CHLORINE OXYFLUORIDES

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I. Introduction

This review is limited to compounds containing both oxygen and fluorine atoms bonded directly to a common chlorine central atom. Therefore, compounds, such as fluorine perchlorate (O_3ClOF), have not been included. Data on O_3ClOF were summarized in a recent review on inorganic hypofluorites (*180*).

The subject of chlorine oxyfluorides* has been reviewed in 1963 by Schmeisser and Brändle (*253*) and in 1969 in "Gmelin's Handbuch der

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* For the sake of clarity, we have not followed a rigid system of nomenclature, such as starting formulas with the central atom followed by the ligands. If, for example, FClO is written as ClOF, an uninformed reader might be induced to think of the compound as a hypofluorite.

Anorganischen Chemie" (*122*). However, both reviews deal only with chloryl fluoride ($FClO_2$) and perchloryl fluoride ($FClO_3$). Since the writing of these reviews, three of the four possible remaining chlorine oxyfluorides i.e., FClO, F_3ClO, and F_3ClO_2, have been characterized, and claims have been made for the synthesis of the fourth one, ClF_5O. Additional information on chlorine oxyfluorides can be found in various monographs and textbooks (*32*, *75*, *77*, *95*, *156*, *169*, *244*) and in particular in "Comprehensive Inorganic Chemistry" in the chapter on the halogens written by Downs and Adams (*84*). A second area of significant recent progress comprises ions derived from chlorine oxyfluorides. Therefore, these are also discussed in detail.

For the present review, the literature cited in *Chemical Abstracts* (Jan. 1965–Dec. 1973) was used in addition to more recent work pub-

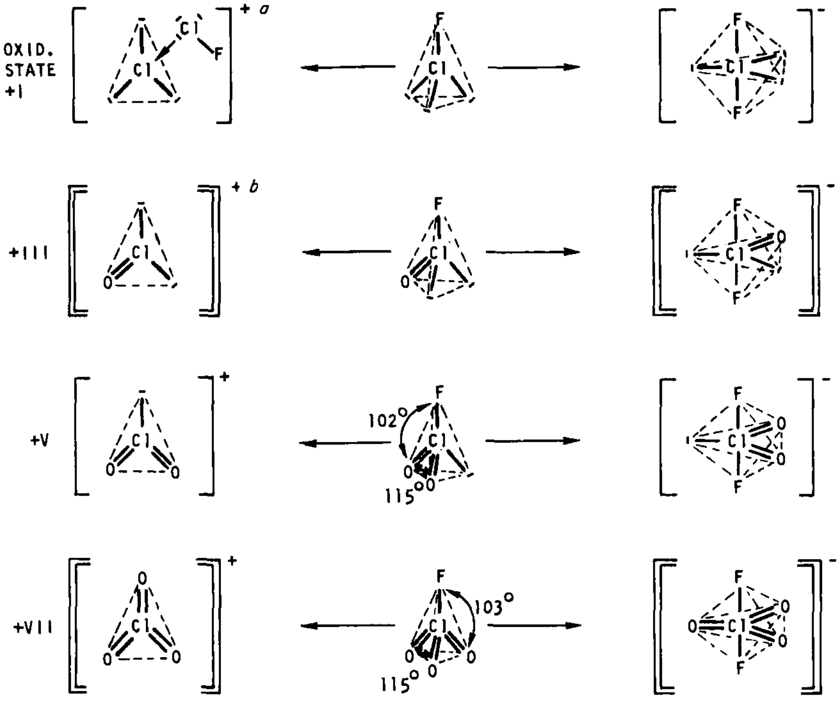


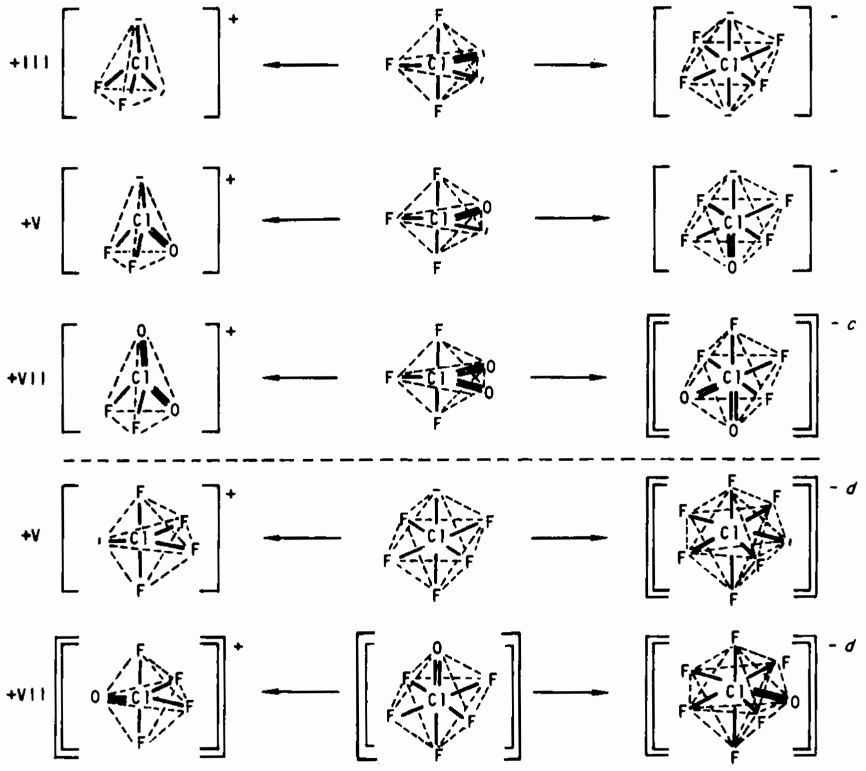
FIG. 1. Geometries of the chlorine oxyfluoride molecules and their ions compared to those of the corresponding chlorine fluorides. [a] Since the Cl^+ cation would possess only an electron sextet, it is stabilized by a ClF molecule to form the Cl_2F^+

lished during 1973 and 1974. For literature before 1965, we have relied mainly on Schmeisser's review (*253*) and Gmelin's handbook (*122*).

In addition to a discussion of the individual compounds, a section was added correlating the physical and chemical properties of the chlorine oxyfluorides with their structure. In the Appendix, full tables of thermodynamic properties are given for each compound, where known.

II. General Aspects

Since most of the physical and chemical properties of the chlorine oxyfluorides can be readily correlated with their molecular structure, we shall discuss briefly some of the more general aspects.



cation. [b] Double brackets indicate yet unknown ions. [c] See text for preference of cis model. [d] These compounds with a coordination number of 7 are unlikely to exist.

A. GEOMETRY

As can be seen from Fig. 1, the structures of all the chlorine oxyfluoride molecules and ions can be derived from those of the corresponding binary chlorine fluorides *(53)* by replacing a free chlorine valence electron pair by a doubly bonded oxygen atom without significant rearrangement of the rest of the molecule.

The only possible exception to this rule could be the yet unknown *(68)* $ClF_4O_2^-$ anion. By comparison with the known structures of the pseudoisoelectronic $IF_4O_2^-$ *(45, 93)* and $TeF_4O_2^{2-}$ *(260)* anions, the 2 oxygens in $ClF_4O_2^-$ should also be in cis and not in trans position. In these and similar oxyfluoride anions, such as SF_5O^- *(65)* or CF_3O^- *(59)*, the negative charge is located mainly on the most electronegative ligands, i.e., fluorine. Furthermore, in pseudo-octahedral species not containing a free valence electron pair on the central atom, such as XF_5O^-, the fluorine trans to the less electronegative ligand appears to be more weakly bonded than the remaining fluorines. This is plausible from molecular orbital arguments. Therefore, for $XF_4O_2^-$ the structure with 2 oxygen atoms trans to 2 fluorines and cis with respect to each other, should favor the resonance structures having the negative charge located on the fluorine ligands.

Since the degree of mutual repulsion decreases in the order, free valence electron pair > double-bonded oxygen > fluorine, the observed bond angles deviate somewhat from those expected for the ideal geometries. Typical examples are $FClO_2$ and $FClO_3$ (Fig. 1).

The structure of radicals and radical ions can also readily be predicted by treating an unpaired electron in the same manner as a free valence

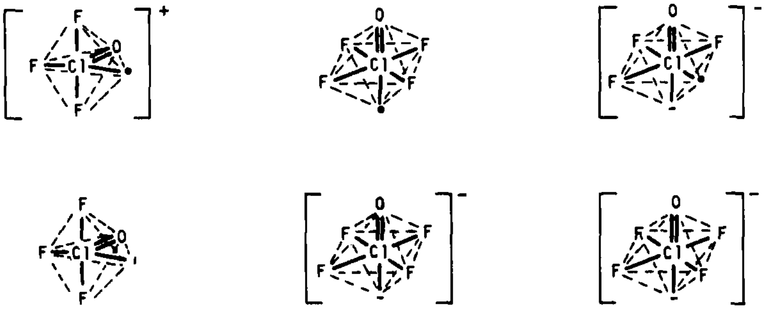


FIG. 2. Structures of the yet unknown ClF_3O^+, ClF_4O, and ClF_3O^- radicals (upper row) predicted by comparison with the known structures (bottom row) of ClF_3O and ClF_4O^-.

electron pair. Therefore, a chlorine oxyfluoride free radical should have the same geometry as the corresponding anion with identical fluorine and oxygen ligands (Fig. 2). Similarly, the structure of a radical cation should be analogous to that of the corresponding molecule having the same ligands. For a radical anion, however, the additional sterically active valence electron will increase the coordination number around the central atom by 1. This should result in a geometry resembling that of the anion containing one F ligand more, but in which one F ligand is replaced by the sterically active free electron. The exact spin distribution would have to be determined experimentally and is not necessarily the same as shown in Fig. 2.

B. Ligand Distribution

As can be seen from Fig. 1, the structures are simple and can be logically predicted if one keeps in mind that free valence electron pairs on the central atom are sterically active and behave as a ligand. For 3, 4, 5, and 6 ligands, always the sterically most favorable arrangements are observed, namely, the triangular plane, tetrahedron, trigonal bipyramid, and the octahedron, respectively (*119*). Based on the information available for halogen oxyfluorides and related compounds such as xenon or chalcogen oxyfluorides the following conclusions concerning the ligand distribution can be reached. In a triangular plane and a tetrahedron all positions are equivalent. In a trigonal bipyramid the two axial positions are occupied by the most electronegative ligands, i.e., F atoms. In octahedrons of the type XF_5A only one arrangement is possible. For XF_4AB, however, the A or B ligands are trans if A and B are either two free electron pairs or one free electron pair and one oxygen ligand. When A and B are 2 O atoms, the cis arrangement appears more favorable (see above). The case of the pentagonal bipyramid is not of practical interest since it appears that the coordination number around a high oxidation state, chlorine central atom is limited to a maximum of 6.

C. Relative Bond Strengths

Unfortunately, exact bond lengths are known only for $FClO_2$ (*220*) and $FClO_3$ (*72*). However, complete vibrational spectra have been published for essentially all of the chlorine oxyfluorides. These can be used for the evaluation of the corresponding force constants. Since the latter are a good measure for the relative strengths of these bonds, their comparison is interesting. As can be seen from Table I, the ClO bonds all

TABLE I

STRETCHING FORCE CONSTANTS OF SOME CHLORINE OXYFLUORIDES

Oxidation state	Compound	f_{ClO} (mdyn/Å)	f_{ClF} (mdyn/Å) I[a]	II[b]	III[c]	Ref.
+VII	$ClF_2O_2^+$	12.1	4.46	—	—	(*69*)
+V	ClF_2O^+	11.20	3.44	—	—	(*58*)
+VII	$FClO_3$	9.4	3.9	—	—	(*174*)
+V	ClF_3O	9.37	3.16	2.34	—	(*55*)
+VII	ClF_3O_2	9.23	3.35	2.70	—	(*57*)
+V	ClF_4O^-	9.13	—	1.79	—	(*56*)
+V	$FClO_2$	9.07	—	—	2.5	(*270*)
+V	ClO_2^+	8.96	—	—	—	(*66*)
+V	$ClF_2O_2^-$	8.3	—	1.6	—	(*54*)
+III	$FClO$	6.85	—	—	2.59	(*5*)

[a] Mainly covalent bonds.

[b] Mainly semi-ionic 3c–4e bonds

[c] Special case of highly polar $(p—\pi^*)\sigma$ bonds.

possess more or less double-bond character. The variation in the values of the ClO-stretching force constants is mainly due to the combination of several effects. For example, a formal positive charge (i.e., in cations), a high oxidation state of the central atom, and a high number of fluorine ligands tend to increase the ClO-stretching force constant (*57*). In contrast to the ClO bonds, the ClF bond strengths are subject to much

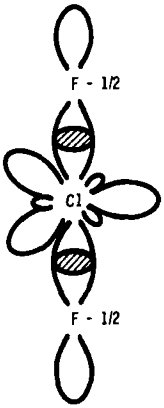


FIG. 3. Schematic bonding in ClF_2^- as explained by a semi-ionic 3c–4e bond model.

larger changes. These strong variations cannot be explained by effects such as listed above for the ClO bonds or by the Gillespie–Nyholm valence shell, electron pair repulsion (VSEPR) theory (*119*) alone. By analogy with the halogen fluorides (*53*), it is necessary to assume contributions from two different kinds of bonding. In addition to the normal covalent bonds possessing a bond order of about 1, the occurrence of semi-ionic 3 center–4 electron bonds (*130*, *232*, *243*) must be invoked. The principle of a semi-ionic 3c–4e bond is demonstrated in Fig. 3. For simplicity, ClF_2^- (*63*) was chosen as an example. Ideally, the two F ligands form two semi-ionic 3c–4e [p--p] σ-bonds with one p electron pair of the chlorine central atom, whereas the free Cl valence electron pairs form an sp^2 hybrid.

Instead of using this semiempirical molecular orbital model, the bonding in ClF_2^- can also adequately be described in the valence-bond representation (*76*) as a resonance hybrid of the following canonical forms: (F—Cl) F^- and F^-(Cl—F). This results in the same average charge distribution as in the molecular orbital model, i.e., $^{-1/2}F\text{-}Cl\text{-}F^{-1/2}$. Another and the simplest bond model, proposed by Bilham and Linnett (*29*) for XeF_2 which is pseudoisoelectronic with ClF_2^-, assumes single electron bonds for each X—F bond. It is relatively immaterial, which of these three descriptions is preferred since all of them result in the same charge distribution and a Cl—F bond order of about 0.5.

As can be seen from Table I, these weak ClF bonds occur only when the central atom has a coordination number in excess of 4 and possesses at least one free Cl valence electron pair. In addition to Gillespie's simple VSEPR theory, the following general rule has been proposed by Christe (*53*), which permits the prediction of whether, and how many, semi-ionic bonds are to be formed:

> The free valence electron pairs on the central atom seek high *s*-character; i.e., sp^n hybridization. If the number of ligands is larger than 4 and one or more of them are free valence electron pairs, then as many F ligands form linear semi-ionic 3 center–4 electron bonds as are required to allow the free electron pairs to form an sp^n hybrid with the remaining F ligands. These semi-ionic 3c–4e bonds are considerably weaker and longer than the mainly "covalent" sp^n hybrid bonds.

This rule also holds for the chlorine oxyfluorides as well as for the chlorine fluorides for which it was originally formulated.

An additional effect, however, must be invoked to be able to rationalize fully the experimental data. Inspection of Table I reveals that the ClF-stretching force constants of $FClO_2$ and FClO are significantly lower than expected from the above discussion. In particular, if the known ClF-stretching force constants and bond distances within the pseudo-

TABLE II

COMPARISON OF ClF-STRETCHING FORCE CONSTANTS AND BOND LENGTHS WITHIN THE PSEUDOTETRAHEDRAL SERIES FCl, FClO, $FClO_2$, $FClO_3$

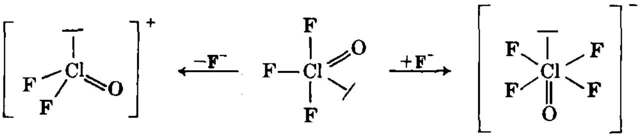
Molecule	f_{ClF} (mdyn/Å)	r_{ClF} (Å)	Ref.	
FCl	4.56	1.628	(*122*)	(*122*)
FClO	2.59	—	(*5*)	—
$FClO_2$	2.5	1.697	(*270*)	(*220*)
$FClO_3$	3.9	1.610	(*174*)	(*72*)

tetrahedral series FCl, FClO, $FClO_2$, $FClO_3$ are compared (see Fig. 1 and Table II), it becomes obvious that the ClF bonds in FClO and $FClO_2$ are abnormally long and weak. Application of the rules discussed above is of no help in explaining the observed trends. However, if a simple molecular orbital description, similar to that proposed by Spratley and Pimentel (*274*) for FNO and F_2O_2, is used, the data can be rationalized. Molecules FCl, FClO, $FClO_2$, and $FClO_3$ can be thought of as being derived from the combination of an F atom with the Cl, ClO, ClO_2, and ClO_3 radicals, respectively. This hypothetical bond formation involves a 2p electron of the fluorine atom and the unpaired electron of the Cl-containing radical. If according to the example of $(NO)_2$ and $(CN)_2$, given by Spratley and Pimentel (*274*), the unpaired electron occupies an antibonding (π^*) orbital, the resulting bond is very weak. On the other hand, if the unpaired electron occupies a bonding orbital the resulting bond is strong. Since the unpaired electron in Cl and ClO_3 occupies a bonding orbital, the resulting Cl—F bond in FCl and $FClO_3$, respectively, should be strong, whereas those in FClO and $FClO_2$, derived from ClO and ClO_2, respectively, with an antibonding (π^*) electron (*193*), should be weak. These predictions are in excellent agreement with the data of Table II. As a consequence of the high electronegativity of fluorine, most of the electron density in the antibonding (π^*) orbital of ClO or ClO_2 is transferred to the F atom. For FClO and $FClO_2$, this results in a long and highly polar ClF bond with a significant negative charge located on F. Since at the same time electron density is removed from an antibonding orbital of the ClO_n part of the molecule, the bond strength of these ClO bonds is increased. As pointed out by Chi and Andrews (*47*) for ClClO, there is a marked difference in behavior between radicals with a first-row element central atom and those with a second-row element central atom. Owing to their larger size and polarizability, the second-row elements facilitate a charge transfer and the XY_n stretching frequencies usually increase upon combination of XY_n with a halogen radical. For first-row element central atoms, the corresponding frequencies usually show a slight decrease. It should be pointed out, however, that in both cases a highly polar and weak bond of the type $\overset{\delta-}{F}—\overset{\delta+}{X}Y_n$ results, provided the unpaired electron in the XY_n parent radical occupies an antibonding orbital. Supporting evidence for the above postulated charge transfer from XY_n to F was recently given by Parent and Gerry (*220*) for $FClO_2$.

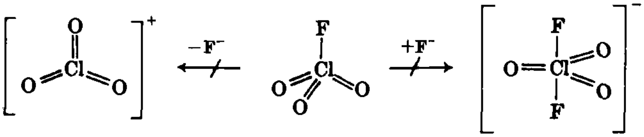
In summary, three types of bonding are invoked to rationalize the remarkable differences in Cl—F bonds encountered for chlorine fluoride oxides. These are (*a*) conventional, mainly covalent bonds, (*b*) weak semi-ionic 3 center–4 electron bonds, and (c) weak highly polar $(p—\pi^*)\sigma$ bonds. It must be kept in mind, however, that all these bond descriptions are idealized extremes, used mainly for didactic reasons. The actual bonds may contain significant contributions from more than one kind of bonding and, as a consequence, there is little black and white, but many shades of gray. Obviously, other bond models can also be used, so long as they adequately account for the experimental data. The steady increase in our knowledge about these compounds is bound to result in significant improvements of these rather empirical and intuitive bond models.

D. AMPHOTERIC NATURE, TENDENCY TO FORM ADDUCTS, AND REACTIVITY

In many respects the chlorine oxyfluorides resemble the chlorine fluorides. For example, they exhibit little or no self-ionization, but are amphoteric. With strong Lewis acids or bases they can form stable adducts. The tendency to form adducts was found (*64*) not to be so much a function of the relative acidity of the parent chlorine oxyfluoride but rather to depend on the structure of the amphoteric molecule and of that of the anion or the cation formed. The preferred structures are the energetically favored tetrahedron and octahedron. Consequently, a trigonal bipyramidal molecule, such as ClF_3O (*64*), exhibits a pronounced tendency to form either a stable pseudotetrahedral cation or a pseudooctahedral anion:



On the other hand, tetrahedral $FClO_3$ does not form an adduct with either Lewis acids or bases (*167*, *209*, *224*):



Similarly, the chemical reactivity of these two chlorine oxyfluorides differs vastly: whereas ClF_3O is extremely reactive and cannot be handled even in a well-dried glass vacuum system, $FClO_3$ reacts only slowly with water.

III. Specific Compounds

A. CHLORINE MONOFLUORIDE OXIDE

According to Ruff and Krug (*242*), FClO is formed during hydrolysis of ClF_3 as a solid melting at −70°C to a red liquid which is unstable in the gas phase. However, no conclusive proof for the existence of FClO was given, and it appears that the red color observed may have been due to the presence of chlorine oxides. Heras and co-workers (*137*) have proposed the formation of FClO as an intermediate in the thermal decomposition of $FClO_2$. More recent studies by Bougon and co-workers on the hydrolysis of ClF_3 (*9*, *36*), by Christe on the reaction of ClF_3 with $HONO_3$ (*51*) and on the reaction of ClF_3O with SF_4 (*60*), by Pilipovich *et al.* on the photochemical synthesis of ClF_3O (*228*), and by Schack *et al.* on the reaction chemistry of ClF_3O (*246*) all point to the formation of FClO as an intermediate that is unstable with respect to disproportionation:

$$2FClO \longrightarrow FClO_2 + ClF$$

Attempts to stabilize the FClO formed as an intermediate by complexing with a strong Lewis acid, such as AsF_5 to give $ClO^+AsF_6^-$, were also unsuccessful. Thus the controlled hydrolysis of $ClF_2^+AsF_6^-$ with stoichiometric amounts of H_2O in HF solution resulted only in the formation of $ClO_2^+AsF_6^-$ (*51*). This is not surprising since Lewis acids are known to catalyze such disproportionation reactions.

Recently, Cooper and co-workers (*74*) succeeded in obtaining direct evidence for the existence of free FClO in the gas phase. During a study of the hydrolysis of excess ClF_3 in a flow reactor, a novel species was observed in the infrared spectrum showing a PQR band centered at 1032 cm^{-1}. The species causing this band was found to decompose at ambient

TABLE III

OBSERVED AND CALCULATED FREQUENCIES FOR THE FClO SPECIES[a]

Isotope	Assignment	Obsd. (cm^{-1})	Calcd. (cm^{-1})
$F^{35}Cl^{16}O$	ν_1	1038.0	1038.3
	ν_2	593.5	593.9
	ν_3	315.2	316.0
$F^{37}Cl^{16}O$	ν_1	1029.0	1028.9
	ν_2	587.5	588.4
	ν_3	315.2	313.8
$F^{35}Cl^{18}O$	ν_1	999.2	999.5
	ν_2	593.5	592.6
	ν_3	307.0	308.3
$F^{37}Cl^{28}O$	ν_1	990.1	989.6
	ν_2	587.5	587.1
	ν_3	307.0	306.2

[a] Data from Andrews *et al.* (*5*).

temperature with a half-life of about 25 sec into $FClO_2$ and ClF. If an excess of H_2O was used in the hydrolysis, no FClO but the expected (*9*, *36*) ClO_2 was observed as the main product.

The results of Cooper *et al.* were confirmed by a matrix isolation study by Andrews and associates (*5*). The latter authors observed the same species during the photolysis (2200–3600 Å) of argon matrix-isolated ClF and O_3 in the temperature range 4°–15°K. All three fundamentals expected for a bent FClO molecule were observed, and their assignment to FClO was confirmed by the measurement of the ^{18}O and ^{37}Cl isotopic

TABLE IV

FORCE FIELD OF FClO ASSUMING A BOND ANGLE OF 120° AND ALL INTERACTION CONSTANTS TO BE ZERO[a]

$f_{ClO} = 6.85$ mdyn/Å
$f_{ClF} = 2.59$ mdyn/Å
$f_{\alpha} = 0.92$ mdyn Å/rad²

[a] Data from Andrews *et al.* (*5*).

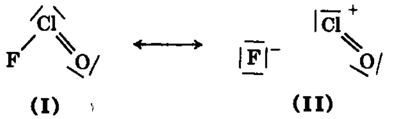
shifts (Table III) and by force field computations (Table IV). For the force field computation, an FClO bond angle of 120° was assumed. However, on the basis of the increased repulsion from the chlorine free valence electron pairs (see Section II, A), we would expect this angle to be less than the tetrahedral angle of 109°, but larger than that found for ClF_2^+ [103.17° in $ClF_2^+AsF_6^-$ (*181*) and 95.9° in ClF_2^+ SbF_6^- (*88*)]. The small size of the molecule, its high dipole moment, the naturally occurring ^{37}Cl isotope, and its half-life at ambient temperature make it ideally suited for a structure determination by microwave spectroscopy in a flow system.

The force field reported (*5*) for FClO allows some conclusions concerning the strength of the bonds in this molecule. Comparison of the ClO-stretching force constant of FClO with those of the higher oxidation state species listed in Table I makes the FClO value appear surprisingly low. However, when compared to species of similar oxidation state and geometry (Table V), FClO exhibits a value very much in line with our expectations for a ClO double bond. The ClF bond is relatively weak,

TABLE V

COMPARISON OF THE ClO-STRETCHING FORCE CONSTANTS AND BOND ORDERS OF FClO WITH THOSE OF RELATED PSEUDOTETRAHEDRAL SPECIES HAVING A COMPARABLE OXIDATION STATE

Species	Oxidation state	f_{ClO} (mdyn/Å)	Bond order	Ref.
ClO_2^-	+III	4.26	1.5	(*266*)
FClO	+III	6.85	2	(*5*)
ClO_2	+IV	7.02	2	(*161*)

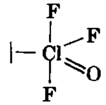


(I) (II)

indicating that contributions from resonance structures, such as II, are significant as is also the case in the related $FClO_2$ molecule. The high ionicity of the Cl—F bond in these two chlorine fluoride oxides has been discussed above (Section II, C) in terms of a $(p—\pi^*)\sigma$ bond.

B. CHLORINE TRIFLUORIDE OXIDE

Chlorine trifluoride oxide,



(III)

was discovered in 1965 at Rocketdyne by Pilipovich *et al.* (*226*, *231*). However, these results were not published until 1972 owing to classification. The same compound was independently discovered in 1970 by Bougon and co-workers (*37*, *39*). A minor modification of Bougon's synthesis by Züchner and Glemser also produced (*300*) ClF_3O. All the data on ClF_3O, except for the short note by Züchner *et al.*, were obtained either at Rocketdyne or at the Centre d'Etudes Nucléaires de Saclay.

Owing to its pseudotrigonal bipyramidal structure with two highly polar Cl—F bonds, ClF_3O possesses only low kinetic stability. This renders it a powerful fluorinating and oxygenating agent requiring the use of metal or Teflon or Kel-F equipment for its handling.

1. *Synthesis*

Several synthetic routes to ClF_3O were developed at Rocketdyne (*226*, *228–231*, *240*). One of these involves the fluorination of Cl_2O at −78°C:

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

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

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. 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 an adduct with ClF_3O (*64*), stabilization of the product by complex formation does not seem to influence the ClF_3O yields strongly.

Owing to unpredictable explosions experienced 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°C provided the fluorine was suitably activated by methods such as glow discharge. Unactivated fluorine did not interact with Cl_2O at −196°C. The relatively low yield of ClF_3O (1–2%) makes this modification impractical.

The low-temperature fluorination of $NaClO_2$ produced ClF_3O in low yield (*175*, *226*). However, the low yields and poor reproducibility make this route unattractive.

The method (*176*, *226*, *229*) most suitable for the preparation of ClF_3O on a larger scale involves the fluorination of chlorine nitrate at −35°C according to:

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

The main advantages of this process are (*a*) less fluorine is required than in the fluorination reactions of Cl_2O yielding ClF_3 as a coproduct, (*b*) the great difference in the volatilities of products FNO_2 and ClF_3O ($\Delta T_{\mathrm{bp}} \sim 100$°C) permits an easy separation by fractional condensation, and (*c*) chlorine nitrate can be made more conveniently and, most importantly, does not appear to be hazardous in its handling. 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 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 ($T < 0$°C) are indicated.

A convenient laboratory method for the synthesis of ClF_3O involves UV photolysis of systems containing Cl, F, and oxygen starting materials. At Rocketdyne (*228*, *230*, *240*), ClF_3O was prepared from seven different systems, including a direct synthesis from the elements Cl_2, F_2, and O_2. Bougon *et al.* (*37*, *39*) obtained ClF_3O in high yield from $ClF_3 + OF_2$. The latter synthesis was modified by Züchner *et al.* (*300*) by replacing ClF_3 with ClF_5.

In small-scale operations, ClF_3O can conveniently be purified by complexing it with KF at room temperature. Impurities, such as $FClO_2$, that do not form an adduct under these conditions can be pumped off.

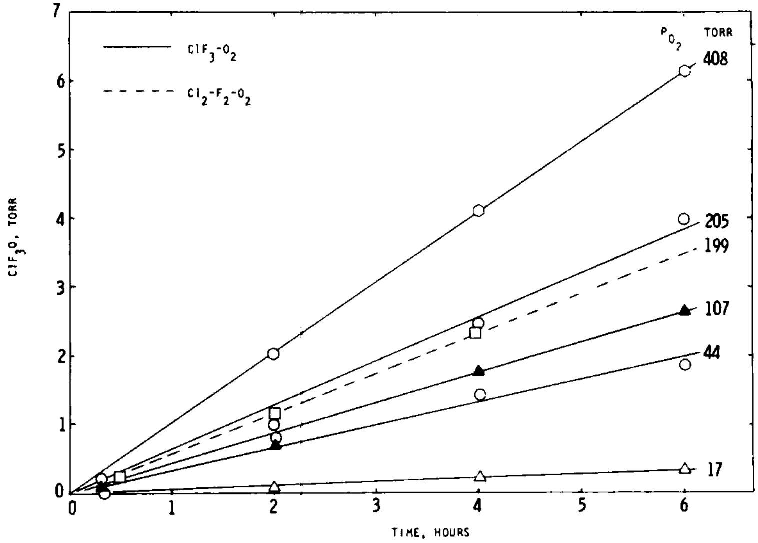


FIG. 4. Chlorine trifluoride oxide formed as a function of time and oxygen partial pressure ($P_{ClF_3} = 10$ torr).

Pure ClF_3O can be obtained by vacuum pyrolysis at 50° to 70°C, whereas compounds, such as ClF_3, which form a more stable KF adduct remain complexed *(226)*.

A detailed kinetic study of the photolyses of the ClF_3—O_2 and of the Cl_2—F_2—O_2 systems was carried out by Axworthy *et al.* *(10)*. Contrary to the original report *(228)*, the rate of ClF_3O formation was demonstrated to be the same for both systems, to increase with O_2 concentration, and to be independent of irradiation time (Fig. 4). Furthermore, the rate of ClF_3O formation was shown to be proportional to the intensity of the 1847 Å band of the Hg spectrum indicating that the dissociation of O_2 to two ground-state, ^{3}p, oxygen atoms is the primary photochemical process. The following mechanism was proposed which requires the photochemical dissociation of ClF_3 as well:

$$O_2 \xrightarrow{h\nu\ (1847\ \text{Å})} O + O$$

$$ClF_3 \xrightarrow{h\nu\ (2000-3500\ \text{Å})} ClF_2 + F$$

$$O + ClF_2 \longrightarrow ClF_2O$$

$$ClF_2O + F_2 \longrightarrow ClF_3O + F$$

The photolysis of ClF_3 was investigated under similar conditions. A photochemical steady state was quickly achieved, where $[F_2] = [ClF] = \alpha[ClF_3]$, and α has a value of about 1 at low and of about 3 at high pressures. These results together with the known photochemical decomposition of OF_2 (*113*) explain why ClF_3O can be readily generated by the photolysis of so many different starting materials.

2. *Molecular Structure*

Although the exact geometry of ClF_3O has not yet been established, its approximate structure is known from vibrational and ^{19}F NMR spectroscopy. Its UV spectrum has also been reported (*228*).

The ^{19}F NMR spectrum of ClF_3O was studied by several groups. A single signal at $\phi = -262$ (*226*) or -253 (*300*) ppm was reported for liquid ClF_3O. For the gas, a singlet at $\phi = -327$ ppm was observed (*226*).

TABLE VI

VIBRATIONAL SPECTRA OF ClF_3O GAS AND LIQUID AND THEIR ASSIGNMENT IN POINT GROUPS C_s[a]

Observed frequencies (cm^{-1}) and relative intensities				Assignment	Approximate description of mode
Gas		Solid matrix IR	Liquid Raman		
IR	Raman				
1228					
1224 s	1222 (1.5) p	1223 s	1224 (1.0) p	$\nu_1(A')$	$\nu(^{35}Cl{=}O)$
1218					
1213	1211 (0.5) p	1212 m		$\nu_1(A')$	$\nu(^{37}Cl{=}O)$
701	694 (2.6) p	686 s	689 (2.7) p	$\nu_2(A')$	$\nu(^{35}Cl{-}F')$
684	686 sh, p	678 m		$\nu_2(A')$	$\nu(^{37}Cl{-}F')$
676 vs		652 vs		$\nu_7(A'')$	$\nu_{as}(F^{35}ClF)$
666		641 s		$\nu_7(A'')$	$\nu_{as}(F^{37}ClF)$
		499 m		$\nu_8(A'')$	$\delta_{rock}(O^{35}ClF')$
501	500 (1)		497 sh		
		498 sh		$\nu_8(A'')$	$\delta_{rock}(O^{37}ClF')$
491 ms	489 (1)	486 mw		$\nu_3(A')$	$\delta_{sciss}(O^{35}ClF')$
		484 w		$\nu_3(A')$	$\delta_{sciss}(O^{37}ClF')$
481	482 (10) p	478 mw	466 (10)	$\nu_4(A')$	$\nu_s FClF$
412 w	414 (0.2) dp	414 w	405 (0.5) sh	$\nu_9(A'')$	τ
323 313 m	319 (0.1)	323 mw	316 (0.3) p	$\nu_5(A')$	$\delta_s FClF$ out of $F\ddot{C}lF$ plane $\equiv \delta_{wag} OClF'$
230 mw	224 (0.4) p		227 (1.2) p?	$\nu_6(A')$	$\delta_s FClF$ in $F\ddot{C}lF$ plane

[a] Data from Christe and Curtis (*55*).

From nuclear relaxation time measurements, Alexandre and Rigny (*3*) were able to determine the chemical shift difference between the equatorial and the 2 axial fluorine atoms as 50 ± 2 ppm. They also obtained a value of 195 Hz for the mean Cl—F coupling constant and values for the exchange time between the fluorine atoms.

Vibrational spectroscopy (*37*, *55*, *300*) provided the best evidence for ClF_3O possessing a pseudotrigonal bipyramidal structure of symmetry C_s, in which 2 fluorines occupy the axial and 1 fluorine, 1 oxygen, and a sterically active free valence electron pair occupy the equatorial positions (see structure III). At Rocketdyne (*55*), a thorough spectroscopic study was carried out including the infrared spectra of gaseous, solid, and matrix-isolated ClF_3O and the Raman spectra of the gas and the liquid.

TABLE VII

INTERNAL FORCE CONSTANTS OF $ClF_3O^{a,b}$

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] Data from Christe and Curtis (*55*).

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

The observed spectra agree well with those reported by the other groups (*37*, *300*), although the latter was incorrectly assigned. The best assignment (*55*) is given in Table VI. A normal coordinate analysis was also carried out for ClF_3O and a modified valence force field was computed (*55*) using the observed ^{35}Cl—^{37}Cl isotopic shifts. Table VII summarizes the internal force constants thus obtained. The geometry of ClF_3O assumed for this computation was $D(ClO) = 1.42$, $R(ClF_{eq}) = 1.62$, and $r(ClF_{ax}) = 1.72$ Å based on the known geometry of ClF_3 and Robinson's correlation between bond length and stretching frequency (*236*, *237*). In the absence of exact structural data, the following ideal bond angle values were assumed: α (OClF′) = 120° and β (OClF) = γ (FClF′) = 90°. However, increased repulsion from the free valence electron pair on chlorine and the double-bonded oxygen should cause some deviations from this ideal structure (see Section II, A).

The force constants of greatest interest are the stretching force constants. The value of 9.37 mdyn/Å obtained for $f_{\mathrm{Cl=O}}$ is similar to those computed for $FClO_2$ and ClO_2^+ (see Table I) 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 (*63*) 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 (*63*) in terms of semi-ionic 3 center–4 electron bonds. The same reasoning holds for the axial ClF bonds of ClF_3O. 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. 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 predominantly covalent bonding. These results are in excellent agreement with a generalized bonding scheme discussed in Section II, C 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 semi-ionic 3 center–4 electron pσ bond.

3. *Physical Properties*

Chlorine trifluoride oxide is colorless as a gas or liquid and white in the solid state. Some of its properties are summarized in Table VIII. The vapor pressure of the liquid can be described according to the Rocketdyne study (*226*) by the equation

$$\log P(\mathrm{mm}) = 8.433 - \frac{1680}{T(°\mathrm{K})}$$

or, according to Bougon *et al.* (*31*), by

$$\log P(\mathrm{mm}) = 8.394 - \frac{1655}{T(°\mathrm{K})}$$

Vapor density measurements (*37*, *226*) and mass spectroscopy (*226*, *300*) were used to show that ClF_3O is monomeric in the gas phase. The relatively high boiling point and Trouton constant of ClF_3O imply its association in the liquid phase. More specific evidence about the nature of this association was obtained from the vibrational spectra

TABLE VIII

SOME PROPERTIES OF ClF_3O

Property	Value	Ref.
Melting point	−42° to −44.2°C	(*16*, *37*, *226*)
Boiling point	29° or 27°C	(*37*, *226*)
ΔH_{fusion}	1.975 kcal $mole^{-1}$	(*16*)
ΔS_{fusion}	8.63 e.u.	(*16*)
ΔH_{vap}	7.7 or 7.57 kcal $mole^{-1}$	(*37*, *226*)
Trouton constant	25.4 or 25.2 e.u.	(*37*, *226*)
Density(l; 20°C)	1.865 gm ml^{-1}	(*226*)
$\Delta H^0_{f\,298}(g)$	-36.5^a or -35.3^b kcal $mole^{-1}$	(*15*, *16*, *269*)
$\Delta H^0_{f\,298}(l)$	$-44.1^{a,c}$, $-42.9^{b,c}$, or -38.7^b kcal $mole^{-1}$	(*16*, *152*, *269*)

[a] Corrected for $\Delta H^0_{f\,HF(g)} = -65.14$ kcal $mole^{-1}$ (*83*).

[b] Corrected for $\Delta H^0_{f\,HF(soln)(75H_2O)} = -77.04$ kcal $mole^{-1}$ (*151*).

[c] Using the $\Delta H^0_{f\,298(g)}$ values of Barberi (*16*) and Sinke (*269*) for the gas and the above listed $\Delta H_{vap} = 7.6$ kcal $mole^{-1}$.

recorded for the liquid and the solid and from a controlled diffusion experiment carried out for matrix-isolated ClF_3O. It was concluded (*55*) that association appears to involve exclusively the axial fluorine atoms. This finding agrees with the association proposed by Frey *et al.* (*102*) for the structurally related, trigonal bipyramidal molecules SF_4 and ClF_3.

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. These properties are given for the range 0–2000°K in the Appendix (Table AI).

4. *Chemical Properties*

Chlorine trifluoride oxide is stable at ambient temperature and can be stored and handled in well-passivated metal, Teflon, or Kel-F containers without decomposition. Its thermal stability is intermediate between that of ClF_3 and ClF_5. When heated to 280–300°C in a Monel cylinder (*37*, *226*), or to 200°C in a stainless steel cylinder, or to 350°C in a flow system (*226*), ClF_3O decomposes:

$$ClF_3O \longrightarrow ClF_3 + \tfrac{1}{2}O_2$$

It reacts rapidly with glass or quartz and, therefore, cannot be handled in standard glass vacuum systems (*226*). It reacts with numerous materials causing oxidation through both fluorination and oxygenation. With hydrogen-containing species, these reactions may occur at quite low temperature and with hydrocarbon type compounds are generally explosive. However, many chlorine-, fluorine-, or oxygen-substituted compounds, even with lower valent central atoms, react only slowly at ambient temperature, or not at all. Thus, no reaction was observed at room temperature between ClF_3O and chlorine, chlorine fluorides, chlorine oxyfluorides, and the nitrogen fluorides, FNO, FNO_2, NF_3, and N_2F_4 (*246*). However, elevated temperatures or UV photolysis have resulted in appreciable reaction of all compounds examined. With Cl_2 no interaction was detected at 25°C, but at 200°C the following reaction occurred:

$$ClF_3O + Cl_2 \longrightarrow 3ClF + 0.5\,O_2$$

Chlorine monoxide and ClF_3O reacted slowly at room temperature (*246*):

$$ClF_3O + Cl_2O \longrightarrow 2ClF + FClO_2$$

Similarly, $ClOSO_2F$ interacts with ClF_3O (*246*):

$$ClF_3O + 2ClOSO_2F \longrightarrow S_2O_5F_2 + FClO_2 + 2ClF$$

and

$$ClF_3O + ClOSO_2F \longrightarrow SO_2F_2 + FClO_2 + ClF$$

All these reactions can be rationalized in terms of a reduction of ClF_3O to the unstable FClO (see Section III, A) which readily decomposes to $FClO_2$ and ClF. At elevated temperature, $FClO_2$ may decompose further to $ClF + O_2$ (*24*, *137*, *183*).

Several reaction systems were discovered in which, in addition to fluorination, oxygenation also occurred. These include SF_4 (*60*); N_2F_4, HNF_2, and F_2NCFO (*246*, *248*); and MoF_5 (*35*). In the following equations, the end products observed for the SF_4–ClF_3O reaction are underlined:

$$ClF_3O + SF_4 \xrightarrow[25^\circ]{CsF} \underline{SF_6} + FClO$$

$$2FClO \longrightarrow \underline{FClO_2} + ClF$$

$$SF_4 + ClF \xrightarrow{CsF} \underline{SF_5Cl}$$

$$SF_4 + ClF_3O \longrightarrow \underline{SF_4O} + ClF_3$$

$$SF_4 + ClF_3 \longrightarrow \underline{SF_6} + ClF$$

In the MoF_5–ClF_3O system, both MoF_6 and MoF_4O were formed, followed by adduct formation. With N_2F_4, an appreciable reaction rate was observed only above 100°C:

$$ClF_3O + 2N_2F_4 \longrightarrow 3\,NF_3 + FNO + ClF$$

In addition to these products, small amounts of NF_3O were obtained. The yield of NF_3O from this reaction system could be increased to about 5% when UV irradiation was used. Higher yields of NF_3O (~70%) could be obtained at low temperature from HNF_2 and ClF_3O:

$$\begin{array}{lll} & ClF_3O + 2HNF_2 \longrightarrow & [FClO] + 2HF + 2NF_2^{\cdot} \\ & 2NF_2^{\cdot} + [FClO] \longrightarrow & \underline{NF_2Cl} + \underline{NF_3O} \\ \text{with the side reactions,} & 2NF_2^{\cdot} \longrightarrow & \underline{N_2F_4} \\ & 2[FClO] \longrightarrow & \underline{FClO_2} + ClF \\ & ClF + HNF_2 \longrightarrow & \underline{HF} + \underline{NF_2Cl} \end{array}$$

The reaction between difluoraminocarbonyl fluoride, F_2NCFO, and ClF_3O yielded again NF_3O and $ClNF_2$ in nearly equimolar amounts. However, the yields were much lower (20% based on ClF_3O consumed) with N_2F_4 being the main N—F containing product.

One reaction was discovered (*246*) in which ClF_3O did not act as an oxidizing but rather as a reducing agent. With the powerful oxidizer PtF_6, it reacted according to

$$ClF_3O + PtF_6 \longrightarrow ClF_2O^+PtF_6^- + 0.5F_2$$

The interaction of ClF_3O with HF, resulting in a fluoride ion abstraction to give the ClF_2O^+ cation (*38*), will be discussed below. With H_2O, an excess of chlorine trifluoride oxide hydrolyzes (*226*) according to

$$ClF_3O + H_2O \longrightarrow FClO_2 + 2HF$$

Mixtures of ClF_3O and ClF_5 (*225*) hold promise as an oxidizer in rocket propulsion.

As discussed in Section II, D, the compound ClF_3O has an energetically unfavorable pseudotrigonal bipyramidal structure. Consequently, it exhibits a pronounced tendency to form adducts with both strong Lewis acids and bases. Adducts containing the ClF_2O^+ cation (see Section III, C) were obtained (*33–35*, *38*, *58*, *64*, *246*, *300*) with the following Lewis acids: BiF_5, SbF_5, AsF_5, PF_5, TaF_5, NbF_5, VF_5, PtF_5, UF_5, MoF_4O, SiF_4, BF_3, and HF. With WF_4O and UF_4O, no stable ionic products were formed (*35*) in spite of the fact that WF_4O is a stronger Lewis acid than MoF_4O. This is caused by the increased tendency of WF_4O to enter the following oxygen–fluorine exchange reaction:

$$ClF_3O + MF_4O \longrightarrow FClO_2 + MF_6 \quad (M = W \text{ or } U)$$

Adducts containing the ClF_4O^- anion (see Section III, D) were prepared (*56*, *64*, *300*) by reaction of ClF_3O with the Lewis bases CsF, RbF, and KF. With the weaker bases FNO and FNO_2, it does not interact even at −95°C (*64*).

C. DIFLUOROOXYCHLORONIUM(V) CATION

Compounds containing the ClF_2O^+ cation with the following counterions are known: BiF_6^-, SbF_6^-, $Sb_2F_{11}^-$, AsF_6^-, PF_6^-, TaF_6^-, NbF_6^-, VF_6^-, PtF_6^-, UF_6^-, SiF_6^{2-}, BF_4^-, HF_2^-, MoF_5O^-, and $Mo_2F_9O_2^-$ (*33–35*, *38*, *58*, *64*, *246*, *300*).

1. *Synthesis*

With the exception of the PtF_6^- salt which was prepared from ClF_3O and PtF_6 [(*246*), Section III, B, 4], all the other salts were prepared by direct combination of ClF_3O with the corresponding Lewis acid. When the Lewis acid is a solid at the reaction temperature, or nonvolatile, it is advisable to use either a large excess of ClF_3O or anhydrous HF as a solvent to avoid polyanion formation (*33–35*, *64*).

2. *Molecular Structure*

The ionic nature of $ClF_3O\cdot$ Lewis acid adducts was established by vibrational (*33–35*, *38*, *58*, *300*) and ^{19}F NMR (*61*) spectroscopy.

The NMR spectrum of $ClF_2O^+AsF_6^-$ in anhydrous HF showed (*61*) the characteristic quadruplet of AsF_6^- at $\phi = 67.5$ ppm in addition to a single signal due to rapidly exchanging HF and ClF_2O^+. Upon acidification of the HF solvent with AsF_5, a separate signal at $\phi = -272$ ppm was observed for ClF_2O^+ in addition to a single signal due to HF, AsF_6^-, and AsF_5. For $ClF_2O^+PtF_6^-$ in HF the ClF_2O^+ signal was also found at $\phi = -272$ ppm. The observation of a singlet for ClF_2O^+ shows the magnetic equivalence of the 2 fluorine atoms.

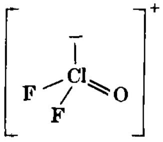
The vibrational spectra were reported (*33–35*, *38*, *58*, *300*) for all of the above-listed ClF_2O^+ salts. In addition to the bands characteristic of the anions, all spectra exhibited bands with frequencies and relative intensities similar to those shown in Table IX. These are characteristic for the ClF_2O^+ cation. The vibrational spectrum of ClF_2O^+ closely resembles that of isoelectronic SF_2O and, therefore, could be readily assigned. The only ambiguity in the assignment existed (*34*, *58*) for the two deformation modes occurring in the 380–400 cm^{-1} region. Recent Raman polarization measurements (*34*) have shown that the 400-cm^{-1} band belongs most likely to ν_4 (A′), and the 380-cm^{-1} band to ν_6 (A″).

TABLE IX

VIBRATIONAL SPECTRUM OF THE ClF_2O^+ CATION

Raman (HF solution) (cm^{-1})	IR (solid) (cm^{-1})	Assignment in point group C_s	Approx. description of mode
1333 (4) 1322 sh } p	1334 s 1323m	ν_1 (A′)	νClO
741 (10) p	734 m	ν_2 (A′)	$\nu_s ClF_2$
715 (1)	694 s	ν_5 (A″)	ν_{as} ClF_2
512 (2) p	512 s	ν_3 (A′)	δ_s $OClF_2$
404 (2) p	405 m	ν_4 (A′)	δ_{sciss} ClF_2
383 (1)	383 m	ν_6 (A″)	δ_{as} $OClF_2$

The spectroscopic evidence is consistent with the following structure of symmetry C_s for ClF_2O^+:



(IV)

A normal coordinate analysis was carried out (*58*) for ClF_2O^+ assuming the following geometry: $R_{ClO} = 1.41$ Å; $r_{ClF} = 1.62$ Å, $\beta(OClF) = 108°$; and $\alpha(FClF) = 93°$. A modified valence force field was computed, and the results are given in Table X. As can be seen from Table I, the ClO-

TABLE X

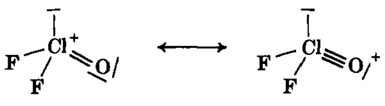
VIBRATIONAL FORCE CONSTANTS OF $ClF_2O^{+\,a,b}$

f_R	11.20
f_r	3.44
f_β	1.65
f_α	1.78
$f_{\beta\beta}$	0.21
f_{rr}	0’39

[a] Data from Christe *et al.* (*58*).

[b] Stretching constants in mdyn/Å and deformation constants in mdyn Å/radian^2.

stretching force constant of ClF_2O^+ exhibits a high value, implying that the positive charge in ClF_2O^+ is partially located on the oxygen atom and that contributions from resonance structures, such as VI,



(V) (VI)

are significant. The ClF-stretching force constant of ClF_2O^+ is within the range expected for a predominantly covalent ClF bond (see Table I and discussion in Section II, C).

3. *Properties*

Except for the following salts, the above-listed ClF_2O^+ salts are stable, white, crystalline solids. The UF_6^- salt is blue-green and of marginal stability at ambient temperature. In HF solution or during exposure of the solid to a laser beam, the UF_6^- anion is slowly oxidized by ClF_2O^+ to UF_6 (*33*). For MoF_5 this instability of the pentavalent metal toward oxidation to the hexavalent state is even more pronounced. When ClF_3O and MoF_5 are combined, no stable MoF_6^- salt is formed, but MoF_6 and MoF_4O are the products with the latter being capable of forming stable adducts (*35*). The $ClF_2O^+PtF_6^-$ salt is a canary yellow solid (*246*). The VF_5 and PF_5 adducts exhibit dissociation pressures of 2.5 and 3.5 mm, respectively, at room temperature (*33, 34*). The $(ClF_2O^+)_2\ SiF_6^{2-}$ salt is unstable at room temperature. It reaches a dissociation pressure of 760 mm at 31°C and its dissociation pressure can be represented (*64*) by the equation

$$\log P(\text{mm}) = 11.8018 - \frac{2712.3}{T(°\text{K})}$$

From these data, the heat of dissociation, $\Delta H_d^0 = 37.24$ kcal mole^{-1}, and the heat of formation of the solid adduct, $\Delta H^0{}_{f298} = -495.7$ kcal mole^{-1} were obtained. For the latter the literature value was corrected by using the more precise value of -35.9 kcal mole^{-1} for the heat of formation of gaseous ClF_3O (see Table VIII). The adduct melts under its own vapor pressure at 50.5°C (*300*).

The Raman spectrum of a solution of ClF_3O in anhydrous HF shows no bands due to ClF_3O but only those of ClF_2O^+ in agreement with the following ionization scheme (*38*):

$$ClF_3O + HF \longrightarrow ClF_2O^+ + HF_2^-$$

However, no attempts were reported to isolate the neat solid at low temperature and to examine its thermal stability.

The thermal stability of the adducts depends on the strength of the Lewis acids and decreases for the ClF_2O^+ salts in the following order: $SbF_5 > AsF_5 > BF_3 > VF_5 > PF_5 > SiF_4 > HF$ (*33–35*, *38*, *64*). The $ClF_2O^+MoF_5O^-$ salt, when heated in vacuum to 75–80°C or when dissolved in anhydrous HF, is converted to ClF_2O^+, $Mo_2F_9O_2^-$, and ClF_3O. It was shown by Raman spectroscopy that this reaction is reversible. Heating of these compounds to higher temperatures results in decomposition to MoF_4O and ClO_2^+ salts of MoF_4O (*35*).

The X-ray powder patterns were reported for the XF_6^- type (*34*, *64*, *246*) and the BF_4^- (*64*) adduct and were tentatively indexed in the orthorhombic system.

D. TETRAFLUOROOXYCHLORATE(V) ANION

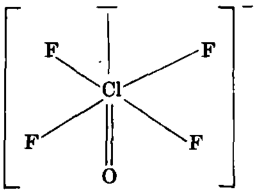
The existence of adducts between ClF_3O and CsF (*56*, *64*, *300*), RbF (*64*), and KF (*64*) has been reported. It was shown (*56*, *300*) by vibrational spectroscopy that these adducts are ionic and contain the ClF_4O^- anion.

1. *Synthesis and Properties*

Chlorine trifluoride oxide was found (*64*) to combine readily with the alkali metal fluorides, CsF, RbF, or KF, at room temperature to form white stable adducts. High conversion to the 1 : 1 adduct appears to be easiest for CsF. The use of a large excess of ClF_3O, agitation, and extended contact times are conducive to nearly complete conversions. These alkali metal ClF_4O^- salts have found use in the purification of ClF_3O (*226*). The thermal stability of the adducts decreases in the order $CsF > RbF > KF$. For example, the $KClF_4O$ salt can be decomposed by vacuum pyrolysis at 50–70°C (*226*), whereas a much higher temperature is required for the pyrolysis of $CsClF_4O$.

2. *Molecular Structure*

The ionic nature of these adducts and the structure of the ClF_4O^- anion were established by vibrational spectroscopy (*56*, *300*). It was shown (*56*) that the observed vibrational spectrum (Table XI) is consistent with the following structure of symmetry C_{4v}:



(VII)

TABLE XI

VIBRATIONAL SPECTRA OF $Rb^+ClF_4O^-$ AND $Cs^+ClF_4O^-$ AND THEIR ASSIGNMENT[a]

Observed frequencies (cm^{-1}) and relative intensities				Assignment for XZF_4 in point group C_{4v}	Type of vibration
$Rb^+ClF_4O^-$		$Cs^+ClF_4O^-$			
IR	Raman	IR	Raman		
1216 s	1211 (0.6)	1201 s	1203 (0.6)	A_1 ν_1	ν XZ
462 w	461 (10)	457 w	456 (10)	ν_2	ν_{sym} in-phase XF_4
339 s	[350][b]	339 s	[345][b]	ν_3	δ_{sym} out-of-plane XF_4
	350 (4.3)		345 (4)	B_1 ν_4	ν_{sym} out-of-phase XF_4
				ν_5	δ_{asym} out-of-plane XF_4
283 vw	285 (0.4)	280 vw	283 (0.4)	B_2 ν_6	δ_{sym} in-plane XF_4
600 } vs	599 (0.1)	600 } vs	594 (0.2)	E ν_7	ν_{asym} XF_4
500	557 (0.4)	560	564 (0.3)		
415 } s	416 (1.4)	415 } s	416 (1.4)		
394	395 (0.1)	396	397 (0.1)	ν_8	δ ZXF
	213 (0.6)		204 (0.7)	ν_9	δ_{asym} in-plane XF_4

[a] Data from Christe and Curtis (*56*).

[b] Calculated frequency.

A normal coordinate analysis was carried out (*56*) for ClF_4O^- assuming the following geometry: $D(ClO) = 1.42$ Å; $r(ClF) = 1.75$ Å; and all bond angles are 90°. The internal force constants obtained are listed in Table XII. Comparison with the stretching force constants of other chlorine fluorides oxides (see Table I) shows that the ClO bond in ClF_4O^- has full double-bond character, but that the ClF bond is a rather weak semi-ionic 3 center–4 electron bond. This implies that the formal negative charge in ClF_4O^- is distributed almost exclusively over the four fluorine

TABLE XII

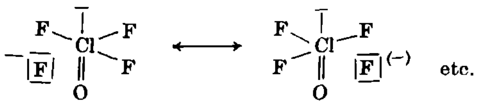
Force Constants of ClF_4O^- [a,b]

f_R	9.13		
f_r	1.79	$f'_{\beta\beta}$	0.29
f_β	1.33	$f'_{\alpha\alpha}$	0.08
f_α	0.61	$f_{r\beta}$	0.15
f_{rr}	0.25	$f''_{r\beta}$	−0.15
f'_{rr}	0.04		

[a] Data from Christe and Curtis (*56*).

[b] Stretching force constants in mdyn/Å and deformation force constants in mdyn Å/radian^2.

ligands. Resonance structures of the following type can be used to describe this effect:



(VIII) (IX)

E. Chlorine Pentafluoride Oxide

The synthesis of ClF_5O was claimed in 1972 by Züchner and Glemser (*300*) by UV photolysis of a mixture of ClF_5 and OF_2 in a nickel vessel fitted with a sapphire window. Although the authors failed to isolate a pure product, they "identified" ClF_5O in the product mixture by negative-ion mass spectroscopy and ^{19}F NMR spectroscopy. However, the following properties attributed to ClF_5O do not agree with the general trends observed for the remaining chlorine fluorides and oxyfluorides: (*a*) low volatility at −78°C, (*b*) a ^{19}F NMR resonance between −146 and −103 ppm relative to $CFCl_3$, and (*c*) exchange broadening in the NMR spectrum even at −76°C. For ClF_5O, we would expect (*a*) a volatility comparable to that of ClF_5 (*227*) or SF_6 (*279*), (*b*) an averaged ^{19}F NMR chemical shift of about −390 ppm (*61*), and (*c*) the absence of intramolecular exchange owing to chlorine having its maximum coordination number and no free valence electron pair, and owing to the lack of a plausible exchange mechanism.

Attempts to duplicate Züchner and Glemser's experiment (*300*) at Rocketdyne and the Centre d'Etudes Nucleaires de Saclay did not result in any evidence for ClF_5O. In the Rocketdyne study, the progress of the ClF_5–OF_2 photolysis in the temperature range –78° to 30°C, using both unfiltered and Pyrex-filtered UV radiation, was continuously monitored by gas chromatography. At the end of an experiment, the products were also separated by fractional condensation in a Teflon–stainless steel vacuum system and were characterized by vibrational spectroscopy. It was shown that in the ClF_5–OF_2 system, when exposed to unfiltered UV radiation, ClF_5 rapidly decomposes to ClF_3 and F_2 and, therefore, yields only the same products obtainable from the photolysis of ClF_3–OF_2 mixtures, i.e., mainly ClF_3O.

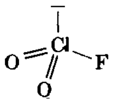
The ^{19}F NMR spectrum observed by Züchner and Glemser (*300*) might be rationalized in terms of a rapidly exchanging mixture of ClF_3 and ClF_3O as was pointed out to us by Dr. Bougon. To verify this, we have recorded the NMR spectra of ClF_3–ClF_3O mixtures over the temperature range 40° to –102°C. It was found that mixtures of pure ClF_3 and ClF_3O yield separate signals for ClF_3 (at about $\phi = -118$ and –10 ppm) and ClF_3O (at about –269 ppm) over the whole temperature range studied. However, upon addition of about 5 mole% of HF, one single signal is observed for all three species with a chemical shift corresponding to the averaged chemical shifts of the three components. The temperature dependence of these spectra is similar to that reported by Züchner and Glemser (*300*). At 40°C the signal was rather broad, became narrower with decreasing temperature, but broadened below –60°C and shifted to higher field. At –102°C a new and relatively narrow signal appeared significantly shifted upfield. The observed shifts and temperature dependence of these spectra are strongly dependent on the exact composition of the mixture.

The only remaining piece of evidence presented (*300*) for ClF_5O was the presence of a low-intensity fragment due to ClF_4O^- in the negative ion mass spectrum of the crude reaction product. However, this fragment might be attributed to a recombination process in the mass spectrometer since a 52% peak was also reported for F_2^- which can form only by recombination. Furthermore, negative-ion spectra frequently show species of higher mass than that of the parent molecule due to attachment of other atoms or groups (*28*), as was recently also demonstrated for BrF_5, of which the negative-ion spectrum shows a rather intense BrF_6^- fragment (*194*). In agreement with the preceding NMR interpretation, the observed (*300*) negative-ion mass spectrum is best ascribed to a mixture of ClF_3O, ClF_3, $FClO_3$, and some ClF_5, with several higher mass peaks and F_2^- being due to recombination in the spectrometer.

Based on the cited evidence it appears unlikely that Züchner and Glemser (*300*) had indeed observed ClF_5O.

F. Chloryl Fluoride

Chloryl fluoride,



(X)

was first obtained in 1942 by Schmitz and Schumacher (*256*) by the low-temperature fluorination of ClO_2 with F_2. The compound itself has not been studied very intensively although it is the most frequently encountered reaction product in systems involving reactions of chlorine mono-, tri-, or pentafluorides with oxides or hydroxides. Its structure can be derived from a tetrahedron with a free valence electron pair of chlorine occupying one of the four corners. Compared to $FClO_3$, this structure is less symmetric, kinetically less stable, and contains a highly polar, long $(p—\pi^*)\sigma$ (see Section II, C) bond. Therefore at moderate temperatures, $FClO_2$ is far more reactive than $FClO_3$ in spite of its lower oxidation state.

1. *Synthesis*

In our experience (*70*), $FClO_2$ is most conveniently prepared by combining $NaClO_3$ with an about equimolar amount of ClF_3 at −196°C in a stainless steel cylinder and holding the mixture at room temperature for a day. Chloryl fluoride (bp = −6°C) is thus obtained in high yield and can be separated from the by-products O_2, Cl_2 (bp = −33.8°C), and unreacted ClF_3 (bp = 11.75°C) either by fractional distillation or by repeated fractional condensation through a series of traps maintained at −95°, −112°, and −126°C. This procedure is safe and does not involve the handling of any shock-sensitive materials. It is based on the previous reports by Engelbrecht and Atzwanger (*92*) and Smith and co-workers (*270*) that gaseous ClF_3 reacts with $KClO_3$ to give $FClO_2$ in high yield. The substitution of $KClO_3$ by $NaClO_3$ is significant since the product NaF does not form an adduct with ClF_3, whereas KF does. This decreases by 60% the amount of ClF_3 required for the reaction. By analogy with the known $KClO_3 + BrF_3$ reaction (*296*), the idealized stoichiometry of the above reaction is

$$6\,NaClO_3 + 4ClF_3 \longrightarrow 6NaF + 2Cl_2 + 3O_2 + 6FClO_2$$

The use of larger than stoichiometric amounts of ClF_3 is advisable to avoid the possible formation of shock-sensitive chlorine oxides.

Woolf's original method (*296*) involved the use of $KClO_3$ and BrF_3, according to

$$6KClO_3 + 10BrF_3 \longrightarrow 6KBrF_4 + 2Br_2 + 3O_2 + 6FClO_2$$

Although the yield of $FClO_2$ is high, it is very difficult to obtain pure colorless $FClO_2$ by this method. When $KClO_3$ is replaced by $KClO_4$ (*285*), $FClO_2$ is obtained in 97% yield:

$$3KClO_4 + 5BrF_3 \longrightarrow 3KBrF_4 + Br_2 + 3O_2 + 3FClO_2$$

The product purification problem for this system is analogous to that encountered for the $KClO_3$–BrF_3 system. Direct fluorination of $KClO_3$ with F_2 (*31*, *89*, *92*, *265*) is not synthetically useful for preparing $FClO_2$, since the main product is always $FClO_3$. The interaction of $HOSO_2F$ with $KClO_3$ was reported (*99*) to produce $FClO_2$ in 30% yield. However, a study of this system carried out at Monsanto (*198*) failed to produce $FClO_2$, probably owing to formation of chloryl fluorosulfate.

An alternative route to $FClO_2$ involves the fluorination of chlorine oxides. The resulting $FClO_2$ is usually very pure but the handling of the shock-sensitive chlorine oxides renders these methods unattractive, particularly for the production of larger amounts of material. The original synthesis of $FClO_2$ by Schmitz and Schumacher in 1942 (*256*) involved direct fluorination of ClO_2. When F_2 was added at −80°C to a quartz vessel containing ClO_2, followed by slow warm-up to 20°C, $FClO_2$ was formed in a moderate reaction. The most favorable conditions were a reaction time of 2 min, a reaction temperature of 0°C, and the use of a mixture consisting of 25.6 mm ClO_2, 54.0 mm F_2, and 540.7 mm air. The reaction was found to be homogeneous and bimolecular (*12*). Modifications of this reaction involve passing gaseous F_2 through liquid ClO_2 at −50° to −55°C (*264*) or, preferably, using $CFCl_3$ as a solvent at −78°C (*162*, *254*). Chlorine dioxide can also be fluorinated to $FClO_2$ by passing ClO_2 diluted with N_2 at room temperature over AgF_2 or CoF_3 or by passing ClO_2 through liquid BrF_3 at 30°C (*255*).

The fluorination of chlorine oxides other than ClO_2 also produces $FClO_2$. Thus, $FClO_2$ was obtained in yields of up to 75% by fluorination of Cl_2O_6 with F_2 between 22° and 48°C (*7*, *8*). The high yield of $FClO_2$ coupled with the absence of $FClO_3$ indicates that the primary step is the decomposition of Cl_2O_6 to $2ClO_2 + O_2$ followed by the fluorination of ClO_2 to $FClO_2$. Similarly, the reaction between Cl_2O_6 and FNO_2, when carried out in $CFCl_3$ solution at 0°C, produces $FClO_2$ in addition to $NO_2{}^+ClO_4{}^-$ (*255*). Chloryl fluoride is also formed during the fluorination of Cl_2O_6 at −40°C with BrF_3 or BrF_5 (*294*) or with HF (*252*). During thermal decomposition of Cl_2O_7 in the presence of F_2 at 100°–120°C in quartz or Pyrex, $FClO_2$ is formed in addition to $FClO_3$ and ClF (*98*).

The risk of explosions is somewhat reduced in the $\mathrm{ClO_2}$–$\mathrm{AgF_2}$ reaction when the $\mathrm{ClO_2}$ is replaced by the less dangerous $\mathrm{Cl_2O}$. The yield of $\mathrm{FClO_2}$ was 35% (*117*, *182*). Similarly, $\mathrm{Cl_2O}$ can be fluorinated at −78°C with either ClF (*51*),

$$\mathrm{2Cl_2O + ClF \longrightarrow FClO_2 + 2Cl_2}$$

or $\mathrm{ClF_3O}$ (*246*),

$$\mathrm{Cl_2O + ClF_3O \longrightarrow FClO_2 + 2ClF}$$

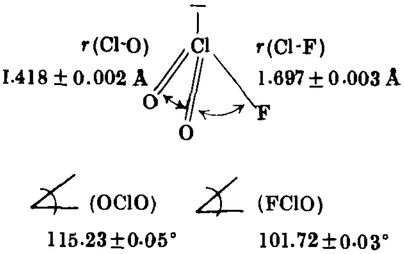
Oxygenation of a chlorine fluoride, if possible, would be more attractive than fluorination of the shock-sensitive chlorine oxides. A process for $\mathrm{FClO_2}$ has been claimed by Faust *et al.* (*97*) furnishing $\mathrm{FClO_2}$ in about 50% yield by simply heating a mixture of ClF and $\mathrm{O_2}$ to 80°–90°C. However, attempts in our laboratory (*70*) to verify this synthesis failed. It appears, that the $\mathrm{FClO_2}$ observed by Faust *et al.* (*97*) in their experiments was due to hydrolysis of ClF (*9*, *36*, *70*).

Numerous reactions have been reported in which $\mathrm{FClO_2}$ is formed as a product. Most of these involve the interaction between a chlorine fluoride or oxyfluoride with an oxide or hydroxide. The oxidation state of the chlorine fluoride is not important since +I, +III, and +V compounds all yield $\mathrm{FClO_2}$ owing to the tendency of the lower oxyfluorides, such as FClO, to disproportionate. The presence of excess chlorine fluoride is important to avoid formation of chlorine oxides. The following equations are typical examples for these types of reactions:

$$\begin{array}{lcl}
\mathrm{5ClF + 2H_2O} & \longrightarrow & \mathrm{4HF + FClO_2 + 2Cl_2} \quad (\mathit{9,\ 36}) \\
\mathrm{2ClF_3 + 2H_2O} & \longrightarrow & \mathrm{4HF + FClO_2 + ClF} \quad (\mathit{9,\ 36}) \\
\mathrm{ClF_5 + 2H_2O} & \longrightarrow & \mathrm{4HF + FClO_2} \quad (\mathit{227}) \\
\mathrm{ClF_3O + H_2O} & \longrightarrow & \mathrm{2HF + FClO_2} \quad (\mathit{226}) \\
\mathrm{2ClF_3 + 2HONO_2} & \longrightarrow & \mathrm{2HF + FClO_2 + ClF + 2FNO_2} \quad (\mathit{51}) \\
\mathrm{ClF_5 + 2HONO_2} & \longrightarrow & \mathrm{2HF + FClO_2 + 2FNO_2} \quad (\mathit{51}) \\
\begin{array}{l}\mathrm{ClF_3O + 2ClOSO_2F} \\ \mathrm{ClF_3O + ClOSO_2F}\end{array} & \begin{array}{c}\longrightarrow \\ \longrightarrow\end{array} & \left.\begin{array}{l}\mathrm{S_2O_5F_2 + FClO_2 + 2ClF} \\ \mathrm{SO_2F_2 + FClO_2 + ClF}\end{array}\right\} (\mathit{246}) \\
\mathrm{2ClF_3 + 3COF_2} & \longrightarrow & \mathrm{2CF_4 + FClO_2 + CF_3OCl} \quad (\mathit{288}) \\
\mathrm{2ClF_3 + UO_2F_2} & \longrightarrow & \mathrm{UF_6 + FClO_2 + ClF} \quad (\mathit{178,\ 179,\ 263}) \\
\mathrm{6ClF + TeO_2} & \longrightarrow & \mathrm{TeF_5Cl + FClO_2 + 2Cl_2} \quad (\mathit{168})
\end{array}$$

2. *Molecular Structure*

The exact structure of $\mathrm{FClO_2}$ was determined by Parent and Gerry (*219*, *220*) using microwave spectroscopy. The molecule was shown to have C_s symmetry with the following internuclear parameters:



(XI)

Values were also reported for the rotational constants, centrifugal distortion constants, and the chlorine nuclear quadrupole coupling constants of the three isotopic species $^{19}F^{35}Cl^{16}O_2$, $^{19}F^{37}Cl^{16}O_2$, and $^{19}F^{35}Cl^{16}O^{18}O$. The molecular dipole moment was found to be 1.722 ± 0.03 D.

The pyramidal structure of symmetry C_s for $FClO_2$ was also confirmed by vibrational spectroscopy. E. A. Smith *et al.* (*271*) and Arvia and Aymonino (*6*) reported the infrared spectrum of the gas. D. F. Smith *et al.* (*270*) studied the infrared spectrum of the gas, measured the ^{35}Cl–^{37}Cl and ^{16}O–^{18}O isotopic shifts, recorded the Raman spectrum of the liquid, and carried out a normal coordinate analysis. The observed frequencies and their assignment are summarized in Table XIII.

Andrews and co-workers have recently reported (*5*) ^{35}Cl–^{37}Cl and ^{16}O–^{18}O isotopic shifts for the infrared spectrum of argon matrix-isolated $FClO_2$. Tantot (*282*) has studied in his thesis work the infrared and Raman spectra of the gas, the Raman spectrum of the neat liquid and of HF solutions, and the infrared and Raman spectra of the solid.

Force fields for $FClO_2$ were computed by D. F. Smith *et al.* (*270*), Robinson *et al.* (*238*), So and Chau (*272*), and Tantot (*282*). The force fields computed by Smith *et al.* (*270*), So and Chau (*272*), and Tantot (*282*) agree relatively well for the two stretching force constants, suggesting values of about 9.0 and 2.5 mdyn/Å for f_{ClO} and f_{ClF}, respectively. Except for Tantot's computation (*282*) which did not give plausible values for the deformation constants ($f_\alpha > f_\beta$), estimates that significantly deviate from the actual (*220*) geometry of $FClO_2$ were used for these computations. Since the deformation constants are more likely to be angle-dependent, a recomputation using the exact geometry and the observed (*270*) isotopic shifts is desirable.

Mean square amplitudes of vibration were calculated by Baran (*14*) based on the frequencies and estimated geometry reported by Smith *et al.* (*270*). The UV absorption spectrum of $FClO_2$ was studied by Sicre and Schumacher (*264*) and Pilipovich *et al.* (*228*). From a mass spectro-

TABLE XIII

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF $FClO_2$[a]

	Assignment	$F^{35}ClO_2$ (cm^{-1})	$F^{37}ClO_2$ (cm^{-1})	$F^{35}Cl^{18}O_2$ (cm^{-1})	$F^{37}Cl^{18}O_2$ (cm^{-1})	$F^{35}Cl^{16}O^{18}O$ (cm^{-1})	$F^{37}Cl^{16}O^{18}O$ (cm^{-1})
A′	ν_1 sym ClO_2 stretch	1105.8	1098.4	1060.4	1052.6	1080.7	1072.4
	ν_2 ClF stretch	630.2	621.6	624.7	616.0	628.6	618.6
	ν_3 ClO_2 scissor	546.5	543.0	529.0	—	537.8	534.0
	ν_4 FClO bend	401.6	—	—	—	—	—
A″	ν_5 asym ClO_2 stretch	1271.4	1258.6	1229.6	1215.0	1253.6	—
	ν_6 FClO bend	367.0	—	—	—	—	—

[a] Data from Smith *et al.* (*270*).

scopic study of $FClO_3$ (*82*) and using a value of 57 kcal mole^{-1} for the Cl—O bond energy, the electron affinity of $FClO_2$ was estimated to be $\geqslant 2.7$ eV.

The ^{19}F NMR spectrum of liquid $FClO_2$ at −80°C was recorded by Carter *et al.* (*43*) and Christe *et al.* (*61*) and consisted of a single peak at $\phi = -328$ or -315 ppm, respectively. A signal at $\phi = -332$ ppm was tentatively assigned by Alexakos and Cornwell (*2*) to gaseous $FClO_2$.

The weak and highly polar Cl—F bond in FClO can be rationalized in terms of either a $(p—\pi^*)\sigma$ bond (see Section II, C) or a simple valence bond model (*66*) resulting in a resonance hybrid of the following canonical forms: $FClO_2 \leftrightarrow F^- + ClO_2^+$. It has been discussed in detail by Parent and Gerry (*220*), by Carter *et al.* (*43*), and in Section II, C of this review.

3. *Physical Properties*

Chloryl fluoride is colorless as a gas and liquid, and white as a solid. It is stable under normal conditions and some of its physical properties are summarized in Table XIV. Although precise measurements of some of its spectroscopic properties have recently been undertaken (*220*, *282*), most of its physical properties are either still unknown or were determined (*256*) at a time when corrosion-resistant metal–Teflon vacuum systems were not yet available. It was shown by vibrational spectroscopy (*282*) that solid $FClO_2$ between −263°C and its melting point exists only in one phase. Neutron diffraction data obtained for this phase at −196°C (*282*) were tentatively indexed based on a monoclinic unit cell with $a = 8.7$, $b = 6.2$, $c = 4.7$ Å, $\beta = 96°$, and $Z = 4$, similar to that of ClF_3.

TABLE XIV

SOME PROPERTIES OF $FClO_2$

Property	Value	Ref.
Melting point	−115° or −123.0° ± 0.4°C	(*15, 16, 256*)
Boiling point	~ −6°C	(*256*)
ΔH_{fusion}	1.440 kcal mole^{-1}	(*15, 16*)
ΔS_{fusion}	9.60 e.u.	(*15, 16*)
ΔH_{vap}	6.2 kcal mole^{-1}	(*256*)
Trouton constant	23.2 e.u.	(*256*)
$\Delta H^0_{f\ 298\ (g)}$	−8.1 ± 2.5 kcal mole^{-1} [a]	(*15, 16*)
Dipole moment (g)	1.722 ± 0.03 D	(*220*)

[a] Corrected for $\Delta H^0_{f\ HF(g)} = -65.14$ kcal mole^{-1} (*83*).

Tantot *et al.* (*190*, *282*, *283*) also studied association effects in the liquid phase using vibrational spectroscopy, pulse ^{19}F NMR spectroscopy, and conductometric measurements. They suggest a dipolar dynamic interaction resulting in short-lived associated forms and, possibly, a short-range local order observable on a vibrational but not on an NMR time scale. The specific conductivity of $FClO_2$ in the temperature range −120° to 23°C varies according to Martin and Tantot (*190*) from 1.2 to 3.12 $\mu S\ cm^{-1}$ ($=10^{-6}\ ohm^{-1}cm^{-1}$). The observed conductivity was taken as evidence for self-ionization:

$$2FClO_2 \rightleftharpoons ClO_2^+ + ClO_2F_2^-$$

However, more conclusive evidence is required in view of the reluctance of $FClO_2$ to form $ClO_2F_2^-$ anions (see Section III, F, 4) and of its known reactivity which renders the preparation and handling of very pure $FClO_2$ quite difficult. The vapor pressure of $FClO_2$ as a function of the temperature was measured by Schumacher *et al.* (*8*, *256*), and is listed in Table XV. It can be described by the equation $\log P(\text{mm}) = 8.23 - [1412/T(°\text{K})]$. Several thermodynamic properties of $FClO_2$ have been estimated by Rips *et al.* (*235*) by means of correlation increments using only the boiling point of the substance. Whereas the correct boiling point of $FClO_2$ was used, its structure was erroneously assumed to be that of the hypofluorite F—O—Cl=O.

TABLE XV

VAPOR PRESSURES OF CHLORYL FLUORIDE

°C	−78	−65.5	−55	−45.5	−38	−30.2	−23.8	−17.2	−9.7	−6.3
mm of Hg	8.8	25.2	55.9	103.8	161.4	244	338	459	645	740

4. *Chemical Properties*

Chloryl fluoride is stable at ambient temperature in well-passivated and dry containers. Its thermal decomposition in quartz was studied by Schumacher *et al.* (*24*, *137*). It reaches a measurable rate only above 300°C. The decomposition reaction is monomolecular and its rate is pressure-dependent. The activation energy was calculated to be 45 ± 2 kcal mole^{-1} and the rate constant was determined as $k_\infty = 2.3 \times 10^{13} \times 10^{-45000/4.5T}\ \text{sec}^{-1}$. The following decomposition mechanism was proposed:

$$FClO_2 \longrightarrow FClO + O$$
$$O + FClO_2 \longrightarrow FClO + O_2$$
$$2FClO \longrightarrow 2ClF + O_2$$

However, based on our present knowledge about FClO (see Section III, A), a more likely decomposition mode for FClO in the above mechanism would be

$$2FClO \longrightarrow ClF + FClO_2$$

The thermal decomposition of $FClO_2$ in Monel was studied by Macheteau and Gillardeau (*183*). Decomposition to ClF and O_2 was observed at 100°C (2.5% in 144 hr) and 200°C (10% in 235 hr), but a temperature $\geqslant$250°C was required for rate measurements. It was found that the decomposition is of first order and monomolecular at temperatures up to 285°C. At 300°C the reaction becomes second-order. The calculated rate constants and half-life times are summarized in Table XVI. The average activation energy between 250° and 285°C was found to be 23.7 kcal mole^{-1}. The results at temperatures >300°C agree with those reported by Schumacher *et al.* (*137*) for the quartz reactor. Glass is only slowly attacked by $FClO_2$ at room temperature, but traces of HF or H_2O catalyze the reaction (*90*, *265*). Chloryl fluoride reacts with water (*9*, *36*) and anhydrous nitric acid (*51*) according to

TABLE XVI

THERMAL DECOMPOSITION OF $FClO_2$ IN MONEL[a]

Temp. (°C)	Initial press. of $FClO_2$ (mm)	Average rate constant (sec^{-1})	Half-life
250	52	6.8×10^{-6}	20 hr
250	101	8.5×10^{-6}	22 hr 30 min
270	52	1.8×10^{-5}	10 hr 30 min
285	52	2.8×10^{-5}	6 hr 40 min

[a] Data from Macheteau and Gillardeau (*183*).

$$2FClO_2 + H_2O \longrightarrow 2HF + 2ClO_2 + \tfrac{1}{2}O_2$$

and

$$2FClO_2 + 2HONO_2 \longrightarrow 2HF + 2ClO_2 + N_2O_5 + \tfrac{1}{2}O_2$$

Both reactions are relatively slow and do not go to completion in several hours at room temperature (*9*, *36*, *51*). In addition, some of the ClO_2

formed can decompose to Cl_2 and O_2 and the nascent oxygen can oxidize $FClO_2$ to $FClO_3$ which is resistant to hydrolysis:

$$FClO_2 + O \longrightarrow FClO_3$$

These results differ from the previous report by Schmeisser and Fink (*255*) that the reaction between $FClO_2$ and $HONO_2$ proceeds at −30°C according to (*46*)

$$2FClO_2 + 2HONO_2 \longrightarrow NO_2ClO_4 + ClO_2 + NO_2 + 2HF$$

The statement made in Gmelin (*122*) and attributed to Bode and Klesper (*31*) that $FClO_2$ hydrolyzes to $FClO_3$ and H_2, is obviously incorrect. Hydrolysis of $FClO_2$ with base (*253*, *264*, *296*) proceeds as follows:

$$FClO_2 + 2OH^- \longrightarrow ClO_3^- + F^- + H_2O$$

Traces of H_2O in $FClO_2$ generate a red-brown color (*256*) which is probably due to ClO_2. With NH_3 it ignites at −78°C and the end products are NH_4Cl and NH_4F (*99*). The observation of a weak band at 1052 cm^{-1} in the Raman spectra of $FClO_2$ in dilute HF solutions in addition to strong bands due to $FClO_2$, was interpreted (*283*) in terms of the equilibrium:

$$HF + FClO_2 \rightleftarrows ClO_2^+ + HF_2^-$$

With HCl, chloryl fluoride reacts (*255*) at −110°C according to

$$HCl + FClO_2 \longrightarrow HF + ClO_2 + \tfrac{1}{2}Cl_2$$

With the stronger reducing agent HBr, it reacts explosively at −110°C (*99*). With $HOSO_2F$, at −78°C (*99*) it forms the stable ClO_2OSO_2F,

$$FClO_2 + HOSO_3F \longrightarrow HF + ClO_2OSO_2F$$

but with $HOSO_2Cl$ at −90°C, only the decomposition products of the analogous ClO_2OSO_2Cl, i.e., SO_3, ClO_2, and Cl_2, are obtained. With anhydrous $HOClO_3$, the following reaction occurs (*87*, *252*):

$$FClO_2 + HOClO_3 \longrightarrow HF + ClO_2OClO_3$$

Sulfur trioxide, at −10°C in $CFCl_3$ solution, undergoes an insertion reaction to yield the orange solid (mp = 27°C) ClO_2OSO_2F (*254*). The same compound was also obtained (*296*) in the absence of a solvent:

$$FClO_2 + SO_3 \longrightarrow ClO_2OSO_2F$$

With the strong reducing agent SO_2, chloryl fluoride reacts explosively at −40°C (*99*). When $FClO_2$ and I_2O_5 are combined at −196°C, then warmed to −50° to −20°C, I_2O_5 is dissolved with formation of O_2, IF_5, ClO_2, Cl_2O_6, and Cl_2O_7 (*294*).

Chloryl fluoride is a fluorinating agent and a moderately strong oxidizer. Thus it can fluorinate AsF_3 to the pentafluoride (*294*):

$$3FClO_2 + AsF_3 \longrightarrow ClO_2^+AsF_6^- + 2ClO_2$$

Sulfur tetrafluoride is oxidized by $FClO_2$ at 50°–300°C to yield a mixture of SF_6, SF_4O, and SF_2O_2 (*4*). Similarly, N_2F_4 is fluorinated at 30°C to give a mixture to NF_3, FNO_2, and FNO (*223*). Uranium tetrafluoride can be oxidized by $FClO_2$ to UF_5 and UF_6, the latter step requiring a reaction temperature between 50° and 150°C (*27*). Metal chlorides are converted by $FClO_2$ into metal fluorides, most of which can form ClO_2^+-containing salts when an excess of $FClO_2$ is used. Typical examples are $SbCl_5$, $SnCl_4$, and $TiCl_4$ which are converted to $ClO_2^+SbF_6^-$, $(ClO_2^+)_2$-SnF_6^{2-}, and $(ClO_2^+)_2TiF_6^{2-}$, respectively. Aluminum trichloride is converted to AlF_3 (*99*, *255*). Oxides, such as I_2O_5 (see above), SiO_2, Sb_2O_5, and B_2O_3 can be converted by $FClO_2$ at −10°C to SiF_4, ClO_2^+-SbF_6^-, and $ClO_2^+BF_4^-$, respectively (*87*). At 50°–100°C, UO_2F_2 reacts only slowly with $FClO_2$, but at 150°C with contact times of 30 min, UF_6, Cl_2, and O_2 are formed (*178*, *179*) according to

$$4FClO_2 + UO_2F_2 \longrightarrow UF_6 + 2Cl_2 + 5O_2$$

Only one reaction was reported in which $FClO_2$ was oxidized from the penta- to the heptavalent state (*49*, *52*, *69*). The powerful oxidizer PtF_6 was required to obtain the following reaction:

$$2FClO_2 + 2PtF_6 \longrightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^-$$

Chloryl fluoride was converted to ClF_3O by UV-photolysis of systems containing mixtures such as $FClO_2$–F_2, $FClO_2$–ClF, $FClO_2$–ClF_3, and $FClO_2$–ClF_5 (*228*, *240*). These reactions probably do not involve a direct oxygen–fluorine exchange in $FClO_2$, since ClF_3O can be synthesized by the same technique either directly from the three elements or from ClF_3 and oxygen (*228*).

Chloryl fluoride, like most of the other known chlorine fluorides and oxyfluorides, possesses amphoteric character. Owing to its weak and polar $(p—\pi^*)\sigma$ Cl—F bond (see Section II, C), it exhibits a much stronger tendency to form adducts with Lewis acids than with Lewis bases. The adducts with Lewis acids result in salts containing ClO_2^+ cations, and those with bases result in $ClO_2F_2^-$ salts. Both ions are discussed in detail in Sections III, G and H, respectively.

G. CHLORYL CATION

Although the chloryl cation does not contain a ClF bond and, therefore, in a strict sense does not belong to the family of the chlorine fluoride oxides, it was included in this review since it is a true derivative of $FClO_2$.

The existence of $FClO_2$ adducts with BF_3, AsF_5, PF_5, SbF_5, SiF_4, SO_3, and TaF_5 was first reported in 1954 by Schmeisser and Ebenhöch (*87*, *254*) and Woolf (*296*). In 1957, Schmeisser and Fink obtained (*99*, *255*) adducts with TiF_4 and SnF_4. In 1958, Clark and Emeleus described (*73*) the existence of a VF_5 adduct, more recently Christe (*52*) obtained a PtF_5 and IrF_5 adduct, and Yeats and Aubke (*298a*) prepared $ClO_2^+ [AsF_5(SO_3F)]^-$ from ClO_2SO_3F and AsF_5.

In a previous review (*253*) the adducts of $FClO_2$ with the stronger Lewis acids, such as AsF_5 or SbF_5, were considered to be ionic and to contain ClO_2^+ cations. However, the corresponding BF_3 and PF_5 adducts were assumed to be molecular adducts. In 1968, Carter *et al.* (*44*) reported evidence for the existence of solvated ClO_2^+ ions in HSO_3F solution. Since then, vibrational spectroscopy has successfully been used to establish the ionic nature of solid $ClO_2^+AsF_6^-$ (*43*, *66*), $ClO_2^+BF_4^-$ (*66*, *155*, *157*), $ClO_2^+SbF_6^- \cdot xSbF_5$ (*42*, *43*, *155*, *157*), $ClO_2^+ClO_4^-$ (*221*), $ClO_2^+PtF_6^-$, and $ClO_2^+IrF_6^-$ (*52*).

1. Syntheses and Properties

Salts containing the ClO_2^+ cation can be prepared either by direct combination of $FClO_2$ with the corresponding perfluorinated Lewis acid with (*254*) or without a solvent (*43*, *66*, *73*, *155*, *209*, *296*), by the interaction of $FClO_2$ with oxides (*87*), chlorides (*99*, *255*), and lower (*294*) or higher (*52*) oxidation state fluorides, or by interaction of the perfluorinated Lewis acid with chlorine oxides (*210*, *247*). The latter reactions, however, produce nonvolatile XF_3O as a by-product:

$$5Cl_2O + 3XF_5 \longrightarrow 2ClO_2^+XF_6^- + XF_3O + 4Cl_2 \quad (X = As, Sb)$$

$$5Cl_2O + 7SbF_5 \longrightarrow 2ClO_2^+Sb_3F_{16}^- + SbF_3O + 4Cl_2$$

$$5ClO_2 + 6SbF_5 \longrightarrow 4ClO_2^+SbF_6^- + 2SbF_3O + \tfrac{1}{2}Cl_2$$

$$5ClO_2 + 14SbF_5 \longrightarrow 4ClO_2^+Sb_3F_{16}^- + 2SbF_3O + \tfrac{1}{2}Cl_2$$

$$Cl_2O_6 + 2SbF_5 \longrightarrow ClO_2^+SbF_6^- + SbF_3O + FClO_3$$

Of the above approaches, the direct combination of $FClO_2$ with the corresponding Lewis acid is generally the most convenient. It yields well-defined products, except for cases, such as SbF_5 (*210*) or TaF_5 (*296*), where polyanion formation is possible. From the $FClO_2$–SbF_5 system, depending on the ratio of the starting materials and the reaction conditions, only $ClO_2^+SbF_6^-$, $ClO_2^+Sb_3F_{16}^-$, or a mixture of the two but no $ClO_2^+Sb_2F_{11}^-$, were obtained (*210*). However, single crystals of

$ClO_2^+Sb_2F_{11}^-$ have been obtained by Edwards and Sills (*88a*) by the interaction of $ClF_2^+SbF_6^-$ solutions with glass.

The $FClO_2$ adducts are generally white solids, except for the yellow PtF_6^- and IrF_6^- salts (*52*) and for $FClO_2 \cdot SO_3$ which was reported to be a red-to-pale yellow low-melting solid (*296*). The properties of the latter compound indicate that in the liquid phase it may exist, by analogy with Cl_2O_6 (*221*), in its covalent form, i.e., O_2ClOSO_2F. The ionicity of chloryl fluorosulfate was also discussed (*298*) in a paper dealing with the liquid range of fluorosulfates. The literature reports on the thermal stability of the ClO_2^+ salts are rather sketchy. In addition to the data given in Table IV of Schmeisser's review (*253*), stability data were published only for the BF_3 and the SbF_5 adducts. The $FClO_2 \cdot BF_3$ adduct reaches a dissociation pressure of 1 atm at 44.1°C (*66*), whereas $ClO_2^+SbF_6^-$ (mp = 220–225°C) and $ClO_2^+Sb_3F_{16}^-$ (mp = 50–53°C) are stable up to 300° and 200°C, respectively (*209*). The PtF_6^- and IrF_6^- salts of ClO_2^+ are stable at room temperature (*52*). It should be pointed out that Table IV of Schmeisser (*253*) implies that the thermal stability of the PF_6^- salt is higher than that of the BF_4^-. However, for related cations the reverse is true, and it appears that the data cited might be inaccurate.

X-Ray powder diffraction data have been reported for $ClO_2^+AsF_6^-$ (*66*) and for $ClO_2^+SbF_6^-$ and $ClO_2^+Sb_3F_{16}^-$ (*209*). All the ClO_2^+ salts react violently with organic compounds and water. With stronger Lewis bases, such as NO, NO_2, $ClNO_2$ (*99*, *255*), FNO, and FNO_2 (*51*, *68*), the following type of displacement reactions can be carried out:

$$ClO_2^+AsF_6^- + NO_x \longrightarrow NO_x^+AsF_6^- + ClO_2$$

$$ClO_2^+AsF_6^- + ClNO_2 \longrightarrow NO_2^+AsF_6^- + ClO_2 + \tfrac{1}{2}Cl_2$$

$$ClO_2^+PtF_6^- + FNO_x \longrightarrow NO_x^+PtF_6^- + FClO_2$$

2. *Molecular Structure*

The ClO_2^+ cation has been well characterized by vibrational spectroscopy (*42*, *43*, *66*, *155*, *157*). Characteristic frequencies and intensities for ClO_2^+ are summarized in Table XVII. The observed ^{35}Cl–^{37}Cl isotopic shifts were used to calculate the bond angle of ClO_2^+. It was shown that the cation is sharply bent and that the bond angle approximates 120° (*66*, *155*). Force constants were computed as a function of the ClO_2^+ bond angle (*66*, *155*) and the preferred set of constants is included in Table XVII. The value of 8.96 mdyn/Å obtained (*66*) for the ClO-stretching force constant of ClO_2^+ demonstrates that the ClO bond has double-bond character (see Table I).

TABLE XVII

CHARACTERISTIC FREQUENCIES[a] AND INTERNAL FORCE CONSTANTS[b] OF ClO_2^+

Obsd. freq. (cm^{-1}) and intensities		Assignment in point group C_{2v}		
IR	Raman			
1296.4 m	1296.4 (1)	$\nu_3(B_1)$	ν_{as}	$^{35}ClO_2$
1282.6 mw	—	$\nu_3(B_1)$	ν_{as}	$^{37}ClO_2$
1043.7 mw	1044.4 (10)	$\nu_1(A_1)$	ν_s	$^{35}ClO_2$
1038.3 w	1039.1 (4)	$\nu_1(A_1)$	ν_s	$^{37}ClO_2$
521.0 m	521.3 (3)	$\nu_2(A_1)$	δ	$^{35}ClO_2$
517 sh	—	$\nu_2(A_1)$	δ	$^{37}ClO_2$

$f_r = 8.96 \pm 0.06$ mdyn/Å
$f_{rr} = -0.45 \pm 0.13$ mdyn/Å
$f_{r\alpha} = 0.24 \pm 0.13$ mdyn/Å
$f_\alpha = 0.82 \pm 0.03$ mdyn/Å

[a] Taken for $ClO_2^+AsF_6^-$ from Christe *et al.* (*66*).
[b] Calculated for ∢ OClO = 120°.

These conclusions concerning the structure of ClO_2^+ were recently confirmed by Edwards and Sills (*88a*) who carried out a crystal structure determination for $ClO_2^+Sb_2F_{11}^-$. They found the ClO_2^+ ion to be V-shaped, with an O-Cl-O angle of 122° and a mean Cl-O bond length of 1.31 Å.

H. DIFLUOROCHLORATE(V) ANION

The existence of difluorochlorates of sodium, potassium, and barium was reported in 1965 by Mitra (*195*). However, this claim was met by skepticism since the reported synthesis involved the use of 40% aqueous hydrofluoric acid. In a subsequent paper (*196*), Mitra withdrew his claim. In 1969, Huggins and Fox reported (*141*, *142*) the synthesis of $CsClF_2O_2$ from CsF and $FClO_2$, and a subsequent spectroscopic study by Christe and Curtis showed (*54*) that the vibrational spectrum of the adduct is consistent with a $ClF_2O_2^-$ anion of symmetry C_{2v}.

1. Synthesis and Properties

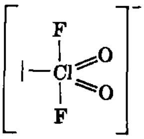
The synthesis of $CsClF_2O_2$ can be readily achieved by the interaction of dry CsF with excess $FClO_2$ at room temperature (*141*, *142*). In the original work (*141*, *142*), activated CsF was used which was obtained by vacuum pyrolysis of the CsF–hexafluoroacetone complex. The conversion of CsF to $CsClF_2O_2$ was 87%. When ordinary CsF (dried by fusion in a platinum crucible and powdered) was used (*54*), the conversion of CsF to $CsClF_2O_2$ was 73%.

The $CsClF_2O_2$ adduct is a white solid, stable at 25°C. Vacuum pyrolysis at 80°–100°C yields CsF and $FClO_2$ (*142*), demonstrating that the formation reaction is reversible. It fumes in moist air and reacts explosively with water (*142*). Controlled hydrolysis (*54*) proceeds according to

$$ClF_2O_2^- + H_2O \longrightarrow ClO_3^- + 2HF$$

2. *Structure*

The nature of the $CsClF_2O_2$ adduct was established (*54*) by vibrational spectroscopy. The observed spectra were consistent with a $ClF_2O_2^-$ anion possessing the following structure of symmetry C_{2v}:



(XII)

The observed bands and their assignments are summarized in Table XVIII. A normal coordinate analysis was carried out (*54*) for $ClF_2O_2^-$ assuming the following geometry: $R(ClO) = 1.43$ Å, $r(ClF) = 1.79$ Å, $\alpha(\angle OClO) = 120°$, $\beta(\angle OClF) = 90°$, and $(\angle FClF) = 180°$. The actual bond angles are expected to deviate slightly from this ideal geometry owing to increased repulsion from the free valence electron pair on Cl (see Section II, A). The internal force constants of $ClF_2O_2^-$ are summarized in Table XIX. As can be seen from Table I and the general discussion in Section II, C, the ClO bonds in $ClF_2O_2^-$ have double-bond character and the ClF bonds are as expected, semi-ionic 3 center–4 electron bonds. The polarity of the latter is increased further by the formal negative charge and the high degree of oxygen substitution. The combination of these effects results in the lowest ClF-stretching force constant value found to date for any ClF bond. As demonstrated for several other oxyfluoride anions (see Section III, D), the negative charge in $ClF_2O_2^-$ resides mainly on the ligands having the highest electronegativity, i.e., on the fluorine, and not on the oxygen atoms.

TABLE XVIII

VIBRATIONAL SPECTRUM OF $Cs^+ClF_2O_2^-$ AND ITS ASSIGNMENT[a]

Obsd. freq. (cm^{-1}) and intensities		Assignment for XO_2F_2 in point group C_{2v}	Approx. description of vibration
IR	Raman		
1225 1191 vs	1221 (0.8)	$\nu_8(B_2)$	$\nu_{as}(XO_2)$
1070 s	1076 (10) 1064 1055	$\nu_1(A_1)$	$\nu_s(XO_2)$
559 m	559 (1.2)	$\nu_2(A_1)$	$\delta_s(XO_2)$
510 vs, br		$\nu_6(B_1)$	$\nu_{as}(XF_2)$
	480 (1), br	$\nu_5(A_2)$?	τ
330–370 m	363 (10)	$\nu_3(A_1)$	$\nu_s(XF_2)$
	337 (8)	$\nu_7(B_1)$, $\nu_9(B_2)$	δ_{rock}, δ_{wag}
	198 (0.7)	$\nu_4(A_1)$	$\delta_s(XF_2)$

[a] Data from Christe and Curtis (*54*).

TABLE XIX

FORCE CONSTANTS OF $ClF_2O_2^-$ [a,b]

f_R	8.3	f_β	1.2
f_{RR}	0.1	$f_{\beta\beta'}$	0.57
f_r	1.6	$f_{\beta\beta}$	0.1
f_{rr}	−0.1	$f_{r\beta} - f_{r\beta'}$	0.3
f_α	1.95		

[a] Data from Christe and Curtis (*54*).

[b] Stretching force constants in mdyn/Å, deformation constants in mdyn Å/radian², and stretch–bend interactions in mdyn/radian.

I. CHLORINE TRIFLUORIDE DIOXIDE

A compound having the empirical composition $(ClF_3O_2)_n$ was reported in 1962 by Streng and Grosse (*128*, *276*, *278*). It was obtained by the interaction of either Cl_2, ClF, or HCl with O_2F_2 between −154°C and −143°C or by UV photolysis of ClF_3 and O_2 mixtures at −78°C. Both methods produced the same product, a violet unstable solid, which irreversibly decomposed above −78°C. In a subsequent study of the infrared and visible spectra of these products, Gardiner and Turner (*108*, *109*) proposed the structure F_2ClOOF for the violet compound. However, both the synthetic and the spectroscopic studies are not convincing and further work is required to establish the composition and structure of this violet species.

A well-defined and characterized compound, having the composition ClF_3O_2 and showing no resemblance to Streng and Grosse's violet compound, was reported in 1972 by Christe (*50*). This work is an excellent example for the perfection of handling techniques for extremely reactive oxidizers. Thus the physical, chemical, and spectroscopic properties of ClF_3O_2 and of its $ClF_2O_2^+$ adducts were determined from a total of 2.2 mmol of material. The fact that ClF_3O_2 as a powerful oxidizer is readily reduced to $FClO_2$ which cannot be removed from ClF_3O_2 by simple fractionation (see below), rendered the handling of this compound puarticlarly difficult.

1. *Synthesis and Properties*

The synthesis of ClF_3O_2 is best described by the following reaction sequence:

$$2FClO_2 + 2PtF_6 \longrightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^-$$

Several side reactions compete with this reaction and the yield of $ClF_2O_2^+$ varies greatly with slight changes in the reaction conditions (*52*, *68*). The ClF_3O_2 is then displaced from its $ClF_2O_2^+$ salt according to

$$ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- + 2FNO_2 \longrightarrow 2NO_2^+PtF_6^- + ClF_3O_2 + FClO_2$$

Chloryl fluoride is slightly less volatile than ClF_3O_2, and, therefore, most of it can be removed from ClF_3O_2 by fractional condensation in a −112°C trap. The remaining $FClO_2$, however, has to be removed by complexing with BF_3:

$$ClF_3O_2 + FClO_2 + 2BF_3 \longrightarrow ClF_2O_2^+BF_4^- + ClO_2^+BF_4^-$$

Since $ClF_2O_2^+BF_4^-$ is stable (*69*) at 20°C, whereas $ClO_2^+BF_4^-$ is not (*66*), the latter can be pumped away at 20°C. The resulting pure $ClF_2O_2^+BF_4^-$ is then treated with an excess of FNO_2 and the evolved ClF_3O_2 and unreacted FNO_2 are readily separated by fractional condensation through a series of −126° and −196°C traps:

$$ClF_2O_2^+BF_4^- + FNO_2 \longrightarrow NO_2^+BF_4^- + ClF_3O_2$$

The overall yield of pure ClF_3O_2 based on the PtF_6 used in step 1 was found to be about 10 mole%.

Pure ClF_3O_2 is colorless as a gas or liquid and white as a solid. Some of its measured (*68*) physical properties are summarized in Table XX. Near its melting point the vapor pressure above liquid ClF_3O_2 was found to be reproducibly lower than expected from the vapor pressure curve given in Table XX. This indicates that close to the melting point some ordering effect occurs in the liquid.

The measured vapor density of ClF_3O_2 indicates that no appreciable association occurs in the gas phase. Its relatively low boiling point and Trouton constant imply little association in the liquid phase. This prediction is confirmed by the vibrational spectra of the liquid and the neat solid which exhibit only minor frequency shifts when compared to the spectra of the gas and the matrix-isolated solid. This finding is somewhat surprising since both ClF_3 (*102*) and ClF_3O (*55*, *226*) show a pronounced tendency to associate in the liquid and solid state through bridges involving the axial fluorine atoms.

TABLE XX

SOME PROPERTIES OF ClF_3O_2[a]

Property	Value
Melting point	−81.2°C
Boiling point	−21.58°C
ΔH_{vap}	5.57 kcal mole^{-1}
Trouton constant	22.13 e.u.
Vapor pressure	$\log P(\text{mm}) = 7.719 - \frac{1217.2}{T\ (°\text{K})}$

[a] Data from Christe and Wilson (*68*).

The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given below assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation. These properties are given for the range 0°–2000°K in the Appendix (Table AII).

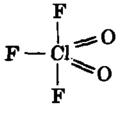
Chlorine trifluoride dioxide resembles chlorine fluorides and oxyfluorides in its corrosive and oxidizing properties. It must be handled in systems consisting of corrosion-resistant metals, Teflon, or sapphire. It appears to be marginally stable in a well-passivated system at ambient temperature. It is a strong oxidative fluorinator as evidenced by its tendency to fluorinate metal surfaces to metal fluorides with $FClO_2$ formation. It reacts explosively with organic materials and care must be taken to avoid such combinations. The hydrolysis of ClF_3O_2 was not quantitatively studied; however, on one occasion a slight leak in an infrared gas cell containing ClF_3O_2 resulted in the formation of $FClO_3$ and HF indicating the following reaction.

$$ClF_3O_2 + H_2O \longrightarrow FClO_3 + 2HF$$

Chlorine trifluoride dioxide forms stable adducts with strong Lewis acids, such as BF_3, AsF_5, or PtF_5 (*49*, *68*, *69*). These adducts have ionic structures containing the $ClF_2O_2^+$ cation (see Section III, I, 2). The high stability of these adducts can be explained by the change from the energetically unfavorable trigonal-bipyramidal structure of ClF_3O_2 to the more favorable tetrahedral $ClF_2O_2^+$ configuration (see Section II, D). Contrary to ClF_3 (*295*), but by analogy with ClF_3O (*64*), it does not form stable adducts with FNO or FNO_2 at temperatures as low as −78°C. This was demonstrated by the various displacement reactions where ClF_3O_2 and unreacted FNO or FNO_2 could be readily removed from the reactor at −78°C. With the stronger base, CsF, it did not form a stable adduct but decomposed to $FClO_2$ and F_2. However, only relatively small amounts of ClF_3O_2 were available for the complex formation study with CsF, and the possibility of preparing salts such as $Cs^+ClF_4O_2^-$ under more favorable reaction conditions cannot entirely be ruled out.

2. *Molecular Structure*

Vibrational (*57*) and ^{19}F NMR (*68*) spectroscopy were used to establish for ClF_3O_2 the following structure of symmetry C_{2v}, which according to semi-empirical linear combination of atomic orbitals–molecular orbitals (LCAO-MO) self-consistent field (SCF) calculations (*239*) is most stable:



(XIII)

The ^{19}F NMR spectrum of liquid ClF_3O_2 was measured in the temperature range −20° to −80°C. It showed at all temperatures one partially resolved signal centered at −413 ppm below the external standard $CFCl_3$. The observed signal is in excellent agreement with an AB_2 pattern with $J/\nu_0\delta = 1.0$ and $J_{FF} = 443$ Hz. The low chemical shift of −413 ppm for ClF_3O_2 is in excellent agreement with a heptavalent chlorine fluoride, and the fluorine–fluorine coupling constant of 443 Hz observed for ClF_3O_2 is similar to that of 421 Hz observed for the structurally related ClF_3 *(61)*. Additional support for the above structure was derived from the fact that the B_2 part of the AB_2 pattern occurs downfield from the A part as expected for the axial fluorine atoms in a trigonal bipyramidal arrangement *(120, 200)*.

The infrared spectra of gaseous, solid, and matrix-isolated ClF_3O_2 and the Raman spectra of gaseous and liquid ClF_3O_2 were reported *(57)* and are summarized in Table XXI. The observed data are in excellent agreement with the preceding model (XIII) of symmetry C_{2v}. A normal coordinate analysis was carried out for ClF_3O_2 assuming the following geometry: $D(ClO) = 1.40$ Å, $R(ClF_{eq}) = 1.62$ Å, $r(ClF_{ax}) = 1.72$ Å, $\alpha(OClO) = 130°$, $\beta(F_{eq}ClF_{ax}) = \delta(OClF_{ax}) = 90°$, and $\gamma(OClF_{eq}) = 115°$, based on the observed geometries of ClF_3 and $FClO_3$ and a correlation between ClO bond length and stretching frequency. The deviation of the OClO bond angle from the ideal 120° was estimated by comparison with the known geometries of SF_4O and $FClO_3$. The force constants thus obtained are summarized in Table XXII. The value of the ClO-stretching force constant (9.23 mdyn/Å) is in excellent agreement with that of

TABLE XXI

VIBRATIONAL SPECTRUM OF ClF_3O_2 AND ITS ASSIGNMENT IN POINT GROUP C_{2v} [a]

IR (cm^{-1})	Ra (cm^{-1})	Assignment for ClF_3O_2 in point group C_{2v}		Approx. description of mode
1093 s	1093 (4) p	A_1	ν_1	Sym ClO_2 str
683 m	683 (10) p		ν_2	ClF_{eq} str
519 w	520 (8) p		ν_3	ClO_2 scissor
487 vw	487 (6) p		ν_4	Sym $F_{ax}ClF_{ax}$ str
287 w	285 (1)		ν_5	$F_{ax}ClF_{ax}$ scissor in ClF_3 plane
(417)[b]	402 (0+)	A_2	ν_6	Torsion
695 vs		B_1	ν_7	Antisym $F_{ax}ClF_{ax}$ str
592 s	586 (0+)		ν_8	ClO_2 wag
372 w			ν_9	Antisym $F_{eq}ClF_{2ax}$ def in ClF_3 plane
1327 vs	1320 (0+)	B_2	ν_{10}	Antisym ClO_2 str
531 m	530 (1)		ν_{11}	ClO_2 rock
[c]	222 (1)		ν_{12}	$F_{ax}ClF_{ax}$ scissor out of ClF_3 plane

[a] Data from Christe and Curtis *(57)*.
[b] Observed only for solid ClF_3O_2.
[c] Below frequency range of spectrometer used.

TABLE XXII

INTERNAL FORCE CONSTANTS OF ClF_3O_2 [a,b]

$f_D = 9.23$	$f_{\beta\beta} = 0.09$
$f_R = 3.35$	$f_{r\beta} = f_{r\beta'} = 0.10$
$f_r = 2.70$	$f_{r\delta} = -f_{r\delta'} = 0.25$
$f_\alpha = 1.41$	$f_{D\alpha} = 0.61$
$f_\beta = 1.40$	$f_{\beta\delta} = -f_{\beta\delta'} = -0.16$
$f_\gamma = 1.33$	$f_{\delta\delta} = -f_{\delta\delta'} = -0.34$
$f_\delta = 1.30$	$f_{\delta\delta''} = -0.17$
$f_{DD} = -0.09$	$f_{\gamma\gamma} = -0.30$
$f_{rr} = -0.04$	$f_{R\alpha} = -0.37$

[a] Data from Christe and Curtis (*57*).

[b] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch–bend interaction constants in mdyn/radian.

9.37 mdyn/Å found for ClF_3O (*55*) and the general valence force field values of 9.07 and 8.96 mdyn/Å reported for $FClO_2$ (*270*) and ClO_2^+, (*66*) respectively. The values of the ClF-stretching force constants are comparable to those previously reported for the related pseudotrigonal bipyramidal molecules ClF_3 (*102*) and ClF_3O (*55*) and are summarized in Table XXIII. In all three molecules, the stretching force constant of the equatorial ClF bond is significantly higher than that of the two axial bonds, although their relative difference decreases with increasing oxidation state of the central atom. The difference in bond strength between equatorial and axial bonds implies significant contributions from semi-ionic 3 center–4 electron bonds to the axial ClF bonds. This bonding scheme has been discussed in detail for the related pseudotrigonal bipyramidal ClF_2^- anion in Section II, C.

TABLE XXIII

ClF STRETCHING FORCE CONSTANTS OF ClF_3O_2 COMPARED TO THOSE OF PSEUDOTRIGONAL BIPYRAMIDAL ClF_3O, ClF_3, ClF_2^-, AND $ClF_2O_2^-$

Compound	f_R (mdyn/Å)	f_r (mdyn/Å)	f_{rr} (mdyn/Å)	$(f_R - f_r)/f_R$	Ref.
ClF_3	4.2	2.7	0.36	0.36	(*102*)
ClF_3O	3.2	2.3	0.26	0.26	(*55*)
ClF_3O_2	3.4	2.7	−0.04	0.19	(*57*)
ClF_2^-	—	2.4	0.17	—	(*63*)
$ClF_2O_2^-$	—	1.6	−0.1	—	(*54*)

Inspection of Table XXIII also reveals that the value of f_r does not depend exclusively on the oxidation state of the central atom. Obviously, formal negative charges (as in the anions) and increasing oxygen substitution facilitate the formation of semi-ionic bonds and, hence, counteract the influence of the oxidation state of the central atom. It is interesting to note that the relative contribution from semi-ionic bonding (see Section II, C) to the axial ClF bonds [$= (f_R - f_r)/f_R$] decreases from ClF_3 to ClF_3O and ClF_3O_2 (see Table XXIII). This can be attributed to the decreasing electron density around the central atom with increasing oxidation state, thus making it more difficult to release electron density to the axial fluorine ligands as required for the formation of semi-ionic bonds.

The bonding in ClF_3O_2 might be described by the following approximation (*53*). The bonding of the three equatorial ligands, ignoring the second bond of the Cl=O double bond, is mainly due to an sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves one delocalized p-electron pair of the chlorine atom for the formation of a semi-ionic 3 center–4 electron pσ bond.

J. DIFLUOROPERCHLORYL CATION

The existence of the $ClO_2F_2^+$ cation in the form of its PtF_6^- salt was reported in 1972 by Christe (*49*). In a subsequent paper (*69*), a full account was given of the synthesis and properties of the PtF_6^-, AsF_6^-, and BF_4^- salts of $ClO_2F_2^+$.

1. *Synthesis and Properties*

It was found (*52*) that PtF_6 and $FClO_2$, when combined at −196°C and allowed to warm up slowly to 25°C, interacted according to

$$2FClO_2 + 2PtF_6 \longrightarrow ClO_2F_2^+PtF_6^- + ClO_2^+PtF_6^-$$

The yield of $ClO_2F_2^+$ was not 50% as expected from the foregoing equation, but generally about 25% owing to the competing reaction

$$2FClO_2 + 2PtF_6 \longrightarrow 2ClO_2^+PtF_6^- + F_2$$

In some of the experiments, small amounts of $ClF_6^+PtF_6^-$ or ClF_5 and $FClO_3$ were observed, depending on the exact reaction conditions. The formation of some $FClO_3$ is not surprising since it is known that $FClO_2$ readily interacts with nascent oxygen to yield $FClO_3$ (*9*, *36*, *51*).

Attempts to suppress the competing reaction by changing the reaction conditions (rapid warm-up from −196° to −78°C and completion of the reaction at −78°C) resulted on one occasion in an entirely different course for the reaction:

$$6FClO_2 + 6PtF_6 \longrightarrow 5ClO_2{}^+PtF_6{}^- + ClF_6{}^+PtF_6{}^- + O_2$$

Further modification of the reaction conditions (rapid warm-up of the $FClO_2$–PtF_6 mixture from −196° to either −78° or 25°C and completion of the reaction at 25°C) did not produce detectable amounts of either $ClO_2F_2{}^+$ or $ClF_6{}^+PtF_6{}^-$, but only $ClO_2{}^+PtF_6{}^-$ and ClF_5, F_2, and O_2. This indicates that the nature of the reaction products is more influenced by the warm-up rate of the starting materials from −196° to about −78°C than by the final reaction temperature. Slow warm-up favors the formation of $ClO_2F_2{}^+$, whereas rapid warm-up yields $ClF_6{}^+$ or ClF_5 and F_2 (*52*).

The $BF_4{}^-$ and $AsF_6{}^-$ salts were prepared (*69*) as follows:

$$ClO_2{}^+PtF_6{}^- + ClO_2F_2{}^+PtF_6{}^- + 2FNO_2 \longrightarrow FClO_2 + ClF_3O_2 + 2NO_2{}^+PtF_6{}^-$$

Unreacted FNO_2 and some of the $FClO_2$ could be separated from ClF_3O_2 by fractional condensation. The remaining $FClO_2$ was separated from ClF_3O_2 by complexing with BF_3. Since the resulting $ClO_2{}^+BF_4{}^-$ has a dissociation pressure (*66*) of 182 mm at 22.1°C while $ClO_2F_2{}^+BF_4{}^-$ is stable, the former salt could be readily removed by pumping at 20°C. Conversion of $ClO_2F_2{}^+BF_4{}^-$ to the corresponding $AsF_6{}^-$ salt was accomplished through displacement of $BF_4{}^-$ by the stronger Lewis acid AsF_5:

$$ClO_2F_2{}^+BF_4{}^- + AsF_5 \longrightarrow ClO_2F_2{}^+AsF_6{}^- + BF_3$$

All three salts, $ClO_2F_2{}^+PtF_6{}^-$, $ClO_2F_2{}^+AsF_6{}^-$, and $ClO_2F_2{}^+BF_4{}^-$, are solids, stable at 25°C, and react violently with water or organic materials. The $PtF_6{}^-$ compound is canary yellow, whereas those of $AsF_6{}^-$ and $BF_4{}^-$ are white.

The salts dissolve in anhydrous HF without decomposing. They are crystallinic in the solid state, and the X-ray powder diffraction patterns of $ClO_2F_2{}^+BF_4{}^-$ and $ClO_2F_2{}^+AsF_6{}^-$ have been reported (*69*). The pattern of the former was tentatively indexed on the basis of an orthorhombic unit cell with $a = 5.45$, $b = 7.23$, and $c = 13.00$ Å. Assuming four molecules per unit cell and neglecting contributions from the highly charged central atoms to the volume, a plausible average volume of 16 $Å^3$ per F or O atom was obtained.

The thermal stability of $ClO_2F_2{}^+BF_4{}^-$ is higher than that of $ClO_2{}^+BF_4{}^-$ (*66*), $ClF_2{}^+BF_4{}^-$ (*259*), or other similar salts. The pronounced tendency of ClF_3O_2 to form stable adducts with Lewis acids is in good agreement with the correlations between the stability of an adduct and the structure of the parent molecule and its ions (see Section II, D). Thus, tetrahedral $ClO_2F_2^+$ (see below) should be energetically much more favorable than trigonal bipyramidal ClF_3O_2.

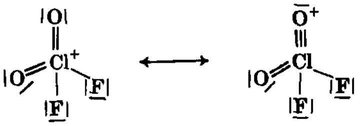
2. *Molecular Structure*

The structure of $ClO_2F_2^+$ salts was established by ^{19}F NMR and vibrational spectroscopy (*69*).

In the ^{19}F NMR spectrum of $ClF_2O_2^+PtF_6^-$ in anhydrous HF, a broad singlet at −310 ppm relative to external $CFCl_3$ was tentatively assigned (*61*) to $ClF_2O_2^+$. Subsequent studies (*69*) of $ClF_2O_2^+BF_4^-$ and $ClF_2O_2^+AsF_6^-$ confirmed the original assignment. The spectrum of $ClF_2O_2^+BF_4^-$ in HF showed a strong temperature dependence. At 30°C it consisted of a single peak at 185 ppm relative to external $CFCl_3$. With decreasing temperature the peak at first became broader and then separated at about 0°C into three signals at −301 ($ClO_2F_2^+$), 146 (BF_4^-), and 194 ppm (HF) which became narrower with further decrease in temperature. The observed peak area ratio of approximately 2 : 1 for the 146- and −301-ppm signals confirmed their assignment to BF_4^- and $ClO_2F_2^+$, respectively, and proved the ionic nature of the $ClF_3O_2 \cdot BF_3$ adduct in HF solution.

The spectrum of $ClF_2O_2^+AsF_6^-$ in HF (which was acidified with AsF_5) consisted of two resonances at −307 ($ClO_2F_2^+$) and 105 ppm (HF, AsF_5, AsF_6^-), respectively. Rapid exchange among HF, AsF_5, and AsF_6^- preempted the measurement of the $ClO_2F_2^+$ to AsF_6^- peak area ratio (*69*).

The vibrational spectra of the BF_4^-, AsF_6^-, and PtF_6^- salts of $ClO_2F_2^+$ were recorded for both the solids and HF solutions (*69*). It was shown that all three salts are ionic containing, in addition to the anions, a common cation. The vibrational spectrum of this cation closely resembled that of SO_2F_2 indicating a pseudotetrahedral structure of symmetry C_{2v}. The observed frequencies together with the stretching force constants obtained from Cl isotopic shifts are listed in Table XXIV. Inspection of Table I shows that $ClO_2F_2^+$ possesses the highest value known for a ClO-stretching force constant. This is not surprising, since the central atom in $ClO_2F_2^+$ has a high oxidation state (+VII), highly electronegative ligands, and a formal positive charge (cation). The influence of these factors on f_{ClO} was discussed in Section II, C. By analogy with ClF_2O^+ (*58*), the only other known species exhibiting a f_{ClO} value of similar magnitude, contributions from the resonance structure,



(XIV) (XV)

TABLE XXIV

OBSERVED FREQUENCIES, APPROXIMATE DESCRIPTION OF MODES, AND MOST IMPORTANT INTERNAL FORCE CONSTANTS COMPUTED TO FIT THE OBSERVED ^{35}Cl AND ^{37}Cl ISOTOPIC SHIFTS AND ASSUMING TWO DIFFERENT BOND ANGLES OF $ClO_2F_2^+$ [a]

Assignment		Obs. freq. (cm^{-1})	Approx. description of mode
A_1	ν_1	1241	$\nu_{sym}(ClO_2)$
	ν_2	756	$\nu_{sym}(ClF_2)$
	ν_3	514	$\delta_{sym}(ClO_2)$
	ν_4	390	$\delta_{sym}(ClF_2)$
A_2	ν_5	390	τ
B_1	ν_6	1479	$\nu_{asym}(ClO_2)$
	ν_7	530	$\delta_{rock}(ClO_2)$
B_2	ν_8	830	$\nu_{asym}(ClF_2)$
	ν_9	514	$\delta_{rock}(ClF_2)$

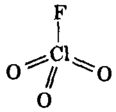
	∠OClO, ∠FClF, deg	
	124, 96	114, 105
f_D (mdyn/Å) (ClO)	12.20	12.04
f_{DD} (mdyn/Å)	–0.46	–0.66
f_R (mdyn/Å) (ClF)	4.40	4.53
f_{RR} (mdyn/Å)	–0.32	0.03

[a] Data from Christe *et al.* (*69*).

might be invoked to explain the high f_{ClO} value. The value of the ClF-stretching force constant (4.46 mdyn/Å) falls within the range expected for a predominantly covalent ClF bond in a cation having a central atom with a +VII oxidation state.

K. Perchloryl Fluoride

Perchloryl fluoride,



(XVI)

the acyl fluoride of perchloric acid, was first obtained by Bode and Klesper in 1951 (*30*) by the action of F_2 on $KClO_3$ at −40°C, but believed to be ClO_2OF. In 1952 it was prepared by Engelbrecht and Atzwanger (*91*) by electrolysis of $NaClO_4$ in anhydrous HF and was correctly identified. In the mid-fifties it became commercially available from Pennsalt Chemical Corporation and can be purchased in research quantities from Ozark Mahoning Company. Owing to its remarkably low reactivity and high specific impulse (see Section III, K, 5), it received considerable interest as a rocket propellant oxidizer, resulting in a rather thorough study of its properties. Unfortunately, its high vapor pressure (53 atm at $T_c = 95°C$) and coefficient of expansion rendered it inferior to other oxidizer candidates. Owing to its relative inertness (it hydrolyzes only slowly in water), it has found use as a fluorinating agent in organic chemistry. In addition to the general reviews, listed in the Introduction, and brief reviews in Japanese (*205*) and Chinese (*48*), reviews that are devoted exclusively to $FClO_3$ have been published by Pennsalt (*222*), Gall (*106*), and Khutoretskii *et al.* (*158*). The inertness of $FClO_3$ is due to its energetically favorable pseudotetrahedral configuration, its highly covalent and strong Cl—F bond (see Section II, C), and its extremely small dipole moment of 0.023 D. Combined, these properties give it a high kinetic stability in spite of its low thermodynamic stability ($\Delta H^0_{f298} = -5.7$ kcal mole^{-1}).

1. *Synthesis*

Perchloryl fluoride can be prepared by electrolysis of a saturated solution of $NaClO_4$ in anhydrous HF with a current efficiency of 10% (*91, 92*).

Fluorination of solid $KClO_3$ by F_2 (*30, 31*) produces $FClO_3$, $FClO_2$, ClF, Cl_2O_6, Cl_2, and O_2 (*89, 92*). The yields of $FClO_3$ were about 45% based on the F_2 used (*92*). When the fluorination was carried out below −20°C, yields of $FClO_3$ as high as 60% were obtained (*265*). The fluorination of $NaClO_3$ with F_2 can also be carried out in aqueous solution at 25°–75°C resulting in a 50% yield of $FClO_3$ (*299*; see also *125*). Replacement of F_2 by other fluorinating agents, such as ClF_3, BrF_3, or SbF_5, gives mainly $FClO_2$ and Cl_2 and only low yields of $FClO_3$ (*92*). Purification of crude $FClO_3$ by washing of the products condensible at −196°C with an alkaline $Na_2S_2O_3$ solution produces material containing less than 1.5% of impurities (*92*).

The thermal decomposition of Cl_2O_7 at 100°C in the presence of F_2 produces a mixture of $FClO_3$ and $FClO_2$ in a yield of about 75% (*98*). Similarly, the fluorination of either Cl_2O_6 or Cl_2O_7 with SbF_5 produces $FClO_3$ in high yield (*210*) according to

$$Cl_2O_6 + 2SbF_5 \longrightarrow ClO_2{}^+SbF_6{}^- + SbF_3O + FClO_3$$

and

$$Cl_2O_7 + nSbF_5 \longrightarrow SbF_3O\cdot(SbF_5)_{n-1} + 2FClO_3$$

The fluorination of NO_2ClO_4 by ClF_3 at room temperature results in the formation of $FClO_3$ and smaller amounts of $FClO_2$, ClO_2, and $ClNO_2$ (*25*). Perchloryl fluoride is also formed by the interaction of $FClO_2$ with nascent oxygen (*9*, *36*, *51*) and in the reaction of gaseous ClF_3 with UO_2, U_3O_8, and UO_3 (*149*) and with UO_2F_2 (*263*), or by the reaction of $ClF_2{}^+BiF_6{}^-$ with metal oxides (*78*). Xenon dioxide tetrafluoride, XeO_2F_4, is capable of oxidizing either ClF_3 or ClF_5 to $FClO_3$ (*143*). Almost quantitative yields of $FClO_3$ and  $R_fC(=O)F$ can be obtained by the alkali metal fluoride-catalyzed decomposition of the corresponding $R_fCF_2OClO_3$ at slightly elevated temperatures (*249*).

The most convenient and commercially attractive methods for preparing $FClO_3$ involve the fluorination of perchlorates. Heating of $KClO_4$ to 70°–120°C in an excess of SbF_5 produces $FClO_3$ in 50% yield (*90*). The yield of $FClO_3$ can be increased to 90% and the reaction temperature can be lowered to 20°–50°C, when a mixture of HF–SbF_5 is used (*292*, *293*). Slightly lower yields were obtained when the HF solvent was replaced by AsF_3, IF_5, or BrF_5.

Most of the commercial processes are based on the use of $HOSO_2F$. This method was proposed in 1956 by Barth-Wehrenalp (*20*). Evolution of $FClO_3$ starts at 50°C and goes to completion at 85°–110°C. The yields of $FClO_3$ vary from 50 to 80% (*20*, *22*, *162*, *163*) and, if necessary, the $HOSO_2F$ can be regenerated (*22*). If desired, the reaction can be carried out in glass apparatus. The influence of certain additives on the yield of $FClO_3$ was studied (*81*). The addition of 5 to 25% of SbF_3 to the $HOSO_2F$ increases the yield of $FClO_3$ to 90% and higher but hinders the regeneration of $HOSO_2F$. The addition of HF–BF_3 increases the $FClO_3$ yield to 85% but requires elevated pressure. Zinc, aluminum, silver, and lead fluorides were found to decrease the yield of $FClO_3$.

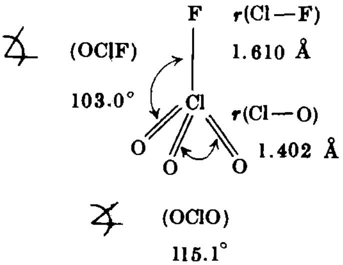
The highest yield of perchloryl fluoride (97%) was achieved with a mixture of fluorosulfonic acid and SbF_5 as fluorinating medium. Potassium, sodium, lithium, magnesium, barium, calcium, and silver perchlorates and perchloric acid itself undergo the reaction. Commercial reagents are used and their additional purification is not necessary; unlike all the previous methods the preparation of perchloryl fluoride by this method can be carried out at room temperature. At high temperature (100°–135°C) the reaction time is 1–10 min in all, which allows the process to be carried out continuously in a packed column. The purity of product obtained after the usual purification reaches 98% and over; air and carbon dioxide are present as trace impurities (*23*).

The exact mechanism of the reaction between ClO_4^- and superacids has as yet not been established, although numerous comments on it were published (*19*, *21*, *167*, *253*, *292*, *297*). Based on our present understanding of superacid chemistry (*67*, *118*, *216*) and of the complex formation of $FClO_3$ (see Section III, K, 4), a mechanism involving ClO_3^+ as an intermediate is very unlikely. Furthermore, the high yields of $FClO_3$ (up to 97%) would be surprising in view of the expected instability of ClO_3^+. In our opinion, other mechanisms, such as the one shown, involving protonated perchloric acid (*166*) are more plausible:

$$\begin{array}{lcl}
4HF + 2SbF_5 & \longrightarrow & 2H_2F^+ + 2SbF_6^- \\
2H_2F^+ + ClO_4^- & \longrightarrow & H_2OClO_3^+ + 2HF \\
H_2OClO_3^+ + HF & \longrightarrow & FClO_3 + H_3O^+ \\
\hline
ClO_4^- + 3HF + 2SbF_5 & \longrightarrow & FClO_3 + H_3O^+ + 2SbF_6^-
\end{array}$$

2. *Molecular Structure*

The structural parameters of $FClO_3$ were determined by Clark, Beagley, and Cruickshank (*72*) by gas-phase electron diffraction. The molecule has symmetry C_{3v} and the following bond angles and distances:



(XVII)

Owing to its small dipole moment, $FClO_3$ exhibits only a very weak microwave spectrum (*171*, *173*). Since only the $J = 4 \rightarrow 5$, $K = 3$ and the $J = 6 \rightarrow 7$, $K = 3$ and $K = 6$ transitions were observed, a complete structure determination was not possible. However, the estimated geometry and dipole moment are in good agreement with the exact values measured by other methods. Table XXV lists the frequency values and constants that were obtained. The rotational constants, B_0, are in good agreement with the values obtained from the high-resolution infrared spectrum (*184*) of the 549- and 589-cm^{-1} fundamentals.

The dipole moment of $FClO_3$ was determined by dielectric relaxation measurements (*192*) as 0.023 ± 0.003 D and from the $J_{11 \rightarrow 12}$ transition in a resonant cavity at 126196 MHz (*101*) as 0.025 ± 0.003 D. This low dipole moment indicates that the electronegativity of F and the ClO_3 group are comparable, thus resulting in a high degree of covalency for the Cl—F bond.

TABLE XXV

FREQUENCY VALUES AND CONSTANTS FOR PERCHLORYL FLUORIDE

Transitions and constants	$F^{35}ClO_3$ (MHz)	$F^{37}ClO_3$ (MHz)
$J = 4 \rightarrow 5, K = 3$	52585.97 ± 0.05	52560.4 ± 0.3
$J = 6 \rightarrow 7, K = 3$	73619.40 ± 0.05	73583.94 ± 0.05
$J = 6 \rightarrow 7, K = 6$	73618.72 ± 0.05	—
B_0	5258.692 ± 0.005	5256.149 ± 0.005
D_J	0.0014 ± 0.0002	
D_{JK}	0.0018 ± 0.0003	
eq$Q$	−19.2 ± 0.5	−15.4 ± 1.5

The ^{19}F NMR spectrum of $FClO_3$, according to Brownstein (*41*) consists of a partially resolved quartet ($J_{ClF} \sim 310$ Hz) of equal intensity at $\phi = -241.5$ ppm. The lack of rapid quadrupole relaxation indicates a highly symmetric electric field around the central atom in good agreement with the small dipole moment observed for $FClO_3$ (see above). The temperature dependence of the ^{19}F NMR spectrum of $FClO_3$ was studied by Bacon *et al.* (*13*). An expression for the line broadening was derived, and a value of 1.0 kcal $mole^{-1}$ was obtained for the activation energy of molecular reorientation. A value of 278 ± 5 Hz was calculated for $J35_{ClF}$. According to Agahigian *et al.* (*1*), the ^{19}F resonance of $FClO_3$ occurs at $\phi = -287$ ppm, but measurements in our laboratory indicate that this value is inaccurate. A value of $\phi = -252.9 \pm 2$ ppm was found by us for liquid $FClO_3$ at −120°C. The ^{35}Cl and ^{19}F NMR spin-lattice relaxation times and rotational diffusion in liquid $FClO_3$ were measured by Maryott *et al.* (*96*, *191*) using pulse techniques.

The mass spectrum of $FClO_3$ was measured (*82*, *138*, *234*). The vertical ionization potential and the F—ClO_3 bond dissociation energy were found to be 13.6 ± 0.2 eV and ~60 kcal $mole^{-1}$, respectively. The average ClO bond dissociation energy and the heat of formation were estimated (*82*) to be 60 and −5.3 kcal $mole^{-1}$, respectively.

The UV absorption spectrum of $FClO_3$ was reported by Sicre and Schumacher (*264*) and Pilipovich *et al.* (*228*).

The vibrational spectrum of $FClO_3$ has been well characterized. The infrared spectrum was thoroughly analyzed by Lide and Mann (*174*) and two of the fundamentals (ν_3 and ν_5) were studied at high resolution by Madden and Benedict (*184*). The Raman spectra of the liquid and of the gas were reported by Powell *et al.* (*233*) and Dunlap *et al.* (*85*) and by Claassen and Appelman (*71*), respectively. The observed fundamentals together with their assignment are summarized in Table XXVI and are in excellent agreement with a molecule of symmetry C_{3v}. The infrared spectrum of $FClO_3$ has also been reported by Engelbrecht *et al.* (*92*), Pennsalt (*222*), Smith *et al.* (*271*), and Karelin *et al.* (*154*). A correlation of ClO-stretching frequencies (*236*) and force constants with bond lengths and bond orders was given by Robinson (*237*); however, his plots and assumptions must be thoroughly updated before being used. Absolute infrared intensities were reported for $FClO_3$ by Kharitonov *et al.* (*157*). Quantum mechanical studies of the atomic, bond, and

TABLE XXVI

VIBRATIONAL SPECTRUM OF GASEOUS $FClO_3$ AND ITS ASSIGNMENT FOR POINT GROUP C_{3v}

		Assignment	Infrared[a] (cm^{-1})	Raman[b] (cm^{-1})
A_1	ν_1	sym ClO_3 stretch	1061 s	1062.8, 1060.9[c] vs, p
	ν_2	ClF stretch	717 s, 707 m	716.8, 706.6 s, p
	ν_3	sym ClO_3 deform.	549 w	548.8 m, p
E	ν_4	asym ClO_3 stretch	1315 vs	1314 w
	ν_5	asym ClO_3 deform.	589 m	573 w
	ν_6	rocking	405 w	414 w

[a] Data from Lide and Mann (*174*).

[b] Data from Claassen and Appelman (*71*).

[c] Splittings are due to ^{35}Cl and ^{37}Cl isotopes.

molecular polarizabilities were carried out by Nagarajan and Redmon (*204*). Numerous force fields (*107, 140, 154, 157, 201, 204, 245, 273*) were computed for $FClO_3$, but owing to the lack of sufficient experimental data, no unique solution was obtained. Values of about 9.4 and 3.9 mdyn/Å for the ClO- and the ClF-stretching force constants, respectively, appear to us most reasonable. Mean square amplitudes of vibration of $FClO_3$ were calculated by Müller *et al.* (*201, 203*) and Nagarajan and Redmon (*204*). Müller *et al.* (*201*) have also computed the Coriolis zeta constants for $FClO_3$; however, their values differ significantly from those given by Hoskins (*140*). Molecular reorientation in liquid $FClO_3$ was studied by Sunder and co-workers (*279a*) using Raman spectroscopy.

The high-resolution photoelectron spectrum of $FClO_3$ was studied by DeKock *et al.* (*80*). The results from this study, including *ab initio* SCF MO calculations of the electronic structures, are summarized in Tables XXVII and XXVIII. These calculations indicate considerable participation by 3d orbitals of the Cl atom, although they tend to overestimate the importance of 3d orbitals in bonding by correcting for some inade-

TABLE XXVII

IONIZATION DATA FOR PERCHLORYL FLUORIDE[a,b]

Band No.	Adiabatic i.p. (eV)	Vertical i.p. (eV)	Vibrational spacing (cm^{-1})	Vibrational assignment	Orbital assignment
1	13.04 (1)	—	370 (40)	ν_3 or ν_4	$6b_2$
	13.57 (2)	—	475 (60)	ν_3	$2a_2$
2	14.85 (1)	15.181 (6)	340 (16)	ν_4	$6b_1$
	15.181 (6)	15.307 (6)	1025 (30)	ν_1	$11a_1$
3	16.676 (5)	16.676 (5)	1135 (16)	ν_1	$5b_2$
			805 (30)	ν_2	
			510 (20)	ν_3	
4	18.07 (3)	18.31 (2)	—	—	$5b_1$
5	19.175 (7)	19.390 (4)	850 (30)	ν_2	$4b_2$
			485 (40)	ν_3	
	19.699 (7)	19.807 (7)	855 (30)	ν_2	$9a_1$
			500 (20)	ν_2	
6	—	21.7 (1)	—	—	$4b_1$
7	—	24.2 (1)	—	—	$8a_1$
		Ground state	1269	ν_1	
			848	ν_2	
			544	ν_3	
			384	ν_4	

[a] Data from DeKock *et al.* (*80*).

[b] Standard deviations are given in parentheses after each quantity.

TABLE XXVIII

CALCULATED EIGENVALUES AND PERCENTAGE CHARACTER OF VALENCE MOLECULAR ORBITALS FOR $FClO_3$[a]

		Atomic character (%)						
		Chlorine orbital			Oxygen orbital		Fluorine orbital	
Orbital	Eigenvalue (eV)	3d	3s	3p	2s	2p	2s	2p
$1a_2$	−12.9	—	—	—	—	100	—	—
7e	−14.1	10.5	—	—	—	78.0	—	11.0
$10a_1$	−15.4	12.6	—	1.9	1.1	44.3	—	39.8
6e	−16.0	16.5	—	—	5.3	74.0	—	3.9
5e	−18.6	9.2	—	1.8	1.3	18.7	—	68.9
4e	−21.5	4.3	—	24.8	19.1	38.0	—	13.3
$9a_1$	−23.3	1.1	4.1	34.1	16.8	29.4	2.6	11.4
$8a_1$	−26.2	—	18.2	10.0	34.2	12.3	7.6	17.2
3e	−40.6	2.9	—	24.5	66.7	5.0	—	—
$7a_1$	−43.0	2.4	3.9	8.1	14.0	1.9	68.7	—
$6a_1$	−47.6	—	44.7	—	29.2	6.5	17.5	1.6

[a] Data from DeKock *et al.* (*80*)

quacy in the s and p bases. Results of MO calculations were also reported by Hillier *et al.* (*129*, *139*) and Ionov and Ionova (*146*). The latter authors calculated the electron density distribution in $FClO_3$ as $Q_{Cl} = +0.83$, $Q_O = -0.23$, and $Q_F = -0.14$, using the geometry, the ionization potential of the molecule and of the free atoms, and the orbital exponents of the Slater functions as input data.

X-Ray diffraction data were reported by Tallman *et al.* (*280*, *281*) for solid $FClO_3$ at liquid air temperature. The data were indexed in terms of a tetragonal unit cell with $a = 7.66$ and $c = 5.31$ Å, $Z = 4$, and $d = 2.18$ gm/cm^3. Barberi (*16*, *17*) has shown that solid $FClO_3$ exists between its melting point and −196°C in only one solid phase. Based on entropy calculations, Koehler and Giauque (*160*) suggested that there is a high degree of disorder in the arrangement of the F and O atoms in crystallinic $FClO_3$.

3. Physical Properties

Some of the physical properties of $FClO_3$ are summarized in Table XXIX. In the Appendix (Table AIII), the temperature dependence of some of the thermodynamic properties is given (*147*). In addition to these data, the viscosity of gaseous $FClO_3$ between 50 and 150°C was reported

(*218*). Some thermodynamic properties of $FClO_3$ were calculated (*235*) using only the boiling point of the compound and correlation increments.

Perchloryl fluoride is white as a solid and colorless as a liquid and gas. It possesses a characteristic sweetish odor (*92*). Its toxicity is moderate and comparable to that of CH_2CHCN or Cl_2. Tests on mice showed an acute vapor toxicity (LD_{50}) of 630 ppm at 4-hr exposure time. Exposure of monkeys to 40 ppm $FClO_3$ in air for 3 months resulted in enlarged spleens and lungs together with some evidence of red cell destruction (*222*).

The dielectric strength of $FClO_3$ is outstanding and over a broad pressure range is about 30% higher than that of SF_6. During irradiation with ^{60}Co γ-rays, the dielectric strength decreased only by 5% (*46*). The correlation between negative-ion formation and electric breakdown of $FClO_3$ was studied by Hickam and Berg (*138*) by mass spectroscopy. Perchloryl fluoride has been used as an insulator in high-voltage systems.

Perchloryl fluoride was reported (*185*, *195*, *205*, *206*, *222*) to be sparingly soluble (1–3 gm/liter at 1 atm and 25°C) in a wide variety of polar and nonpolar solvents, such as aqueous solutions, alcohols, ketones, esters, ethers, and aromatic and halogenated solvents. However, more recent measurements by Golub *et al.* (*124*) show that these solubilities are substantially (several-fold) higher. When working with larger amounts of $FClO_3$ in organic solvents, all necessary precautions should be taken since mixtures of this kind are potentially explosive. Hammond *et al.* (*132–134*) have extensively studied the extremely weak electron acceptor–donor (ball-plane) interactions between $FClO_3$ and aromatic hydro- and fluorocarbons. Several inorganic acid halides, $HOSO_2F$, PCl_3, $POCl_3$, SO_2Cl_2, $SOCl_2$, $TiCl_4$, and $SiCl_4$ dissolve gaseous $FClO_3$ to the extent of 20–30 gm/liter at 25°C and 1 atm pressure (*106*).

Liquid perchloryl fluoride is a typical nonpolar solvent. Most inorganic and organic salts are insoluble in it. Conversely, most covalent, essentially nonpolar substances, boiling within about 50°C of perchloryl fluoride, are completely miscible, e.g., chlorine, boron trifluoride, sulfur hexafluoride, silicon tetrafluoride, phosgene, nitrous oxide, chlorine trifluoride, chlorofluorocarbons, silicon tetrachloride, sulfuryl chloride, dinitrogen tetroxide, and thionyl chloride (*106*).

Blends of perchloryl fluoride with halogen fluorides are homogeneous and stable. When these are used as storable liquid oxidizers for rocket propulsion, the halogen fluoride usually confers hypergolicity, increased density, and lowered vapor pressure; whereas the perchloryl fluoride provides oxygen needed for efficient combustion of carbon in the fuel or of certain metal additives. The mixtures are thermally stable and their

TABLE XXIX

SOME PHYSICAL PROPERTIES OF $FClO_3$

Property	Value	Ref.
Melting point	-147.75°C	(*92*, ***160***[a])
Boiling point	-46.67°C	(*30*, *92*, ***160***)
T_{crit}	95.17°C	(*92*, *100*, ***148***)
P_{crit}	53.0 atm	(*148*)
Crit. density	0.637 gm cm^{-3}	(***92***, *100*)
Crit. molar volume	161 cm^3	(*92*)
Vapor pressure (for $T = -109°$ to $-44°$C)	Log P(mm) $= -1652.3/T$(°K) $-8.62625 \log T$ $+0.0046098T$ $+28.44780$	(*92*, *148*, ***160***)
Density of solid (-190°C)	2.19 gm cm^{-3}	(*281*)
Density of liquid (for $T = -142°$ to -39°C)	$\rho(\text{gm cm}^{-3}) = 2.266 - 1.603 \times 10^{-3}T$ $-4.080 \times 10^{-6}T^2$(°K)	(*92*, *100*, ***148***, *222*)
(for $T = 29.9°$ and 53.8°C)	$\rho(\text{gm cm}^{-3}) = 1.390$ and 1.276	(*268*)
Viscosity of liquid (for $T = -77°$ to 54°C)	Log $\eta = 299\ T^{-1} - 1.755$ (centipoise)	(*222*, ***268***)
Surface tension (for $T = -75.2°$ to -55.6°C)	24.1 to 21.3 dyn cm^{-1}	(*268*)
ΔH_{fusion}	0.9163 kcal $mole^{-1}$	(*16*, *17*, ***160***)
ΔS_{fusion}	7.12 e.u.	(*16*, *17*)
ΔS_{vap} (-46.67°C)	4.619 kcal $mole^{-1}$	(*30*, *92*, *148*, ***160***)
Trouton constant	20.395 e.u.	(*30*, *92*, ***160***)
ΔH^0_{f298} (g)	-5.7 kcal $mole^{-1}$	(*15–18*, *82*, *204*, ***291***)
ΔG^0_{f298} (g)	11.5 kcal $mole^{-1}$	(*291*)
S^0_{298}	66.65 e.u.	(*147*, *148*, *172*, *208*, ***291***)
$C_{p\ 298}$ (g)	15.517 e.u.	(*147*, ***160***, *204*, *291*)
$C_{p\ 298}$ (l)	27.19 e.u.	(***150***, *160*)
Specific heat ratio, C_p/C_v, gas at 25°C	1.12	(*174*, ***189***)

[a] Bold face reference number indicates reference from which the listed value is quoted.

compatibility with container materials is determined mainly by the halogen fluoride. The density and vapor pressure of perchloryl fluoride–chlorine trifluoride blends have been summarized in tables by Gall (*106*). The miscibility and compatibility of $FClO_3$ at low temperatures was studied by Streng (*277*) for O_2, O_3, O_2F_2, ClF, ClF_3, SF_4, SF_6, CF_3Cl, and C_4H_{10}.

4. Chemical Properties

Owing to its pseudotetrahedral configuration, its highly covalent strong Cl—F bond, and low dipole moment, $FClO_3$ possesses high kinetic stability in spite of $\Delta H_f{}^0$ being only −5.7 and $\Delta G_f{}^0$ being positive (11.5 kcal $mole^{-1}$). This is reflected in its high thermal stability and its reluctance to hydrolyze. It is not shock-sensitive and at room temperature is relatively inert. At elevated temperature, however, or under conditions supplying a sufficient amount of activation energy, it is a powerful oxidizer (*211*).

Perchloryl fluoride is thermally stable up to about 400°C. The thermal decomposition of $FClO_3$ in quartz at pressures between 5 and 930 mm and temperatures between 465° and 495°C was studied by Gatti *et al.* (*112*). They found that the decomposition reaction,

$$2FClO_3 \longrightarrow 2ClF + 3O_2$$

is unimolecular and homogeneous with an activation energy of 58.4 ± 2 kcal $mole^{-1}$. The rate constant at 495.4°C was found to be $k = 9.25 \times 10^{-4}$ sec^{-1} and the following decomposition mechanism was suggested:

$$\begin{aligned} FClO_3 &\longrightarrow FClO_2 + O \\ O + FClO_3 &\longrightarrow FClO_2 + O_2 \\ FClO_2 &\longrightarrow ClF + O_2 \end{aligned}$$

The decomposition kinetics were also calculated by Usmanov and Magarra (*287*) using a dimensionless molecular transfer equation. Perchloryl fluoride can be heated almost to the softening point of glass without explosion (*92*).

Hydrolysis of $FClO_3$ is very slow even at 250°–300°C (*92*). For quantitative hydrolysis, heating of $FClO_3$ with concentrated aqueous hydroxide solution to 300°C in a sealed tube is required:

$$FClO_3 + 2NaOH \longrightarrow NaClO_4 + NaF + H_2O$$

For quantitative analysis, $FClO_3$ can conveniently be reduced at 25°C by an alcoholic solution of KOH resulting in dissolved KF and a precipitate of $KClO_4$ (*222*).

The reaction of $FClO_3$ with metallic sodium or potassium starts only at ~300°C, although it proceeds vigorously (*92*). At room temperature $FClO_3$ is unreactive with a considerable number of gases, liquids, and solids. Again, however, if sufficient activation energy, such as heating to 100°–300°C, is supplied, violent reactions usually occur. With reducing agents, oxides, fluorides, and chlorides are formed. Typical examples are H_2, N_2O, H_2S, SO_2, SCl_2, PCl_3, CaC_2, KCN, NaI, KSCN, $CH_2{=}CCl_2$, and hydrocarbons (*122*, *158*, *222*). Using dilute mixtures, the H_2S–$FClO_3$ reaction can be controlled and the following products are obtained (*222*):

$$3FClO_3 + 4H_2S \longrightarrow 4SO_2 + 3HF + 3HCl + H_2O$$

In the spectra of H_2S–$FClO_3$ and H_2–$FClO_3$ flames, bands due to S_2, SO_2, OH and to ClO, OH, respectively, were observed (*177*). With HCl at 200°–300°C, the following gas-phase reaction occurs:

$$FClO_3 + 7HCl \longrightarrow HF + 4Cl_2 + 3H_2O$$

Many inorganic ions are oxidized by $FClO_3$ in aqueous solution (*112*). The oxidation rate often depends on the pH of the solution and the temperature. For example: the oxidation of KI in the presence of $NaHCO_3$ is barely detectable; in caustic soda, a slow oxidation occurs; and in 0.1 *M* mineral acid one observes (*92*) quantitative reaction within 4 hr according to

$$FClO_3 + 8I^- + 6H^+ \longrightarrow Cl^- + F^- + 4I_2 + 3H_2O$$

Other ions oxidized by $FClO_3$ include NO_2^-, SO_3^{2-}, and CN^- which are converted to NO_3^-, SO_4^{2-}, and NCO^-, respectively (*106*, *122*, *222*).

Whereas $FClO_3$ is rather inert toward most compounds, including gaseous NH_3, at room temperature it reacts (*92*, *186*, *187*) easily with liquid NH_3 at −78°C or its aqueous solutions:

$$FClO_3 + 3NH_3 \longrightarrow NH_4F + NH_4NHClO_3$$

The reaction is complete in several hours and, in liquid NH_3, it is greatly accelerated by $NaNH_2$ (*186*, *187*). From the ammonium perchloryl amide, which could not be isolated in pure form, the corresponding Ag^+, Cs^+, and K^+ salts and K_2NClO_3 and Cs_2NClO_3 have been obtained. These salts, especially when dry, are impact- and friction-sensitive.

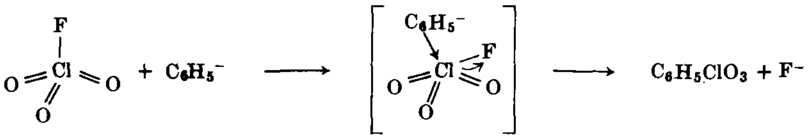
Perchloryl fluoride does not attack glass at moderate temperature, but decomposes at 25°C on contact with activated SiO_2 or Al_2O_3, particularly in the presence of small amounts of H_2O. With other surface-active materials, such as charcoal, ignition may take place. However, there is no reaction at room temperature with synthetic zeolites. It passes freely through a 4 Å molecular sieve, but is completely absorbed by a 5 Å molecular sieve (*188*). Most combustible substances in contact with liquid $FClO_3$ form shock-sensitive explosive compositions. Generally, metal oxides, fluorides, or chlorides do not react with $FClO_3$ at temperatures up to 400°C (*186*). Lalande reported (*164*) that $FClO_3$ oxidizes UF_4 to UF_6. However, a subsequent study by Rude *et al.* (*241*) showed that an intermediate uranium oxyfluoride that disproportionates to UF_6 and UO_2F_2 is formed. Photolysis of mixtures of $FClO_3$ with F_2 or ClF_5 produces ClF_3O (*228, 240*).

Perchloryl fluoride shows no tendency to form adducts with either strong Lewis acids or bases. This behavior has been rationalized in Section II, D. The binary systems of $FClO_3$ with BF_3, PF_5, AsF_5, SbF_5, or SO_3 were studied by Lang (*167*), at Pennsalt (*224*), and by Nikitina and Rosolovskii (*209*). Similarly, at Pennsalt (*224*) no evidence was found for complexing of $FClO_3$ with either CsF or FNO_2.

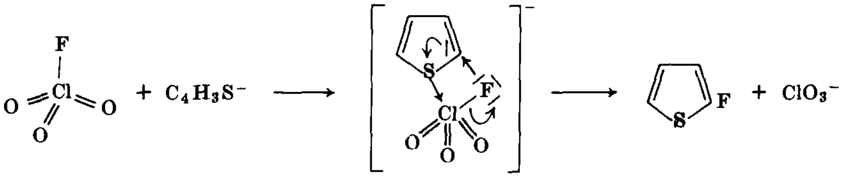
Anhydrous $FClO_3$ does not corrode most of the common metals, but, in the presence of moisture, slow hydrolysis may occur causing corrosion (*40*, *122*, *127*, *222*). The compatibility of various elastomers with 1:1 mixtures of $FClO_3$ and N_2F_4 was studied by Green *et al.* (*126*) and Grigger *et al.* (*127*).

In reactions with organic compounds, $FClO_3$ behaves as either an oxidant or a 1- or 2-center electrophile which, depending on the reaction conditions, can be used for the introduction of either fluorine, a ClO_3 group, or both fluorine and oxygen. A large number of publications have appeared on this subject and have been extensively reviewed by Khutoretskii *et al.* (*158*). Additional general information can be found in Refs. (*106, 122, 169, 262,* and *284*). Since a systematic coverage of this subject is beyond the scope of this review, we give examples only of the most important type of reactions, in addition to references to some of the more recent publications not covered in the previous reviews.

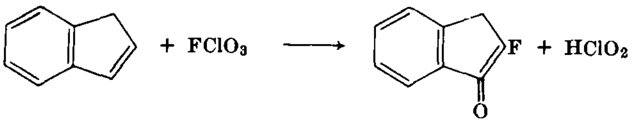
Since $FClO_3$ is highly susceptible to nucleophilic attack at the chlorine atom, it reacts readily with anions. These reactions are relatively well-understood, and Sheppard has proposed (*261*) a general mechanism for these reactions by which the most nucleophilic center in the anion (oxygen or other heteroatom related to carbon) always attacks the chlorine and never the more electronegative fluorine. For localized nucleophiles (such as alkoxides), simple fluoride ion displacement occurs, but, for the mesomeric ions (ambient electrophiles), an intramolecular (cyclic) transfer of F^- can occur in the intermediate to give a C—F bond. The high energy gained by the formation of the C—F bond provides a strong driving force for this fluoride transfer, and fluorine never has to achieve a highly unfavorable energy state with positive charge. This mechanism explains why phenyllithium reacts with $FClO_3$ to give perchloryl benzene, whereas 2-lithiothiophene gives 2-fluorothiophene in high yield (*257*):



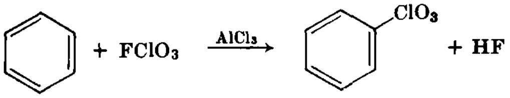
and



Compounds having a cyclic double bond conjugated with an aromatic ring are capable of reacting with $FClO_3$ to give α-fluoroketones. This type of reaction was named oxofluorination and in it $FClO_3$ acts as a 2-center electrophile as shown for indene (*207*):



In the presence of Friedel–Crafts catalysts, such as $AlCl_3$, the $FClO_3$ can be used for introducing a ClO_3 group (perchlorylation) into an aromatic ring (*144*):

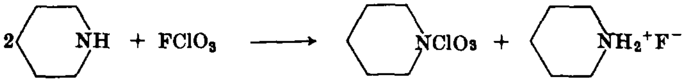


Hydrogenolysis (*258*) of perchloryl aromatic compounds yields ArH and not ArOH, thus confirming the presence of a C—Cl bond. Another useful reaction of $FClO_3$ involves the replacement of the active hydrogens of methylene compounds by fluorine (*145*, *262*, *284*). A typical example is the fluorination of malonic esters:

$$CH_2(COOR)_2 \xrightarrow{+FClO_3} CF_2(COOR)_2$$

Since $FClO_3$ is a very mild fluorinating agent, it has found widespread use for the selective fluorination of compounds such as steroids.

The reaction of cyclic amines with $FClO_3$ is similar to that of $FClO_3$ with NH_3 (see above). For example, the following reaction takes place with piperidine (*110*):



(For additional recent publications dealing with the use of $FClO_3$ as a reagent for the synthesis of organic compounds, see Refs. *94*, *103*, *111*, *114–116*, *153*, *159*, *212*, *213*, *217*, *250*, *286*, *289* and *290*.)

5. *Uses*

The most thoroughly studied application of $FClO_3$ is its use as an oxidant. The spectra of fuel–$FClO_3$ flames were studied (*177*), and the flame speed in mixtures of CH_4 with air and $FClO_3$ was measured (*131*). The H_2–$FClO_3$ flame was found (*251*) to be readily controllable with a low background and useful as an excitation source for flame photometry. For rocket propulsion, the performance of either neat $FClO_3$ or combinations with other oxidizers, such as halogen fluorides (*11*, *26*), was studied and typical performance data (*106*) are given in Table XXX. Small amounts of ClF_3 can be added to neat $FClO_3$ to provide self-ignition. The performance of $FClO_3$ as an oxidizer is similar to that of N_2O_4 (*106*, *136*), and the burning rate of solid propellants is increased by $FClO_3$ (*267*). It has also been proposed to use an acetylene–$FClO_3$ torch

TABLE XXX

PERFORMANCE OF SELECTED STORABLE LIQUID OXIDIZERS FOR ROCKET PROPULSION[a]

Oxidizer	Fuel	Specific impulse[b] (sec)	Density impulse (gm sec/cm^3)
$FClO_3$	UDMH[c]	290	337
ClF_3	UDMH	279	382
65 ClF_3/35 $FClO_3$	UDMH	288	386
$FClO_3$	LiH solid[d]	273	337
ClF_3	LiH solid	288	436
88 ClF_3/12 $FClO_3$	LiH solid	291	433
$FClO_3$	N_2H_4	295	358
ClF_3	N_2H_4	292	436
N_2O_4	N_2H_4	291	354

[a] Data from Gall (*106*).

[b] Pound force × sec/lb mass; shifting equilibrium; pressure ratio 1000:14.7.

[c] Unsymmetrical dimethylhydrazine.

[d] LiH, 85%; organic binder, 15%.

for cutting and welding of metals, in the Sterling cycle engine, in high-pressure gas generation for turbine drive, in fuel cells, and in explosives similar to Sprengel liquid O_2–carbon powder combinations (*105*), and as a deodorant in aerosol sprays (*170*). However, the latter application appears very doubtful in view of the substantial toxicity of $FClO_3$ (see above).

The use of $FClO_3$ as a chemical reagent for the introduction of fluorine or a ClO_3 group has been discussed in detail in Section III, K, 4 and is of special value for the synthesis of fluorine-containing steroids. The polymerization of ethylene under a pressure of hundreds of atmospheres and a temperature of about 200°C in the presence of $FClO_3$ has been patented (*135*).

There are patents on the use of $FClO_3$ as a heat transfer medium in refrigeration (*165*) and as an insecticide–fungicide (*123*). Owing to its ability to absorb intensively slow electrons (*138*), $FClO_3$ can be used as a gaseous insulator. Its dielectric properties are superior to those of SF_6, and it hardly deteriorates on exposure to γ-irradiation (*104*).

General information on shipping, handling, safety, etc., of $FClO_3$ can be found in Gall's review (*106*).

L. Chlorine Fluoride Oxide Radicals

Very little is known about chlorine fluoride oxide radicals. Although the formation of the $FClO_3^-$ radical anion in the reaction of $FClO_3$ with nucleophilic agents has been postulated (*286*), it has not been isolated and characterized.

The only well-known species is the $FClO^+$ radical cation. The ESR spectrum of this species was first reported by Olah and Comisarow (*214*, *215*) for both the ClF_3–SbF_5 and the ClF_5–SbF_5 system. However, the spectrum was incorrectly interpreted in terms of a ClF^+ radical cation. Eachus, Slight, and Symons (*86*) suggested that the observed spectrum is due to $FClO^+$ and not to ClF^+. This conclusion was supported by Christe and Muirhead (*62*) who showed that, in the pure ClF_3–SbF_5 and ClF_5–SbF_5 systems, this species could not be observed but was generated by impurities in the starting materials. Additional evidence for this species containing oxygen was obtained by Gillespie and Morton (*121*) who investigated the reaction of ClF and of Cl_2–ClF with the superacid medium HSO_3F–SbF_5–SO_3. It was shown that the addition of H_2O to solutions of $ClF_2^+SbF_6^-$ in SbF_5 strongly enhanced the ESR signal attributed to ClF^+ by Olah and Comisarow. They suggested that the species was due either to $FClO^+$ or $FClO_2^+$, although their attempts to detect ^{17}O hyperfine splitting in a sample treated with enriched water were unsuccessful. The conclusive identification of this species was recently reported by Morton and Preston (*199*). By using ^{17}O substitution techniques, they succeeded in proving that the species contains 1 oxygen atom and is best described as $FClO^+$. This radical cation is characterized by its g value of 2.0059 and the following hyperfine interactions: $a_{17} = 18.0$, $a_{19} = 20.4$, and $a_{35} = 12.9$ G.

During a matrix-isolation infrared study of the F_2–Cl_2O and ClF–O_3 systems, a new species was observed by Andrews *et al.* (*5*) at 733.8 cm^{-1} which was tentatively assigned to the $ClF_2O\cdot$ radical. However, more data are needed for the positive identification of this species.

M. MISCELLANEOUS

The ClO_3F^{2-} anion has been reported by Mitra and Ray (*197*). However, in our opinion their claim is almost certainly incorrect.

A compound of the empirical composition FCl_2O_6 was claimed by DeGuevara (*79*). The following self-explanatory abstract of this patent was found in *Chemical Abstracts* and, we are confident, will be enjoyed by the more knowledgeable readers:

> The title compd. which is claimed to be novel is prepd. by reacting in a hermetically sealed flask 500 ml. 55° Be H_2SO_4, $Ca(OCl)_2$ 5–10, $KClO_2$ 9–20, $KClO_3$ 10–20, and $Mg(ClO_4)_2$ 10–20 g. Cl and a Cl oxide are given off, washed, and collected as a stabilized aq. soln. Simultaneously, F is produced from CaF_2 and H_2SO_4 and washed and dried. The F is passed into the stabilized aq. soln. of FCl_2O_6, which is suitable for use as an antiseptic, preservative, and purifier in the food, wine, perfume, and water industries and as a humectant and bleach for textiles.

IV. Appendix: Tables of Thermodynamic Properties for Some Chlorine Oxyfluorides

TABLE AI

THERMODYNAMIC PROPERTIES FOR ClF_3O GAS[a]

T(°K)	$C_p{}^0$ [cal/(mole deg)]	H^0–$H_0{}^0$ (kcal/mole)	$-(F^0$–$H_0{}^0)/T$ [cal/(mole deg)]	S^0 [cal/(mole 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

TABLE AI—*continued*

T(°K)	$C_p{}^0$ [cal/(mole deg)]	H^0–$H_0{}^0$ (kcal/mole)	$-(F^\circ$–$H_0{}^0)/T$ [cal/(mole deg)]	S^0 [cal/(mole deg)]
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

[a] Data from Christe and Curtis (*55*).

TABLE AII

THERMODYNAMIC PROPERTIES FOR ClF_3O_2 GAS[a]

T(°K)	$C_p{}^0$ [cal/(mole deg)]	H^0–$H_0{}^0$ (kcal/mole)	$-(F^\circ$–$H_0{}^0)/T$ [cal/(mole deg)]	S^0 [cal/(mole deg)]
0	0	0	0	0
100	10.127	0.847	48.967	57.437
200	16.511	2.179	55.516	66.411
298.15	21.256	4.049	60.375	73.956
300	21.327	4.089	60.459	74.088
400	24.384	6.386	64.711	80.675
500	26.362	8.930	68.484	86.344
600	27.685	11.636	71.881	91.275
700	28.599	14.453	74.968	95.615
800	29.251	17.347	77.795	99.479
900	29.727	20.298	80.400	102.953
1000	30.085	23.289	82.816	106.105
1100	30.360	26.312	85.066	108.985
1200	30.574	29.359	87.171	111.637
1300	30.745	32.425	89.148	114.091
1400	30.883	35.507	91.012	116.375
1500	30.995	38.601	92.775	118.509
1600	31.089	41.705	94.447	120.513
1700	31.167	44.818	96.036	122.400
1800	31.233	47.938	97.551	124.183
1900	31.289	51.064	98.997	125.873
2000	31.337	54.196	100.382	127.480

[a] Data from Christe and Curtis (*57*).

TABLE AIII: Thermodynamic Properties for $FClO_3$ Gas[a]

	cal mole^{-1} deg^{-1}			kcal mole^{-1}			
T(°K)	C_p^0	S^0	$-(F^0-H^0_{298})T$	$H^0-H^0_{298}$	ΔH_f^0	ΔF_f^0	Log K_P
0	0.000	0.000	Infinite	−3.178	−3.034	−3.034	Infinite
100	8.462	54.278	78.032	−2.375	−3.996	1.097	−2.397
200	12.073	61.160	67.968	−1.362	−4.715	6.493	−7.095
298	15.517	66.653	66.653	0.000	−5.120	12.090	−8.861
300	15.573	66.749	66.653	0.029	−5.125	12.196	−8.884
400	18.152	71.602	67.297	1.722	−5.298	18.002	−9.835
500	20.000	75.863	68.593	3.635	−5.312	23.831	−10.416
600	21.319	79.633	70.125	5.704	−5.226	29.653	−10.801
700	22.271	82.994	71.728	7.886	−5.076	35.455	−11.069
800	22.967	86.016	73.328	10.150	−4.884	41.231	−11.263
900	23.487	88.753	74.893	12.474	−4.665	46.983	−11.408
1000	23.883	91.249	76.405	14.843	−4.426	52.710	−11.519
1100	24.189	93.540	77.860	17.248	−4.175	58.410	−11.604
1200	24.430	95.655	79.256	19.679	−3.914	64.090	−11.672
1300	24.624	97.619	80.594	22.132	−3.649	69.746	−11.725
1400	24.780	99.449	81.876	24.602	−3.382	75.380	−11.767
1500	24.909	101.164	83.106	27.087	−3.112	80.998	−11.801
1600	25.016	102.775	84.285	29.584	−2.843	86.596	−11.828
1700	25.105	104.294	85.418	32.090	−2.574	92.179	−11.850
1800	25.181	105.731	86.507	34.604	−2.311	97.744	−11.867
1900	25.246	107.094	87.555	37.125	−2.051	103.297	−11.881
2000	25.301	108.391	88.564	39.653	−1.795	108.833	−11.892
2100	25.349	109.626	89.538	42.185	−1.544	114.359	−11.901
2200	25.391	110.807	90.478	44.723	−1.300	119.871	−11.908
2300	25.428	111.936	91.387	47.264	−1.060	125.374	−11.913
2400	25.461	113.019	92.266	49.808	−0.828	130.868	−11.917
2500	25.489	114.059	93.117	52.356	−0.605	136.347	−11.919
2600	25.515	115.059	93.942	54.906	−0.386	141.823	−11.921

2800	25.558	116.952	95.518	60.013	0.027	152.747	–11.922
2900	25.577	117.849	96.273	62.570	0.223	158.199	–11.922
3000	25.593	118.716	97.007	65.129	0.411	163.641	–11.921
3100	25.608	119.556	97.721	67.689	0.593	169.082	–11.920
3200	25.622	120.369	98.416	70.250	0.767	174.513	–11.918
3300	25.635	121.158	99.093	72.813	0.935	179.937	–11.916
3400	25.646	121.923	99.753	75.377	1.095	185.360	–11.914
3500	25.657	122.667	100.398	77.942	1.249	190.776	–11.912
3600	25.666	123.390	101.026	80.508	1.396	196.192	–11.910
3700	25.675	124.093	101.640	83.075	1.537	201.600	–11.907
3800	25.683	124.778	102.240	85.643	1.673	207.009	–11.905
3900	25.691	125.445	102.827	88.212	1.803	212.404	–11.902
4000	25.698	126.096	103.400	90.782	1.926	217.803	–11.900
4100	25.704	126.730	103.961	93.352	2.043	223.200	–11.897
4200	25.711	127.350	104.511	95.922	2.156	228.592	–11.894
4300	25.716	127.955	105.049	98.494	2.264	233.986	–11.892
4400	25.721	128.546	105.577	101.066	2.366	239.370	–11.889
4500	25.726	129.124	106.093	103.638	2.464	244.755	–11.886
4600	25.731	129.690	106.600	106.211	2.558	250.143	–11.884
4700	25,735	130.243	107.097	108.784	2.646	255.525	–11.881
4800	25.739	130.785	107.585	111.358	2.731	260.904	–11.879
4900	25.743	131.316	108.064	113.932	2.812	266.277	–11.876
5000	25.747	131.836	108.534	116.507	2.889	271.652	–11.873
5100	25.750	132.346	108.996	119.082	2.961	277.029	–11.871
5200	25.753	132.846	109.450	121.657	3.030	282.399	–11.868
5300	25.756	133.336	109.896	124.232	3.097	287.779	–11.866
5400	25.759	133.818	110.335	126.808	3.158	293.140	–11.863
5500	25.762	134.290	110.766	129.384	3.220	298.518	–11.861
5600	25.765	134.755	111.190	131.960	3.274	303.881	–11.859
5700	25.767	135.211	111.608	134.537	3.327	309.248	–11.857
5800	25.769	135.659	112.019	137.114	3.378	314.621	–11.855
5900	25.771	136.099	112.423	139.691	3.425	319.982	–11.852
6000	25.773	136.533	112.821	142.268	3.470	325.349	–11.850

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[a] JANAF Thermochemical Tables (*147*).

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