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Contribution from Rocketdyne,
a Division of Rockwell International, Canoga Park, California 91304

Halogen Perchlorates. Reactions with Fluorocarbon Halides

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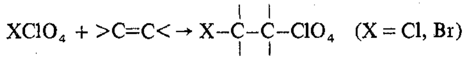
Received March 28, 1974 AIC40205V

The reactions of chlorine perchlorate and bromine perchlorate with numerous fluoroalkyl halides were examined. In the case of fluorocarbon iodides, these reactions were generally found to produce high yields of the novel fluorocarbon perchlorates CF_3ClO_4, $CF_3CF_2ClO_4$, *n*-$C_7F_{15}ClO_4$, $O_4ClCF_2CF_2ClO_4$, and $ICF_2CF_2ClO_4$. Important insight into the mechanism of formation of these compounds was obtained through the isolation of complex intermediates such as $(CF_3)_2CFI(ClO_4)_2$ and *n*-$C_7F_{15}I(ClO_4)_2$. Based on their vibrational spectra, these intermediates have the ionic structure $[(R_f)_2I]^+[I(ClO_4)_4]^-$. Fluorocarbon bromides reacted less readily but sometimes did produce perchlorate derivatives such as $(O_4ClCF_2CFBr-)_2$, $CF_3CFBrCF_2ClO_4$, and $BrCF_2CF_2ClO_4$. Neither mono nor di, primary nor secondary chlorine contained in saturated R_fCl materials interacted with these halogen perchlorates. These and other related reactions are discussed and characteristic data are given for this new and interesting class of compounds.

Introduction

Until recently the study of covalent perchlorates was restricted to a few derivatives,[1,2] mainly inorganic, because of the extreme shock sensitivity of the known hydrocarbon derivatives. Also the available intermediates for forming covalent perchlorates were quite limited and themselves difficult to manipulate. With the discovery of chlorine perchlorate ($ClOClO_3$ or Cl_2O_4)[3] and bromine perchlorate ($BrOClO_3$ or $BrClO_4$),[4] useful reagents became available for the synthesis of new perchlorate species. This has been realized and has led to the preparation of the new inorganic materials $I(ClO_4)_3$,[5] $CsI(ClO_4)_4$,[5] and $CsBr(ClO_4)_2$[6] and improved syntheses of $Ti(ClO_4)_4$ and $CrO_2(ClO_4)_2$.[7] Furthermore, the reactions of Cl_2O_4 and $BrClO_4$ with perhaloolefins were shown[8] to produce the previously unknown perhaloalkyl perchlorates, in high yield, as illustrated



$$XClO_4 + {>}C{=}C{<} \rightarrow X{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}ClO_4 \quad (X = Cl, Br)$$

Of paramount interest though, was the finding that these fluorocarbon perchlorates were stable, tractable species quite unlike their hydrocarbon and some of their inorganic analogs. Thus it was decided to investigate further this new class of compounds and, in particular, to search for additional preparative routes which result exclusively in the introduction of a perchlorato group without simultaneous addition of bromine or chlorine atoms.

Experimental Section

Caution! The halogen perchlorates and the alkyl perchlorates are potential explosives. Safety precautions should be taken in handling and using these materials.

Apparatus and Materials. The equipment used in this work has been described.[5] Chlorine perchlorate[3] and bromine perchlorate[4] were prepared as reported. The fluoroalkyls were purchased (except where noted) and purified by fractional condensation. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å line of an Ar ion laser as the exciting line and a Claassen filter[9] for the elimination of plasma lines. Sealed quartz tubes (~2-mm i.d.) or glass melting point capillaries were used as sample containers in the transverse-viewing, transverse-excitation technique. While exposed to the laser beam, the sample tube was kept below -80° in a vacuum-jacketed flow tube by flowing a stream of dry N_2 through it. Mass spectra were recorded using a Quad 300 (Electronic Associates, Inc.) quadrupole mass spectrometer equipped with a passivated all stainless steel inlet system. The ^{19}F nmr spectra were recorded on a Varian Model DA60 spectrometer at 56.4 MHz using $CFCl_3$ as internal standard. Chemical shifts and coupling constants were determined by the side-band technique. Analytical data were obtained using Orion specific ion electrodes (F^-, Cl^-, or ClO_4^-) and solutions prepared after Na fusion or hydrolysis. These data together with some physical properties are summarized in Table I.

CF_3I–Cl_2O_4 Reactions. Trifluoromethyl iodide (2.02 mmol) and Cl_2O_4 (4.24 mmol) were combined at -196° in a 30-ml stainless steel cylinder which was subsequently slowly warmed to -45° during several days. Recooling to -196° showed the absence of noncondensable products. While rewarming to room temperature, the volatile products evolved were separated by fractional condensation. These consisted essentially of Cl_2 (2.07 mmol), trapped at -196°, and CF_3ClO_4 (2.01 mmol), trapped at -112°; the yield of CF_3ClO_4 was 99% based on CF_3I. The molecular weight observed by vapor density measurements was 167 *vs.* a value of 168.4 calculated for CF_3ClO_4. Measured quantities of CF_3ClO_4 and $CFCl_3$ reference were used to confirm by ^{19}F nmr peak area ratio measurements that the compound contains three fluorine atoms per molecule. The purity of the product was further indicated by its tensiometric homogeneity. The mass spectrum showed *m/e* peaks for $CF_3ClO_4^+$ (parent), $CF_3ClO_2^+$, CF_3ClO^+, ClO_3^+ (base peak), CF_3^+, ClO_2^+, COF_2^+, ClO^+, CF_2^+, COF^+, CO_2^+, O_2^+, CF^+, and CO^+ ions.

On standing at room temperature, the nonvolatile product of this reaction, "$IClO_4$," evolved O_2, Cl_2, and Cl_2O_7 in a manner similar to $I(ClO_4)_3$[5] eventually leading to the formation of I_2O_5. Occasionally the reaction of CF_3I with Cl_2O_4 deflagrated, particularly when warmed up too rapidly. The deflagration resulted in the generation of much O_2 (*e.g.*, 9.4 mmol from 6.0 mmol of Cl_2O_4), CO_2, COF_2,

Table I. Physical Properties and Analytical Data of Several Novel Fluorocarbon Perchlorates

Compd[a]	Vapor pressure	ΔS, eu	ΔH_v, kcal/mol	Elemental analysis, %			
				Calcd		Found	
				F	Cl	F	Cl
CF_3ClO_4	7.4828, 1301.0 (9.5[b])	23.3	5.94	33.84	21.04	33.3	21.5
$CF_3CF_2ClO_4$	7.6356, 1430.8 (27.7[b])	21.8	6.54	43.49	16.23	42.9	16.0
n-$C_7F_{15}ClO_4$	2[c]			60.84	7.57	60.4	7.42
$ICF_2CF_2ClO_4$	15			23.29	10.86	22.9	10.9
$BrCF_2CF_2ClO_4$	74			27.20	12.69	27.1	12.5
$(-CFBrCF_2ClO_4)_2$	<1			21.89	13.62	21.4	13.8
$C_4F_6(ClO_4)_2Cl_2$	2			26.40	32.84	26.3	32.7

[a] All compounds listed are clear, colorless liquids. [b] $\log P_{mm} = A - B/T(°K)$; bp, °C. [c] In mm at 20°.

Cl_2, and a trace of CF_3Cl. All the iodine was recovered as I_2 and IF_5. No solid residue was produced and no CF_3ClO_4 was obtained.

Trifluoromethyl perchlorate (0.456 mmol) was loaded into a 10-ml cylinder containing ~1 g of CsF cooled at −196°. The closed cylinder was heated at 100° for 18 hr prior to fractionation of the products. Most of the CF_3ClO_4 was recovered (0.321 mmol) unchanged. The decomposition products were $FClO_3$ (0.134 mmol) and COF_2 (0.134 mmol obtained on vacuum pyrolysis of the $Cs^+OCF_3^-$ salt formed).

CF_3CF_2I–Cl_2O_4 Reactions. Perfluoroethyl iodide (1.97 mmol) and Cl_2O_4 4.65 mmol) were allowed to react as described for CF_3I but during the work-up the reactor was initially not warmed above −45°. The only volatile species found were Cl_2 (2.03 mmol) and some Cl_2O_4. However, after 3 days at −25°, the reactor was again examined and additional volatile materials were present. These were $CF_3CF_2ClO_4$ (1.84 mmol) and small amounts of Cl_2 and unreacted CF_3CF_2I. The yield was 94% and the vapor density molecular weight was 216; calculated for $CF_3CF_2ClO_4$, 218.4. The mass spectrum of $CF_3CF_2ClO_4$ exhibited prominent m/e peaks for the fragment ions $CF_2ClO_4^+$, $C_2F_5^+$, ClO_3^+, CF_3^+ (base peak), ClO_2^+, ClO^+, CF_2^+, COF^+, CF^+, and CO^+. The "$IClO_4$" solid left in the reactor was as described before.

Other examples of this reaction which were worked up somewhat differently gave the same final result. However, at the intermediate stages there was even more definite evidence for the formation of an $R_fI(ClO_4)_2$ complex. For example, at the completion of the −45° reaction, the reaction cylinder was warmed directly to room temperature while pumping and fractionating the volatiles. After 1.5 hr the cylinder was closed and the fractions obtained were examined. These were one Cl_2 for each C_2F_5I and a little $FClO_3$ but no R_f species from a starting mixture of 1:2 C_2F_5I–Cl_2O_4. After 2 hr at room temperature, the reactor was reopened and was now found to contain "free" $CF_3CF_2ClO_4$ in approximately 95% yield, together with trace amounts of Cl_2 and Cl_2O_7. The stability of $CF_3CF_2ClO_4$ is shown by the fact that a 0.598-mmol sample did not react on contact with 1.6 g of CsF for 1 week at ambient temperature. However, heating the mixture at 120° for 12 hr completely decomposed the perchlorate to $FClO_3$ (0.60 mmol) and CF_3CFO (0.60 mmol obtained on vacuum pyrolysis of the formed $Cs^+CF_3CF_2O^-$).

$(CF_3)_2CFI$–Cl_2O_4 Reactions. 2-Iodoperfluoropropane was prepared from perfluoropropene and I_2–IF_5 by a method similar to that previously reported[10] and its identity was verified by infrared, mass, and ^{19}F nmr spectra. Chlorine perchlorate (3.31 mmol) and $(CF_3)_2CFI$ (1.53 mmol) were allowed to react as in the preceding examples. Fractional condensation of the volatile products on work-up showed Cl_2 (1.55 mmol), Cl_2O_4 (0.36 mmol), and $(CF_3)_2CFI$ (0.09 mmol). The nonvolatile residue weighed 0.703 g, and it did not decompose on standing. The weight calculated for 1.44 mmol of $(CF_3)_2CFI(ClO_4)_2$ was 0.711 g. Examination of the residue in the drybox showed a loose, finely powdered, white solid, mp 71–73° dec. *Anal.* Calcd for $C_3F_7I(ClO_4)_2$: ClO_4, 40.2. Found: ClO_4, 40.6. The solid fumes in air and liberates some I_2 together with oily droplets on treatment with water. When heated at 105° for 16 hr in a 10-ml cylinder, 0.62 mmol produced O_2 (1.13 mmol) and 2.42 mmol of the condensable species CO_2 and Cl_2 with some COF_2 and small amounts of CF_4 and C_2F_6. Iodine was found exclusively as I_2 and IF_5. No solid products were recovered.

ICF_2CF_2I–Cl_2O_4 Reactions. 1,2-Diiodotetrafluoroethane was prepared from $CF_2{=}CF_2$ and I_2. The purified product was allowed to react with 4–6-fold molar equivalents of Cl_2O_4 at and below −45°. Generally the chlorine by-product obtained indicated that even after 1 week only slightly more than one I per ICF_2CF_2I had reacted. In addition to unreacted ICF_2CF_2I and Cl_2O_4, typical products included $ICF_2CF_2ClO_4$ (~60%), ICF_2CF_2Cl (~20%), and Cl_2O_7. Purification of $ICF_2CF_2ClO_4$ was difficult, especially the removal of Cl_2O_7. The $ICF_2CF_2ClO_4$ is a clear, colorless liquid stable at ambient temperature. Under dynamic vacuum it slowly passes through traps cooled to −45°. This compound gave a most definitive mass cracking pattern including an easily detectable parent ion. Important m/e peaks noted corresponded to the ions $IC_2F_4ClO_4^+$, $IC_2F_4^+$, $IC_2F_3O^+$, $C_2F_4ClO_4^+$, CF_2I^+, $C_2F_4^+$, $C_2F_3O^+$, ClO_3^+, CF_3^+ (base peak), ClO_2^+, COF_2^+, ClO^+, CF_2^+, COF^+, and CF^+.

When carried out at −25° the reaction deflagrated, giving the usual O_2, Cl_2, CO_2, COF_2 and I_2–IF_5. No nonvolatile products were recovered. With the aid of a solvent (FC-78, 3M Co.) reactions of Cl_2O_4 with both ICF_2CF_2I and $ICF_2CF_2ClO_4$ were carried out at −45°. Again poor results were obtained and poor yields of R_fClO_4 but minor amounts of a viscous, colorless liquid of low volatility (~2 mm at 20°) were recovered. Based on its ^{19}F nmr and infrared spectrum, this material has been identified as the bisperchlorate $O_4ClCF_2CF_2ClO_4$.

$ICF_2CF_2CF_2I$–Cl_2O_4 Reaction. 1,3-Diiodoperfluoropropane was prepared as reported[11] from $AgO_2CCF_2CF_2CF_2CO_2Ag$ and I_2. A 1.29-mmol sample of it was allowed to react with 5.63 mmol of Cl_2O_4 at −45° for several days. Products volatile at −45° consisted of Cl_2 (2.91 mmol) and Cl_2O_4 (0.47 mmol). However when the closed reactor was allowed to warm to room temperature for 4 hr, the nonvolatile product $(O_4Cl)_2ICF_2CF_2CF_2I(ClO_4)_2$, according to the observed stoichiometry, deflagrated. The deflagration products were O_2 (~7 mmol), Cl_2, CO_2, COF_2, CF_4, and some C_2F_6 (~6 mmol total), together with I_2 and IF_5. No nonvolatile species was observed.

n-$C_7F_{15}I$–Cl_2O_4 Reactions. n-Perfluoroheptyl iodide (1.42 mmol) and Cl_2O_4 (3.60 mmol) were allowed to react at −45° for several days and gave Cl_2 (1.48 mmol) and Cl_2O_4 (0.66 mmol) as products volatile at this temperature. After several hours of pumping at room temperature, the white solid product left in the reactor weighed 0.985 g. The weight calculated for 1.42 mmol of $C_7F_{15}I(ClO_4)_2$ was 0.987 g. The solid had a melting point with decomposition of 56–58° and it fumed in air. *Anal.* Calcd for $C_7F_{15}I(ClO_4)_2$: ClO_4, 28.6. Found: ClO_4, 28.3. Upon standing for several days at ambient temperature the solid appeared shiny and sticky as if it were decomposing. Therefore it was heated to 40° under vacuum while collecting the volatile material in cold traps. Traces of Cl_2 and Cl_2O_7 were obtained, along with a clear, colorless, mobile liquid. The mass spectrum of this liquid resembled those reported[12] for n-C_7F_{15}– compounds. Some of the more important characteristic peaks were attributable to the ions $C_7F_{14}ClO_4^+$, $C_7F_{15}O^+$, $C_7F_{15}^+$, $C_nF_{2n-1}O^+$ and $C_nF_{2n-1}^+$ (n = 3–6), and ClO_x^+ (x = 1–3). This liquid was identified as $C_7F_{15}ClO_4$.

A sample of $C_7F_{15}ClO_4$ (0.22 mmol) was heated with 1.1 g of CsF for 1 hr at 110°. This produced $FClO_3$ (0.22 mmol) and $C_6F_{13}CFO$ (0.21 mmol obtained on pyrolysis of the $Cs^+C_7F_{15}O^-$ salt formed). The n-perfluoroheptoyl fluoride was identified on the base of its infrared and mass spectrum, which included the parent ion peak, $C_7F_{14}O^+$.

$BrCF_2CFBrCFBrCF_2Br$–Cl_2O_4 Reactions. Perfluorobutadiene and Br_2 were employed to prepare 1,2,3,4-tetrabromoperfluorobutane.[13] The latter (1.27 mmol) and Cl_2O_4 (7.37 mmol) were allowed to react at −25° for 4 weeks. Vacuum fractionation of the products, while keeping the reactor at 0°, showed the volatile products to be Cl_2 (2.67 mmol), Cl_2O_4 (2.42 mmol), and a large but unmeasured amount of $BrClO_4$. From the recovered materials, it appeared that 2 Br had been replaced by ClO_4 to give $C_4F_6Br_2(ClO_4)_2$. The residue was a stable, clear, colorless liquid with less than 1 mm vapor pressure at room temperature. It was identified as $(O_4ClCF_2CFBr-)_2$ by the comparison of its infrared, mass, and ^{19}F nmr spectra with those of a sample of $(O_4ClCF_2CFBr-)_2$ prepared from bromine perchlorate and perfluorobutadiene (see below).

Samples of $C_4F_6Br_2(ClO_4)_2$ (1.34 mmol) and Cl_2O_4 (2.00 mmol) were allowed to react in a 30-ml cylinder at −45° for 3 weeks. Very little Cl_2 by-product was noted at that time and therefore more Cl_2O_4 was added and the temperature changed to −25° for 5 weeks. The evolved Cl_2 (1.03 mmol) indicated about 40% of the bromine had reacted. However, some degradation was also evident since fluorocarbon acyl fluoride and $FClO_3$ were found. Removal of these volatile species as well as $BrClO_4$ and excess Cl_2O_4 left a clear, colorless, nonvolatile liquid which was characterized by vibrational and ^{19}F nmr spectroscopy.

$CF_2{=}CFCF{=}CF_2$–$BrClO_4$ and –Cl_2O_4 Reactions. Perfluorobutadiene (2.58 mmol) and $BrClO_4$ (5.80 mmol)[14] were gradually warmed from −78 to 0° over several days followed by removal and separation of volatile products which consisted of a small amount of $BrClO_4$ and an unidentified fluorocarbon acyl fluoride. The residue consisted of the clear, colorless, mobile liquid $(O_4ClCF_2CFBr-)_2$ (2.25 mmol, 87% yield). The ^{19}F nmr showed only two types of fluorine with a 2:1 peak area ratio indicating a symmetrical adduct. The mass spectrum was complex and the parent ion was beyond the range of the instrument (*m/e* 500). No ion containing more than 2 Br atoms was found. Several $C-ClO_4^+$ fragments were noted as well as intense ClO_3^+, ClO_2^+, and ClO^+ ions.

Similarly, perfluorobutadiene (2.24 mmol) and Cl_2O_4 (4.98 mmol) were allowed to react at −78 to 0° furnishing $C_4F_6Cl_2(ClO_4)_2$ (2.15 mmol, 96% yield). The infrared spectrum was typical for a covalent perchlorate while the mass spectrum was very complex apparently due to the presence of isomeric species which was also indicated by the ^{19}F nmr spectrum (see Discussion). In the mass spectrum intense ClO_x^+ (x = 1–3) ion fragments were observed.

Miscellaneous R_fBr–$XClO_4$ Reactions. 1,2-Dibromoperfluoropropane was prepared from $CF_3CF{=}CF_2$ and Br_2. In a typical reaction, $CF_3CFBrCF_2Br$ (2.01 mmol) and Cl_2O_4 (2.68 mmol) were allowed to react for 3 days at 0° followed by 4 days at room temperature. Several fractional condensations were carried out, after O_2 (3.49 mmol) was removed by pumping, resulting in the isolation of $CF_3CFBrCF_2ClO_4$ (0.90 mmol, 45% yield) as the only detectable fluorocarbon perchlorate. It was identified by comparison to an authentic sample.[8] At −25° for 4 weeks, these same reactants gave a 31% yield of the $CF_3CFBrCF_2ClO_4$.

Bromine perchlorate and $CF_3CFBrCF_2Br$ were allowed to react using these same conditions and produced a 23% yield of $CF_3CFBrCF_2ClO_4$ with all of the unreacted R_fBr being recovered. For this system the possibility was examined for catalytically accelerating the displacement of Br by ClO_4 using added $Cs^+ClO_4^-$ or $NO_2^+ClO_4^-$. However, no effect was noted, with both the reaction rates and yields being unchanged.

1,2-Dibromoperfluorethane (2.01 mmol) and Cl_2O_4 (4.60 mmol) were contacted at −25° for 6 weeks. Separation of the products revealed that most of the $BrCF_2CF_2Br$ (1.70 mmol) was unchanged. A trace of $ClCF_2CF_2Br$ was found, and as the only R_fClO_4, $BrCF_2CF_2ClO_4$ (0.23 mmol, 11% yield). This perchlorate was identified by comparison to an authentic sample prepared from tetrafluoroethylene and $BrClO_4$. Furthermore, the known $BrCF_2CFO$ and $FClO_3$ were formed in qualitative experiments by CsF-catalyzed decomposition.

Tetrafluoroethylene (1.23 mmol), $BrClO_4$ (1.34 mmol), and CF_3Cl (∼9 mmol) were allowed to react at −45° for several days. Trapping at −78° separated $BrCF_2CF_2ClO_4$ (1.12 mmol) from the CF_3Cl and other trace products which were more volatile. When no solvent was used to moderate this reaction only decomposition products were obtained. In addition to characterization of $BrCF_2CF_2ClO_4$ by CsF-catalyzed decomposition to $BrCF_2CFO$ and $FClO_3$, other data are presented in the tables.

Dibromodifluoromethane (2.02 mmol) and Cl_2O_4 (8.16 mmol) were added to a 30-ml cylinder cooled at −196°. After 3 weeks at −45°, the products were separated by fractional condensation. Analysis by infrared and gc showed COF_2 (1.9 mmol), COFCl (0.1 mmol), and Cl_2 (4.1 mmol), together with $BrClO_4$ and Cl_2O_7.

Discussion

Fluorocarbon Iodide Reactions. Chlorine perchlorate and fluorocarbon iodides have been found to react vigorously at −45° and below to produce, at first, a complex intermediate of the composition $R_fI(ClO_4)_2$ and eventually the corresponding fluorocarbon perchlorate.[15] The equations for these reactions are

$$R_fI + 2Cl_2O_4 \rightarrow R_fI(ClO_4)_2 + Cl_2$$

$$R_fI(ClO_4)_2 \rightarrow R_fClO_4 + [IClO_4]$$

Yields of R_fClO_4 from these reactions were often high (90+%) and excellent material balances served to define the stoichiometry of the reactions. The vigor of the reaction is exemplified by the fact that with the simplest R_f (=CF_3–) occasional deflagrations were encountered, particularly when the requirement of very slow warming of the reactants was not rigorously followed. In other instances, the intermediate deflagrated at some higher temperature (>−45°). These deflagrations always produced much O_2, Cl_2, CO_2, and COF_2 together with small amounts of CF_4, CF_3Cl, and sometimes C_2F_6. Furthermore, all of the iodine originally present as R_fI was always recovered as a mixture of I_2 and IF_5. This is remarkable in view of the fact that the only fluorine in the system was bound to carbon in supposedly inert perfluoralkyl groups. Thus, an interhalogen compound has been formed from a C–F compound.

To our knowledge, this is the first time that such an unusual reaction has been observed. This is an efficient process also, since all the iodine is involved. This process probably entails an initial formation of IF, which is known to disproportionate[16] readily to the observed species according to

$$5IF \rightleftharpoons 2I_2 + IF_5$$

The fluorocarbon perchlorates prepared from iodides were CF_3ClO_4, $CF_3CF_2ClO_4$, $C_7F_{15}ClO_4$, $ICF_2CF_2ClO_4$, and $O_4ClCF_2CF_2ClO_4$. Combinations of spectral data (infrared and Raman, Table II and Figures 1 and 2; ^{19}F nmr, Table III; and mass spectra) together with elemental analyses, vapor density molecular weight measurements, and derivative formation were used to identify these new compounds. The results of all these observations were unequivocal, agreed with earlier results for similar compounds,[8] and established these products as covalent monodentate perchlorates.

A combination of infrared and Raman spectroscopy is a very useful tool for establishing the identity of these perchlorates.

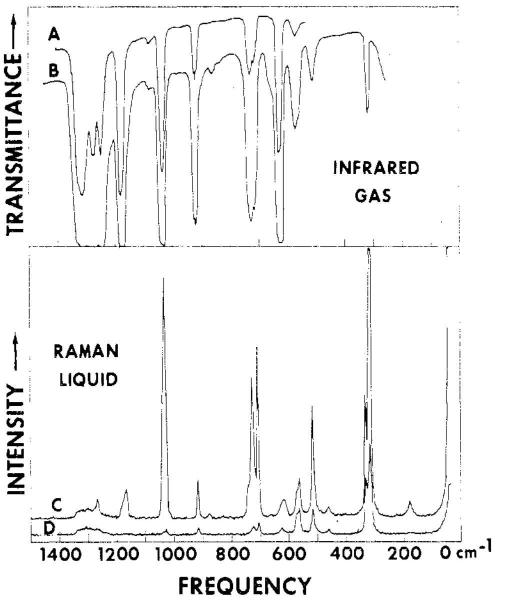


Figure 1. Infrared spectrum of CF_3ClO_4 gas: A, 5 mm in 5-cm path length cell with AgCl windows; B, 18 mm in 10-cm path length cell with AgBr windows. Raman spectrum of liquid CF_3ClO_4 at −100°: C, incident polarization parallel; D, incident polarization perpendicular.

Table II. Infrared and Raman Spectra of Fluorocarbon Perchlorates (4000–500-cm^{-1} Range)

CF_3ClO_4 Ir[a]	CF_3ClO_4 Raman[b]	$CF_3CF_2ClO_4$ Ir[a]	$BrCF_2$-CF_2ClO_4 Ir[a]	$ICF_2CF_2ClO_4$ Ir[a]	n-$C_7F_{15}ClO_4$ Ir[b]	n-$C_7F_{15}ClO_4$ Raman[b]	$(O_4ClCF_2$-$CFCl$-$)_2$ Ir[b]	$(O_4ClCF_2$-$CFBr$-$)_2$ Ir[b]	Tentative assignment
					1368 sh	1375 w			
	1330 vw		1320 vs	1320 vs	1350 sh	1332 w	1310 vs	1310 vs	
1308 vs	1300 vs	1308 vs	1305 vs	1303 vs	1295 vs	1300 w	1295 vs	1290 vs	Antisym ClO_3 str
1265 s	1267 vw	1250 vs	1250 s	1288 s	1245 vs		1245 m	1225 ms	
1241 s	1240 vw	1204 s	1204 s	1197 s	1210 vs	1215 vw	1227 m	1190 s	
1171 vs	1169 vw	1180 s	1187 m		1153 vs	1160 w	1180 vs	1150 s	C–F str region
			1168 s			1140 vw	1135 s	1115 sh	
		1093 vs	1112 s	1105 s	1108 m	1112 w	1100 m	1098 w	
			1068 w	1076 w	1052 m	1051 m	1058 w		
1028 vs	1031 s	1035 vs	1037 vs	1038 vs	1028 vs	1035 vs	1032 vs	1028 vs	Sym ClO_3 str
							960 s		
914 m	917 w	930 w	940 s	922 s	947 w	948 vw	943 s	933 m	C–O str
				906 s	900 mw	908 w	892 m	900 m	
		848 mw	850 w		852 w		861 s	860 mw	
					840 w		848 m	843 mw	
			810 w	805 m	825 w	823 w	809 w	804 w	C–C str + certain C–Hal str
					785 w		784 m	780 m	
					770 w	767 s	770 m	762 m	
					750 m	750 w		750 m	
					743 m	742 w	732 w		
724 m	726 m	752 m			728 m	728 s			δ umbrella CF_3
706 sh	708 m				713 ms	714 m			δ scissor FCF_2
660 sh	660 vw	675 s	665 m	670 s	660 s	660 s			δ CF_2
			643 m	640 s	643 s	645 s	650 vs	645 vs	
615 s	616 vw	612 s	615 m	614 s	612 s	617 m	610 vs	608 vs	Cl–O str
568 mw	570 vw	582 m			565 sh	578 w	572 w	570 sh	δ antisym ClO_3
560 sh	564 w								δ scissor $OClO_2$
512 w	516 m[c]	530 w				515 m[d]			δ umbrella ClO_3

[a] Gas. [b] Liquid. [c] Raman peaks below 500 cm^{-1} for CF_3ClO_4 were at 462 (vw), 342 (m), 320 (vw), 316 (vs), and 178 (vw) cm^{-1}. [d] Raman peaks below 500 cm^{-1} for n-$C_7F_{15}ClO_4$ were at 470 (vw), 388 (m), 322 (m), 300 (m), 285 (w), and 223 (mw) cm^{-1}.

Table III. ^{19}F Nmr Data[a,b]

Compd	CF_3-	-CF_2-	>CFX (X = Cl, Br)	-CFX-ClO_4 (X = F, Cl)
CF_3ClO_4	60.4			
$CF_3CF_2ClO_4$	84.6			93.2
$CF_3(CF_2)_5CF_2ClO_4$	81.2	121.9–126.4		88.0
$ClCF_2CF_2ClO_4$		72.7		92.5
$BrCF_2CF_2ClO_4$		68.2		91.4
$ICF_2CF_2ClO_4$		63.3		90.4
$O_4ClCF_2CF_2ClO_4$		92.2		92.2
$ClCF_2CFClClO_4$		69.0		79.0
$Cl_2CFCFClClO_4$			69.8	76.0
$(-CFBrCF_2ClO_4)_2$			125	79.3
$CF_3CFClCF_2ClO_4$	76.5		122	84.7
$CF_3CFBrCF_2ClO_4$	78.4		139	85.8

[a] Chemical shift in ppm relative to internal $CFCl_3$; a peak area ratio measurements agreed with the assignments. [b] Data not from this work are taken from ref 8.

All of the more than 12 members of this class of compounds now known show very strong infrared bands near 1300 cm^{-1} (antisymmetric ClO_3 stretches) and 1030 cm^{-1} (symmetric ClO_3 stretch). In addition, another strong band due to the Cl–O single bond stretch of the O–ClO_3 group appears near 615 cm^{-1} in all –CF_2ClO_4 terminated species and at 630 cm^{-1} in all –$CFClClO_4$ terminated[8] species. Previously[8] we had assigned the Cl–O stretch in –CF_2ClO_4 examples to the bands at ~645 cm^{-1} in those compounds. Now with many more examples available, it is clear that the Cl–O stretch occurs at ~615 cm^{-1} while the ~645-cm^{-1} band is due to a CF_2 deformational mode (see Table II). The C–O stretch for these compounds is also characteristic and is emphasized in Table II along with other significant correlations. Raman spectra alone are less characteristic than the infrared for these materials but they always exhibit a very intense symmetric ClO_3 stretching band at ~1030 cm^{-1}. Infrared and Raman spectra of CF_3ClO_4 and n-$C_7F_{15}ClO_4$ are shown in Figures 1 and 2 as typical representatives of this class of compounds.

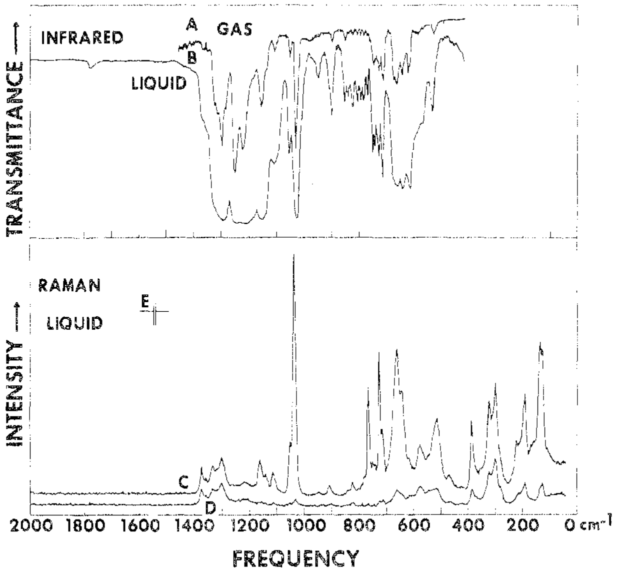


Figure 2. Infrared spectrum of $C_7F_{15}ClO_4$: A, 2 mm of gas in 10-cm path length cell with AgBr windows; B, liquid between AgCl plates. Raman spectrum of liquid n-$C_7F_{15}ClO_4$ at –80°: C, incident polarization parallel; D, incident polarization perpendicular; E, spectral slit width.

Trifluoromethyl perchlorate is the simplest fluorocarbon perchlorate, the "parent" member of the series. Some of its properties were described in a preliminary communication.[17] The stability of this compound is noteworthy. A sample stored in a stainless steel cylinder for nearly 2 years was unchanged. Even at elevated temperature (100° for 18 hr) in the presence of the known decomposition catalyst CsF,[8] only 30% of the material cleaved according to

$$CF_3ClO_4 \xrightarrow[\Delta]{CsF} COF_2 + FClO_3$$

The quantitative decomposition of R_fClO_4 compounds into

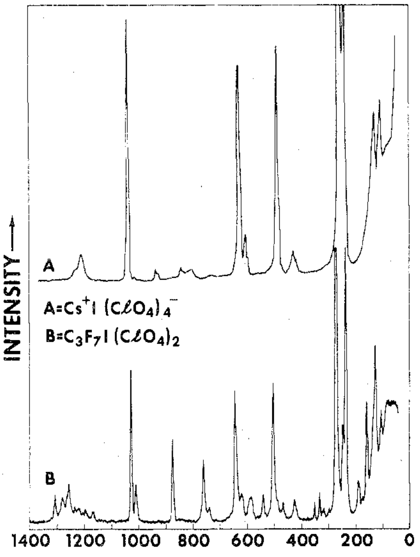


Figure 3. Raman spectra of solids at −100°.

Table IV. Infrared and Raman Spectra of Solid Iodine Perchlorates (cm^{-1}, Intensity)

i-$C_3F_7I(ClO_4)_2$		n-$C_7F_{15}I(ClO_4)_2$		$Cs^+I(ClO_4)_4^-$
Ir	Raman	Ir	Raman	Raman
		1371 ms	1376 mw	
		1337 mw	1332 w	
	1308 w		1295 vw	
1295 vs	1281 w	1278 sh	1278 w	
1250 vs, br	1257 mw	1230 vs, br	1259 w	
	1235 vw		1250 vw	1243 w, sh
	1220 vw		1236 vw	
	1205 vw		1218 vw	1207 mw
1190 sh	1196 vw			
1168 s	1168 vw	1157 s		
		1138 w		
		1074 mw	1074 mw	
		1048 mw	1048 vw	
1032 s	1028 s	1023 s	1023 s	1038 s
	1011 mw			1016 mw
971 s		959 ms	959 m	
874 s	875 m	857 w		
		828 w		
		810 mw	806 m	
765 m	762 m	755 m	755 w	
746 s	741 vw	730 mw	742 m	
718 s				
667 s		675 s	664 w	
640 s	646 s	640 s	639 s	630 s
620 sh	622 w			607 mw
584 m	588 w	584 m	590 w	
		568 m	576 w	
542 m	543 w	533 m		
496 s	502 s	494 m	499 s	489 s
425 w	429 w	423 vw	428 w	430 mw
	352 w	382 w	383 w	
	333 w		345 vw	
	320 vw		322 vw	
	298 vw		311 vw	
	272 vvs		261 vvs	261 vs
	249 w			
	228 vs			240 s
	191 w		197 w	
	175 vw			
	159 ms		152 w	
	129 ms		125 w	131 ms
	106 w			106 ms

their corresponding acyl fluorides and perchloryl fluoride is a very useful characteristic reaction as reported previously.[8] The mass spectrum of CF_3ClO_4 was slightly unusual in that it is the only example of a perfluorocarbon perchlorate for which we have observed a parent ion. Typical of covalent perchlorates in general, no ClO_4^+ ions were found although intense ClO_3^+, ClO_2^+, and ClO^+ ion peaks were present. This is reasonable since the C–O bond energy is almost twice that of the Cl–O bond. The ^{19}F nmr spectrum exhibited only one line at 60.4 ppm, quite close to that of related CF_3O– moieties.[18,19] An analysis of the infrared and Raman spectra of gaseous and liquid CF_3ClO_4 has been completed.[20] Nineteen of the twenty-one fundamental modes of vibration expected for a nine-atom molecule of symmetry C_s with hindered rotation of the CF_3 and ClO_3 groups were observed and assigned. This thorough spectral study is fully consistent with the covalent monodentate perchlorate formulation.

Iodine monoperchlorate, postulated as the by-product in the synthesis equations, seems not to be a monomeric covalent material since it shows no volatility. At ambient temperature, on standing the "$IClO_4$" gradually loses Cl_2 and Cl_2O_7, eventually leading to the formation of I_2O_5. The same solid decomposition product results from the ambient-temperature degradation of $I(ClO_4)_3$.[5]

In view of the facile synthesis noted for CF_3ClO_4, it was of interest to extend the method to analogous perfluoroalkyl iodides. With CF_3CF_2I this led to the formation of $CF_3CF_2ClO_4$ whose characterization was analogous to that used for CF_3ClO_4 proving that this was a covalent perchlorate. However, during the synthesis, observations were made which indicated a complex, metastable intermediate had been formed. At −45° all the by-product Cl_2 was formed but not the $CF_3CF_2ClO_4$. To obtain $CF_3CF_2ClO_4$ it was necessary to raise the temperature somewhat which decomposed the intermediate. From several reactions it was found that this metastable intermediate had the empirical composition $CF_3CF_2I(ClO_4)_2$.

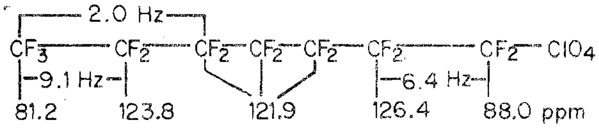
With other precursors, $(CF_3)_2CFI$ and n-$C_7F_{15}I$, it was found that this intermediate was an isolable solid, stable at ambient temperature. The empirical compositions were analogous to those of the ethyl case, *i.e.*, $(CF_3)_2CFI(ClO_4)_2$ and n-$C_7F_{15}I(ClO_4)_2$. These solids fumed in air and formed ClO_4^- and some I_2 on hydrolysis. From their infrared and Raman spectra (Table IV and Figure 3) it was evident that the covalent perchlorate function was still present. However, comparison of the Raman spectra of both solids with that of the salt $Cs^+I(ClO_4)_4^-$ (Table IV and Figure 3), which was obtained from CsI and Cl_2O_4,[5] revealed striking similarities. All of the bands observed for the $I(ClO_4)_4^-$ ion are also shown by these two $R_fI(ClO_4)_2$ solids. They correspond quite closely in both frequency and relative intensity. Furthermore, the only other moderately intense bands in the spectra of the fluorocarbon-containing compounds are in the C–C stretching region and thus not associated with the perchlorate functions. Therefore, it can be concluded the intermediates having the empirical composition $R_fI(ClO_4)_2$ possess the ionic structure $(R_f)_2I^+I(ClO_4)_4^-$. The related ionic structure $(R_f)_2I^+IF_4^-$ has been postulated[21] for solids obtained "not infrequently" from the fluorination of R_fI compounds with ClF_3. However, experimental proof for such a structure was not offered.

That these solid intermediates are the precursors to the covalent R_fClO_4 products was shown for the perfluoroheptyl case. Thus, it was found that, slowly at ambient temperature or more rapidly at 40°, this solid produced n-$C_7F_{15}ClO_4$ and the decomposition products of "$IClO_4$," *i.e.*, Cl_2, O_2, Cl_2O_7, and I_2O_5. Care is required in heating the solid complex. On one occasion when heated just to its melting point under dynamic vacuum, the n-$C_7F_{15}I(ClO_4)_2$ exploded, also the solid tetraperchlorate $(O_4Cl)_2ICF_2CF_2CF_2I(ClO_4)_2$ deflagrated on warming to ambient temperature, as did $(CF_3)_2CFI(ClO_4)_2$ on heating above its melting point.

The high-yield conversion of $(R_f)_2I^+I(ClO_4)_4^-$ to $2R_fClO_4$ is an unusual and very interesting reaction. In addition, the

$(R_f)_2I^+$ cation might be a very useful alkylating reagent for the introduction of perfluoroalkyl groups.

n-Perfluoroheptyl perchlorate exhibited the typical covalent perchlorate mass spectrum and vibrational spectra (Table II). Its ^{19}F nmr spectrum was especially informative with regard to the fluorocarbon part of the molecule but it was more complex than the other R_fClO_4 moieties owing to the presence of several closely similar CF_2 groups. The *n*-$C_7F_{15}ClO_4$ nmr spectrum exhibited five peaks showing relative area ratios of 3:2:6:2:2. A schematic of the analyzed spectrum is shown below.



The lowest field peak at 81.2 ppm (area 3), was shown to be composed of triplets. This peak is assigned to the terminal CF_3 group with coupling to the nearest CF_2 (9.1 Hz) and the next nearest CF_2 (2.0 Hz) groups. Assignment of the next peak, 88.0 ppm (area 2), to the $-CF_2ClO_4$ fluorine resonances can be readily made by comparison with known R_fCF_2OX values.[18,22] This peak is a poorly resolved triplet due to coupling (6.4 Hz) with the adjacent CF_2 group. Since CF_2 groups α to CF_3- are generally of lower field shift than those α to $-CF_2OX$,[18,22,23] the remaining two peaks of area 2 are assigned respectively to the CF_2 (123.8 ppm) α to the terminal CF_3- and the CF_2 (126.4 ppm) α to the $-CF_2ClO_4$ termination. The remaining peak, 121.9 ppm (area 6), is thus assigned to the three central CF_2 groups which are nearly equivalent. This peak is not symmetrical but has a weak shoulder at 122.5 ppm which can be ascribed to a slight nonequivalence of one of the three CF_2's, perhaps the central one in the seven-carbon chain. Further verification of the identity of this perchlorate was obtained through its quantitative CsF-catalyzed decomposition into $FClO_3$ and *n*-$C_6F_{13}CFO$.

The synthesis of 1,2-bis(perchlorato)tetrafluoroethane was attempted from ICF_2CF_2I and Cl_2O_4. In the absence of a solvent, it was found that the consumed Cl_2O_4 amounted to only slightly more than that required for reaction of one I atom. This occurred despite relatively long (1 week) reaction periods at −45°. One of these reactions which had gone smoothly but incompletely at −45° deflagrated while being maintained at −25°. Normally, the volatile products recovered from this reaction were $ICF_2CF_2ClO_4$, ICF_2CF_2Cl (a minor amount usually), Cl_2, and Cl_2O_7. The R_fClO_4 yield (50–60%) was generally nowhere near so good as that obtained with other R_fI compounds.

When a solvent was used to promote the substitution of both iodines in ICF_2CF_2I, $ICF_2CF_2ClO_4$ was still the main product. However, a viscous liquid of low volatility was isolated in very small amounts which was identified as $O_4ClCF_2CF_2ClO_4$ by ^{19}F nmr and ir spectroscopy. The infrared spectrum agreed very well with that of $FSO_3CF_2CF_2SO_3F$[24] when vibrations caused by the different end groups were discounted and only $-OCF_2CF_2O-$ bands were considered. An improved synthetic technique is required to study this perchlorate more fully.

Fluorocarbon Bromide Reactions. Attempts were made to displace bromine from R_fBr substrates in analogy to the corresponding iodine systems. Again reactant ratios of Cl_2O_4 to R_fBr greater than 1 were required since any liberated bromine (BrCl or Br_2) can react with Cl_2O_4 to give $BrClO_4$.[4] The latter might or might not participate in additional displacement of bromine from R_fBr. A 4-week reaction of $BrCF_2CFBrCFBrCF_2Br$ and excess Cl_2O_4 proceeded according to

$$C_4F_6Br_4 + 4Cl_2O_4 \rightarrow C_4F_6Br_2(ClO_4)_2 + 2BrClO_4 + 2Cl_2$$

The ^{19}F nmr spectrum of this bisperchlorate showed it to be a single isomer. It exhibited only two basic types of C–F. These peaks were readily assignable by comparison with known species[8,25] to terminal $-CF_2ClO_4$ fluorine atoms (79.3 ppm) and internal >CFBr fluorine atoms (125 ppm). The resonance characteristic of $-CF_2Br$ fluorines (~60 ppm) was totally absent. Also, the peak area ratio of 2:1 established that this product was wholly $O_4ClCF_2CFBrCFBrCF_2ClO_4$. However, the absorption of the >CFBr fluorines was split into two lines (124.6 and 126.1 ppm) with the low field line having about one-fourth the intensity of the other. The proximity of these peaks indicates strongly that they are due to two different rotational isomers. This is not surprising in view of the many bulky groups on the carbon backbone. With Br atoms on adjacent carbons, the trans isomer would be expected to be preferred as previously demonstrated[26] for $BrCF_2CFBr_2$.

The identification of $O_4ClCF_2CFBrCFBrCF_2ClO_4$ was aided by examining the product of the reaction

$$CF_2{=}CFCF{=}CF_2 + 2BrClO_4 \rightarrow C_4F_6Br_2(ClO_4)_2$$

This interaction proceeded smoothly and efficiently below room temperature to give the identical bisperchlorate in 87% yield. Thus, the first reaction step must have been the following polar 1,2 addition of $BrClO_4$ to the diolefin

$$CF_2{=}CFCF{=}CF_2 + BrClO_4 \rightarrow O_4ClCF_2CFBrCF{=}CF_2$$

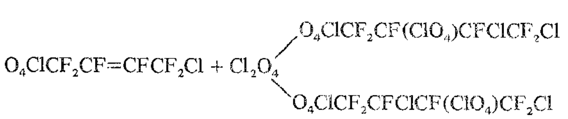
followed by the addition of a second $BrClO_4$ in the same fashion

$$O_4ClCF_2CFBrCF{=}CF_2 + BrClO_4 \rightarrow O_4ClCF_2CFBrCFBrCF_2ClO_4$$

Thus, the symmetrical bisperchlorate is formed with all perchlorate groups in the 1,4 positions as expected on the basis of our previous studies.[8]

The corresponding Cl_2O_4 adduct of perfluorobutadiene was also prepared in 96% yield. The physical appearance, vapor pressure, and infrared spectrum (ClO_4 and C–F bands) of the adduct were much like its Br counterpart. However, the ^{19}F nmr spectrum clearly indicated that a more random addition had occurred. The observed resonances were of three basic types, all of which were well separated and readily assignable:[8,25] (1) 62 ppm $-CF_2Cl$, (2) 83 ppm $-CF_2ClO_4$, and (3) 130 ppm >CFZ (Z = Cl or ClO_4). The finding of both perchlorate and chlorine terminal groups and peak area measurements show that both 1,2 and 1,4 additions occurred as the first step. Equations illustrating the 1,4 addition are

$$CF_2{=}CFCF{=}CF_2 + Cl_2O_4 \rightarrow O_4ClCF_2CF{=}CFCF_2Cl$$



$$O_4ClCF_2CF{=}CFCF_2Cl + Cl_2O_4 \begin{cases} \nearrow O_4ClCF_2CF(ClO_4)CFClCF_2Cl \\ \searrow O_4ClCF_2CFClCF(ClO_4)CF_2Cl \end{cases}$$

Based on peak area measurements and assuming that 1,2 attack gives a single product as discussed for the $BrClO_4$ example, then Cl_2O_4 addition gave somewhat more 1,4 than 1,2 products.

Further substitution of bromine in (O_4ClCF_2CFBr-) by a perchlorato ligand was sought using Cl_2O_4. From the evolved Cl_2, it appeared that ~40% reaction had occurred after 8 weeks at −45 to −25°. In appearance, the liquid product was unchanged—still clear, colorless, and mobile. Its infrared spectrum exhibited minor but distinct differences from the starting material. In particular, the ClO_4 absorptions appeared relatively more intense and broad than they did in the starting material. The ^{19}F nmr spectrum confirmed the changed nature of this liquid compared to the bisperchlorate compound. Rather than just two types of C–F as in the starting material (79.3 ppm for CF_2ClO_4 and 125 ppm for >CFBr), this material had three different types of C–F resonances: 81 ppm $-CF_2ClO_4$, 125 ppm >CFBr, and 135 ppm >CFClO$_4$. The relative area ratios for these types indicated about 35% of the $>CFX$ fluorines were of the $X = ClO_4$ type. Furthermore, each of the three types of C–F found consisted of two or more unequal-area peaks of similar shifts (±1 ppm), indicating the presence of different isomers. Since only 35% of the original Br had been substituted, the above nmr spectrum is that of a mixture of starting material with either a tris- or a tetrakisperchlorate. Distinction between these two possibilities is not possible owing to their low volatilities. However, we would expect the formation of the trisubstituted compound to be favored over that of the tetrakisperchlorate.

Another R_fBr compound tested with Cl_2O_4 and $BrClO_4$ was $CF_3CFBrCF_2Br$. Yields of $CF_3CFBrCF_2ClO_4$ as high as 45% were obtained. The product was identical in its physical and spectral properties with the material previously synthesized[8] by $BrClO_4$ addition to the corresponding olefin. Added $Cs^+ClO_4^-$ or $NO_2^+ClO_4^-$ did not catalyze the above reactions.

Further studies with R_fBr species showed that $BrCF_2CF_2Br$ reacted very slowly and incompletely with Cl_2O_4 giving $BrCF_2CF_2ClO_4$ in 11% yield (after purification) according to

$$BrCF_2CF_2Br + 2Cl_2O_4 \rightarrow BrCF_2CF_2ClO_4 + Cl_2 + BrClO_4$$

The infrared and ^{19}F nmr spectra of the product correlate well with those of the known $ClCF_2CF_2ClO_4$[8] and of $ICF_2CF_2ClO_4$ which was discussed above. In addition, it was shown that CsF decomposed this perchlorate to $BrCF_2CFO$ and $FClO_3$ as expected.

Other R_fBr compounds found not to react with either Cl_2O_4 or $BrClO_4$ despite long contact times were CF_3CF_2Br, $BrCF_2CF_2CF_2Br$, and $CF_3CFBrCF_2ClO_4$.

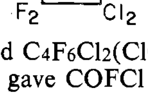
From these various R_fBr–Cl_2O_4 studies, the pattern emerged that some primary and even some secondary Br can be displaced by ClO_4. There are, however, marked differences in the rate and degree of these displacements: $C_4F_6Br_4 > CF_3CFBrCF_2Br > BrCF_2CF_2Br >>> C_2F_5Br$. Furthermore, the reaction appears to be sensitive to the nature of the group adjacent to the C–Br bond. When these are perfluorinated, as in CF_3CF_2Br or $BrCF_2CF_2CF_2Br$ or $CF_3CFBrCF_2ClO_4$, no substitution takes place. If the group is either $-CFBr-$, $-CF_2Br$, or $-CF_2ClO_4$, some substitution occurs.

Attempted Synthesis of Geminal Bisperchlorates. All of the preceding experiments were aimed at the introduction of a single perchlorato group per carbon atom. It appeared very interesting to examine the possibility of synthesizing compounds containing more than one perchlorato group per carbon atom. To this end, dibromodifluoromethane and Cl_2O_4 were allowed to react at −45° for 3 weeks producing the anticipated Cl_2 and $BrClO_4$ by-products. However, the only carbon-containing materials accompanying those compounds were COF_2 and COFCl, accounting for 95 and 5%, respectively, of the carbon in CF_2Br_2. Chlorine heptoxide constituted the other significant product. These moieties most certainly arose from the sequence

$$CF_2Br_2 + 4Cl_2O_4 \rightarrow 2Cl_2 + 2BrClO_4 + [CF_2(ClO_4)_2] \rightarrow COF_2 + Cl_2O_7$$

Apparently geminal ClO_4 groups are unstable toward decomposition into carbonyl compounds and Cl_2O_7.

Fluorocarbon Chloride Reactions. Numerous R_fCl compounds were investigated and it was ascertained that mono or di, primary or secondary chlorine contained in saturated R_fCl materials was unreactive. Those compounds examined that did not react with Cl_2O_4 were CF_3Cl, $ClCF_2CF_2Cl$, $ClCF_2CFCl_2$, $CF_3CFClCF_2Cl$,



$CF_3CFClCF_2ClO_4$, and $C_4F_6Cl_2(ClO_4)_2$. Trichlorofluoromethane did react but gave COFCl and Cl_2O_7 as primary products. Once again apparently geminal ClO_4 groups were unstable with respect to the formation of $>C{=}O$ and Cl_2O_7.

General Considerations. In spite of the large amount of experimental data, it remains difficult to rationalize all of the observed reactions. For the alkyl iodides, a simple halogen elimination reaction according to

$$\geqslant \underset{\delta+}{C}\text{–}\underset{\delta-}{Hal} + \underset{\delta+}{Hal}\text{–}\underset{\delta-}{OClO_3} \rightarrow\ \geqslant C\text{–}OClO_3 + Hal\text{–}Hal$$

certainly is not applicable, since the isolation of the $(R_f)_2I^+ I(ClO_4)_4^-$ intermediate suggests an oxidation of iodine to a +III oxidation state followed by complex rearrangements. In the case of chlorine compounds, such as $CFCl_3$, which interacted with Cl_2O_4, the halogen elimination mechanism shown above is more likely owing to the fact that Cl_2O_4 is probably not a strong enough oxidizer to oxidize Cl to the +III state. Thus, it is possible that the reaction chemistry of the alkyl iodides might be entirely different from that of the corresponding chlorides. Obviously, systematic and more sophisticated kinetic and structural studies should be carried out on these interesting systems to determine reliably the mechanisms involved and to avoid undue speculation.

Acknowledgment. We are very grateful for support of this work in part by the Air Force Armaments Test Laboratory, Eglin Air Force Base, and in part by the Office of Naval Research, Power Branch. In addition, we wish to thank Dr. L. R. Grant for helpful discussions.

Registry No. CF_3ClO_4, 52003-45-9; $CF_3CF_2ClO_4$, 53011-52-2; n-$C_7F_{15}ClO_4$, 53011-53-3; $ICF_2CF_2ClO_4$, 53011-54-4; $BrCF_2CF_2ClO_4$, 53011-55-5; $C_4F_6(ClO_4)_2Br_2$, 53011-56-6; $C_4F_6(ClO_4)_2Cl_2$, 53011-57-7; $CF_3CFBrCF_2ClO_4$, 38126-26-0; i-$C_3F_7I(ClO_4)_2$, 53078-08-3; n-$C_7F_{15}I(ClO_4)_2$, 53078-09-4; $Cs^+I(ClO_4)_4^-$, 53078-10-7; CF_3I, 2314-97-8; CF_3CF_2I, 354-64-3; $(CF_3)_2CFI$, 677-69-0; ICF_2CF_2I, 354-65-4; $ICF_2CF_2CF_2I$, 422-91-3; n-$C_7F_{15}I$, 335-58-0; $BrCF_2CFBrCF_2Br$, 661-94-9; $CF_2{=}CFCF{=}CF_2$, 685-63-2; $CF_3CFBrCF_2Br$, 661-95-0; $BrCF_2CF_2Br$, 124-73-2; $CF_2{=}CF_2$, 116-14-3; Cl_2O_4, 27218-16-2; $BrClO_4$, 32707-10-1.

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(14) An excess of $BrClO_4$ over that required by the 2:1 stoichiometry for reaction of the two olefinic bonds is considered important. Previously[8] a monoperchlorate adduct of $CF_2{=}CFCF{=}CF_2$ had exploded on warming to room temperature. It is believed that a molecule of that type, *i.e.*, $CF_2{=}CFCFXCF_2ClO_4$, with an oxidizable unsaturated link in close proximity to the oxidizing perchlorate group may be inherently unstable.
(15) For succinctness and clarity, the notation ClO_4 is used to denote the covalent perchlorate group $-OClO_3$. Ionic perchlorate is distinguished by a negative change sign, ClO_4^-.
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