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

Chlorine Trifluoride Oxide. III. Vibrational Spectrum, Force Constants, and Thermodynamic Properties

BY KARL O. CHRISTE* AND E. C. CURTIS

Received September 8, 1971

The infrared spectra of gaseous, solid, and matrix isolated ClF_3O and the Raman spectra of gaseous and liquid ClF_3O are reported. Nine fundamental vibrations were observed, consistent with symmetry C_s. The vibrational spectrum of ClF_3O agrees well with a trigonal-bipyramidal model with two fluorine atoms at the apexes and one fluorine atom, one oxygen atom, and one localized free electron pair at the remaining corners. A modified valence force field was computed for ClF_3O. These data indicated that the axial ClF bonds (f_r = 2.34 mdyn/Å) are considerably weaker than the equatorial one (f_R = 3.16 mdyn/Å) and that the bond order of the ClO bond is close to two (f_D = 9.37 mdyn/Å). The Raman spectrum of the liquid and the infrared spectrum of the solid indicate association through the axial fluorine atoms. Thermodynamic properties were computed for ClF_3O in the range 0–2000°K.

Introduction

As part of our extensive study[1–5] of the novel chlorine oxyfluoride, ClF_3O, we have investigated the vibrational spectra of the molecule. In their recent paper, Bougon, *et al.*, have proposed[6] a structure of symmetry C_{3v} for ClF_3O on the basis of infrared and Raman spectra. In this paper, we report the complete vibrational spectrum, force constants, and thermodynamic properties of ClF_3O. The vibrational spectra, force constants, and structure of the two ions, ClF_2O^+ and ClF_4O^-, derived from ClF_3O are discussed elsewhere.[7,8]

Experimental Section

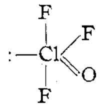
The preparation of ClF_3O and its purification and handling have previously been described.[2,3] The ClF_3O samples used in this investigation had a purity of better than 99.8% and our spectra did not reveal any impurities. The infrared spectra were recorded either on a Beckman Model IR-7 spectrophotometer with NaCl and CsI interchange in the range 4000–200 cm^{-1} or a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The instruments were calibrated by comparison with standard gas calibration points.[9] The gas cells were made of 304 stainless steel and had a path length of 5 cm. Silver chloride and CsI windows were used in the ranges 4000–450 and 450–200 cm^{-1}, respectively. The inside of the CsI windows was protected against chemical attack by Teflon FEP sheet (1-mil thickness). To ensure close contact between the CsI window and the Teflon sheet, a thin film of Halocarbon grease (high-temperature grade from Halocarbon Products) was put on the CsI window prior to attaching the Teflon sheet. The Teflon sheet did not come loose or show blisters even upon evacuation of the cell provided all gas pockets between the CsI window and the thin Teflon sheet were carefully eliminated before assembling the cell. Compensation for bands due to the window material was achieved by placing an empty cell into the reference beam.

The apparatus, materials, and technique used for the matrix isolation study have previously been described.[10,11] Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of ~1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier, and a dc ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. A stainless steel cell with Teflon O-rings and sapphire windows was used for obtaining the spectra of gases and liquids. The design of this cell was similar to that of a cell described previously.[12]

Results and Discussion

Vibrational Spectra.—Figure 1 shows the infrared spectrum of gaseous ClF_3O recorded at various sample pressures. Figures 2 and 3 show the Raman spectra of gaseous and liquid ClF_3O, respectively. Figure 4 shows the infrared spectra of pure and N_2-matrix isolated ClF_3O at 4°K. Figure 5 shows the most intense infrared bands of matrix isolated ClF_3O under high resolution conditions allowing the determination of the ^{35}Cl–^{37}Cl isotopic shifts. Table I lists the observed frequencies which can be attributed to fundamental vibrations. Table II lists the infrared frequencies attributed to overtones and combination bands.

In ClF_3O, the chlorine central atom possesses a nonbonding valence-electron pair. In related molecules (*e.g.*, SF_4 and ClF_5), such an electron pair appears to be sterically active, and similar behavior is anticipated here. The resulting structure can best be described as a trigonal bipyramid. In this type of structure, the apical positions are always occupied by the most electronegative ligands.[13] Hence, structure I of symmetry



I

C_s (possessing one symmetry plane as the only symmetry element) might be expected for ClF_3O. The arrangement of the axial FClF group may not be exactly linear owing to the different degrees of repulsion expected from the three equatorial ligands. However, possible deviations from 180° should be relatively small and symmetry C_s would be retained. A second structure of symmetry C_s (II) can be written for ClF_3O in which one fluorine and one oxygen atom occupy the axial positions. However, comparison with related

---

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

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

[3] D. Pilipovich, H. H. Rogers, and R. D. Wilson, *ibid.*, **11**, 2192 (1972).

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

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

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

[7] K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, **11**, 2212 (1972).

[8] K. O. Christe and E. C. Curtis, *ibid.*, **11**, 2209 (1972).

[9] E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand.*, **64**, 841 (1960).

[10] K. O. Christe and D. Pilipovich, *J. Amer. Chem. Soc.*, **93**, 51 (1971).

[11] K. O. Christe, *Spectrochim. Acta, Part A*, **27**, 631 (1971).

[12] E. L. Gasner and H. H. Claassen, *Inorg. Chem.*, **6**, 1937 (1967).

[13] R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **6**, 749 (1967).

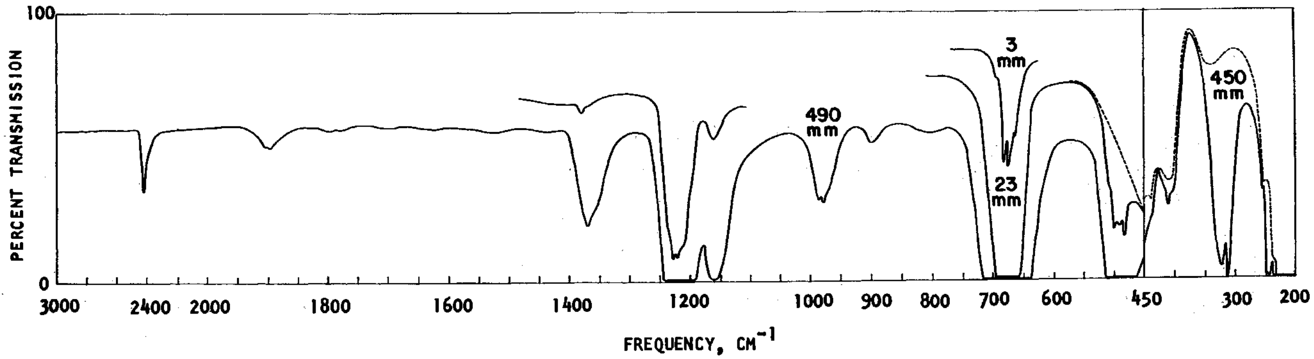
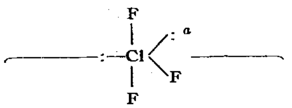
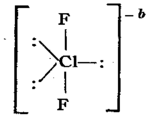
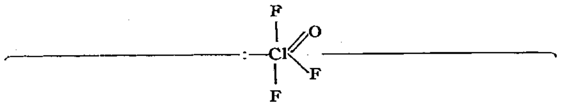
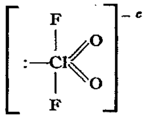
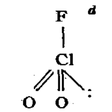


Figure 1.—Infrared spectrum of gaseous ClF_3O at various sample pressures. The broken lines indicate the cell background in this particular region.

TABLE I

VIBRATIONAL SPECTRA OF ClF_3O GAS AND LIQUID COMPARED TO THOSE OF SIMILAR MOLECULES AND IONS

Observed frequencies, cm^{-1}, and relative intensities														
 [a]			 [b]						 [c]		 [d]			
Gas		Liquid			Gas		Solid	Liquid			Gas	Liquid	Assignment for ClF_3O in point group C_s	Approx description of mode
Ir	Raman	Raman	Ir	Raman	Ir	Raman	Matrix ir	Raman	Ir	Raman	Ir	Raman		
					1228 1224 1218 } s	1222 (1.5) p	1223 s	1224 (1.0) p	1225 1191 } vs	1221 (0.8)			$\nu_1(A')$	$\nu(^{35}Cl{=}O)$
					1213	1211 (0.5) p	1212 m		1070 s	1076 (10)			$\nu_1(A')$	$\nu(^{37}Cl{=}O)$
751 s	752 s, p	753 ms			701	694 (2.6) p	686 s	689 (2.7) p			630 s	602 (2) p	$\nu_2(A')$	$\nu(^{35}Cl{-}F')$
					684	686 sh, p	678 m						$\nu_2(A')$	$\nu(^{37}Cl{-}F')$
702 vs			635 vs		676 } vs		652 vs						$\nu_7(A'')$	$\nu_{as}(F^{35}ClF)$
					666		641 s		510 vs				$\nu_7(A'')$	$\nu_{as}(F^{37}ClF)$
							499 m						$\nu_8(A'')$	$\delta_{rock}(O^{35}ClF')$
					501	500 (1)		497 sh	330–370 m	378 (8)				
							498 sh						$\nu_8(A'')$	$\delta_{rock}(O^{37}ClF')$
					491 } ms	489 (1)	486 mw						$\nu_3(A')$	$\delta_{sciss}(O^{35}ClF')$
		514 vs					484 w						$\nu_3(A')$	$\delta_{sciss}(O^{37}ClF')$
530 m	529 vs, p			475 (10)	481	482 (10) p	478 mw	466 (10)	330–370 m	363 (10)			$\nu_4(A')$	ν_sFClF
		502 vs												
					412 w	414 (0.2) dp	414 w	405 (0.5) sh					$\nu_9(A'')$	τ
442 w	431 w, dp	424 vw			323 313 } m	319 (0.1)	323 mw	316 (0.3) p	330–370 m	337 (8)			$\nu_5(A')$	$\delta_sF\ddot{Cl}F$ out of $F\ddot{Cl}F$ plane ≡ $\delta_{wag}OClF'$
328 s	329 w, p	321 vw			230 mw	224 (0.4) p		227 (1.2) p?		198 (0.7)			$\nu_6(A')$	$\delta_sF\ddot{Cl}F$ in $F\ddot{Cl}F$ plane

[a] H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, **52,** 3517 (1970). [b] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, **6,** 1159 (1967). [c] K. O. Christe and E. C. Curtis, *ibid.*, **11,** 583 (1972). [d] D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, **20,** 1763 (1964).

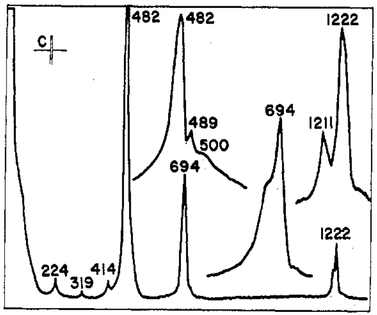


Figure 2.—Raman spectrum of gaseous ClF_3O at a sample pressure of 490 mm. The inserts show the three most intense bands at higher resolution and scale expansion. C indicates equivalent slit width.

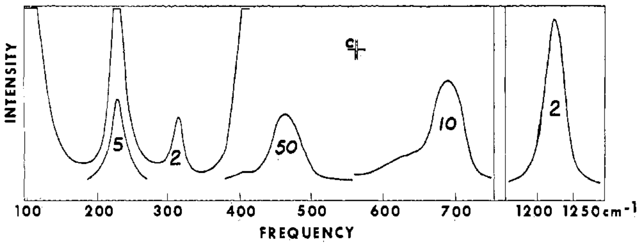


Figure 3.—Raman spectrum of liquid ClF_3O. C indicates equivalent slit width.

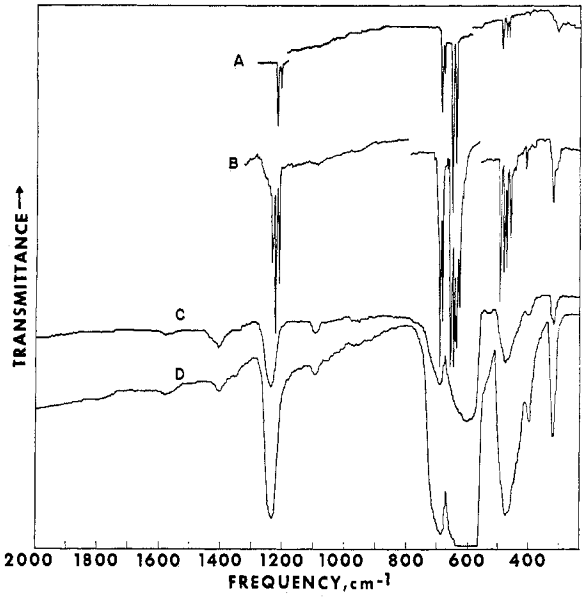
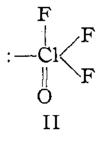


Figure 4.—Infrared spectra of solid ClF_3O at 4°K: (A) 1.0 μmol of ClF_3O in 10,000 μmol of N_2; (B) 10 μmol of ClF_3O in 10,000 μmol of N_2 after controlled diffusion at 27°K; (C and D) pure ClF_3O at two different concentrations.



II

molecules and the observed ^{35}Cl–^{37}Cl isotopic shifts (see below) eliminate this model. If the free electron pair of the chlorine atom in ClF_3O would not be sterically active, a tetrahedral molecule of symmetry C_{3v} would result, as proposed[6] by Bougon, *et al.*

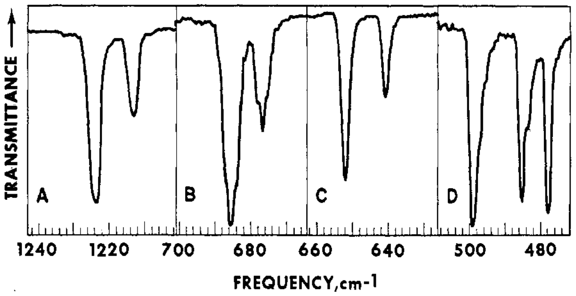
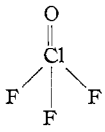


Figure 5.—Infrared spectra of ClF_3O in N_2 matrix at 4°K recorded at tenfold scale expansion under high resolution conditions: (A) 2.9 μmol of ClF_3O (matrix ratio (mr) 1:1000); (B) 2.0 μmol (mr 1:10,000); (C) 0.24 μmol (mr 1:10,000); (D) 10 μmol (mr 1:1000).

Table II

Overtones and Combination Bands Observed in the Infrared Spectrum of ClF_3O Gas

Frequencies, cm^{-1}		
Obsd	Calcd	Assignment
800 vvw, br	475 + 318 = 793	$(\nu_8 + \nu_5)$
899 vw	408 + 491 = 899	$(\nu_4 + \nu_3)$ or $(\nu_4 + \nu_8)$
980 w	2 × 491 = 982	$2\nu_3$ or $2\nu_8$ or $(\nu_3 + \nu_8)$
1161 mw	491 + 680 = 1171	$(\nu_3 + \nu_7)$ or $(\nu_8 + \nu_7)$
1372 mw	2 × 680 = 1360	$2\nu_7$
1899 vw	680 + 1221 = 1901	$(\nu_7 + \nu_1)$
2436 w	2 × 1221 = 2442	$2\nu_1$



III

For structures I and II, one would expect nine fundamental vibrations active in both the infrared and Raman spectrum. For structure III, one would expect only six fundamental vibrations, again, active in both the infrared and Raman spectrum. Since nine fundamental vibrations were unambiguously observed for ClF_3O (see Table I), structure III can be ruled out. Consequently, assignments for ClF_3O were made in point group C_s (see Table I) contrary to the conclusions[6] reached by Bougon, *et al.*, on the basis of incomplete experimental data. Further evidence against symmetry C_{3v} is based on the band shapes observed for the infrared spectrum of the gas showing that ClF_3O cannot be a symmetric top molecule. For example, in the case of C_{3v}, the Cl=O stretching mode at about 1220 cm^{-1} should show well-separated PQR branches. Since the geometry of ClF_3O of symmetry C_s can be estimated (see below), the three principal moments of inertia were computed for structure I resulting in A = 0.216, B = 0.129, and C = 0.0934 cm^{-1}. Based on these values, the infrared band contours were estimated for ClF_3O, according to the method of Ueda and Shimanouchi.[14] The observed band contours were consistent with those predicted. However, they cannot be used to distinguish structures I and II due to the interference by the ^{37}Cl isotope bands, the double and triple coincidences of bands in the infrared spectrum occurring at about 680 and 490 cm^{-1}, respectively, and the fact that most bands are blends of the A, B, and C type.

The assignments (see Table I) for ClF_3O in point group C_s (structure I) are based on the following argu-

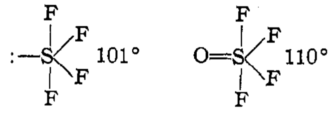
---

[14] T. Ueda and T. Shimanouchi, *J. Mol. Spectrosc.*, **28**, 350 (1968).

ments. The band at about 1220 cm^{-1} occurs at a frequency much too high for any Cl—F fundamental vibration and, hence, must be assigned to the stretching vibration involving the Cl=O double bond. Comparison with related Cl—F containing compounds[15–18] indicates that of the three Cl—F stretching vibrations, at least two should show a frequency higher than 600 cm^{-1} (see Table I). Indeed two bands were observed at about 690 and 650 cm^{-1}. These were assigned to the equatorial Cl—F and the antisymmetric axial FClF stretching vibrations, respectively. These assignments were made on the basis of the observed ^{35}Cl–^{37}Cl isotopic shifts (see below), the relative infrared and Raman intensities, and the Raman polarization measurements. The fourth stretching vibration, *i.e.*, the symmetric FClF mode, should be polarized and of the highest relative intensity in the Raman spectrum. Furthermore, it should be relatively weak in the infrared spectrum and show no detectable Cl isotopic shift if the F–Cl–F group is approximately linear. Hence, this mode must be assigned to the band at about 480 cm^{-1}.

The remaining five bands must be assigned to deformation modes. Of these, three involve a motion of the doubly bonded oxygen atom and, consequently, should occur at higher frequencies. The two lowest frequency bands are assigned to the two F—Cl—F bending modes, ν_5 and ν_6, by analogy with ClF_3.[15] Of the remaining modes, the torsional motion should result in a band of very low intensity in both the infrared and the Raman spectrum. Obviously, only the 414-cm^{-1} band fulfills these requirements. The two highest frequency bands should belong to the F′—Cl=O scissoring and the rocking mode. On the basis of the observed and computed (see below) Cl isotopic shifts, we prefer to assign the scissoring mode, $\nu_3(A')$, to the 480-cm^{-1} band and the rocking mode, $\nu_8(A'')$, to 500 cm^{-1}. These assignments are supported by simple valence force field arguments and by comparison with the vibrational spectra of the related species, ClF_3,[15] ClF_2^-,[16] $ClF_2O_2^-$,[17] and ClO_2F[18] (see Table I).

Force Constants and Bonding.—The potential and kinetic energy metrics for chlorine trifluoride oxide were computed by a machine method.[19] The geometry assumed for this computation was $D(ClO) = 1.42$ Å, $R(ClF') = 1.62$ Å, $r(ClF) = 1.72$ Å, $\alpha(OClF') = 120°$, $\beta(OClF) = \gamma(FClF') = 90°$, based on the observed geometry for ClF_3[20] and a correlation between ClO bond length and stretching frequency.[21] In the absence of structural data, we assumed the oxygen atom, the fluorine atom, and the lone pair to require about the same space and, hence, to be about 120° apart. However, comparison with the known geometry of the trigonal-bipyramid type molecules SF_4[22] and SF_4O[23] indicates that the repulsion from a double bonded oxygen atom should be intermediate between that of a free electron pair and that of a fluorine ligand. Consequently, the true structure of ClF_3O might be expected to deviate somewhat from that used for our computations.



The symmetry coordinates used for ClF_3O are given in Table III. The bending coordinates were weighted by unit (1 Å) distance so the stretching force constants have units of mdyn/Å, the deformation force constants units of mdyn Å/radian², and the stretch–bend interaction constants mdyn/radian. The *G* matrix and *Z* transformation were found by the computer and, hence, are not given here.

TABLE III

SYMMETRY COORDINATES FOR ClF_3O

A′	S_1	$D(ClO)$
	S_2	$R(ClF')$
	S_3	$\alpha(OClF')$
	S_4	$(1/\sqrt{2})[r_1(ClF) + r_2(ClF)]$
	S_5	$(1/\sqrt{2})[\beta_1(OClF) + \beta_2(OClF)]$
	S_6	$(1/\sqrt{2})[\gamma_1(FClF') + \gamma_2(FClF')]$
A″	S_7	$(1/\sqrt{2})[r_1(ClF) - r_2(ClF)]$
	S_8	$(1/\sqrt{2})[\beta_1(OClF) - \beta_2(OClF)]$
	S_9	$(1/\sqrt{2})[\gamma_1(FClF') - \gamma_2(FClF')]$

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. The computed force constants are given in Table IV. An uncertainty estimate is difficult to make. However, numerical experiments with this and similar molecules indicate the uncertainties in the valence force constants to be 0.2 to 0.3 for Cl=O and 0.2 mdyn/Å for Cl—F. The force constants of greatest interest are the stretching force constants since they are a direct measure for the strength and covalent character of the various bonds. The value of 9.37 mdyn/Å obtained for $f_{Cl=O}$ is similar to those computed for ClO_2F (9.07 mdyn/Å)[18] and ClO_2^+ (8.96 mdyn/Å)[24] indicating double bond character. The value of 2.34 mdyn/Å computed for the axial Cl—F stretching force constant f_r is almost identical with that of 2.34 mdyn/Å, previously calculated[16] for ClF_2^-. The corresponding interaction constant, f_{rr}, is also very similar for both species. The relatively low value of f_r in ClF_2^- has previously been interpreted[16] in terms of semiionic three-center four-electron bonds. The same rea-

TABLE IV

INTERNAL FORCE CONSTANTS OF ClF_3O[a]

f_D	9.37	f_{rr}	0.26
f_R	3.16	$f_{\beta\beta}$	0.11
f_r	2.34	$f_{\gamma\gamma}$	0.13
f_α	1.84	$f_{r\beta} = -f_{r\beta'}$	0.25
f_β	1.69	$f_{\beta\gamma} = f_{\beta\gamma'}$	0.22
f_γ	1.87		

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian², and stretch–bend interaction constants in mdyn/radian.

---

(15) H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, **52**, 3517 (1970).

(16) K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, **6**, 1159 (1967).

(17) K. O. Christe and E. C. Curtis, *ibid.*, **11**, 35 (1972).

(18) D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, **20**, 1763 (1964).

(19) E. C. Curtis, *Spectrochim. Acta, Part A*, **27**, 1989 (1971).

(20) D. F. Smith, *J. Chem. Phys.*, **21**, 609 (1953).

(21) E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963).

(22) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963).

(23) J. L. Hencher, D. W. Cruickshank, and S. H. Bauer, *ibid.*, **48**, 518 (1968).

(24) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969).

soning[16] holds for the axial ClF bonds of ClF_3O and, hence, will not be repeated here. It should be pointed out, however, that in ClF_3O, enhancement of the ionic character of the axial ClF bonds is due to oxygen substitution, whereas in ClF_2^- it is due to the formal negative charge. Since the influence of oxygen substitution on the remaining ClF bonds has previously been discussed[17] at length for $ClO_2F_2^-$, it will not be reiterated. The value of 3.16 mdyn/Å computed for the equatorial ClF bond of ClF_3O is considerably larger than that of the axial bonds indicating[16] predominantly covalent bonding. In summary, the results from the force constant analysis are in excellent agreement with a generalized bonding scheme previously discussed[25] for a large number of halogen fluorides and suggest that the overall bonding in ClF_3O might be described by the following approximation. The bonding of the three equatorial ligands (including the free electron pair on Cl as a ligand and ignoring the second bond of the Cl=O double bond) is mainly due to a sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves mainly one delocalized p-electron pair of the chlorine atom for the formation of a semiionic three-center four-electron $p\sigma$ bond.

The deformation force constants computed for ClF_3O are as expected. The values for interaction constants cannot be unique; those not given in Table IV were assumed zero. The values for f_{rr}, $f_{\beta\beta}$, $f_{\gamma\gamma}$, and $f_{r\beta}$ are in accord with those for similar molecules.[26] Fitting ν_5 and ν_6 required nonzero values for $f_{\beta\gamma}$ and $f_{\beta\gamma'}$. Similarly, ν_7 and ν_8 required nonzero values for $f_{r\beta}$ and $f_{r\beta'}$. While these four interaction constants are strictly indeterminant, numerical experiments showed that the observed frequencies could not be fitted with significantly different values.

The computed potential energy distribution is given in Table V. The results were normalized, but the sums do not add up to 1.0 since the less important terms are not listed. As can be seen from Table V, most vibrations are highly characteristic except for ν_5 and ν_6, which are almost an equal mixture of the symmetry coordinates, S_5 and S_6. The ν_5 and ν_6 modes can be visualized as a symmetric bending motion of the two axial fluorine atoms in a plane perpendicular to the direction of the lone pair, and ν_6 as a symmetric bending motion in the plane containing the lone pair.

TABLE V

POTENTIAL ENERGY DISTRIBUTION FOR ClF_3O

Assignment		Frequency, cm^{-1}	Potential energy distribution
A′	ν_1	1223	$0.96f_D$
	ν_2	694	$0.76f_R + 0.16f_\alpha$
	ν_3	490	$0.76f_\alpha + 0.17f_r$
	ν_4	482	$0.90f_r + 0.10f_{rr}$
	ν_5	319	$0.61f_\gamma + 0.53f_\beta - 0.14(f_{\beta\gamma} + f_{\beta\gamma'})$
	ν_6	227	$0.41f_\beta + 0.30f_\gamma + 0.09(f_{\beta\gamma} + f_{\beta\gamma'})$
A″	ν_7	652	$0.89f_r + 0.14f_\beta - 0.09(f_{r\beta} + f_{r\beta'})$
	ν_8	500	$0.97f_\beta$
	ν_9	414	$0.80f_\gamma$

The ^{35}Cl–^{37}Cl isotopic shifts computed for ClF_3O from the above force constants are listed in Table VI.

TABLE VI

OBSERVED AND COMPUTED ^{35}Cl–^{37}Cl ISOTOPIC SHIFTS FOR ClF_3O

Normal mode		Isotopic shift, cm^{-1} Computed	Isotopic shift, cm^{-1} Obsd
A′	ν_1	11.8	10.9
	ν_2	9.0	8.8
	ν_3	2.7	2.0
	ν_4	0	0
	ν_5	1.4	
	ν_6	0.8	
A″	ν_7	11.2	11.2
	ν_8	0.5	1.2 or less
	ν_9	0	

As can be seen, the agreement between the observed and computed shifts is good and lends further support to the assignments suggested above. Thus, the possibility of assigning the bands at 686, 652, and 478 cm^{-1} to $\nu_{sym}(ClF_2(eq))$, $\nu_{asym}(ClF_2(eq))$, and $\nu(ClF(ax))$, respectively, of structure II can be ruled out based upon the lack of observing any ^{35}Cl–^{37}Cl isotopic splitting for the 478-cm^{-1} band.

Association in the Liquid and Pure Solid.—The relatively high boiling point and Trouton constant[2] of ClF_3O imply its association in the liquid phase. More specific evidence about the nature of this association can be obtained from the vibrational spectra recorded for the liquid and the solid and from a controlled diffusion experiment carried out for matrix isolated ClF_3O. Principally, association could involve either oxygen or fluorine bridges. In the case of fluorine bridges, distinction might be made between equatorial and axial fluorine bridges. The stretching frequencies of the bonds involved in the bridging should decrease when going from the gas or matrix isolated solid to the liquid or pure solid. On the other hand, the bonds not involved in the bridging should show no decrease or possibly a very small increase in frequency. Comparison between the infrared spectra of matrix isolated (trace A, Figure 4) and pure solid ClF_3O (trace C, Figure 4) reveals that the Cl=O stretching mode frequency increases by about 10 cm^{-1}, that the equatorial ClF stretching mode shows no detectable change, but that the antisymmetric axial FClF stretching frequency decreases by about 50 cm^{-1}. Similarly, the controlled diffusion experiment carried out for matrix isolated ClF_3O (trace B, Figure 4) shows the appearance of new bands on the high-frequency side of $\nu(Cl{=}O)$ and $\nu(Cl{-}F')$ and on the low frequency side of $\nu_{as}(FClF)$. Furthermore, a weak band observed at 468 cm^{-1} in the infrared spectrum of matrix isolated ClF_3O must be due to associated ClF_3O owing to its strong increase in relative intensity upon controlled diffusion. In addition, the Raman spectrum of the liquid (Figure 3) shows a pronounced frequency decrease only for $\nu_{sym}(FClF)$. Consequently, association appears to involve exclusively the axial fluorine atoms. This finding agrees with the association proposed[27] by Frey, Redington, and Aljibury for the structurally related, trigonal-bipyramidal molecules SF_4 and ClF_3.

A decrease of the volatility of ClF_3O due to extensive self-ionization (*i.e.*, $2ClF_3O \rightleftarrows ClF_2O^+ClF_4O^-$) in the liquid or solid phase can be ruled out since it should result in more dramatic changes in the spectra upon phase change. Furthermore, no evidence for the presence of

---

(25) K. O. Christe, paper presented at the Fourth International Fluorine Symposium, Estes Park, Colo., July 1967.

(26) K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **357**, 125 (1968).

(27) R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, **54**, 344 (1971).

the bands characteristic for ClF_2O^+[7] and ClF_4O^-[8] could be detected in the spectra of liquid or solid ClF_3O.

Thermodynamic Properties.—The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation.[28] These properties are given for the range 0–2000°K in Table VII.

Acknowledgment.—The authors wish to express their gratitude to Dr. D. Pilipovich for continuous encouragement of this work and stimulating discussions, and to Mr. R. D. Wilson for his help in the preparation of some of the samples. We are indebted to Dr. J. Cape of the Science Center of North American Rockwell Corporation for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch, and by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under Contract AF 49(638)-1734.

TABLE VII

THERMODYNAMIC PROPERTIES FOR ClF_3O

T, °K	C_p°, cal/mol	$H° - H_0°$, kcal/mol	$-(F° - H_0°)/T$, cal/(mol deg)	$S°$, cal/(mol deg)
0	0	0	0	0
100	9.721	0.837	49.255	57.624
200	14.932	2.072	55.613	65.971
298.15	18.593	3.732	60.159	72.675
300	18.646	3.766	60.237	72.790
400	20.875	5.751	64.108	78.486
500	22.260	7.913	67.478	83.305
600	23.160	10.187	70.470	87.448
700	23.771	12.536	73.159	91.067
800	24.200	14.936	75.602	94.271
900	24.512	17.372	77.838	97.141
1000	24.744	19.835	79.900	99.736
1100	24.921	22.319	81.813	102.103
1200	25.059	24.818	83.595	104.277
1300	25.168	27.330	85.265	106.288
1400	25.256	29.851	86.834	108.156
1500	25.328	32.380	88.314	109.901
1600	25.387	34.916	89.715	111.538
1700	25.437	37.458	91.044	113.078
1800	25.479	40.003	92.309	114.533
1900	25.514	42.553	93.516	115.912
2000	25.545	45.106	94.668	117.221

[28] J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York, N. Y., 1940.

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

Chlorine Trifluoride Oxide. IV. Reaction Chemistry

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

Received September 8, 1971

Reactions of chlorine trifluoride oxide, ClF_3O, with Cl_2, Cl_2O, $ClOSO_2F$, N_2F_4, HNF_2, and NF_2CFO are reported. In these reactions, ClF_3O either fluorinates, oxygenates, or both oxygenates and fluorinates the substrates. The interaction of ClF_3O with PtF_6 is also described. In this reaction, ClF_3O liberates F_2 and forms the new complex, $ClF_2O^+PtF_6^-$. Characterizing data for the complex are given.

Introduction

In the preceding papers,[1-3] we reported the preparation and properties of the new chlorine oxyfluoride, ClF_3O. Since ClF_3 is a powerful oxidative fluorinating agent, it was anticipated that ClF_3O would be similarly reactive as a fluorinating, as well as an oxygenating agent. This paper describes some of the reaction chemistry of ClF_3O.

Experimental Section

Apparatus.—Experimental techniques used in these studies were essentially the same as those described elsewhere.[1-4] Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries (~0.5 mm o.d.). Gas chromatographic analyses were performed using the method of Dayan and Neale.[5] A Hanovia utility lamp (catalog no. 30620) was used for the photolyses.

Materials.—The preparation and purification of ClF_3O, Cl_2O, $ClOSO_2F$, HNF_2, and NF_2CFO are described elsewhere.[1,6-9] Chlorine (Matheson Co.), tetrafluorohydrazine (Allied Chemical Corp.), and platinum hexafluoride (Ozark Mahoning Co.) were purchased and purified by fractional condensations.

Reactions of Chlorine Trifluoride Oxide. With Chlorine.—At room temperature, chlorine and ClF_3O do not interact. An equimolar mixture (100 cm³, 4.46 mmol each) of the two when heated at 200° for 16 hr in a 30-ml stainless steel cylinder did result in complete consumption of the ClF_3O. The products were separated by fractional condensation at −142 and −196° and analyzed by infrared spectroscopy and gas chromatography. Chlorine monofluoride was the principal product (262 cm³, 11.7 mmol) with only a small amount of ClO_2F (6.7 cm³, 0.3 mmol) and unreacted Cl_2 (15.7 cm³, 0.7 mmol) being observed. Noncondensables (O_2) were also produced. When kept at 100° for 2 days, ClF_3O reacted with Cl_2 only partially (~30%) to give ClF_3, ClF, and ClO_2F as the major reaction products.

With Dichlorine Monoxide.—Chlorine trifluoride oxide (76.5 cm³, 3.42 mmol) and an equal quantity of Cl_2O were separately condensed at −196° into a Kel-F reactor fitted with a Teflon valve. (Previous experiments in stainless steel cylinders resulted in extensive decomposition of the Cl_2O, apparently due to

---

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

[2] D. Pilipovich, R. H. H. Rogers, and D. Wilson, *ibid.*, **11**, 2192 (1972).

[3] K. O. Christe and E. C. Curtis, *ibid.*, **11**, 2196 (1972).

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

[5] V. H. Dayan and B. C. Neale, *Advan. Chem. Ser.*, **No. 54**, 223 (1966).

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

[7] C. J. Schack and R. D. Wilson, *Inorg. Chem.*, **9**, 311 (1970).

[8] E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. G. Warner, *J. Inorg. Nucl. Chem.*, **17**, 188 (1961).

[9] G. W. Fraser and J. M. Shreeve, *Inorg. Chem.*, **4**, 1497 (1965).