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DER UNIVERSITAT GÖTTINGEN, GÖTTINGEN, GERMANY

Preparation of Substituted Fluorosulfonyl Isocyanides. XXVII[1]

BY HERBERT W. ROESKY, HORST H. GIERE, AND DANIEL P. BABB

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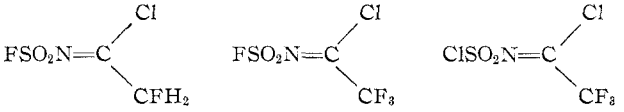
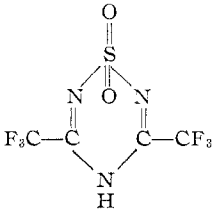
$FSO_2NHC(O)CFH_2$ was prepared by the reaction of FSO_2NCO with monofluoroacetic acid with evolution of carbon dioxide. A study of the reactions of $FSO_2NHC(O)CFH_2$ and $FSO_2NHC(O)CF_3$ with PCl_5 has resulted in the preparation and characterization of the compounds



The reaction of $FSO_2N{=}CClCF_3$ with ammonia and several amines led to compounds of the general formula $FSO_2N{=}CCF_3$ where X = NH_2, $N(CH_3)_2$, and $N(C_2H_5)_2$. Partial hydrolysis of $FSO_2N{=}CClCF_3$ gave $FSO_2NHC(O)CF_3$. The compounds have been isolated and their structures characterized by infrared, nmr, and mass spectrometry and elemental analyses.

Introduction

Recently the preparation of the heterocyclic compound[2]



was reported as resulting from the reaction of $ClSO_2N{=}PCl_3$ and trifluoroacetic acid. The purpose of this work was to examine some of the reactions of $FSO_2N{=}PCl_3$ and FSO_2NCO with fluorinated acetic acids in an attempt to prepare linear or cyclic fluorosulfonyl–nitrogen compounds. The resulting compounds, $FSO_2NHC(O)R$, were treated with phosphorus pentachloride to form additional members of the series $FSO_2N{=}CClR$[3-5] by elimination of HCl and $POCl_3$. Reaction of $FSO_2NHC(O)CF_3$ with PCl_5 produced $ClSO_2N{=}CClCF_3$, in addition to the FSO_2 compound. Compounds of the general formula $FSO_2N{=}CXCF_3$ where X = NH_2, $N(CH_3)_2$, and $N(C_2H_5)_2$ resulted from the reaction of $FSO_2N{=}CClCF_3$ with NH_3, $(CH_3)_2NH$, and $(C_2H_5)_2NH$. Hydrolysis of $FSO_2N{=}CClCF_3$ produced $FSO_2NHC(O)CF_3$.

Experimental Section

Reagents.—CF_3COOH, PCl_5, and the amines were obtained from Merck A.G. or Fluka A.G. These reagents were used without further purification. FSO_2NCO was prepared by the fluorination of $ClSO_2NCO$ with antimony trifluoride.[6] Monofluoroacetic acid, CFH_2COOH, was prepared by the reaction of $(FCH_2COO)_2Ba$ with sulfuric acid.[7]

General Methods.—All reactions were carried out in Pyrex flasks under an atmosphere of nitrogen. Prior to use the nitrogen was dried over a column of P_4O_{10}. Because the compounds could be extremely toxic, all operations were performed in a well-ventilated hood. Infrared spectra (Table I) were recorded using a Leitz infrared spectrophotometer. The spectra of liquids were obtained in the liquid phase as capillary films with potassium bromide windows and as gases in a gas cell of 10-cm length.

Nuclear magnetic resonance spectra (Table II) were recorded using a Varian A-56/60 spectrometer. Tetramethylsilane and trichlorofluoromethane were used as external standards.

Elemental analyses (Table III) were performed by Beller Microanalytical Laboratory, Göttingen, Germany. Boiling points of liquids are given in Table III.

Mass spectra were obtained using an Atlas UFCH 4 spectrometer and the spectrum of $FSO_2N{=}CClCF_3$ is given in Table IV.

Preparation of Monofluoroacetylfluorosulfonylimide, $FSO_2NHCOCFH_2$.—The reaction was carried out in a one-neck 500-ml flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen T adapter. A 125.0-g sample (1.0 mol) of FSO_2NCO and 78.0 g (1.0 mol) of FCH_2COOH were heated to 80° and maintained at that temperature for about 5 hr. After cooling to room temperature crystals of $FSO_2NHC(O)CH_2F$ were formed. This compound was not characterized in detail.

Preparation of N-Fluorosulfonylfluoromethylcarbimide Chloride, $FSO_2N{=}CClCH_2F$.—In a two-neck flask equipped with a mechanical stirrer and a reflux condenser with a drying tube were placed 600 ml of CCl_4, 159.0 g (1.0 mol) of $FSO_2NHC(O)CH_2F$, and 208.0 g (1.0 mol) of PCl_5. The mixture was heated for 1 hr at 80°. The resulting $POCl_3$ and CCl_4 were removed by means of a water pump vacuum and the residue was distilled under vacuum; yield, 91.0 g (51%) (0.51 mol).

Preparation of Trifluoroacetylfluorosulfonylimide.—$FSO_2NHCOCF_3$ was first prepared by Heinze.[8] A sample of 234.5 g (1.0 mol) of $FSO_2N{=}PCl_3$ and 114.0 g (1.0 mol) of CF_3COOH was heated for 60 hr at 90–100° in a flask equipped with a reflux condenser topped with a drying tube. The $POCl_3$ formed in the reaction was removed under water pump vacuum (10–12 mm) and the product purified by distillation under high vacuum (0.01 mm); yield, 156 g (80%) (0.8 mol).

Preparation of N-Fluorosulfonyltrifluoromethylcarbimide Chloride, $FSO_2N{=}CClCF_3$.—The reaction was carried out in a 500-ml three-neck flask equipped with a distillation head, a dropping funnel, and a mechanical stirrer. To 206 g (1.0 mol) of PCl_5 was added 195 g (1.0 mol) of $FSO_2NHC(O)CF_3$, and the mixture

(1) Paper XXVI: H. W. Roesky and D. P. Babb, *Inorg. Nucl. Chem., Letters*, in press.
(2) H. W. Roesky, *Angew. Chem.*, **81**, 493 (1969).
(3) H. W. Roesky, *ibid.*, **81**, 119 (1969).
(4) H. W. Roesky and H. H. Giere, *Chem. Ber.*, **102**, 3707 (1969).
(5) H. W. Roesky and S. Tutkunkardes, *Z. Anorg. Allgem. Chem.*, in press.
(6) H. W. Roesky and A. Hoff, *Chem. Ber.*, **101**, 162 (1968).
(7) M. Hudlicky, "Chemie der organischen Fluorverbindungen," VEB Verlag der Wissenschaften, Berlin, 1960, p 124.
(8) P. R. Heinze, Dissertation, Göttingen, 1968.

TABLE I

INFRARED SPECTRA (CM^{-1})

$FSO_2N{=}CClCH_2F$	FSO_2NH-$COCF_3$	$FSO_2N{=}CClCF_3$	$ClSO_2N{=}CClCF_3$
~2940 m	~3330 s	1670 s	1650 s
1660 vs	~2950 m	1468 vs	1411 vs
1430 vs	1840 s	1285 s	1280 s
1218 vs	1800 vs	1229 vs	1235 vs
1137 m	1502 s	1198 vs	1183 vs
1119 m	1445 m	973 vs	970 s
1031 vs	1297 vs	862 vs	803 s
889 vs	1235 vs	810 m	714 s
825 vs	1180 vs	722 w	649 w
673 s	1098 vs	649 w	585 m
613 m	907 s	584 m	549 w
573 m	872 s	542 w	510 m
506 w	813 s		
465 m	763 s		

$FSO_2N{=}CCF_3NH_2$	$FSO_2N{=}CCF_3N(CH_3)_2$	$FSO_2N{=}CCF_3N(C_2H_5)_2$
~3390 s	~2920	~2980 w
~3260 m	1620 vs	1612 vs
1663 s	1518 m	1519 m
1596 m	1469 w	1490 m
1382 s	1426 m	1463 m
1198 vs	1410 m	1431 m
1123 w	1369 vs	1396 m
865 s	1278 s	1372 s
811 vs	1250 s	1350 m
754 w	1197 vs	1322 w
712 m	1170 vs	1311 w
604 s	1142 s	1219 vs
565 vs	1062 w	1165 vs
554 m	947 s	1075 m
	879 vs	966 vs
	783 s	930 s
	753 m	850 vs
	721 w	785 vs
	630 vs	750 m
	560 w	726 w
	521 m	626 s
	513 w	606 s
		563 m
		535 m
		517 w
		505 w

TABLE II

^1H AND ^{19}F NMR SPECTRA

Compound	Chem shift, ppm: FSO_2	CF	C–H	NH
$FSO_2N{=}CClCH_2F$	−54.5	211.8[a]	−5.14[b]	...
$FSO_2NHCOCF_3$	−53.8	77.0	...	−10.2
$FSO_2N{=}CClCF_3$	−55.2	73.7	...	...
$ClSO_2N{=}CClCF_3$	...	71.5	...	...
$FSO_2N{=}CCF_3NH_2$	−51.6	76.6	...	−8.34
$FSO_2N{=}CCF_3N(C_2H_5)_2$	−57.5[c]	62.6[d]	−1.24[e]	...
$FSO_2N{=}CCF_3N(CH_3)_2$	−57.0[f]	63.6[g]	−3.25[h]	...

[a] J_{F-H} = 45.7 cps, triplet. [b] J_{F-H} = 45.7 cps, doublet. [c] J_{F-F} = 8.5 cps, quartet. [d] J_{F-F} = 8.5 cps, doublet. [e] J_{H-H} 7.5 cps, triplet; δ_{CH_2} = 3.60 ppm, quartet. [f] J_{F-F} = 7.7 cps, quartet. [g] J_{F-F} = 7.7 cps and J_{F-H} = 1.5 cps, two septets. [h] J_{F-H} = 1.5 cps, quartet.

was maintained at 80°. As the product was formed, it was distilled into a receiving flask by means of the distillation head. Purification was accomplished by redistilling the crude product through a 25-cm Rasching column. The quantity of $ClSO_2N{=}CClCF_3$ formed, which remained in the reaction flask, was not measured; yield, 93 g (43%) (0.43 mol).

Preparation of N-Chlorosulfonyltrifluoromethylcarbimide Chloride, $ClSO_2N{=}CClCF_3$.—In a one-neck flask equipped with a reflux condenser a mixture of 136 g (0.69 mol) of $FSO_2NHC(O)CF_3$ and 143 g (0.69 mol) of PCl_5 was heated for 5 hr at about 80°. After allowing the mixture to cool to room temperature, the oil pump volatile products were collected in a trap cooled with liquid nitrogen. Distillation under normal pressure yielded 35 g (0.157 mol) (22%) of $ClSO_2NCClCF_3$. The quantity of $FSO_2N{=}CClCF_3$ formed in this reaction was not measured.

Reactions of $FSO_2N{=}CClCF_3$. (a) **With $POCl_3$.**—A sample of 15 g (0.07 mol) of $FSO_2NCClCF_3$ and 2.55 g (0.017 mol) of $POCl_3$ was refluxed for 2 hr. No volatile products were isolated. $FSO_2NCClCF_3$ was recovered unchanged from the flask.

(b) **With PCl_5.**—A sample of 15 g (0.07 mol) of $FSO_2NCClCF_3$ and 2.9 g (0.014 mol) of PCl_5 was heated to 60° for 4 hr. PF_5 and POF_3 were determined by ir analysis to be in the volatile products. From the liquid residue $ClSO_2NCClCF_3$ was recovered by distillation; yield, 11.0 g (0.05 mol) (68%). The ir spectrum and boiling point were identical with those of an original sample.

Preparation of N-Fluorosulfonyltrifluoromethylcarbimide Amide, $FSO_2N{=}CCF_3NH_2$.—The reaction was carried out in a three-neck, 1-l. flask equipped with a Dry Ice condenser maintained at −80°, a stirring motor, and a nitrogen T adapter. To 55.9 g (0.26 mol) of $FSO_2N{=}CClCF_3$ dissolved in 800 ml of dry ethyl ether was added 8.9 g (0.52 mol) of ammonia over a period of 20 min through the Dry Ice condenser. The flask was maintained at about −80°. After the addition was complete, the flask was slowly warmed to room temperature. The solid was removed by filtration under dry nitrogen. The solvent of the resulting solution was removed by means of a water pump vacuum and the residue was sublimed under oil pump vacuum at 65° and 0.01 Torr; yield, 10.5 g (0.054 mol) (20.6%).

TABLE III

ELEMENTAL ANALYSES

Compound	% C Calcd	% C Found	% F Calcd	% F Found	% N Calcd	% N Found	% H Calcd	% H Found	% S Calcd	% S Found	% Cl Calcd	% Cl Found	Bp,° C (mm) [mp, °C]
$FSO_2N{=}CClCH_2F$	13.53	13.8	21.40	21.0	7.90	7.7	1.13	1.2	18.03	18.1	20.01	20.2	61.5 (12)
$FSO_2NHCOCF_3$	12.31	12.2	39.00	39.0	7.20	7.1	...	...	16.42	16.2	...	...	38 (0.01)
$FSO_2N{=}CClCF_3$	11.25	11.2	35.61	35.2	6.57	6.5	...	...	15.00	14.8	16.61	16.5	42 (760)
$ClSO_2N{=}CClCF_3$	10.45	10.5	25.02	25.2	6.02	6.1	...	...	13.90	13.9	30.80	30.5	111 (760)
$FSO_2N{=}CCF_3NH_2$	12.40	12.4	39.10	38.7	14.43	14.3	1.03	1.1	16.52	16.8	...	...	[66–67]
$FSO_2N{=}CCF_3N(CH_3)_2$	21.62	21.8	34.20	33.9	12.61	12.7	2.72	2.9	14.41	14.5	...	...	[73]
$FSO_2N{=}CCF_3N(C_2H_5)_2$	28.80	28.8	30.35	29.9	11.20	11.3	4.04	3.9	12.80	12.8	...	...	[75] 107 (0.01)

Preparation of N-Fluorosulfonyltrifluoromethylcarbimide Dimethylamide, $FSO_2N{=}CCF_3N(CH_3)_2$.—To a mixture of 42 g (0.20 mol) of $FSO_2N{=}CClCF_3$ and 800 ml of dry ethyl ether in a flask cooled to −60° was added 18.1 g (0.39 mol) of $HN(CH_3)_2$ in a method analogous to that described above. The product was purified by recrystallization from ether; yield, 23.2 g (0.104 mol) (53%).

Preparation of N-Fluorosulfonyltrifluoromethylcarbimide Diethylamide, $FSO_2N{=}CCF_3N(C_2H_5)_2$.—A 50.0-g (0.24-mol) sample of $FSO_2N{=}CClCF_3$ and 700 ml of dry ethyl ether were

TABLE IV
MASS SPECTRUM OF $FSO_2N{=}CClCF_3$

m/e	Rel intens	Species
31	5.95	CF
32	2.16	S
35	2.16	Cl
37	0.54	
48	11.35	SO
50	5.95	CF_2
51	2.70	SF
61	2.16	
63	0.81	NCCl
64	11.35	SO_2
67	39.46	SOF
69	79.46	CF_3
76	23.24	$NCCF_2$
83	100.00	SO_2F
85	42.16	
87	8.11	CF_2Cl?
144	83.24	FSO_2NCCl
146	72.97	$FSNCCF_3$
178	51.89	FSO_2NCCF_3
194	1.62	
196	0.54	$SO_2NCClCF_3$
213	8.11	
215	2.70	$FSO_2NCClCF_3$

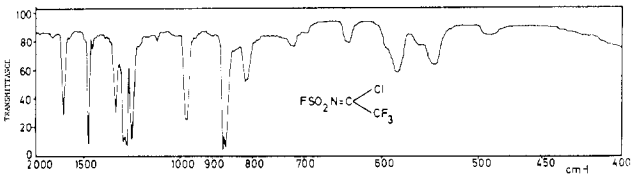


Figure 1.—The infrared spectrum for $FSO_2NCClCF_3$.

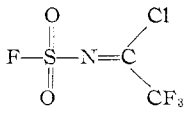
placed in a flask cooled to −70°. $HN(C_2H_5)_2$ (34.3 g, 0.47 mol) was added using a dropping funnel. The addition was carried out over a period of 1 hr. The compound was purified by distillation; yield, 18.2 g (0.073 mol) (31%).

Hydrolysis of $FSO_2NCClCF_3$.—A 15-g (0.07-mol) sample of $FSO_2NCClCF_3$ was allowed to stand in open air for 1 day and was then distilled in oil pump vacuum; yield, 7.8 g (0.04 mol) (57%) of $FSO_2NHC(O)CF_3$. The ir spectrum and boiling point were identical with those of an original sample.

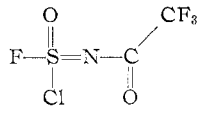
Results and Discussion

The reaction of FSO_2NCO with CF_3COOH does not occur even after refluxing the products for several days. The corresponding reaction with CH_2FCOOH led to the desired product, $FSO_2NHC(O)CH_2F$, in high yield. This reaction is dependent on the pK value of the acid. To prepare $FSO_2NHC(O)CF_3$ we used as a starting material $FSO_2N{=}PCl_3$, because the direction of the reaction is favored by the formation of $POCl_3$.

The reaction of $FSO_2NHC(O)CF_3$ or $FSO_2NHC(O)CFH_2$ with phosphorus pentachloride produced only one of the two possible isomers which, for the CF_3 compound, could be either structure I or II.



I

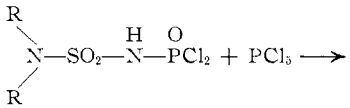


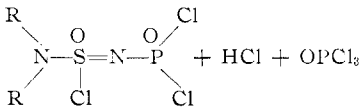
II

An unambiguous structural assignment could be made by mass spectrometric and infrared investigation. The molecule ion peak was present at *m/e* 213 with a peak at *m/e* 215 consistent with one chlorine in the molecule. The largest peak was that for SO_2F^+ with the second largest at *m/e* 144 assigned to FSO_2NCCl^+. As can be seen from Table IV there are no ions at *m/e* 28 or 97 which should be present, as CO^+ or $OCCF_3^+$ if isomer II is present. The infrared spectrum for this compound shows no C=O stretch.

The ir spectrum for $FSO_2NHC(O)CF_3$ shows a strong absorption at 1800 cm^{-1} in the liquid phase which is assigned to the C=O stretch. In the case of $FSO_2NCClCF_3$ we found an absorption at 1670 cm^{-1} in the gas phase which is assigned to the C=N stretching frequency (Figure 1). This assignment is consistent with other C=N compounds, *e.g.*, $FSO_2N{=}CClCH_3$.[4,9,10] The $\nu_{as}(SO_2)$ is tentatively assigned at 1467 cm^{-1} and the ν(SF) at 862 cm^{-1}. The ν_{as} (SO_2) is in agreement with bands of other fluorosulfonyl compounds.[11] In $ClSO_2N{=}CClCF_3$ the band at 862 cm^{-1} disappeared, whereas in $FSO_2N{=}CClCF_3$ it is one of the strongest bands. The ν(SO) and ν(CF) are in the same region between 1200 and 1300 cm^{-1}. An unambiguous assignment is therefore not possible.

When the fluorine atom on the fluorosulfonyl group is replaced by a dialkylamine group the reactions take the course[12]

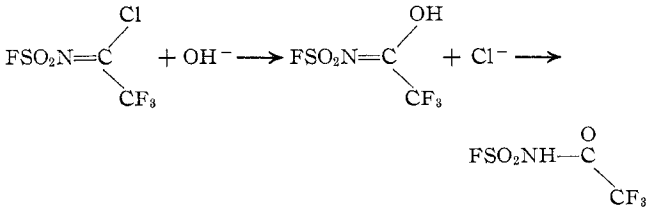




Whether isomer I or II is formed probably depends mainly on the nature of the substituents at the sulfur atom. Substituents with an inductive effect form isomers of type I.[3-5]

The reaction of $FSO_2NHCOCF_3$ with PCl_5 also produces $ClSO_2N{=}CClCF_3$. That the chlorine for fluorine substitution is due to the reaction of $FSO_2N{=}CClCF_3$ with PCl_5 and not with $POCl_3$ was shown by separate experiments. Even after prolonged heating $FSO_2N{=}CClCF_3$ did not react with $POCl_3$. Selective substitution of the chlorine atom in $FSO_2NCClCF_3$ by another group takes place in ether at low temperatures. The C–Cl bond is very reactive and is easily cleaved by nucleophilic reagents. No attack of the S–F bond was observed under these conditions. In the presence of water $FSO_2N{=}CClCF_3$ is rapidly hydrolyzed yielding the compound $FSO_2NHC(O)CF_3$ which was identified by ir spectroscopy. The initial attack is probably on the chlorine atom with subsequent rearrangement to $FSO_2NHC(O)CF_3$.

(9) E. Kühle, *Angew. Chem.*, **79**, 663 (1967).
(10) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen & Co. Ltd., London, 1968.
(11) H. W. Roesky and A. Hoff, *Chem. Ber.*, **101**, 162 (1968).
(12) H. W. Roesky, *Inorg. Nucl. Chem. Letters*, in press.



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).

(13) H. W. Roesky, *Angew. Chem.*, **79**, 724 (1967).
(14) H. W. Roesky and D. P. Babb, *ibid.*, **81**, 494 (1969).

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).

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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

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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 $\log P_{NSCl}(mm) = 12.321 - 3360/T$. 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 $\log P_{S_3N_3Cl_3}(mm) = 14.270 - 5316/T$. 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.

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