Table III. Mass Spectrum of CF_3OCClO

m/e	Ion	Rel intensity	m/e	Ion	Rel intensity
12	C^+	1.7	50	CF_2^+	2.7
16	O^+	1.4	63	$CO_2{}^{35}Cl^+$	31.6
19	F^+	0.4	65	$CO_2{}^{37}Cl^+$	10.3
28	CO^+	10.7	69	CF_3^+	100.0
31	CF^+	3.0	85	CF_3O^+	0.23
35	$^{35}Cl^+$	8.8	113	$CF_3CO_2^+$	4.2
37	$^{37}Cl^+$	2.7	148	$CF_3CO_2{}^{35}Cl^+$	0.16
44	CO_2^+	2.5	150	$CF_3CO_2{}^{37}Cl^+$	0.05
47	COF^+	1.9			

perature for days, and easily handled in Pyrex or metal equipment without decomposition.

$$CF_3CF_2OCl \longrightarrow CF_3CF_2O + Cl\cdot$$
$$CF_3CF_2O\cdot \longrightarrow CF_3CFO + F\cdot$$
$$CF_3CF_2O\cdot \longrightarrow COF_2 + CF_3\cdot$$
$$CF_3\cdot + Cl\cdot \longrightarrow CF_3Cl$$

Chloroxypentafluoroethane decomposes readily with either thermal or photolytic initiation. Both conditions give products which are readily accounted for in terms of the intermediacy of the C_2F_5O radical. The thermal decomposition gives predominantly CF_3CFO, ClF, and Cl_2, the latter arising, in part perhaps, through reaction of ClF with the metal walls. Decomposition in this manner is essentially a reversal of the synthetic reaction. Photodecomposition yields COF_2 and CF_3Cl almost exclusively, presumably because of the pronounced instability of the C_2F_5O radical under such conditions. Analogous products (CF_4 and COF_2) are obtained from C_2F_5OF[1] by thermal or radical initiation of decomposition. The instability of the C_2F_5O radical is indicated also by the failure to form $C_2F_5ONF_2$ through reactions with N_2F_4. Irradiation of a mixture of C_2F_5OCl and N_2F_4 gave a mixture of COF_2, CF_3CFO, CF_3Cl, CF_3NF_2, and Cl_2 but no $-ONF_2$ species.

Gradual, but sometimes instantaneous, decomposition of $(CF_3)_2CFOCl$ occurs at room temperature and below. The products found were CF_3CFO, CF_3Cl, CF_3CF_3, and Cl_2; the products can be rationalized through radical fragmentation and recombination.

$$(CF_3)_2CFOCl \longrightarrow (CF_3)_2CFO\cdot + Cl\cdot$$
$$(CF_3)_2CFO\cdot \longrightarrow CF_3CFO + CF_3\cdot$$
$$CF_3\cdot + Cl\cdot \longrightarrow CF_3Cl$$
$$2CF_3\cdot \longrightarrow CF_3CF_3$$

Similarly, $(CF_3)_2CFOF$[1] and reducing agents gave CF_3CFO, CF_4, and $(CF_3)_2C{=}O$. When decomposition of the $(CF_3)_2CFOCl$ was gradual, minor amounts of $(CF_3)_2C{=}O$ were obtained along with CF_3CFO and CF_3Cl.

Acknowledgment. We are pleased to acknowledge support for this work by the Office of Naval Research, Power Branch. We also are indebted to Dr. D. Pilipovich for encouragement and helpful discussions, to Dr. J. S. Muirhead for determination of the ^{19}F nmr spectra, and to Mr. S. N. Cohz for obtaining the mass spectral patterns.

Chloroxysulfur Pentafluoride

C. J. Schack, R. D. Wilson, J. S. Muirhead, and S. N. Cohz

Contribution from Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California 91304. *Received November 16, 1968*

Abstract: The preparation, identification, and characterization of chloroxysulfur pentafluoride are reported. Reactions of SF_5OCl leading to SF_5OOSF_5, SF_5ONF_2, and the new compound SF_5OCClO are described.

The reaction of thionyl tetrafluoride or fluorocarbonyls with fluorine in the presence of alkali metal fluorides has been shown[1,2] to be an excellent method for the synthesis of the corresponding fluoroxy compounds, SF_5OF or R_fOF. The previous part of this work[3] reports a similar reaction of fluorocarbonyls with chlorine monofluoride in place of fluorine that results in the formation of chloroxyperfluoroalkanes. This paper describes an extension of the ClF addition reaction to thionyl tetrafluoride which resulted in the new compound, chloroxysulfur pentafluoride, SF_5OCl. Derivatives prepared from SF_5OCl include SF_5OOSF_5,[4] SF_5ONF_2,[5] and the previously unknown chloroformate, SF_5OCClO.

Experimental Section

Apparatus. Synthetic reactions were conducted in stainless steel cylinders, and the products were separated and purified using a stainless steel–Teflon vacuum line. Pressures were measured by means of a Heise, bourdon tube type, pressure gauge. Infrared spectra were taken on Perkin-Elmer Infracords 137 and 337 using 5-cm path length stainless steel or Kel-F cells fitted with AgCl windows. The ^{19}F nmr spectra were obtained at −40° using a Varian Associates high-resolution nmr spectrometer operating at 56.4 Mc. Samples were sealed in Pyrex tubes with $CFCl_3$ as the internal standard. Mass spectral data were obtained with a CEC 21-103 C mass spectrometer modified with a metal inlet system, CEC Part No. 285400.

---

[1] J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

[2] M. Lustig, A. R. Pitochelli, and J. K. Ruff, *J. Am. Chem. Soc.*, **89**, 2841 (1967).

[3] C. J. Schack and W. Maya, *ibid.*, **91**, 2902 (1969).

[4] C. I. Merrill and G. H. Cady, *ibid.*, **83**, 298 (1961).

[5] W. H. Hale, Jr., and S. M. Williamson, *Inorg. Chem.*, **4**, 1342 (1965).

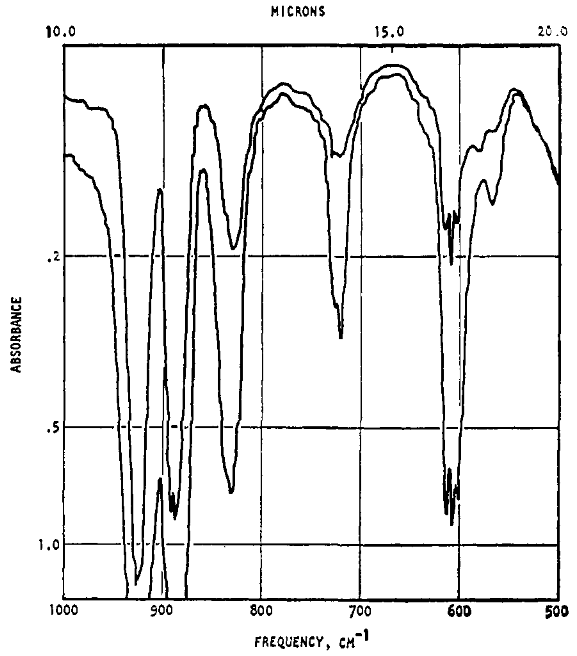


Figure 1. Infrared spectrum of SF_5OCl at 20 and 2.5. mm.

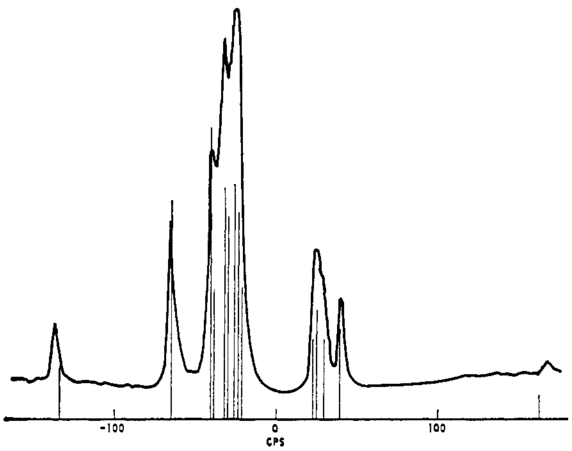


Figure 2. Nmr spectrum of SF_5OCl.

Materials. Chlorine monofluoride was prepared by heating an equimolar mixture of chlorine and fluorine to 150° for several hours in a stainless steel cylinder. Thionyl fluoride was made from thionyl chloride and NaF in acetonitrile[6] and was fluorinated to thionyl tetrafluoride using elemental fluorine.[1] Tetrafluorohydrazine (Air Products Co.) and carbon monoxide (Matheson Co.) were purchased. The alkali metal fluorides were fused and then powdered in a drybox prior to use. Gaseous reactants were purified by fractional condensations.

Preparation of SF_5OCl. In a typical reaction, CsF powder (3.32 g, 21.8 mmol) was loaded into a 30-ml prepassivated cylinder in the drybox. After evacuation, SOF_4 (413 cm^3, 18.4 mmol) and ClF (430 cm^3, 19.2 mmol) were separately condensed into the reactor at $-196°$. The cold bath was changed to $-78°$ and the reaction allowed to proceed overnight. Products of the reaction were separated by fractional condensation at -112 and $-196°$ as the cylinder was warmed to ambient temperature. The trap cooled at $-196°$ contained 37 cm^3 (1.65 mmol) which was identified by infrared examination as a mixture of unreacted ClF with minor quantities of SOF_4 and SF_6. The high-temperature fraction was pure, colorless SF_5OCl (402 cm^3, 17.9 mmol), 97% yield. Preparations of SF_5OCl generally were carried out using ClF in excess as its high volatility facilitated product separation. Some syntheses were conducted at approximately $-40°$ instead of $-78°$ with equally good results. The catalytic activity of KF was also examined, and it was found to be effective in forming SF_5OCl. In the absence of any added CsF or KF, no reaction between ClF and SOF_4 occurred at either $-78°$ or room temperature. Cesium fluoride promotes the formation of SF_5OCl more readily than KF. Thus a synthesis of SF_5OCl ($\sim$10 mmol scale) using CsF gave a 15% yield in 1 hr at $-78°$ whereas KF produced a 13% yield in 2 hr.

Properties of SF_5OCl. Chloroxysulfur pentafluoride is a clear, water-white liquid and is stable for very limited periods at room temperature in clean, dry, prepassivated stainless steel or perhalogenated plastic equipment. Storage at $-40°$ in stainless steel cylinders has resulted in only a few per cent decomposition over a 3-4 week period. This decomposition can be limited to a negligible amount by low-temperature storage in the presence of KF or CsF since the products of the decomposition are generally SOF_4 and ClF, *i.e.*, the starting materials. Cleanliness and passivation of equipment is as absolutely necessary in handling and transferring SF_5OCl as with chlorine fluorides. Even then, some loss of material may result due to its limited thermal stability.

Molecular Weight. The molecular weight of SF_5OCl as determined by gas density assuming ideal gas behavior was 177 (calculated 178.5).

Vapor Pressure and Boiling Point. The vapor pressures of SF_5OCl over the temperature range -65 to 0° are [given as T (°K), P (mm)]: 208.5, 16; 225.3, 52; 241.7, 128; 245.4, 155; 250.2, 186; 273.2, 520. The vapor pressure-temperature relationship is described by the equation $\log P_{\text{mm}} = 7.57604 - 1324.37/T(°\text{K})$. The normal boiling point calculated from the equation is 8.9°, with a heat of vaporization of 6.06 kcal/mole and a Trouton constant of 21.5.

Reactions of SF_5OCl. Photolysis. A sample of SF_5OCl (70.0 cm^3, 3.12 mmol) was condensed at $-196°$ into a Pyrex ampoule fitted with a stopcock (Halocarbon grease). The ampoule was warmed to room temperature and irradiated for 3 hr (Hanovia 100-W utility lamp, Catalog No. 30620). Products of the photolysis were separated by several fractional condensations in traps cooled to -95 and $-196°$. Identification of the products was made from infrared spectra and mass spectra. The $-196°$ trap contained 62.2 cm^3 (2.78 mmol) of a mixture consisting of 34 cm^3 of Cl_2, 22 cm^3 of SOF_4, 5 cm^3 of SiF_4, and a small amount of SO_2F_2. No unreacted SF_5OCl was observed. The high-temperature fraction (23.0 cm^3, 1.03 mmol) was nearly pure SF_5OOSF_5,[4] contaminated with approximately 3% SF_5OSF_5,[7] corresponding to a peroxide yield of 65%. The mass cracking pattern found for SF_5OOSF_5 agreed with the qualitative pattern reported earlier.[4] The principal ions observed (greater than 2% relative intensity) were (given as ion, relative intensity): SF_5^+, 100; SF_3OO^+, 2.6; SF_4^+, 2.4; SF_3O^+, 92.0; SF_2OO^+, 2.0; SF_3^+, 27.0; SF_2O^+, 19.2; $SFOO^+$, 3.2; SF_2^+, 12.0; SFO^+, 20.0; SF^+, 3.0; SO^+, 3.5; S^+, 7.8; O^+, 2.2.

Reaction with N_2F_4. A sample of SF_5OCl (105 cm^3, 4.69 mmol), was condensed into a 250-ml Pyrex ampoule at $-196°$ together with N_2F_4 (47.3 cm^3, 2.11 mmol). After warming to room temperature the ampoule was irradiated for 35 min and recooled to $-196°$. Subsequent fractionations through traps cooled to -112 and $-196°$ gave SF_5ONF_2 (14.0 cm^3, 0.62 mmol) in the high-temperature trap. Identification of the SF_5ONF_2 was based on its infrared spectrum[5] and vapor density. The low-temperature trap contained a mixture (181 cm^3, 8.08 mmol), composed mostly of SOF_4 and Cl_2 with lesser amounts of N_2F_4 and FNO. No SiF_4 was detected but a small amount of white solid remained in the reactor which was probably $(NO_x)_2SiF_6$[5] and which on standing evolved some NO_2. The yield of SF_5ONF_2 was 14%.

Reaction with CO. Chloroxysulfur pentafluoride (127 cm^3, 5.67 mmol) was condensed into a 500-ml Pyrex ampoule at 196° followed by approximately 150 cm^2 of CO (measured by pressure difference). As the ampoule was warming to ambient temperature, it was irradiated for 25 min. Unreacted CO was pumped out of the ampoule after cooling to $-196°$, and the contents were vacuum fractionated through traps cooled to -95 and $-196°$. The latter fraction (20.8 cm^3, 0.93 mmol) was a mixture of SOF_4, $COFCl$,[8] and a trace of SO_2F_2 as indicated by an infrared spectrum. The

---

[6] F. A. Fawcett, C. W. Tullock, and D. D. Coffmann, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

[7] H. L. Roberts, *J. Chem. Soc.*, 2774 (1960).

[8] A. H. Nielsen, T. G. Burke, P. J. Woltz, and E. A. Jones, *J. Chem. Phys.*, **20**, 596 (1952).

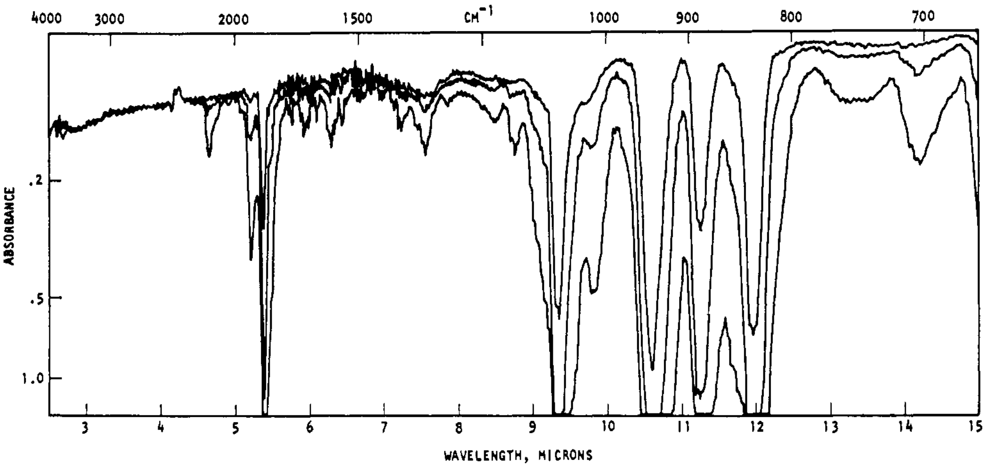


Figure 3. Infrared spectrum of SF_5OCClO at 40, 9, and 2.3 mm.

−95° fraction was pure SF_5OCClO (117 cm^3, 5.22 mmol), a 92% yield.

Properties of SF_5OCClO. Pentafluorosulfur chloroformate is a water-clear liquid and a colorless gas. It is stable at room temperature in glass, stainless steel, or Kel-F apparatus.

Molecular Weight. The molecular weight of SF_5OCClO as determined by vapor density assuming ideal gas behavior was 202 (calculated 206.5).

Vapor Pressure and Boiling Point. The vapor pressures of SF_5OCClO over the temperature range −64 to 23° are [given as T(°K), P(mm)]: 209.0, 3; 226.8, 12; 251.0, 54; 273.2, 128; 296.8, 319. The vapor pressure-temperature relationship is described by the equation $\log P_{mm} = 7.33542 - 1423.85/T(°K)$. The normal boiling point calculated from the equation is 46.4°, with a heat of vaporization of 6.51 kcal/mole and a Trouton constant of 20.4.

Discussion

Synthesis of the new compound, chloroxysulfur pentafluoride, has been accomplished by means of the alkali metal fluoride catalyzed addition of ClF to SOF_4 at −40 to −78°. Evidence obtained from material balances in the synthetic reactions, molecular weight data, derivative formation, and decomposition products supports the assigned composition. Confirmation of the structure of the compound was obtained from infrared, ^{19}F nmr, and mass spectra.

$$SOF_4 + ClF \xrightarrow{MF} SF_5OCl$$

$$M = K, Cs$$

The infrared spectrum of SF_5OCl is shown in Figure 1. Assignments of S–F vibrations in many SF_5X compounds[4,5,9–11] make it possible to assign similar absorptions in SF_5OCl. Thus the intense bands found at 925 and 888 cm^{-1} are assigned, respectively, to the planar SF_4 stretching vibration and the axial S–F stretching vibration. The band at 604 cm^{-1} is assigned to the symmetrical out-of-plane SF_4 square deformation. Less intense absorptions at 830 and 720 cm^{-1} may be due to asymmetric and symmetric stretching vibrations of the Cl–O–S group. It cannot be ruled out that the 720-cm^{-1} band is simply the Cl–O stretching vibration, but this seems unlikely since this absorption appears at higher frequencies (780–750 cm^{-1})[3] in R_fOCl compounds. In the same manner it appears that the 830-cm^{-1} band is probably not a simple S–O stretching vibration as such vibrations generally absorb at 780–790 cm^{-1} in comparable highly fluorinated sulfur oxides.[5]

The ^{19}F nmr spectrum of SF_5OCl is shown in Figure 2. The center of the SF_4 resonance is taken as the zero value on the scale. Because of pronounced second-order spin-spin interactions between the apical and four basal fluorine atoms of the SF_5 groups, the experimental ^{19}F nmr spectrum is complex. Analysis and assignment of the spectral features of this AB_4 system is best accomplished by the method of Merrill, Williamson, Cady, and Eggers.[12] The chemical shifts and coupling constants were obtained using a version of the computer program described by Ferguson and Marquardt.[13] The basal fluorine resonance occurs at −60 ppm relative to $CFCl_3$ with derived values of 156 Hz for the coupling constant and −2.44 ppm for the chemical shift of the apex fluorine relative to the basal fluorines. Figure 2 shows the experimental and calculated spectra using these parameters and supports the assignment of the spectra as an AB_4 compound. Zero on the scale is the center of the basal fluorine resonance pattern. The values of the chemical shifts and coupling constant are in good agreement with those reported[12] for other SF_5 groupings.

A mass fragmentation pattern of SF_5OCl was obtained and is given in Table I. Peaks for fragments containing other sulfur isotopes served to check the assignment of ^{32}S-containing ions. No parent peak

Table I. Mass Spectrum of SF_5OCl

m/e	Ion	Rel intensity	m/e	Ion	Rel intensity
127	SF_5^+	0.50	51	SF^+	3.02
124	SF_4O^+	0.35	51	ClO^+	0.49
105	SF_3O^+	100.00	48	SO^+	4.18
89	SF_3^+	8.48	37	Cl^+	1.05
86	SF_2O^+	23.50	35	Cl^+	0.35
70	SF_2^+	5.95	19	F^+	2.94
67	SFO^+	23.16	16	O^+	3.51

---

(9) L. H. Cross, H. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 945 (1960).

(10) L. H. Cross, G. Cushing, and H. L. Roberts, *Spectrochim. Acta*, **17**, 334 (1960).

(11) C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 909 (1963).

(12) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

(13) R. C. Ferguson and D. W. Marquardt, *J. Chem. Phys.*, **41**, 2087 (1964).

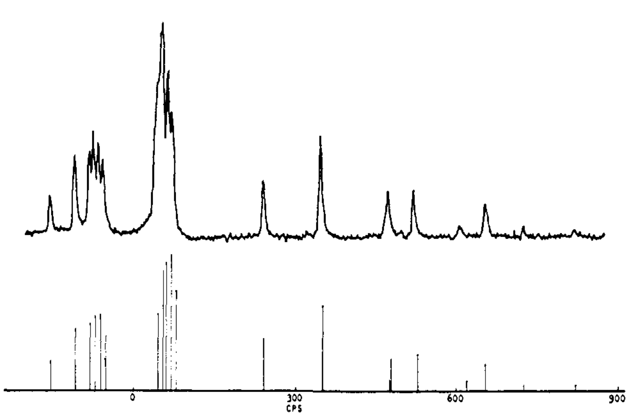


Figure 4. Nmr spectrum of SF_5OCClO.

was observed as is generally typical of pentafluorosulfur compounds.[4,14] The mass spectrum is compatible with the SF_5OCl formulation. Unlike most SF_5OX compounds, however, the SF_3O ion is the base peak and not the SF_5 ion. A similar observation has been reported[5] for the SF_5ONF_2 mass spectrum.

No chemical or physical evidence was found to indicate the presence of any isomeric species, such as $ClSF_4OF$, as a product of the synthetic reaction. The formation of SF_5OCl only, by this synthesis, indicates the ionic nature of the effective intermediate. This intermediate is presumed to be the SF_5OM complex.[1] The inherent polarization of ClF due to the high electronegativity of the fluorine atom results in a reaction with the above complex yielding only one product, SF_5OCl. In addition, the SOF_4–ClF system was shown to be unreactive in the absence of any added alkali metal fluoride.

The stability of SF_5OCl at room temperature appears to be somewhat marginal. More often than not, samples underwent slow, continuous decomposition at room temperature. The products of this decomposition were always SOF_4 and ClF. Very careful passivation of all metal or Teflon parts of the container systems did serve to slow this process but did not always eliminate the decomposition.

Study of the chemistry of SF_5OCl has been limited to photochemical reactions. These reactions have been found to involve the SF_5O radical as would be expected from the reported[5,11] chemistry of other SF_5OX compounds. Photolysis of SF_5OCl yields products consistent with a twofold reaction path for the SF_5O radical. Primarily, the generated radical couples with

$$SF_5OCl \xrightarrow{h\nu} SF_5O\cdot + Cl\cdot$$

$$2SF_5O\cdot \longrightarrow SF_5OOSF_5$$

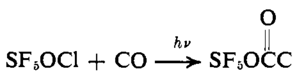
$$SF_5O\cdot \longrightarrow SOF_4 + F\cdot$$

itself to form the peroxide. A secondary process gives SOF_4. The yield of SF_5OOSF_5 (66%) is sufficiently high to make this process a good one for the synthesis of this compound.

Reactions of N_2F_4 and fluoroxy compounds have been shown to be an effective method of forming oxydifluoramines.[5,15] The perfluoromethyl derivative has also been readily prepared from CF_3OCl and N_2F_4.[3] Examination of the N_2F_4–SF_5OCl system showed that SF_5ONF_2 could be formed but in low yield only (14%). The principal products were SOF_4, Cl_2, FNO, and a white solid, probably $(NO_x)_2SiF_6$. Several unsuccessful reactions were conducted in an attempt to increase the yield of SF_5ONF_2. To a lesser degree similar undesired reactions were noted[5] in the original preparation of SF_5ONF_2 from SF_5OF and N_2F_4. Furthermore, a somewhat critical set of reactant pressures and irradiation conditions was necessary for the synthesis. These optimum conditions were not found for the SF_5OCl–N_2F_4 reaction.

$$SF_5OCl + 0.5N_2F_4 \xrightarrow{h\nu} SF_5ONF_2 + 0.5Cl_2$$

Insertion of carbon monoxide into the oxygen–halogen bond of perfluoromethylfluoroxy[16] or -chloroxy[3] compounds is a proven method of forming the respective fluoroformate or chloroformate. Chloroxysulfur pentafluoride and carbon monoxide were also observed to form the chloroformate derivative upon photolysis in very high yield (97%). This new compound was identified by its molecular weight and infrared, ^{19}F nmr, and mass spectra. The infrared spectrum of SF_5OCClO[17] is shown in Figure 3. Several features of the spectrum are noteworthy. Retention of the SF_5 group is indicated[9–11] by the two strong bands at 942 and 890 cm^{-1} attributable to the SF_4 square stretching and axial S–F stretching vibrations, respectively. These assignments are supported by the band found at 600 cm^{-1} arising from the symmetrical out-of-plane SF_4 square deformation. The presence of a carbonyl group in the compound is shown by the strong band at 1855 cm^{-1}, the region in which perfluoroacyl chlorides are known[18] to have a C=O stretching vibration. A comparable band in CF_3OCClO[3] is found at 1835 cm^{-1}. Assignment of the remaining strong bands, 1070 and 835 cm^{-1}, is not certain. They are probably due to C–O and S–O stretching vibrations which may be coupled due to the S–O–C link.



$$SF_5OCl + CO \xrightarrow{h\nu} SF_5O\overset{\overset{\displaystyle O}{\|}}{C}Cl$$

Pentafluorosulfur chloroformate also exhibits the complex ^{19}F nmr spectrum typical of SF_5 derivatives. In this case the basal fluorine resonance occurs at -65 ppm relative to $CFCl_3$. A chemical shift of 8.47 ppm is found for the apex fluorine relative to the basal fluorines with a coupling constant of 156 Hz. Excellent agreement is found with an AB_4 spectrum calculated using these values as is shown in Figure 4. No extraneous resonances were observed. The values of the spectral parameters are also in agreement with previously described[12] SF_5 groupings.

Table II shows the mass cracking pattern of SF_5OCClO. No parent peak was observed. Unlike SF_5OCl, however, this derivative has the SF_5 ion as the most abundant fragment as is more normal for SF_5OX compounds. The observed fragments are in agree-

---

[14] B. Cohen and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 754 (1962).

[15] J. M. Shreeve, L. C. Duncan, and G. H. Cady, *ibid.*, **4**, 1516 (1965).

[16] P. J. Aymonion, *Chem. Commun.*, 241 (1965).

[17] Absorptions for SF_5OCClO were found at 1855 (s), 1070 (vs), 1020 (w), 942 (vs), 890 (s), 835 (vs), 750 (w), 705 (m), 660 (m), and 600 cm^{-1} (m).

[18] D. G. Weiblen in "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press, New York, N. Y., 1954, p 457.

Table II. Mass Spectrum of SF_5OCClO

m/e	Ion	Rel intensity	m/e	Ion	Rel intensity
129	$^{34}SF_5^+$	4.00	63	$CO^{35}Cl^+$	48.57
127	$^{32}SF_5^+$	100.00	51	SF^+	2.86
108	SF_4^+	3.71	44	CO_2^+	3.43
105	SF_3O^+	25.71	37	Cl^+	2.14
89	SF_3^+	24.71	35	Cl^+	7.14
86	SF_2O^+	4.86	32	S^+	1.92
70	SF_2^+	12.86	19	F^+	0.97
67	SFO^+	6.00	16	O^+	1.32
65	$CO^{37}Cl^+$	15.71	12	C^+	0.83

ment with the proposed structure. Differences between this fragmentation pattern and that of CF_3OCClO[3] are related to the breaking of the different carbon-oxygen single bonds of the compounds. The pentafluorosulfur compounds breaks at this bond giving fragments leading to the intense ion peaks, SF_3O and CClO. The trifluoromethyl compound breaks at the adjacent C-O bond giving strong CF_3 and OCClO peaks.

Pentafluorosulfur chloroformate is colorless and stable at room temperature in glass or metal equipment. Samples stored in infrared cells for several weeks did not decompose to a detectable degree.

Acknowledgment. The authors gratefully acknowledge support for this work by the Office of Naval Research, Power Branch. We are also indebted to Dr. D. Pilipovich and Dr. K. O. Christe for helpful discussion and suggestions.

Some Exchange Reactions Involving Boron Lewis Acids

A. H. Cowley and J. L. Mills

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712.

Received September 11, 1968

Abstract: The ^1H nmr spectra of solutions of the adducts of $B(CH_3)_3$, BF_3, or BH_3 with $(CH_3)_3N$ or tertiary phosphines have been recorded at various temperatures in an effort to establish which of these systems undergo ambient-temperature intermolecular exchange reactions. The trimethylamine–trimethylborane system was selected for more detailed study. Concentration dependence studies together with the energies and entropies of activation establish that the reactions $(CH_3)_3NB(CH_3)_3 + B(CH_3)_3$ and $(CH_3)_3NB(CH_3)_3 + (CH_3)_3N$ proceed by dissociative mechanisms.

There is considerable interest in the relative Lewis acidities of boron compounds. One way of inferring orders of acceptor ability relates to the measurement of nmr chemical shifts.[1] A complicating feature which can arise in such a method is the possibility of rapid intermolecular exchange reactions of the following general categories

$$AB + B^* \rightleftharpoons AB^* + B \qquad (1)$$

$$A^*B + AB^* \rightleftharpoons A^*B^* + AB \qquad (2)$$

$$\left.\begin{aligned} AB &\overset{\text{slow}}{\rightleftharpoons} A + B \\ A + B^* &\overset{\text{fast}}{\rightleftharpoons} AB^* \end{aligned}\right. \qquad (3)$$

where A and B denote the Lewis acid and base, respectively. In such cases the chemical shifts and coupling constants are sensitive to both changes in temperature and relative acid-base concentration. In order to assess the Lewis acidity of a particular acid or the Lewis basicity of a particular base or to measure the nmr parameters of the acid-base complex, it is necessary to cool the system to a temperature such that the intermolecular exchange becomes slow on the nmr time scale.

This point appears to have been appreciated first by Diehl and Ogg[2] in their study of the relative basicity of aliphatic alcohols toward BF_3. Subsequently other authors have studied the exchange between BF_3 and ethers and amines.[3]

Since $B(CH_3)_3$ and BH_3 are employed frequently as reference Lewis acids, we became interested in the possibility that these acids might also undergo rapid intermolecular exchanges. Trimethylamine and trimethylphosphine were selected as reference bases because of their simple ^1H nmr spectra. Of the systems investigated in this work, the trimethylamine-trimethylborane system was selected as the most suitable for more detailed study on the same basis. The reaction was studied with both excess acid and excess base. An additional point of interest concerns the fact that Oliver and coworkers have investigated the mechanisms of the corresponding trimethylamine exchange reactions with $Ga(CH_3)_3$[4] and $In(CH_3)_3$.[5]

Experimental Section

Diborane,[6] trimethylborane,[7] and trimethylphosphine[8] were prepared by previously described procedures and were fractionated

---

(1) For a review of boron acids, see T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 83 (1964).

(2) P. Diehl, *Helv. Phys. Acta*, **31**, 685 (1958); R. A. Ogg and P. Diehl, *J. Inorg. Nucl. Chem.*, **8**, 468 (1958).

(3) (a) R. A. Craig and R. E. Richards, *Trans. Faraday Soc.*, **59**, 1962 (1963); (b) S. Brownstein, A. M. Eastham, and G. A. Latremouille, *J. Phys. Chem.*, **67**, 1028 (1963); (c) A. C. Rutenberg, A. A. Palko, and J. S. Drury, *J. Am. Chem. Soc.*, **85**, 2702 (1963); (d) *J. Phys. Chem.*, **68**, 976 (1964); (e) A. C. Rutenberg and A. A. Palko, *ibid.*, **69**, 527 (1965); (f) E. Gore and S. S. Danyluk, *ibid.*, **69**, 89 (1965).

(4) J. B. DeRoos and J. P. Oliver, *Inorg. Chem.*, **4**, 1741 (1965); *J. Am. Chem. Soc.*, **89**, 3970 (1967).

(5) K. L. Henold and J. P. Oliver, *Inorg. Chem.*, **7**, 950 (1968).

(6) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952).