the low coordination number, will be considerably shorter than in tetrahedral or octahedral derivatives of these ions. The fact that the e'_π parameters increase monotonically across the transition series and do not follow the occupation numbers of the π orbitals suggests a considerable electrostatic polarization interaction similar to that proposed[19] to occur in fluorochromium(III) derivatives.

Smith[9] formally separated the covalent from the electrostatic interaction in these complexes by defining the energies E_1 and E_2 as functions of the orbital angular overlap parameters and of the crystal-field radial integrals a_n. In dealing with the experimental data, values of E_1 and E_2 are derived and broken down into covalent and electrostatic components by direct calculation of the overlap and radial integrals. As a consequence of this calculation there is a monotonic increase in σ^* from Cr(II) to Cu(II), which does not therefore follow the σ occupation numbers, as far as Cr(II) and Fe(II) are concerned, while with the exception of Cu(II), π^* is almost independent of the metal ion, an observation which seems difficult to justify. While the fault may lie not so much with the approach but rather with the procedures by which the various parameters were calculated, it would seem more profitable at this time to combine the electrostatic and covalent parameters together within e'_σ and e'_π as inferred in our treatment.

Because of the large amount of spectroscopic data needed to define, unequivocally, values of the $e'_{\sigma,\pi}$ parameters, there is little information in the literature with which to compare the values derived here. In the complex $Ni(NH_3)_4(NCS)_2$ the parameter e'_σ(N) is 3500–4000 cm^{-1} while the e'_π parameter is very small.[17] In a wide series of six-coordinate tetragonal nickel complexes,[17,24] dπ (being $e'_\pi(Z) - e'_\pi(L)$ in NiL_4Z_2) is always very small suggesting that the e'_π values in these complexes are very small. Certainly it was concluded[17] that π bonding plays very little part in six-coordinate nickel(II) derivatives, unlike the situation observed with the analogous chromium(III) derivatives.[19] The value of close to 5000 cm^{-1} for e'_σ(Cl) in gaseous nickel chloride is consistent with the value for e'_σ(N) for $Ni(NH_3)_4(NCS)_2$ to the extent that changing coordination number from 6 to 2 might generally be expected to increase e'_σ by virtue of decreasing the internuclear nickel–ligand distance. Note that if e'_π(Cl) in octahedral complexes is presumed to be zero, then from the observation that $10Dq = 7200$ cm^{-1} for a hexacoordinate chloronickel(II) complex,[20] $e'_\sigma(\text{Cl}) = 2400$ cm^{-1} in octahedral complexes. A doubling of this value in linear gaseous $NiCl_2$ does not seem unreasonable.

The success of this treatment in solving a considerable amount of data in terms of a small number of variables suggests that the orbital angular overlap paramenters do have chemical significance. It seems that they can be used, in a relative sense, as a measure of σ and π bonding. Accepting this, then clearly the π interaction in these gaseous dihalides is extremely important. Since, as alluded to above, these parameters contain an electrostatic component when derived in a semiempirical fashion, the π interaction may not be entirely covalent in orgin. A strong electrostatic component may be present in view of the observation that the e'_π parameters do not follow the π occupation numbers. In closing it is of interest to note that as a consequence of this strong π interaction, the $10Dq$ values vary a great deal across the transition series and are of little value in themselves to identify the nature of the metal–ligand bond. In complexes of higher coordination number where e'_π is much smaller, the Dq values mimic changes in e'_σ and are therefore of greater qualitative significance.

Acknowledgments.—We are indebted to the National Research Council (Ottawa) for financial support.

---

[24] M. Keeton and A. B. P. Lever, unpublished observations.

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Chlorine Trifluoride Oxide. I. Preparation and Properties

BY D. PILIPOVICH,* C. B. LINDAHL, C. J. SCHACK, R. D. WILSON, AND K. O. CHRISTE

Received September 8, 1971

Chlorine trifluoride oxide, ClF_3O, has been prepared by either direct fluorination of Cl_2O, $NaClO_2$, or $ClONO_2$, or by glow discharge of F_2 in the presence of solid Cl_2O. A number of physical properties are reported as well as the ^{19}F nmr spectrum and the mass cracking pattern.

Introduction

Chlorine trifluoride oxide, ClF_3O, was prepared and characterized at Rocketdyne in 1965.[1] However, these results were not reported in the open literature. Recently, Bougon, Isabey, and Plurien have independently discovered[2] ClF_3O. In this paper, we report several synthetic routes and some physical and spectroscopic properties for ClF_3O.

Experimental Section

Materials and Apparatus.—Chlorine nitrate, $ClONO_2$, was prepared by the method of Schack.[3] Dichlorine oxide, Cl_2O, was generated as required from a Cl_2–HgO mixture as reported[4] by Schack and Lindahl. Mercuric oxide was prepared by the method of Cady.[5] Sodium chlorite was purchased from Matheson Coleman and Bell. Alkali metal fluorides were obtained from American Potash and Chemical Co. Prior to their use, they

---

[1] D. Pilipovich and R. D. Wilson, U. S. Patent, to be issued, 1972.

[2] R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, **271**, 1366 (1970).

[3] C. J. Schack, *Inorg. Chem.*, **6**, 1938 (1967).

[4] C. J. Schack and C. B. Lindahl, *Inorg. Nucl. Chem. Lett.*, **3**, 387 (1967).

[5] G. H. Cady, *Inorg. Syn.*, **5**, 156 (1957).

were fused, allowed to cool in the glove box, and subsequently ground.[6] Fluorine of 99+% purity was produced at Rocketdyne. Metal reactors were either Monel or 304 stainless steel Hoke cylinders equipped with high-pressure Hoke Y3002H needle valves. All manipulations were carried out either in well-passivated (with ClF_3) metal–Teflon FEP vacuum systems or in the dry nitrogen atmosphere of a glove box, except for the glow discharge reaction which was run in a Pyrex glass vessel with copper electrodes.

Infrared spectra were taken on a Beckman IR7 fitted with CsI and NaCl interchange and a Perkin-Elmer Model 337 grating spectrophotometer. The infrared cell used was constructed of nickel and fitted with AgCl windows or CsI windows protected by Teflon FEP film. The ^{19}F nmr spectra were recorded using a Varian high-resolution nmr spectrometer operating at 56.4 Mc. The samples were sealed in Teflon FEP tubes. Mass spectra were obtained with a CEC Model 21-103 C mass spectrometer using an ionizing voltage of 70 eV and a high-range magnet current of 0.60 mA.

Fluorination of Dichlorine Oxide.—*Caution!* Owing to the shock sensitivity of chlorine oxides, proper precautions (*i.e.*, shielding, etc.) must be taken. One explosion was encountered in the course of this work during the purification of about 5 g of Cl_2O.

In a typical experiment, powdered CsF was loaded into a passivated 300-ml 304 stainless steel cylinder in a glove box. The cylinder was then attached to a vacuum line, and after evacuation 246 cm^3 (11 mmol) of Cl_2O was condensed into the cylinder at −196°. The cylinder was warmed to −78° to permit the Cl_2O to liquefy and contact the CsF. After recooling to −196°, 2 l. of F_2 was added and the cylinder was then maintained at −78° for 6 days. The unreacted F_2 was removed by pumping at −196°. The cylinder contents was then warmed to ambient temperature and fractionated through traps maintained at −95 and −196°. The chlorine trifluoride oxide (8.9 mmol) was trapped at −95° and corresponded to a yield of 75 mol %/mol of Cl_2O used. The −196° trap contained ClF_3, ClF, and some ClO_2F.

Fluorination of Cl_2O Absorbed on Mercuric Salts.—Yellow HgO and Cl_2 were allowed to interact at −80° for 24 hr in a 304 stainless steel cylinder. Fluorine was added at −196° and the reaction was allowed to proceed for several days at −80°. The reaction products were separated by fractional condensation and consisted of mostly ClF_3 and ClO_2F. In addition, ClF_5 and ClF_3O were obtained in low yields.

Glow-Discharge Fluorination of Solid Cl_2O.—Dichlorine oxide was deposited at −196° as a solid on the walls of a U-shaped Pyrex glass discharge vessel. During discharge, gaseous fluorine at 20 mm pressure was circulated over the solid in a closed-loop system. After consumption of 5 mol of F_2/mol of Cl_2O, the unreacted F_2 was removed at −196° and the products were separated by fractional condensation in a metal–Teflon FEP vacuum system. The main products were ClF_5 (∼45 mol %) and ClO_2F. In addition, the products contained some ClF_3 and 1 to 2% of ClF_3O.

Fluorination of $NaClO_2$.—Sodium chlorite (33 mmol) was placed in a 300-ml 304 stainless steel cylinder. Fluorine (45 mmol) was added at −196°. The mixture was allowed to warm to −80° and was kept at this temperature for 16 hr. The reaction products consisted of mostly ClO_2F, ClF_3, ClF, and Cl_2, but contained also a small amount of ClF_3O.

Fluorination of Chlorine Nitrate.—Chlorine nitrate (29.7 mmol) and F_2 (110 mmol) were condensed into a passivated 75-ml 304 stainless steel cylinder cooled to −196°. The cylinder was then maintained at −35°, resulting in an initial pressure of 480 psi. After 4 hr, the reactor was cooled to −196° and the noncondensables were removed. The products were separated by fractional condensation using cold traps at −95, −142, and −196°. The −95° fraction contained 19.3 mmol of ClF_3O, representing a 65% yield based on $ClONO_2$. The −142° fraction contained ClO_2F and Cl_2 while FNO_2 was trapped at −196°.

Purification of ClF_3O.—An alternate method of purifying ClF_3O may be used when significant amounts of ClF_3 are present and repeated fractionations of larger quantities of materials are not practical. Chlorine trifluoride oxide contaminated with substantial quantities of ClF_3 and ClO_2F was condensed onto KF (at −196°) and then maintained at ambient temperature for 24 hr. The cylinder was cooled to 0° and the ClO_2F, which does not form a stable adduct with KF, was removed by pumping. Pure ClF_3O was removed *in vacuo* at 50–70°, while ClF_3 remained complexed.

Elemental Analysis.—Chlorine and fluorine were determined by potentiometric titration with $AgNO_3$ solution and by $Th(NO_3)_4$–alizarin titration, respectively, after the combustion of a sample of ClF_3O with anhydrous NH_3 in a metal–Teflon FEP ampoule. (Caution!)

Oxygen was directly determined by reaction of ClF_3O with NaCl according to

$$3NaCl + ClF_3O \longrightarrow 3NaF + {}^1/_2O_2 + 2Cl_2$$

The technique involved condensing a measured quantity of ClF_3O onto reagent grade NaCl contained in a passivated cylinder. The cylinder was then heated to 100° to ensure complete reaction. After cooling to −196°, the noncondensables were measured using a Toepler pump. The gas was identified as O_2 by mass spectrometry. *Anal.* Calcd for ClF_3O: Cl, 32.7; F, 52.5; O, 14.7. Found: Cl, 32.6; F, 52.5; O, 13.1.

Results and Discussion

Synthesis.—The synthesis of ClF_3O is readily carried out through the fluorination of an inorganic, covalent hypochlorite. Those that have received the most attention in this study were dichlorine oxide, Cl_2O, and chlorine nitrate, $ClONO_2$. The fluorination of the dangerous[7] Cl_2O proceeds according to the following equations.

$$2F_2 + Cl_2O \longrightarrow ClF_3O + ClF$$

$$3F_2 + Cl_2O \longrightarrow ClF_3O + ClF_3$$

When no catalyst is used or if KF and NaF are present as catalysts, ClF is the main by-product. When the more basic alkali metal fluorides, RbF and CsF, are used, ClF_3 is the favored coproduct. The formation of ClF_3 rather than ClF is presumably associated with the more ready formation of ClF_2^- intermediates with RbF and CsF. A similar catalytic effect has been noted[8] in the preparation of ClF_5 from ClF_3 in the presence of alkali metal fluorides.

Yields of ClF_3O from Cl_2O are rather variable and may be affected by the particular alkali fluoride present. Yields of over 40% have been consistently obtained and have reached over 80% using either NaF or CsF. Since NaF does not form[9] an adduct with ClF_3O, stabilization of the product by complex formation does not seem to strongly influence the ClF_3O yields.

Owing to unpredictable explosions experienced[7] with liquid Cl_2O, attempts were made to circumvent the Cl_2O isolation step. For this purpose, the crude Cl_2O, still absorbed on the mercuric salts, was directly fluorinated. Again, ClF_3O was formed, but its yield was too low to make this synthetic route attractive.

The fluorination of solid Cl_2O to ClF_3O proceeded at temperatures as low as −196° provided the fluorine was suitably activated by methods such as glow discharge. Unactivated fluorine does not interact with Cl_2O at −196°, and after completion of the discharge unreacted F_2 was removed at −196°. Consequently, the observed ClF_3O could not have formed by fluorina-

---

(6) We are indebted to Mr. M. G. Warner of our laboratories for devising this technique of preparing active alkali metal fluorides. The method produces salts of activity comparable to the precipitation method used by C. T. Ratcliffe and J. M. Shreeve, *Chem. Commun.*, 674 (1965), but is more convenient.

(7) Extreme caution should be used in handling Cl_2O. We have found that the material is readily exploded during adiabatic compression in a U tube, and even inexplicably during routine handling.

(8) D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, Jr., and V. G. Bedwell, *Inorg. Chem.*, **6**, 1918 (1967).

(9) K. O. Christe, C. J. Schack, and D. Pilipovich, *ibid.*, **11**, 2205 (1972).

tion of Cl_2O during warm-up of the reaction products. The relatively low yields of ClF_3O (1 to 2%) could be partially due to the high reactivity of ClF_3O toward glass, although little interaction is to be expected at $-196°$, and the transfer of the products to a metal system was done rapidly and at the lowest possible temperature.

The low-temperature fluorination of $NaClO_2$ produced ClF_3O in low yields. However, the low yields and poor reproducibility make this route unattractive.

The fluorination of chlorine nitrate, $ClONO_2$, proceeds according to

$$2F_2 + ClONO_2 \longrightarrow ClF_3O + FNO_2$$

This reaction offers the most convenient route to ClF_3O for several reasons: (1) less fluorine is required than in the fluorination reactions of Cl_2O yielding ClF_3 as a coproduct, (2) the great difference in the volatilities of the products FNO_2 and ClF_3O ($\Delta T_{bp} \sim 100°$) permits an easy separation by fractional condensation, and (3) chlorine nitrate can be made more conveniently and, most importantly, does not appear to be hazardous in its handling. The yields of ClF_3O using $ClONO_2$ as a starting material are somewhat higher than those from Cl_2O.

In the fluorination of both Cl_2O and $ClONO_2$, side reactions compete with the actual fluorination step. These are caused by the thermal decomposition of the starting materials due to inefficient removal of the heat of reaction. Hence, the rate of the competing reactions is markedly affected by the reaction temperature. At reaction temperatures near or above ambient, the decomposition of the hypochlorite appears to be favored and little or no ClF_3O is formed, resulting in rapid, rather uncontrolled reactions. Apparently, thermal decomposition preceding the fluorination step yields only intermediates incapable of producing ClF_3O. Thus, in order to maximize the desired fluorination reaction, long reaction times at low temperature ($T < 0°$) are indicated.

Properties.—Pure ClF_3O is colorless as a gas or liquid and white in the solid state. It boils at 29° and freezes at $-42°$. Vapor pressures were measured over the range -23 to 31° and the data were fitted to the equation $\log P_{mm} = 8.433 - 1680/T(°K)$. Measured vapor pressures at the noted temperatures are [T (°C), P (mm)]: -23.0, 54.5; -12.4, 98; 0, 200; 5.9, 253; 15.6, 410; 21.0, 525; 25.0, 635; and 31.9, 822. The latent heat of vaporization is 7.7 kcal/mol and the derived Trouton constant is 25.4, indicating some association in the liquid phase. The density at 20° of 1.865 g/ml is similar to those observed for ClF_3[10] and ClF_5.[8] The molecular weight was determined from the vapor density and found to be 106.0 (calcd for ClF_3O, 108.5). The good agreement indicates little or no association in the gas phase at the pressures used ($P < 1$ atm). A complete elemental analysis was carried out for ClF_3O and confirms its composition. The physical properties reported in this paper agree well with those reported[2] by Bougon, *et al.*

Chlorine trifluoride oxide resembles most chlorine fluorides in its corrosive and oxidizing properties. However, it appears to be somewhat more corrosive than either ClF_3 or ClF_5. Care must be taken to passivate all equipment with ClF_3 (or preferably ClF_3O) prior to manipulating ClF_3O. Just as do ClF_3[11] and ClF_5,[8] ClF_3O forms chloryl fluoride upon contact with a number of hydroxylic reagents. The gas reacts rapidly with flamed-out quartz even at low pressures.

Mass Spectrum.—A stable mass cracking pattern for ClF_3O has been obtained. Observed ions[12] (excluding *m/e* due to ^{37}Cl isotopes) were [*m/e*, ion, abundance (%)]: 89, ClF_2O^+, 80.6; 70, $ClFO^+$, 100.0; 54, ClF^+, 21.23; 51, ClO^+, 14.78; 35, Cl^+, 29.35; 19, F^+, 27.29; and 16, O^+, 13.19. Several features of the mass cracking pattern are noteworthy. A comparison with the spectrum of IOF_5,[13] for example, shows that IOF_5 gives a significant parent peak (32%) while ClF_3O has no detectable peak at the same ionizing voltage. Also the ions ClF_2O^+ and $ClFO^+$ have a very high intensity which precludes an extensive thermal rupture of the ClO bond prior to electron bombardment.

Infrared Spectrum.—The infrared spectrum of ClF_3O has been recorded over the range 4000–240 cm^{-1}, showing the following absorptions (cm^{-1}, intensity): 1220, s; 678, vs; 667, vs; 490, ms (broad); 413, w; 319, m; and 245, mw. A detailed study of the vibrational spectrum of the gas and the liquid will be given in a separate paper.[14]

^{19}F Nmr Spectrum.—The ^{19}F nuclear magnetic resonance spectrum of ClF_3O has been investigated in both the liquid and gaseous state. A single broad line is observed for the neat liquid at -262 ppm relative to the external standard $CFCl_3$. Similarly, only a single line ascribable to ClF_3O has been found in the gas-phase spectrum at -327 ppm relative to the same standard. This significant shift to a lower field, when going from the liquid to the gas, lends further support to the association in the liquid phase derived from the vapor pressure measurement and the Raman spectrum of the liquid.[14] Attempts to observe a splitting of the ^{19}F resonance line by cooling of either neat ClF_3O or solutions in ClF_5 were unsuccessful. This indicates a rapid exchange in the liquid phase and line broadening in the liquid and gas phase due to interaction with the large chlorine quadrupole moment. This line broadening is sufficient to obscure any information concerning chemical shift differences and spin–spin coupling between the nonequivalent fluorines even in the gas phase.

Pyrolysis.—It was of interest to determine whether the thermal decomposition of ClF_3O would result in the elimination of F_2, as do ClF_3[15] and ClF_5,[16] or O_2, as do IOF_5[17] and $FClO_2$.[18] When ClF_3O was heated to 280° in Monel, for 16 hr, 70% of the ClF_3O was decomposed to ClF_3 and oxygen, while in stainless steel decomposition was already complete at 200°. Under dynamic conditions at $T > 350°$, ClF_3O decomposed again according to

$$ClF_3O \xrightarrow{\Delta} ClF_3 + {}^1/_2O_2$$

---

[10] A. A. Banks and A. J. Rudge, *J. Chem. Soc.*, 2779 (1955).

[11] R. Bougon, M. Carles, and J. Aubert, *C. R. Acad. Sci., Ser. C*, **265**, 179 (1967).

[12] This pattern is corrected for SiF_4, ClO_3F, Cl_2, ClO_2, COF_2, O_2, and HF, all of which were generated through reaction with the inlet system of the mass spectrometer.

[13] C. J. Schack, D. Pilipovich, S. N. Cohz, and D. F. Sheehan, *J. Phys. Chem.*, **72**, 4697 (1968).

[14] K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 2196 (1972).

[15] H. Schmitz and H. J. Schumacher, *Z. Naturforsch. A*, **2**, 362 (1947).

[16] H. F. Bauer and D. F. Sheehan, *Inorg. Chem.*, **6**, 1736 (1967).

[17] C. J. Schack and D. Pilipovich, unpublished results, this laboratory.

[18] H. J. Heras, P. J. Aymonino, and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, **22**, 161 (1959).

and not to the unknown chlorosyl fluoride, ClFO, and F_2. Its thermal stability thus appears to be intermediate between that of ClF_3[15] and ClF_5.[16] The reaction chemistry of ClF_3O will be described in a separate paper.[19]

Acknowledgment.—We are pleased to acknowledge support for this work by the Office of Naval Research, Power Branch. We wish to thank Mr. S. Cohz for the mass-spectral work, Drs. J. S. Muirhead and J. D. Ray for the ^{19}F nmr measurements, and J. Quaglino for the density measurement. We are also indebted to Dr. E. A. Lawton for his help and encouragement.

---

[19] C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *Inorg. Chem.*, **11**, 2201 (1972).

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Chlorine Trifluoride Oxide. II. Photochemical Synthesis

BY D. PILIPOVICH,* H. H. ROGERS, AND R. D. WILSON

Received September 8, 1971

Chlorine trifluoride oxide, ClF_3O, was synthesized from several gaseous reaction systems using uv activation. The fluorination of both ClO_2F and ClO_3F, using ClF_5 or F_2 as fluorinating agents, gave excellent yields of ClF_3O. In addition, the direct photochemical synthesis of ClF_3O from the elements Cl_2, F_2, and O_2 was successfully achieved. Other systems yielding ClF_3O were ClF_3–O_2 and ClF–IF_5O. Attempts were unsuccessful to photochemically prepare either BrF_5O from BrF_5 and O_2 or BrF_7 from $BrF_5 + F_2$.

Introduction

Halogen fluorides can be readily synthesized by direct fluorination of the corresponding halogens at appropriate temperatures and pressures.[1] Consequently, little attention has been devoted to their photochemical synthesis. When the novel chlorine oxyfluoride, ClF_3O, was discovered[2,3] in 1965, its original synthesis involved handling of the treacherous[3] starting material, Cl_2O. Therefore, alternate approaches, such as photochemical reactions, were studied which might yield ClF_3O. Of initial interest to us was the use of uv irradiation to achieve the "deoxygenation" of either ClO_2F or ClO_3F. One of these, ClO_2F, had previously been shown[4] to degrade thermally to give ClF and O_2. A stepwise deoxygenation of these oxyfluorides *via* the intermediate (and unknown) chlorosyl fluoride, ClOF, might in the presence of F_2 yield ClF_3O. In addition, the alternate approach, *i.e.*, the photochemical addition of oxygen to various chlorine fluorides, was investigated. Of particular interest was whether ClF_3 could combine with oxygen to form ClF_3O and the direct synthesis of ClF_3O from the elements, Cl_2, F_2, and O_2. After the successful completion of our study, Bougon, Isabey, and Plurien independently discovered[5] the formation of ClF_3O when exposing a mixture of ClF_3 and OF_2 to uv irradiation. In this paper, we report the results of our original photochemical studies.

Experimental Section

Materials and Apparatus.—Perchloryl fluoride was purchased from Pennsalt Chemical Co. and used as received after verifying its purity through its infrared spectrum and vapor tension at −80°. Chloryl fluoride was synthesized by a modification of Woolf's procedure[6] and involved the fluorination of $NaClO_3$ with ClF_3. Fluorine was produced at Rocketdyne and Cl_2 and ClF_3 were obtained from the Matheson Co. The ClF_3 was purified by complexing with KF, removing volatiles at ambient temperature, and subsequently pumping off ClF_3 at temperatures above 140°. Chlorine pentafluoride was prepared according to the method of Pilipovich, *et al.*,[7] while chlorine monofluoride was synthesized from ClF_3 and Cl_2.[8] Bromine pentafluoride (Matheson) was treated with F_2 at ambient temperature until the material was colorless. It was purified by fractional condensation through traps kept at −64 and −95°. The BrF_5 was retained in the −95° trap and showed no detectable impurities. The preparation and purification of IF_5O[9] and ClF_3O[3] have previously been described.

All the results listed in this paper was obtained with a Hanovia high-pressure Hg lamp, No. 679-A-36 (power input 450 W). The spectral energy distribution of radiated Hg lines for the lamp includes (Å, W): 2967, 4.3; 2652, 4.0; 2537, 5.8; 2482, 2.3; 2380, 2.3; and 2224, 3.7, according to the manufacturer's specifications. In addition, this lamp emits lines of shorter wavelength down to about 1700 Å (quartz limit). The distance between the lamp and the cell window was about 2 in.

The photolyses were carried out in a cell consisting of a stainless steel cylindrical body (3 in. long, 3 in. i.d., and 388 cm^3 volume). One end of the cell was sealed with a welded plate. The other end was a machined flange onto which a 4-in. diameter optical grade sapphire window was clamped. A vacuum seal was obtained by using Teflon O-rings. Provision was made to condense materials into the cell *via* a stainless steel coldfinger (3 in. long, $^3/_8$ in. o.d.) appended to the main cell body. An outlet was provided which was connected to a stainless steel–Teflon FEP vacuum line for product work-up. Cooling coils were brazed onto the outside of the cell body, and cold methanol was circulated to provide the cooling. The cell wall temperature was automatically controlled to within 3° of a preset temperature over the range −60° to ambient temperature. A removable metal lamphousing was positioned over the sapphire window and dry N_2 was passed over the window to cool the window, prevent condensation prior to the irradiation, and exclude atmospheric oxygen which might act as a filter for short wavelength uv radiation.

---

(1) L. Stein in "Halogen Chemistry," Vol. 1, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, Chapter 3.

(2) D. Pilipovich and R. D. Wilson, U. S. Patent, to be issued, 1972.

(3) D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11**, 2189 (1972).

(4) M. J. Heras, P. J. Aymonino, and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, **22**, 161 (1959).

(5) R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, **271**, 1366 (1970).

(6) A. A. Woolf, *J. Chem. Soc.*, 4113 (1954).

(7) D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, R. D. Wilson, N. N. Ogimachi, F. C. Gunderloy, Jr., and V. G. Bedwell, *Inorg. Chem.*, **6**, 1918 (1967).

(8) H. Schmitz and H. J. Schumacher, *Z. Naturforsch. A*, **2**, 362 (1947).

(9) C. J. Schack, D. Pilipovich, S. N. Cohz, and D. F. Sheehan, *J. Phys. Chem.*, **72**, 4697 (1968).