_3N_3Cl_3$.—The equilibrium pressure of $S_3N_3Cl_3(g)$ over $S_3N_3Cl_3(s)$ was determined by a saturated gas flow method using a mixture of helium and chlorine as the carrier gas. The presence of about 10% chlorine was necessary in order to avoid significant decomposition of the $S_3N_3Cl_3$. The apparatus is diagrammed in Figure 2. A fixed flow of helium (adjusted with a pressure regulator and needle valve) passed through a large tube packed with Drierite and magnesium perchlorate followed by a liquid nitrogen trap to remove any water. The helium was then mixed with a stream of purified[15] chlorine (10.3–12.6% of the total flow) from a Matheson lecture bottle equipped with a needle valve. The gas mixture flowed through a tube which entered the constant-temperature bath, where it flowed through a coiled tube for temperature equilibration and then through a saturator tube packed with ~50 g of $S_3N_3Cl_3$. The bottom of the saturator tube had a Kel-F-waxed 24/40 joint for loading, and the top had a Delmar–Urry O-ring stopcock. The exit of this stopcock led underwater through a 12/5 ball joint (well clamped and sealed with Kel-F wax) to a tared trap in which the passing gases were cooled first to room temperature (~22°) and then to 0°. Both the trap entrance and a by-pass tube leading to the vacuum line between the saturator and the trap were fitted with Fischer–Porter 0–1-mm needle valves which were positioned under the bath liquid. After leaving the 22°–0° trap, the gas then passed through two −78° traps and a series of −196° traps before exiting to the hood.

The $S_3N_3Cl_3$ vapor in the gas stream was trapped out in the first trap (22°–0°); the completeness of this condensation is attested by the fact that no $S_3N_3Cl_3$ collected in the second trap when it was cooled to −22° during part of a run. The NSCl vapor was trapped out in the −78° traps; the completeness of this condensation is attested by the fact that no NSCl could be detected in the −196° traps after a run in which chlorine was omitted from the gas stream. In the regular runs, chlorine collected in the −196° traps. The amounts of NSCl collected corresponded to partial pressures of NSCl far below the 0° equilibrium vapor pressure extrapolated from the data of Table II. Therefore no NSCl could condense out in the first trap, and the contents of the trap corresponded only to the $S_3N_3Cl_3$ of the vapor stream. The helium flow rate was measured with a soap film flowmeter. The chlorine flow rate was determined from the change in weight of the lecture bottle; its approximate magnitude was estimated from the rate of bubbling through a calibrated sulfuric acid bubbler. The flow through the saturator by-passed the traps for at least 6 hr after heating the bath to temperature to purge the saturator and to stabilize the system.

---

(14) When decomposition products from previous runs were present, these were also accounted for.

(15) Chlorine was freed of water by several rapid vacuum-line fractionations through a −112° trap (keeping the condensate) followed by slowly pumping the chlorine from a bulb at −78° (discarding the last 10% of the liquid).

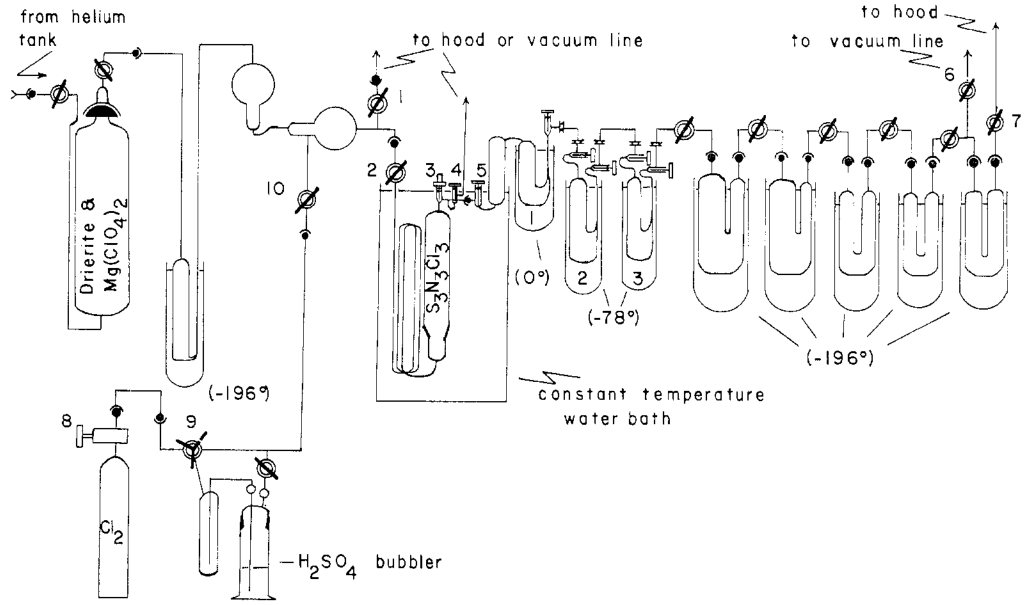


Figure 2.—Saturated gas flow apparatus used to determine equilibrium $S_3N_3Cl_3$ pressures.

The evacuated trap system with all baths in place was filled backward to 1 atm with helium from another tank, and the actual run was begun by closing stopcock 4 and opening stopcock 5. Periodically the cold baths were replenished. The constancy of the chlorine flow was occasionally checked by briefly switching in the sulfuric acid bubbler; the helium flow was checked by closing the drying tube and momentarily passing the helium through the flowmeter. The back-pressure in the line (always ≤ 1 mm) was checked by opening stopcock 1 to a U tube of mercury, and the atmospheric pressure was measured.[16] At the end of each run, traps 1–3 were weighed, after evacuation (traps 2 and 3 took as much as 8 hr pumping at $-78°$ to remove condensed chlorine), to determine the weights of $S_3N_3Cl_3$ and NSCl collected.

The gas volumes of chlorine, $S_3N_3Cl_3$, and NSCl were calculated at STP by assuming them to be perfect gases. The helium flow rate was also converted to STP and added to the chlorine flow rate to obtain the total flow rate. Assuming saturation of the gas with $S_3N_3Cl_3$, we calculated the sublimation pressure of $S_3N_3Cl_3$ using the formula

$$P_{S_3N_3Cl_3}(\text{mm}) = \frac{(\text{pressure of He} + Cl_2)}{(\text{volume of He} + Cl_2)}(\text{volume of } S_3N_3Cl_3)$$

The average pressure of NSCl was calculated similarly. The data for 11 runs are given in chronological order in Table III.

Table III

Results of Gas-Flow Saturation Experiments

Temp, °C	Flow rate, ml/min (STP)	% Cl_2	Time, min	$10^3P_{S_3N_3Cl_3}$, mm		Amt of NSCl, mg
				Obsd	Calcd[c]	
45.0[a]	104.7	12.6	5739	3.69[b]	3.65	26
45.0	132.4	11.5	6365	3.29		30
45.0[a]	172.3	10.3	5010	2.52		34
45.0	59.0	11.5	14243	3.46		294
40.0	100.2	10.4	9306	1.97[b]	1.97	58
35.0	101.4	10.6	18940	1.05[b]	1.05	27
45.0	100.4	10.3	7040	3.44[b]	3.65	111
50.0[a]	101.0	10.6	3745	5.58		70
55.0	100.9	11.6	2775	8.01		332
50.0[a]	146.1	11.7	2605	6.67[b]	6.62	60
50.0	195.2	11.8	2277	6.50[b]	6.62	75

[a] Freshly recrystallized $S_3N_3Cl_3$ used. [b] These data were used in the thermodynamic treatment. [c] Equation 3.

The weights of $S_3N_3Cl_3$ collected in the first trap ranged from 29 to 42 mg; assuming an error of ±1 mg in these weights, we estimate that weighing errors contributed an uncertainty of about ±3% to the calculated vapor pressures of $S_3N_3Cl_3$. A much more serious source of uncertainty in the vapor pressures was the difficulty of completely saturating the gas with $S_3N_3Cl_3$ without having appreciable amounts of the $S_3N_3Cl_3$ depolymerize to NSCl before reaching the first cold trap. The previously described studies of the sublimation of $S_3N_3Cl_3$ showed that, when the compound is sublimed in the presence of a static inert gas so that the subliming molecules must spend an appreciable time in the vapor state, most of the molecules depolymerize to NSCl. Thus the experimental problem was the adjustment of the gas flow so that it was slow enough to ensure saturation with $S_3N_3Cl_3$ but fast enough to avoid appreciable depolymerization. The first four runs of Table III were performed at 45° with various flow rates in order to determine the effect of flow rate on calculated vapor pressure. A maximum pressure was found at a flow rate of approximately 100 ml/min; therefore the runs at 35 and 40° were also run at that flow rate. At 50°, however, flow rates of 146 and 195 ml/min gave considerably higher $S_3N_3Cl_3$ vapor pressures than a 101 ml/min flow rate, probably because of depolymerization at the lower flow rate. Consequently only the higher flow rate data for 50° were used. Undoubtedly the one 55° run had too low a flow rate; the $S_3N_3Cl_3$ in the saturator discolored, and an abnormally large amount of NSCl formed. Therefore the vapor pressure calculated for 55° was not used.

Thermodynamic Treatment of Data

Derivation of Thermodynamic Functions.—A plot of log P_{NSCl}(mm) *vs.* $1/T$, using the data of Table II, is given in Figure 3. The straight line through the points corresponds to the equation

$$\log P_{NSCl}(\text{mm}) = 12.321 - 3360/T \qquad (1)$$

From this equation we calculate $\Delta H° = 46.2 \pm 1.5$ kcal mol^{-1} and $\Delta S° = 129.6 \pm 4.8$ cal deg^{-1} mol^{-1} for the reaction

$$S_3N_3Cl_3(s) \longrightarrow 3NSCl(g) \qquad (2)$$

The indicated limits of error correspond to the deviation of the line in Figure 2 after applying uncertainties of ±0.2 mm in pressure and ±0.1 in temperature to the points.

A plot of log $P_{S_3N_3Cl_3}$(mm) *vs.* $1/T$, using the data

---

[16] Atmospheric pressure ranged from 753 to 765 mm.

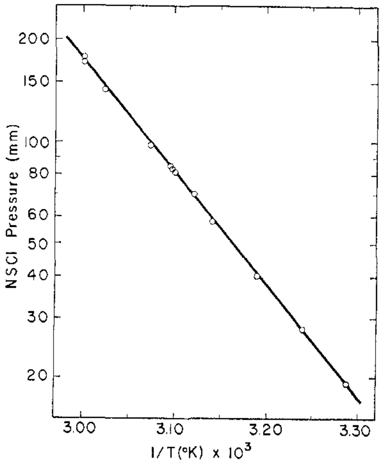


Figure 3.—Plot of log P_{NSCl}(mm) *vs.* $1/T$.

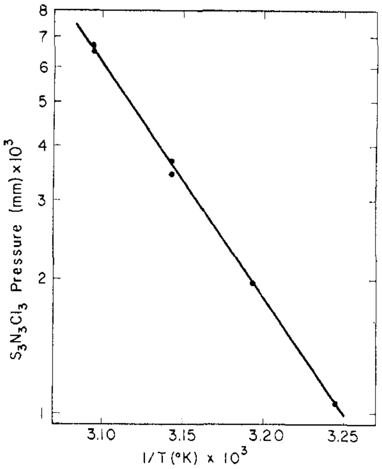


Figure 4.—Plot of log $P_{\mathrm{S_3N_3Cl_3}}$(mm) *vs.* $1/T$.

of Table III, is given in Figure 4. The straight line through the points corresponds to the equation

$$\log P_{\mathrm{S_3N_3Cl_3}}(\mathrm{mm}) = 14.270 - 5316/T \qquad (3)$$

From this equation we calculate $\Delta H^\circ = 24.3 \pm 1.5$ kcal mol^{-1} and $\Delta S^\circ = 52.1 \pm 4.6$ cal deg^{-} mol^{-1} for the reaction

$$\mathrm{S_3N_3Cl_3(s)} \longrightarrow \mathrm{S_3N_3Cl_3(g)} \qquad (4)$$

By combining these values with the corresponding values for reaction 2 we calculate $\Delta H^\circ = 21.9 \pm 3.0$ kcal mol^{-1} and $\Delta S^\circ = 77.5 \pm 9.4$ cal deg^{-1} mol^{-1} for the gaseous detrimerization reaction

$$\mathrm{S_3N_3Cl_3(g)} \longrightarrow \mathrm{3NSCl(g)} \qquad (5)$$

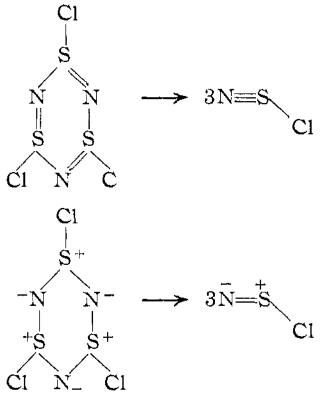
The absolute entropy of NSCl(g) has been calculated from spectroscopic data[8] to be 63.66 cal deg^{-1} mol^{-1}. By combining this datum with the above data, we caluclated, for the absolute entropies of $S_3N_3Cl_3$(s) and $S_3N_3Cl_3$(g), 61.4 and 113.5 cal deg^{-1} mol^{-1}, respectively.

Discussion of Thermodynamic Functions.—It is interesting to compare the thermodynamic functions with those for analogous processes of compounds having similar structure. For example, the structure of γ-SO_3 (a lattice of six-membered ring trimers)[17] is similar to that of $S_3N_3Cl_3$,[18] and the molecular weight of S_3O_9 is close to that of $S_3N_3Cl_3$. Thus it is not surprising that the value of ΔS° (122.1 cal deg^{-} mol^{-1})[19] for the process $S_3O_9(s) \rightarrow 3SO_3(g)$ is similar to that for reaction 2 (129.6 cal deg^{-1} mol^{-1}).

The entropy of sublimation of $S_3N_3Cl_3$ (52.1 cal deg^{-1} mol^{-1}) is remarkably large; its magnitude indicates the existence of many degrees of freedom in the gaseous $S_3N_3Cl_3$ molecule. Indeed this conclusion is consistent with the highly puckered S_3N_3 ring in the $S_3N_3Cl_3$ molecule.[18] For this process the trimer of phosphonitrilic chloride, $P_3N_3Cl_6$ ($\Delta S_{\mathrm{subl}}{}^\circ = 38.0$ cal deg^{-1} mol^{-1}), is a poor analog because of the stiffness of the planar P_3N_3 ring. However the tetramer $P_4N_4Cl_8$ ($\Delta S_{\mathrm{subl}}{}^\circ = 45.3$ cal deg^{-1} mol^{-1}) is a better analog because of its puckered P_4N_4 ring.

Many analogs of the gaseous detrimerization reaction (reaction 5) can be found. Values of ΔS° (in cal deg^{-1} mol^{-1}) for the following six-membered ring compounds are given: $B_3O_3H_3$, 81.0;[20] $B_3O_6H_3$, 88.8;[20] $B_3O_3Cl_3$, 78.8;[20] $B_3O_3F_3$,[20] 90.1; C_6H_6, 79.7;[21] C_9H_{12} (mesitylene), 85.8;[21] C_6H_{12}, 86.3;[21] C_6F_6, 89.3;[22] Be_3O_3, 76.3.[20] The value of 77.5 for $S_3N_3Cl_3$ falls in the 76–90 cal deg^{-1} mol^{-1} range of the above compounds.

The ΔS° value for the gaseous detrimerization reaction is more difficult to rationalize. The reaction may be represented with structural formulas in various ways, such as



Using a consistent bonding scheme, the formal N–S bond order is doubled in the reaction, and the number of N–S linkages is halved. On the basis that bond energy is proportional to bond order, we would expect $\Delta H^\circ = 0$ for the reaction—and indeed the observed value of ΔH° (21.9 kcal mol^{-1}) is rather small. It will be noted that, in the reaction, the number of σ bonds decreases and the number of π bonds increases. The finite ΔH° value is probably a consequence of the fact that, in general, σ bonds are stronger than π bonds.

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

---

(17) R. Westrich and C. H. MacGillavry, *Rec. Trav. Chim.*, **60**, 794 (1941).

(18) G. A. Wiegers and A. Vos, *Acta Cryst.*, **20**, 192 (1966).

(19) National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(20) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich.

(21) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Research Project 44, American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

(22) D. R. Douslin, H. L. Finke, W. D. Good, and D. W. Scott, Quarterly Technical Summary Report No. 20, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla., Dec 31, 1963.