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ORGANIC PERCHLORATES

ROCKETDYNE DIVISION
NORTH AMERICAN ROCKWELL CORPORATION

TECHNICAL REPORT AFATL-TR-72-127

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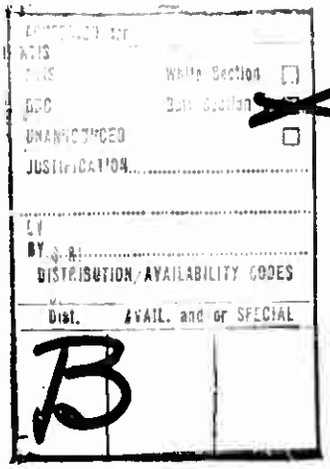
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Organic Perchlorates

C.J. Schack

FOREWORD

This research was conducted by Rocketdyne, a division of North American Rockwell Corporation, 6633 Canoga Avenue, Canoga Park, California 91304, under Contract F08635-71-C-0101 with the Air Force Armament Laboratory, Eglin Air Force Base, Florida 32542. Major Duncan E. Dodds (DLIW) was project monitor for the Armament Laboratory. This report covers work performed under Project 2511, Task 01, Work Unit 12, during the period from 6 March 1971 through 5 June 1972.

This program was directed for the contractor by Dr. D. Pilipovich, Manager, Exploratory Chemistry. Staff members responsible for the scientific effort were Dr. C. J. Schack and Mr. R. D. Wilson. The contractor number assigned to this report is R-9019.

This technical report has been reviewed and is approved.

FRANKLIN C. DAVIES, Colonel, USAF
Chief, Flame, Incendiary, and Explosives Division

ABSTRACT

A variety of new, covalent perchlorates were synthesized, including perfluorinated perchlorates and halofluorocarbon perchlorates. The synthetic approach utilized was a new development and entailed the displacement of halogen from substituted fluorocarbons by the use of chlorine perchlorate.

Simple, saturated mono or di, primary or secondary chlorofluorocarbons did not react with Cl_2O_4 under any conditions. The trichloro compound, $CFCl_3$, was substituted but decomposed to carbonyl compounds and chlorine heptoxide.

Bromofluorocarbons were successfully employed in several instances to furnish new perchlorates with the degree of reactivity and the amount of substitution varying greatly. New perchlorates prepared were $BrCF_2CF_2ClO_4$, $CF_3CFBrCF_2ClO_4$, $O_4ClCF_2CFBrCFBrCF_2ClO_4$, and $C_4F_6Br(ClO_4)_3$. Mono Br Compounds with perfluorinated groups in the α position were unreactive.

Iodofluorocarbons reacted vigorously and usually completely. From CF_3I and C_2F_5I nearly quantitative yields of the new perchlorates, CF_3ClO_4 and $C_2F_5ClO_4$, were obtained. Important physical and chemical properties were measured for these compounds.

In addition, $ICF_2CF_2ClO_4$ and probably $O_4ClCF_2CF_2ClO_4$ were prepared. Novel intermediate complexes of the composition, $R_fI(ClO_4)_2$, were noted in several of these displacement reactions. With $(CF_3)_2CFI$, this complex was isolated as a stable, white, solid powder. Iodine tris-perchlorate did not add ClO_4 groups to perfluoropropene.

Electronegatively substituted chlorocarbons were examined also. Picryl chloride did not react with Cl_2O_4 either as a neat solid or in solution. Cyanuric chloride and trichloroacetonitrile were oxygenated to produce CO_2 and NO_2ClO_4 as significant products. Dichlorodinitromethane reacted incompletely but also formed CO_2 and NO_2ClO_4.

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SECTION I

INTRODUCTION

The chemistry of high-energy chemicals for the most part has paralleled the development of explosive ingredients and subsequently the massive R&D efforts on solid propellants initiated in the 1950s. Traditionally, the conferring of high energy in a covalent molecule is accomplished with the nitro and nitrato functional groups. The nitro group has found its niche in explosives and the nitrato group in double-base propellants.

Two other energetic groups are the perchlorate and the difluoramino, NF_2, moieties. The latter is of extremely high energy and has been extensively evaluated in various solid-propellant applications. Unfortunately, compounds containing the NF_2 group are exceedingly sensitive and appear not to be useful in practical new high-energy explosive formulations. The perchlorate group has been only briefly investigated in covalent compounds such as $C_2H_5ClO_4$. Development was contraindicated because of the extreme thermal sensitivity of the few known compounds. On the other hand, salts of perchloric acid, such as ammonium perchlorate, are workhorse oxidizers in solid propellants.

Generally, the attributes of ionic perchlorate materials are well known and documented. However, examples of useful covalent derivatives are fewer and less well defined. In part, the paucity of data for covalent perchlorates is due to the lack of suitable synthetic intermediates able to serve as vehicles for its introduction in substrate molecules. Recently, two new and useful perchlorate compounds were discovered by the contractor (References 1 and 2), which, in part, fill this void. These compounds are chlorine perchlorate and bromine perchlorate. Both are covalent liquid materials, which are stable below ambient temperature. Most importantly, both compounds are reactive and capable of furnishing perchlorate substituents in covalent or ionic materials.

The objective of this program was the utilization of these new halogen perchlorates in the synthesis of new covalent perchlorates. Of principal concern was the demonstration of model reactions and their subsequent use in preparing a variety of new perchlorates. Structural and physico-chemical characterization of the new materials was sought with the aim of uncovering properties pertinent to explosive end product use.

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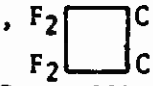
SECTION II

SUMMARY

The excellent properties realized for the perhalo perchlorate compounds prepared earlier at the contractor facility indicated that a thorough investigation should be made of related compounds obtainable through other procedures. In all instances, the halogen perchlorates, and especially chlorine perchlorate, were used as sources of the ClO_4 functionality. Screening reactions were carried out with a wide variety of perhaloalkyl substrates. By the elimination of elemental halogen or mixed halides, the incorporation of ClO_4 groups in these alkyls was sought.

With chlorofluorocarbons, 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, $ClCF_2CF_2Cl$, $ClCF_2CFCl_2$, $CF_3CFClCF_2Cl$,  Cl_2, $CF_3CFClCF_2ClO_4$, and $C_4F_6Cl_2(ClO_4)_2$. Chlorotrifluoromethane (Freon 11) did react but gave $COFCl$ and Cl_2O_7 as primary products.

In the case of bromofluorocarbons, several new covalent perchlorates were synthesized by Br displacement from R_fBr. The degree of reactivity and the amount of substitution obtained varied. An order of reactivity toward Cl_2O_4 was established: $CF_2Br_2 > C_4F_6Br_4 > CF_3CFBrCF_2Br > BrCF_2CF_2Br$. The methyl compound, CF_2Br_2, gave unstable products leading to COF_2 and Cl_2O_7, while the other R_fBr's produced 11- to 100-percent yields of new mono and bis perchlorates. One example was substituted with ClO_4 approaching the composition $C_4F_6Br(ClO_4)_3$. Highly Br- and ClO_4- substituted fluorobutanes were rotationally hindered. Other Br compounds in which the Br was attached to a carbon adjacent to a perfluorinated carbon were unreactive toward Cl_2O_4.

Iodofluorocarbons and Cl_2O_4 combined quite vigorously to undergo high-yield substitution processes leading to the new covalent perchlorates, CF_3ClO_4, $C_2F_5ClO_4$, $ICF_2CF_2ClO_4$, and probably $O_4ClCF_2CF_2ClO_4$. These reactions encompassed an intermediate complex adduct, $R_fI(ClO_4)_2$, as a precursor to the free, substituted end product R_fClO_4. Occasional deflagrations of these intermediates occurred. With $(CF_3)_2CFI$, the bis ClO_4 adduct, $(CF_3)_2CFI(ClO_4)_2$ was obtained. It was found to be a thermally stable, white solid and constituted a new composition of matter. From these results on R_fX-Cl_2O_4 reactions, it appears that the prime factor determining reactivity and substitution is the ability of X to undergo oxidation by Cl_2O_4.

The use of $I(ClO_4)_3$ to form a bis ClO_4 derivative of perfluoropropene was not successful in that no reaction occurred. Several other electronegatively substituted C-Cl compounds were tested with Cl_2O_4 for potential ClO_4 substitution on carbon. Picryl chloride was totally unreactive at all temperatures, with or without a solvent. Cyanuric chloride was oxygenated to form appreciable CO_2 while trichloroacetonitrile underwent attack on the -C≡N group, producing $CCl_3C(O)X$ and NO_2ClO_4. Dichlorodinitromethane reacted incompletely with Cl_2O_4, giving CO_2 and NO_2ClO_4 rather than simple ClO_4 substitution.

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SECTION III

DISCUSSION

Chlorine perchlorate, $ClOClO_3$ (or empirically Cl_2O_4), is a reactive molecule and an excellent source of the perchlorate group in anhydrous environments. Elementary examples of this reactivity are shown by the equations*:

$$HCl \text{ (anhydrous)} + Cl_2O_4 \longrightarrow HClO_4 + Cl_2$$
$$CsCl + Cl_2O_4 \longrightarrow Cs^+ClO_4^- + Cl_2$$
$$AgCl + Cl_2O_4 \longrightarrow Ag^+ClO_4^- + Cl_2$$

All of these reactions are related in that the positively polarized terminal chlorine from Cl_2O_4 combines with a negative chlorine to drive the reaction to completion. Furthermore, both covalent and ionic chloride species react and perchlorates are formed. Bromine perchlorate, $BrOClO_3$ (or empirically $BrClO_4$), also reacts in this manner to provide perchlorates accompanied by the evolution of BrCl.

Several further extensions of the above were possible. It had been reported (Reference 3) that bromine fluorosulfate could condense with chlorocarbons to form polyfluorosulfatomethanes:

$$CCl_4 + 4BrOSO_2F \longrightarrow C(OSO_2F)_4 + 4BrCl$$

Apparently the formation of BrCl is accomplished by the combination of the positive bromine and the chloride. In contractor independent research and development (IR&D) studies, two chlorocarbons were reacted with $ClOClO_3$ to test the extension to covalent perchlorates. The first reaction involved $ClOClO_3$ and CH_3Cl.

$$ClOClO_3 + CH_3Cl \longrightarrow CH_3OClO_3 + Cl_2$$

Methyl perchlorate was quantitatively formed at temperatures below ambient in the absence of any solvent.

Methylene chloride, when reacted with $ClOClO_3$ under similar conditions, gave two new compounds:

$$CH_2Cl_2 + ClOClO_3 \longrightarrow CH_2ClOClO_3 + Cl_2$$
$$CH_2Cl_2 + ClOClO_3 \longrightarrow CH_2(OClO_3)_2 + 2Cl_2$$

The latter compound was the first example, known to the contractor, of a gem bisperchlorate. Very recently, a preliminary report revealing the preparation of another gem bisperchlorate, 2,2-diperchloratopropane, has appeared (Reference 4).

*Throughout this report for purposes of succinctness and clarity, the notation ClO_4 will be used to denote the covalent perchlorate group, $-OClO_3$. Ionic perchlorate will be distinguished by a negative charge sign, ClO_4^-.

Another method for introducing the perchlorate group into molecules is through the addition of either Cl_2O_4 or $BrClO_4$ to olefins (Reference 5):

$$CF_2{=}CF_2 + Cl_2O_4 \longrightarrow ClCF_2CF_2ClO_4$$
$$CF_3CF{=}CF_2 + Cl_2O_4 \longrightarrow CF_3CFClCF_2ClO_4$$
$$CF_3CF{=}CF_2 + BrClO_4 \longrightarrow CF_3CFBrCF_2ClO_4$$

Several noteworthy observations were made regarding these fluorocarbon perchlorates. These compounds and others like them are all clear, colorless, mobile liquids that have the typical low melting points of fluorocarbons. In addition, they are thermally stable, e.g., $CF_3CFClCF_2ClO_4$ was recovered unchanged after several hours in stainless steel at 120°C. With the addition of the perchlorate group, the volatility of the parent structure decreased dramatically. For example, the boiling point of $CF_3CFClCF_2ClO_4$ based on vapor pressure data was calculated at about 115°C, an increase of 70°C over that of $CF_3CFClCF_2Cl$.

The density of chlorofluorocarbons was raised significantly by substituting a ClO_4 group for a Cl atom. The densities of several of these fluoroalkyl perchlorates have been measured and are shown in Table I along with the density of the parent halocarbon.

TABLE I. DENSITY CHANGES WITH ClO_4 SUBSTITUTION

	ρ, g/ml at 20°C	Δρ, g/ml
CF_2ClCF_2Cl	1.47	0.28
$CF_2ClCF_2ClO_4$	1.75	
$CFCl_2CF_2Cl$	1.58	0.19
$CFCl_2CF_2ClO_4$	1.79	
$CF_3CFClCF_2Cl$	1.59	0.21
$CF_3CFClCF_2ClO_4$	1.80	

The substantial density increases resulting from one ClO_4 substitution would be expected to be enhanced by further ClO_4 substitution. Overall then, polyperchlorato fluorocarbon compounds have potentially useful and attractive characteristics.

PREPARATION OF HALOGEN PERCHLORATES

Halogen perchlorates are not commercial materials and must be prepared. Also, some of the reagents required for the synthesis of Cl_2O_4, namely ClF and $ClSO_3F$, were prepared. The overall preparative scheme is shown in the equations:

$$Cl_2 + ClF_3 \xrightarrow{\Delta} 3ClF$$
$$ClF + SO_3 \longrightarrow ClSO_3F$$
$$ClSO_3F + Cs^+ClO_4^- \longrightarrow Cl_2O_4 + Cs^+SO_3F^-$$

Chlorine monofluoride is stable at ambient temperature and was made in sufficient amount, in one run, for the duration of the program. Purified ClF was reacted with SO_3 to form $ClSO_3F$ (Reference 6), which is also storable at ambient conditions. Finally, purified $ClSO_3F$ was used to obtain Cl_2O_4 by contacting liquid $ClSO_3F$ with excess $CsClO_4$ at approximately -45°C for several days. The conversion is approximately quantitative, although 2 to 3 percent of unreacted $ClSO_3F$ has sometimes been encountered.

Chlorine perchlorate is not stable for long periods at ambient temperature and is shock sensitive. However, it can be stored indefinitely at approximately -30°C or lower. Therefore, because low-temperature storage space is limited and because safety considerations prohibit keeping too large a quantity of Cl_2O_4 in one place, this compound was made in multiple, small (9 millimole) batches on a periodic basis.

Bromine perchlorate can be prepared from $BrSO_3F$ and $CsClO_4$, but it is difficult to transfer without partial decomposition. Therefore, bromine perchlorate is better synthesized according to the reaction:

$$Br_2 + 2Cl_2O_4 \longrightarrow 2BrClO_4 + Cl_2$$

Removal of byproduct Cl_2 affords pure $BrClO_4$ in a container to which a reactant may be added and thus eliminates the necessity for $BrClO_4$ transfers.

FLUOROCARBON CHLORIDE REACTIONS

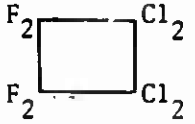
Chlorine containing fluorocarbon compounds are more generally available and cheaper than the corresponding bromine or iodo species; thus, they are more desirable intermediates than the latter. Furthermore, the preparation of new ClO_4-substituted moieties by substitution for halogen, a prime goal of this program, seemed to be more likely with the more electronegative Cl than with the others. This would be the case provided the substitution process is favored by the greatest difference in electronegativity (or degree of polarization) in the C-X component of the reagent. Thus, the positively polarized terminal Cl of Cl_2O_4 would combine with the halogen from C-X to furnish ClX and lead to substitution of the ClO_4 group onto the carbon. However, if other factors such as the C-X bond strength were the most important traits in determining the efficacy of the substitution process, then R_fCl might not be the best intermediate for the synthesis of new covalent perchlorates.

A relatively large number of chlorine-containing, saturated aliphatic fluorocarbons were reacted with Cl_2O_4 in an attempt to effect the general reaction:

$$R_fCl + Cl_2O_4 \longrightarrow R_fClO_4 + Cl_2$$

The R_fCl substrates examined were:

CF_3Cl $\quad$ $ClCF_2CF_2Cl$ $\quad$ $ClCF_2CFCl_2$ $\quad$ $CF_3CFClCF_2Cl$



$CF_3CFClCF_2ClO_4$ $\quad$ $C_4F_6Cl_2(ClO_4)_2$-Isomer Mixture

All of these compounds were tested with Cl_2O_4 statically, without solvent (both components were generally liquid), for prolonged periods at -45° or -25°C. Prior to workup, most of the compounds were allowed to react with Cl_2O_4 at temperatures up to and including ambient. Greater thermal activation was not practical since Cl_2O_4 decomposes slowly at about -20°C and in a matter of 2 days or less at room temperature. Without exception, these substrates failed to react with Cl_2O_4 in any manner. All were completely recoverable at any stage of the reaction. Thus, saturated chlorofluorocarbons, whether mono or di (vicinal or geminal) located in primary or secondary positions, were uniformly unreactive toward Cl_2O_4.

One chlorofluorocarbon was found that would react with Cl_2O_4. This was $CFCl_3$, Freon 11, which was observed to be completely reacted in 3 weeks at -25°C. The desired reaction was:

$$CFCl_3 + 3Cl_2O_4 \longrightarrow CF(ClO_4)_3 + 3Cl_2$$

This was not found although displacement of Cl occurred. Apparently, the intermediate ClO_4 species were unstable, and approximately 85 percent of the $CFCl_3$ was converted to COFCl. The probable reaction path is:

$$CFCl_3 + 2Cl_2O_4 \longrightarrow 2Cl_2 + [CFCl(ClO_4)_2] \longrightarrow COFCl + Cl_2O_7$$

Minor products were CO_2, COF_2, and CF_2Cl_2. The appropriate amount of the byproducts Cl_2 and Cl_2O_7 were found. On a concurrent program concerned with the reaction of CCl_4 and Cl_2O_4 (Reference 7), it was similarly determined that Cl substitution occurred. Again though, the intermediate perchlorate species decomposed to $CO_2/COCl_2$ and Cl_2O_7.

POLYPERCHLORATE HALOBUTANES

Simultaneous with the studies regarding ClO_4 displacement of Cl from fluorocarbon chlorides, attempts were made to accomplish the same displacement with Br compounds. One of the first selected was sym-tetrabromo perfluorobutane. Because this work and other experiments with fluorobutanes are closed related, they will be discussed separately from the remaining R_fBr systems.

The reaction sought for $C_4F_6Br_4$ was:

$$BrCF_2CFBrCFBrCF_2Br + 4Cl_2O_4 \longrightarrow (O_4ClCF_2CFClO_4 \rightarrow)_2 + 4BrCl$$

In practice, twice the above amount of Cl_2O_4 might be required because of the side reaction:

$$BrCl + Cl_2O_4 \longrightarrow Cl_2 + BrClO_4$$

This would occur if $BrClO_4$ were ineffective in the displacement, or if $BrClO_4$ were always preferentially formed from BrCl or Br_2 rather than R_fClO_4 from R_fBr.

It was found that a 4-week reaction of $1C_4F_6Br_4$ and $\sim 6Cl_2O_4$ resulted in the consumption of $4Cl_2O_4$ molecules according to the equation:

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

This new fluorocarbon perchlorate was a stable, clear, colorless mobile liquid with <1 mm vapor pressure at room temperature. The clearly defined presence of ClO_4 groups in the molecule is illustrated by its infrared spectrum*.

Covalent ClO_4 groups have three strong, characteristic infrared vibrations (Reference 5) located at approximately: 1300 cm^{-1}, asym Cl=O stretch; 1020 cm^{-1}, sym Cl=O stretch; and 650 cm^{-1}, Cl-O stretch. These are often the strongest bands in the infrared spectra of these simple molecules and such is also the case here. The fact that there are three such strong absorptions for the ClO_4 group in the infrared region is of great help in establishing the presence of perchlorate substituents. For example, the starting material, $C_4F_6Br_4$, has a strong absorption at about 1015 cm^{-1}, yet it has no bands above about 1220 cm^{-1} and only relatively weak ones near 650 cm^{-1}. Thus, while the first cited band might be mistaken as a ClO_4 band, the absence of the other two shows that no ClO_4 is contained in that compound.

Although two ClO_4 groups were substituted overall per C_4 molecule, numerous possibilities relating to the position and degree of substitutions on individual C_4 species existed. Given equal reactivities of C-Br moieties, 1,2; 1,3; 1,4; and 2,3 ClO_4 substituted isomers could be formed. If varying degrees of substitution occurred, then mono, bis, tris, and even tetrakis ClO_4 derivatives might have been produced in a very complex mixture. Fortunately, the situation was found to be much simpler. The ^{19}F nmr spectrum of the liquid showed only two basic types of C-F were present. These peaks were readily assignable by comparison with known species (References 5 and 8) and were attributed to terminal $-CF_2ClO_4$ fluorine atoms (79.3 ppm relative to external $CFCl_3$) and internal >CFBr fluorine atoms (125 ppm). The well-separated absorption of $-CF_2Br$ fluorines (~60 ppm) was totally absent. Also, because the peak areas were nearly 2:1, this was further proof that this product was wholly the isomer $O_4ClCF_2CFBrCFBrCF_2ClO_4$.

However, the absorption of the >CFBr fluorines was not a single line but was instead two lines (124.6 and 126.1 ppm) with the low field line having about one-quarter the intensity of the other. The proximity of these peaks indicates

*All the illustrated infrared spectra discussed in this report are contained in Appendix I.

strongly that they are due to very similar fluorine substituents. It is probable that they represent two different rotational conformations. Thus, the many bulky groups on the carbon backbone cause preferred, though not exclusive, conformations. With Br atoms on adjacent carbons, it would be expected that these would preferentially acquire positions trans to one another. Nevertheless, even though rotation is hindered, still another configuration could be frozen in and give rise to the second type of $>CFBr$ resonance. An example of this type has been reported (Reference 9) for $BrCF_2CFBr_2$ which at -110°C did not rotate freely and was found to adopt multiple conformations, with the most populated one being that with two bromine atoms trans. Variable-temperature studies of the nmr spectrum could resolve this point, but such work was beyond the scope of the present effort. A final point of evidence aiding the identification of the perchlorate derived from this reaction was obtained by examining the product of the reaction:

$$CF_2=CFCF=CF_2 + 2BrClO_4 \longrightarrow C_4F_2Br_2(ClO_4)_2$$

This interaction proceeded smoothly and efficiently below room temperature to give the bis adduct in 87 percent yield. In all respects--appearance, physical properties, and spectral properties--this product was indistinguishable from that derived from $C_4F_6Br_4$ and Cl_2O_4. Thus, there had occurred an exclusive and stepwise 1,2 addition to the diolefin.

$$CF_2=CFCF=CF_2 + BrClO_4 \longrightarrow O_4ClCF_2CFBrCF=CF_2$$

Additions to perfluorovinyl groups have previously been shown to be oriented in this manner (Reference 5) and can be readily rationalized as occurring through a polar mechanism, i.e., the relatively negative ClO_4 group of $BrClO_4$ always becomes bonded to the positively polarized terminal carbon. Once this mono adduct forms in this fashion, the remaining olefinic bond would be expected to behave similarly in the addition of another $BrClO_4$.

$$O_4ClCF_2CFBrCF=CF_2 + BrClO_4 \longrightarrow O_4ClCF_2CFBrCFBrCF_2ClO_4$$

Thus, the symmetrical bis perchlorate would be formed with all perchlorate groups in the 1,4 positions.

The corresponding bis Cl_2O_4 adduct of perfluorobutadiene was also prepared to provide a sample for possible further ClO_4 substitution. At the same time, a small amount of the bis $ClSO_3F$ adduct was synthesized to furnish corollary and comparative structural data. For the ClO_4 compound, a 96-percent yield was obtained, while for the $ClSO_3F$ compound, the yield was 76 percent. In the latter case, a too vigorous reaction occurred, leading to some C-C bond breaking. Both liquids are stable at ambient temperature in glass, stainless-steel, or Teflon containers. Both are clear, colorless, mobile liquids with about 1 mm vapor pressure at room temperature. The infrared spectrum of the Cl_2O_4 adduct is much like that of the $BrClO_4$ compound especially for the ClO_4 and C-F vibrations.

In contrast to the mode of addition of $BrClO_4$, the Cl_2O_4 and $ClSO_3F$ additions were more random. Both of these materials gave closely related nmr spectra, except that the latter compound also had S-F fluorine peaks. The observed ^{19}F resonances were of three basic types, all of which were well separated and easily distinguished (References S and B): (1) 62 ppm $-CF_2Cl$; (2) B3 ppm $-CF_2ClO_4$ or $-CF_2SO_3F$; and (3) 130 ppm $\geq CFZ$ (Z = Cl or ClO_4). The finding f both chlorine and perchlorate or fluorosulfate terminal groups indicates that 1,4 addition occurred as a first step. The subsequent addition probably then occurs randomly. Equations illustrating this process for the ClO_4 case follow:

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

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

In addition to the species resulting from 1,4 addition, the spectra also showed significant amounts of product resulting from the 1,2 process. Based on crude peak area estimates and assuming that 1,2 attack gives a single product as discussed for the $BrClO_4$ example, then the $ClSO_3F$ reaction proceeded approximately 4S percent in the 1,4 manner and SS percent in the 1,2 manner. The Cl_2O_4 addition gave somewhat more 1,4 products.

Further evidence for the formation of these isomers was obtained from the mass spectra. The 1,4 addition products were indicated by the observation of m/e values corresponding to the loss of a $-CF_2Cl$ group from the molecule upon fragmentation. However, m/e peaks were also found for the ions $C_2(SO_3F)_2^+$ and $C_2Cl(SO_3F)^+$. These ions can be considered indicative for still other positional isomers in these liquids. It is certain, whatever the product mix, that the smaller size of the Cl atom compared to Br puts a much less severe restriction on the mode of addition to the diolefin.

Having acquired these bis perchlorates, an effort was made to further substitute ClO_4 in them. For the chloro compound, this was unsuccessful for those reasons stated in the previous section of this report. For the bromine compound, a limited degree of success was achieved. The reaction of $C_4F_6Br_2(ClO_4)_2$ was carried out at -45° and -25°C with excess Cl_2O_4 for approximately eight weeks. The attempted reaction was

$$(O_4ClCF_2CFBr)_2 + 4Cl_2O_4 \longrightarrow (O_4ClCF_2CFClO_4)_2 + 2Cl_2 + 2BrClO_4$$

From the evolved Cl_2, it appeared that ~40 percent reaction had occurred. In appearance, the liquid product was unchanged, still clear, colorless, and mobile. Its infrared spectrum exhibited minor but distinct difference from the starting material. In particular, the ClO_4 absorptions appeared slightly more intense and broad, relative to other bands, than they did in the starting material. Some changes in the C-Br region were also noted.

The ^{19}F nmr spectrum confirmed the changed nature of this liquid compared to the bis ClO_4 compound. Rather than just two types of C-F as in

$C_4F_6Br_2(ClO_4)_2$ (79.3 ppm for CF_2ClO_4 and 125 ppm for $>CFBr$), this material had three different types of C-F resonance: 81 ppm $-CF_2ClO_4$; 125 ppm $>CFBr$; and 135 ppm $>CFClO_4$. The relative area ratios for these types indicated about 55 percent of the $>CFX$ fluorines were of the $X = ClO_4$ type. It should be noted too that the changes in chemical shifts for the C-F's are in keeping with the substitution of a more electronegative group for Br. Furthermore, each of the three types of C-F found was observed as two or more unequal area peaks. Nevertheless, these were so close to one another (±1 ppm) for each type that they were concluded to represent different preferable rotational isomers. That a still more pronounced effect of this kind should occur is to be anticipated since ClO_4 is larger than Br; therefore, it causes even more rotational hindrance in the normal mixture of meso and dl isomers.

FLUOROCARBON BROMIDE REACTIONS

In addition to the Cl_2O_4 reactions of fluorobutyl bromides, several related but simpler R_fBr compounds were tested. Also, some experiments were run using $BrClO_4$ and the R_fBr substrates. Dibromodifluoromethane and Cl_2O_4 were reacted at -45°C for three weeks producing the anticipated Cl_2 and $BrClO_4$ byproducts.

Unfortunately, the only carbon-containing materials accompanying those compounds were COF_2 and COFCl, accounting for 95 and 5 percent, respectively, of the CF_2Br_2. Chlorine heptoxide constituted the other significant product. These moieties most certainly arose from the sequence:

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

This result echoes that discussed for $CFCl_3$ earlier and reported for CCl_4 (Reference 7) in their reactions with Cl_2O_4. Apparently, bis-perchlorato halomethanes are unstable.

Directly contrary to this facile reaction of C-Br bonds was the finding that CF_3CF_2Br was completely unreactive toward Cl_2O_4. This result could not be altered despite prolonged reactions (months) at -25°C or reactions up to room temperature. In the latter instance, only the quantitative decomposition of Cl_2O_4 to the elements was effected.

Further studies with R_fBr species involved the discovery that $BrCF_2CF_2Br$ reacted very slowly and incompletely with Cl_2O_4. After six weeks reaction at -25°C, these reactants had given $BrCF_2CF_2ClO_4$ but in 11 percent purified yield only.

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

The product was characterized principally by its infrared and ^{19}F nmr spectra. The former fits well as intermediate to that of the known $ClCF_2CF_2ClO_4$ (Reference 5) and that of $ICF_2CF_2ClO_4$ which was prepared under this program. In agreement with this formulation, the nmr spectrum showed two equal intensity absorptions: 68.2 ppm $-CF_2Br$, and 91.4 ppm $-CF_2ClO_4$. Some reported related chemical shifts (References 5 and 8) are 69.4 ppm for $-CF_2Br$ in $BrCF_2CF_2SO_3F$,

and 92.5 ppm for $-CF_2ClO_4$ in $ClCF_2CF_2ClO_4$. Qualitative experiments showed that this compound decomposed on contact with CsF according to:

$$BrCF_2CF_2ClO_4 \xrightarrow{CsF} BrCF_2CFO + FClO_3$$

This is behavior characteristic of R_fClO_4 compounds (Reference 5). Effort was not expended in making more $BrCF_2CF_2ClO_4$ this way since it can be easily derived from $CF_2=CF_2$ and $BrClO_4$ if required.

A sample of $BrCF_2CF_2CF_2Br$ was also reacted with Cl_2O_4 at temperatures up to room temperature. Either the mono or bis ClO_4 was desired. Instead, it was determined that this substrate was even less susceptible to displacement of Br by ClO_4 than $BrCF_2CF_2Br$. No reaction was detected other than the decomposition of Cl_2O_4 to the elements and some ClO_2. Completely analogous results were noted when $BrClO_4$ was used in place of Cl_2O_4.

Yet another R_fBr compound tested was $CF_3CFBrCF_2Br$. Other than with $C_4F_6Br_4$, the best results for ClO_4 substitution for Br were derived from studies with this compound. As before, the objective was to replace both bromines with ClO_4 groups. When the reaction was conducted by letting the reactants warm slowly from 0°C to ambient temperature, there was obtained a 45-percent yield of 1-perchlorato derivative.

$$CF_3CFBrCF_2Br + 2Cl_2O_4 \longrightarrow CF_3CFBrCF_2ClO_4 + 2O_2 + BrCl + Cl_2$$

The identification of this perchlorate was straightforward since it was identical in its physical and spectral properties to the material previously synthesized (Reference 5) by means of the reaction.

$$CF_3CF=CF_2 + BrClO_4 \longrightarrow CF_3CFBrCF_2ClO_4$$

Other Cl_2O_4 reactions of $CF_3CFBrCF_2Br$ were conducted at -25°C for up to four weeks. This produced a 35-percent yield of the same R_fClO_4. Also, experiments of this type were run at -25°C or from 0°C to room temperature in the presence of added $Cs^+ClO_4^-$ or $NO_2^+ClO_4^-$ to discover any possible catalytic effect. The ionic perchlorates were unaffected by the reagents and did not change the yield of $CF_3CFBrCF_2ClO_4$ which still ran about 35 percent. Bromine perchlorate was substituted for Cl_2O_4 and the reaction conducted by slow warming from 0 C to room temperature. This gave a 23-percent yield of the same R_fClO_4.

In a final attempt to ascertain whether secondary Br atoms can be displaced by ClO_4 in compounds of this kind, a reaction was run, employing $CF_3CFBrCF_2ClO_4$ as the starting material.

$$CF_3CFBrCF_2ClO_4 + 2Cl_2O_4 \xrightarrow{?} CF_3CF(ClO_4)CF_2ClO_4$$

At either -25°C for four weeks or at 0°C to ambient temperature for several days, the R_fClO_4 material was unaffected and recovered.

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.

FLUOROCARBON IODIDE REACTIONS

The reaction of CF_3I and Cl_2O_4 was examined as a possible route to CF_3ClO_4. It was anticipated that this reaction, if it occurred, might be complicated by the unavoidable oxidation of displaced iodine to $I(ClO_4)_3$. This is a facile reaction, and it occurs at low temperature. Potentially then, 4 Cl_2O_4 might be required for each R_fI.

$$R_fI + 4\ Cl_2O_4 \longrightarrow R_fClO_4 + I(ClO_4)_3 + 4\ Cl_2$$

Nevertheless, CF_3I and Cl_2O_4 were reacted in an approximate 1:2 ratio as a first test. Slow warming from -196°C to about -45°C was used for maximum temperature moderation. After three weeks at -45°C, the reaction was worked up and a very simple fractional condensation procedure produced a 99-percent yield of CF_3ClO_4.

The observed stoichiometry of the preparation was:

$$CF_3I + 2Cl_2O_4 \longrightarrow CF_3ClO_4 + Cl_2 + [IClO_4]$$

The identification of this colorless compound was unequivocal, based on its infrared spectrum, mass spectrum, ^{19}F nmr, vapor density molecular weight, and CsF catalyzed decomposition. The infrared spectrum shows the quite typical, strong ClO_4 group vibrations at 1310, 1035, and 620 cm^{-1}, together with characteristic CF_3 group vibrations (Table II). The ^{19}F nmr spectrum exhibited only one line at 60.0 ppm, quite close to that of related CF_3O moieties, as shown in Table III. Also, measured quantities of CF_3ClO_4 and $CFCl_3$ were used to prove, by means of comparative area ratios of the nmr absorptions, that there are three F's per molecule in the compound. The mass spectrum is shown in Table IV. A distinct though weak parent ion was detected.

TABLE II. GAS-PHASE INFRARED SPECTRA

CF_3OClO_3		$ClOClO_3$		
cm^{-1}	Relative Intensity	cm^{-1}	Relative Intensity	Assignment
1310	vs	1280	vs	ν_{as} ClO_3
1275	s			ν CF_3
1250	s			ν CF_3
1180	vs			ν CF_3
1035	vs	1040	s	ν_s ClO_3
920	m			ν C-O
		750	w	ν Cl-O
725	m			δ CF_3
620	s	650	vs	ν ClO-Cl
575	w	560	mw	δ ClO_2
510	vw	510	w	δ ClO_3

TABLE 111. ^{19}F NMR CHEMICAL SHIFTS* FOR R_FClO_4 AND SIMILAR COMPOUNDS**

Compound	δ (ppm) and Assignments			
	CF_3-	-CF_2-	-CF_2-	>CFZ
CF_3ClO_4	60.4			
CF_3OCl	64.0			
CF_3OCF_3	60.0			
$CF_3CF_2ClO_4$	B4.6	93.2		
CF_3CF_2OCl	B3	90		
$CF_3CF_2OCF_3$	B7.6	91.2		
$O_4ClCF_2CF_2ClO_4$		92.2	92.2	
$O_4ClCF_2CF_2Cl$		92.S	72.7	
$FOCF_2CF_2Cl$		96.0	69.3	
$O_4ClCF_2CF_2Br$		91.4	68.2	
$FO_3SCF_2CF_2Br$		B6.1	69.4	
$O_4ClCF_2CF_2I$		90.4	63.3	
$ClCF_2CF_2I$		67.0	59.6	
ICF_2CF_2I		S2.9	S2.9	
$(CF_3)_2CFI$	76.9			149
$(BrCF_2CFBr)_2$		52.6		11S
$(O_4ClCF_2CFBr)_2$		79.3		12S
$CF_3CFBrCF_2ClO_4$	7B.4	85.8		139
$CF_3CFClCF_2ClO_4$	76.S	84.7		142

*Relative to $CFCl_3$

**Chemical shifts given are from this report or References 5, 8, and 11

TABLE IV. MASS SPECTRA OF FLUOROCARBON PERCHLORATES*

Ion	m/e	Abundances		
		CF_3ClO_4	$CF_3CF_2ClO_4$	$ICF_2CF_2ClO_4$
CO^+	28	90		
CF^+	31	2	14	24
O_2^+	32	35		
CO_2^+	44	19		
COF^+	47	23	10	42
CF_2^+	50	2	12	18
ClO^+	51	32	15	9
COF_2^+	66	9		8
ClO_2^+	67	64	22	18
CF_3^+	69	71	100.0	100.0
Cl_2^+	70	7		8
ClO_3^+	83	100.0	46	46
$C_2F_3O^+$	97			19
$C_2F_4^+$	100			37
$C_2F_5^+$	119		9	32
CF_3ClO^+	120	0.4		
I^+	127			64
$CF_3ClO_2^+$	136	0.5		
$CF_2ClO_4^+$	149		1.6	
ICl^+	162			12
$CF_3ClO_4^+$	168	0.7		
CF_2I^+	177			12
$C_2F_4ClO_4^+$	199			8
$IC_2F_3O^+$	224			9
$IC_2F_4^+$	227			3.5
I_2^+	254			26
$IC_2F_4ClO_4^+$	326			2.8

*Excluding ^{37}Cl containing ions

Iodine perchlorate, depicted as the byproduct in the preceding equation, is not a covalent material like the other halogen perchlorates. Rather, it is almost certainly a polymeric species. At ambient temperature, on standing the $IClO_4$ gradually loses Cl_2 and Cl_2O_7. Eventually, this process ceases, leaving a nearly colorless solid of indefinite composition, $IO_x(ClO_4)y$. This solid is identical to that obtained by the ambient-temperature degradation of $I(ClO_4)_3$ (Reference 10).

Moderation of the synthetic reaction is required as attested to by the fact that another preparation, much like the preceding example, took a completely different course. Slightly faster warming was used, and when the reaction was worked up, it was found to have deflagrated, going almost quantitatively to O_2, CO_2, COF_2, and Cl_2. Quite interestingly, all the iodine from the CF_3I was recovered as a mixture of I_2 and IF_5. Because the only F-source was the CF_3 group, there had occurred a most unusual fluorination of iodine by fluorine from carbon. Most probably this occurred initially to give IF, which is unstable and disproportionates rapidly according to: $5IF \longrightarrow 2I_2 + IF_5$ (Reference 12). It will be seen in the following discussion that this type result was not unique to CF_3I.

The CsF catalyzed decomposition of CF_3ClO_4 demonstrated the inherent stability of the molecule since only 30 percent of the sample was cleaved during 18 hours at 100°C.

$$CF_3ClO_4 \xrightarrow{CsF} COF_2 + FClO_3$$

The quantitative generation of COF_2 and $FClO_3$ served further to prove that this compound was indeed CF_3ClO_4.

Pentafluoroethyl iodide reacted with Cl_2O_4 quite like CF_3I with the minor but significant difference that there was formed a metastable complex, as shown:

$$CF_3CF_2I + 2Cl_2O_4 \xrightarrow{-45°C} CF_3CF_2I(ClO_4)_2 + 2Cl_2$$

$$CF_3CF_2I(ClO_4)_2 \xrightarrow[RT\ rapidly]{-25°C\ slowly} CF_3CF_2ClO_4 + IClO_4$$

The complex was never isolated and characterized as such because of its instability, but it was shown to have been formed by its quantitative synthesis at -45°C. Its formation perhaps provides an insight into the mechanism of the ClO_4 displacement of I.

Pentafluoroethyl perchlorate, which was obtained in 94-percent yield, exhibits the physical and chemical properties by now known to be typical of R_fClO_4 compounds. The definitive spectral data are shown in Tables III and IV and Appendix I.

Vapor density molecular weight data confirmed the composition as $CF_3CF_2ClO_4$. This was further reinforced by the observed quantitative decomposition:

$$CF_3CF_2ClO_4 \xrightarrow{CsF} CF_3CFO + FClO_3$$

This reaction was complete in 12 hours at 120°C but was undetectable at room temperature after one week.

The synthesis of 1,2 bis perchlorato tetrafluoroethane was attempted from ICF_2CF_2I and Cl_2O_4 based on the foregoing results. In each instance, 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 (one week) reaction periods at -45°C. One reaction of these materials which had gone smoothly but incompletely at -45°C, deflagrated while being maintained at -25°C. This uncontrolled degradation converted all the reactants to O_2, CO_2, COF_2, Cl_2, and a mixture of I_2 and IF_5. Thus, as with CF_3I, great care is required to avoid this vigorous oxygen-fluorine exchange and C-C bond rupture.

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 was generally nowhere near as good (50 to 60 percent) as that obtained with other R_fI compounds. The $ICF_2CF_2ClO_4$ was difficult to separate from Cl_2O_7, but even with traces of that material, it was observed to be a clear, colorless liquid of low volatility (~15 mm at 20°C) and stable at ambient temperature. The spectral properties of $ICF_2CF_2ClO_4$ (Tables III and IV, and Appendix IV) demonstrate reliably its identification. Particularly noteworthy is the good parent peak found in the mass pattern.

In one experiment, FC-78 was used as a solvent to aid the continuance of the substitution process by enhancing mixing and contact. This was only partially successful since $ICF_2CF_2ClO_4$ was still the predominant product. However, a very small amount (~0.1 millimole) was obtained of a liquid less volatile than $ICF_2CF_2ClO_4$. Based on its ^{19}F nmr spectrum (one peak at 92.2 ppm assignable to $-CF_2ClO_4$) and infrared spectrum, this material was tentatively identified as $O_4ClCF_2CF_2ClO_4$. The infrared spectrum--1305, vs; 1250, s; 1210, s; 1175, sh; 1160, s; 1070, vs; 1025, vs; 675, s; 645, s; 615 cm^{-1}, vs--agrees well with that of $FO_3SCF_2CF_2SO_3F$ (Reference 13) when vibrations caused by the different substituents are discounted and only $-OCF_2CF_2O-$ bands are considered. The infrared spectrum of the bis SO_3F derivative shows bands at 1496, vs; 1263, vs; 1230, s; 1170, sh; 1163, s; 1077, vs; 906, w; 846, vs; 758 cm^{-1}, m; (not reported below 700 cm^{-1}).

Unfortunately, more of the $C_2F_4(ClO_4)_2$ was not secured before the conclusion of this program. At this point, a possible reason for the bis compound not being obtained directly is that once one I atom has been replaced, the generated $IClO_4$ is more reactive toward the remaining Cl_2O_4 than the unreacted I atom and is oxidized to $I(ClO_4)_3$. This is supported by the appearance of Cl_2O_7 consistently in this system. Chlorine heptoxide is the primary product from the decomposition of $I(ClO_4)_3$. This would indicate that a stepwise Cl_2O_4 reaction to give first $ICF_2CF_2ClO_4$ which, on purification, could be re-exposed to Cl_2O_4 to complete the formation of the bis derivative.

The corresponding Cl_2O_4 reaction of $ICF_2CF_2CF_2I$ was conducted in an attempt to prepare the 1,3 bis perchlorate. After three weeks at -45°C, the reactor was warmed to room temperature and excess Cl_2O_4 together with byproduct Cl_2 were removed. The amount of these agreed extremely well with the reaction stoichiometry:

$$ICF_2CF_2CF_2I + 4Cl_2O_4 \longrightarrow (O_4Cl)_2ICF_2CF_2CF_2I(ClO_4)_2 + 4Cl_2$$

After the analysis of the Cl_2O_4 products, when the reactor had been at room temperature for about two hours, it was reopened. At this time, the complex, nonvolatile perchlorate was found to have deflagrated, producing O_2, CO_2, COF_2, Cl_2, and some CF_4. As before, iodine also was recovered as I_2-IF_5. Thus, still another example of a metastable, complex R_f-I-ClO_4 was observed.

Up to this point, all the R_fI compounds examined had I on primary carbons; accordingly, an example of a secondary iodine species, CF_3CFICF_3, was tested. The reaction with Cl_2O_4 excess was carried out at -45°C for several days whereupon work-up and warming to room temperature showed the usual $2Cl_2O_4$: 1 R_fI reactant ratio giving a nearly quantitative reaction:

$$CF_3CFICF_3 + 2Cl_2O_4 \longrightarrow (CF_3)_2CFI(ClO_4)_2 + 2Cl_2$$

This complex product differed markedly, however, from the aforementioned unstable compositions. It was completely stable at room temperature and was also completely nonvolatile. When examined in the dry box, the $(CF_3)_2CFI(ClO_4)_2$ material was observed to be a white, fluffy powder that fumed very vigorously in air as does $I(ClO_4)_3$ (but not R_fClO_4). An infrared spectrum (see Appendix I) of the neat solid powder between AgCl disks revealed typical, strong, covalent ClO_4 group absorptions as well as intense C-F bands. Obviously, the spectrum of such a large, complicated molecule is not amenable to either an immediate or a complete analysis. Nevertheless, the dominant features are such that it can be stated that this solid is almost certainly a covalent compound and does not contain the ClO_4^- anion.

When a sample of this solid was heated in a closed vessel at 105°C overnight, it deflagrated giving products similar to those noted in the earlier deflagrations. Thus, O_2, CO_2, COF_2, and Cl_2 were the principal products. Some CF_4 and C_2F_6 (the only two carbon species noted from any of these decompositions) were also generated, and the iodine was reclaimed as I_2-IF_5.

This sealed pyrolysis contrasted sharply with the process that occurred at 60° to 90°C for four hours with continuous pumping. In this case, gradual but partial decomposition took place, liberating some Cl_2(O_2?). The solid itself was not obviously changed, and no indication of any sublimation was encountered. The residue was confirmed as still having a ClO_4 group by its infrared spectrum. After this pyrolysis, it did not fume in air but was deliquescent. Additional characterization of this novel solid was not made.

In conclusion, regarding R_fX-Cl_2O_4 reactions, it is apparent that mono or di, primary or secondary Cl in saturated, aliphatic chlorofluorocarbons is unreactive. Trichloromethyl groups and Cl_2O_4 produce $>C=O$ and Cl_2O_7 rather

than simple substitution. With X=Br, several successful ClO_4 substitutions were performed. The order of reactivity was:

$$CF_2Br_2 > C_4F_6Br_4 > CF_3CFBrCF_2Br > BrCF_2CF_2Br$$

Compounds in which the Br was attached to a carbon adjacent to a perfluorinated carbon were unreactive toward Cl_2O_4. Iodofluorocarbons were very reactive with Cl_2O_4 first giving complex adducts through oxidation of C-I to C-$I(ClO_4)_2$. These adducts were of extremely variable stability. However, under the proper conditions they decomposed to produce the sought-after R_fClO_4 derivatives. Therefore, from the accumulated evidence it appears that the ability of the displaced halogen to be oxidized by Cl_2O_4 is the important factor governing the efficacy of this substitution process. The relative R_f-X bond strengths and the degree of polarization seem unimportant.

IODINE tris PERCHLORATE-PERFLUOROPROPENE REACTION

The facile and useful reactivity of Cl_2O_4 and $BrClO_4$ with respect to fluoroolefins (Reference 5), which produces fluorocarbon perchlorates, is well established. However, the corresponding $IClO_4$ moiety is unknown. Recently, the new covalent perchlorate, $I(ClO_4)_3$, was prepared and characterized at the contractor facility (Reference 10). This compound had obvious potential as a perchlorating reagent, and this was examined with perfluoropropene. Two possible reactions that were considered as desirable were:

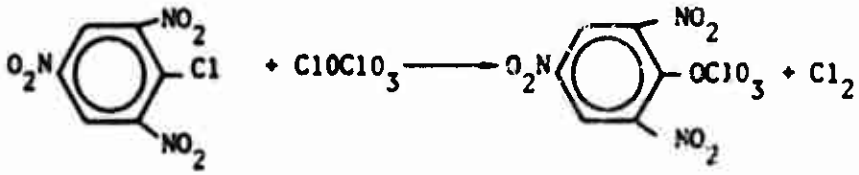
$$CF_3CF{=}CF_2 + I(ClO_4)_3 \longrightarrow CF_3CF(ClO_4)CF_2ClO_4 + IClO_4$$

$$CF_3CF{=}CF_2 + IClO_4 \longrightarrow CF_3CFICF_2ClO_4$$

Accordingly, a sample of $I(ClO_4)_3$ was prepared and contacted with perfluoropropene at -45°C for a week. The olefin did not react with the $I(ClO_4)_3$ and was recovered except for a small amount that was converted to $CF_3CFClCF_2ClO_4$, undoubtedly by Cl_2O_4 that was present as an impurity. Because $I(ClO_4)_3$ begins to decompose at about -25°C, this system was not investigated further.

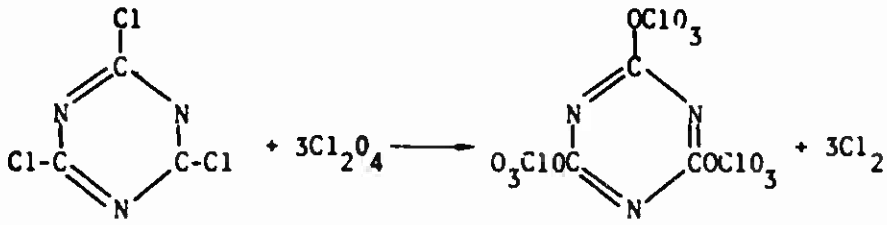
OTHER CHLORINE PERCHLORATE REACTIONS

Concurrent with the work concerning R_fX displacement reactions, experiments were conducted involving a variety of chlorocarbon compounds without any fluorine substituents. The objective was the displacement of Cl by perchlorate. In the case of picryl chloride, the desired reaction is shown by the equation:



The neat, solid picrate was treated with excess Cl_2O_4 at temperatures of -80°C to ambient. No evidence of any reaction was obtained. Picryl chloride, which was partially dissolved in FC-78, was also treated with Cl_2O_4 at -25°C for three weeks. Again no reaction occurred and the picryl chloride was fully recovered.

With cyanuric chloride, a three-fold substitution of Cl by ClO_4 was sought.



After exposure at -45°C for three weeks, it was found that Cl_2 had been eliminated, but it was accompanied by appreciable quantities of CO_2. Because of this evident, undesired degradation, no further effort was expended on this system.

Trichloroacetonitrile presented two probable reaction paths with Cl_2O_4: a possible addition to the -C≡N unsaturated group or displacement of Cl.

$$CCl_3C{\equiv}N + 2Cl_2O_4 \longrightarrow CCl_3C(ClO_4)NCl_2$$

$$CCl_3C{\equiv}N + XCl_2O_4 \longrightarrow C(ClO_4)_XCl_{3-X}C{\equiv}N + Cl_2$$

When first investigated at -20°C (perchlorate/nitrile = 2), appreciable CO_2 and $COCl_2$ were obtained, together with Cl_2 and Cl_2O_7 as volatile products. On repetition with the 2:1 reactant ratio, but employing a slow (16-hour) warm-up to near room temperature, the generation of CO_2 and $COCl_2$ was very slight. Again, however, Cl_2 and Cl_2O_7 were produced in major amounts, the latter accounting for about 75 percent of the charged Cl_2O_4. Both reactions produced a white solid product that was slightly volatile. On subjecting this solid to vacuum sublimation, it was found to be a mixture. The relatively nonvolatile portion was identified as NO_2ClO_4 by its infrared spectrum. The sublimate was a low melting, 40°C, crystalline material shown to contain the $CCl_3C{=}O$ group but no perchlorate. Therefore, it is certain that attack on the nitrile function occurs readily, perhaps to form the illustrated $CCl_3C(ClO_4)_2NCl_2$. Subsequent decomposition of the $CCl_3C(ClO_4)_2$- group would then produce the observed $CCl_3C{=}O$, while substitution of the NCl_2 group with ClO_4, followed by decomposition, furnishes NO_2ClO_4. The last process has been noted under another program (Reference 10), in which NCl_3 and Cl_2O_4 yielded NO_2ClO_4 readily. Under the present conditions, no evidence was found of attack on the CCl_3 group and this system was not pursued further.

Dichlorodinitromethane was reacted with Cl_2O_4 to determine the feasibility of replacing chlorine and forming the mixed nitro-perchlorato derivative.

$$Cl_2C(NO_2)_2 + 2Cl_2O_4 \longrightarrow (ClO_4)_2C(NO_2)_2 + 2Cl_2$$

Early evidence of the course of this reaction at -20°C showed a slow Cl_2 evolution but gave no evidence of a side reaction. After several weeks, however, some CO_2 had been generated also, together with various chlorine oxides Cl_2O_7, ClO_2, and probably Cl_2O_6. Most of the $Cl_2C(NO_2)_2$ was recovered, and the NO_2 of that which had reacted was found to have been converted to NO_2ClO_4. These products are evidence of a substitution process but indicate unstable intermediates result which decompose.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

During this program, a new procedure has been discovered and developed in a preliminary manner for the synthesis of new, stable, covalent perchlorates. This procedure involves the displacement of halogen from saturated aliphatic halofluorocarbons by the action of chlorine perchlorate. The various screening reactions of the wide variety of substrates investigated provide a good indication of the scope of the ClO_4 substitution process. Thus, chlorofluorocarbons were generally unreactive while bromofluorocarbons, depending on the type and place of other substituents, were often successfully converted to the perchlorate derivative. This delineation of the limits of possible Br displacement points the way to the preparation of many new and potentially useful perchlorate species.

Of great significance to an understanding and development of this substitution reaction was the discovery of the uniformly facile interaction of iodofluorocarbons with Cl_2O_4. The nearly quantitative synthesis of CF_3ClO_4 and $C_2F_5ClO_4$ resulted. These are the first examples of perfluorinated aliphatic perchlorates and are thus the parent members of this class of compounds. Furthermore, the R_fI-Cl_2O_4 reactions showed that a hitherto unknown type of complex, covalent perchlorate existed, $R_fI(ClO_4)_2$. These materials are covalent species also and ranged through solids completely stable at ambient temperature.

All of the fluorocarbon perchlorates prepared under this program confirmed the previously observed properties of this class of compound. They are stable, mobile, dense, and relatively high boiling point liquids; e.g., b.p.-CF_3Cl, -81°C; CF_3I, -22°C; CF_3ClO_4, +9°C. Within the scope and limitations defined through this effort, there are many potentially useful perchlorates that are obviously synthetically attainable. The continued development of these materials is warranted. The preparation and characterization of one or more perchlorates with a ClO_4 content of at least one per carbon would be one approach that is now possible. In addition, a more thorough investigation of the $R_fI(ClO_4)_2$ compounds should be conducted to determine their character and utility. In addition, it should be ascertained how these compounds participate in reactions involving conversion of C-F fluorine to IF_5.

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SECTION V

EXPERIMENTAL SECTION

APPARATUS

Volatile materials were separated or purified using a calibrated stainless-steel vacuum line equipped with an FEP-Teflon U-trap and Heise Bourdon tube-type pressure gage. Infrared spectra of gases were obtained using 5-cm path length stainless-steel cells fitted with AgCl windows. Spectra were recorded over the range of 4000 to 400 cm^{-1} on a Perkin-Elmer Model 337 Infracord. Gaseous compounds were separated and analyzed on a contractor-built gas chromatograph (GC) operating at ambient temperature with 25-psi helium at 25 cc/min and with a 3/16-inch x 16.4-foot column filled with 25 percent perfluorokerosene on Fluoropak 80. Retention times (in minutes) for some compounds of interest: CO_2, 2.8; Cl_2, 3.9; $FClO_3$, 5.5; $COCl_2$, 8.7. Liquids were analyzed on a Hewlett-Packard Model 700 chromatograph equipped with temperature programming and automatic attenuation. A 3/16-inch x 11-foot column was packed with 3 percent QF-1 on Chromasorb-T. Mass spectra were obtained using a Quad 300 quadruple mass spectrometer (EAI Inc.) equipped with an all stainless-steel inlet system. Fluorine nmr spectra were obtained with a Varian Associates high resolution nmr spectrometer operating at 56.4 Mc with $CFCl_3$ as the standard.

MATERIALS

Unless noted otherwise, chemicals employed in this work were of the best quality commercially available. Their identity and purity were verifed by two or more of the following methods: IR, nmr, GC, or mass spectra.

CHLORINE MONOFLUORIDE

A 1-liter stainless-steel cylinder was loaded at -196°C with approximately 12.5 liters each of gaseous Cl_2 and ClF_3 (from the Matheson Company). After warming to ambient temperature, the reactor was electrically heated overnight at approximately 150°C. After recooling to room temperature, the product ClF was stored until needed. Purification as it was used was accomplished by fractionation through U-traps cooled to -142 and -196°C. The material trapped at -196°C was retained.

CHLORINE FLUOROSULFATE

Purified ClF was condensed onto SO_3 (Allied Chemical Company) contained in a 150-milliliter stainless-steel cylinder (Reference 6). Generally, a 0.2-mole scale was used with about a 10-percent excess of ClF. The reaction was completed by slow warming of the reactor to ambient temperature. Purification of $ClSO_3F$ was effected by vacuum fractionation through U-traps cooled to -80, -112, and -196°C. The middle fraction (-112°C) was essentially pure $ClSO_3F$.

CHLORINE PERCHLORATE

A 30-milliliter stainless-steel cylinder which had been passivated with ClF_3 was loaded in the dry box with 4.0 g (~16 millimole) of anhydrous $CsClO_4$ (Research Inorganic Chemical Corporation). The evacuated cylinder was then

charged with purified $ClSO_3F$ (~10 millimoles) at -196°C. Warming to -45°C for two days (or until needed) supplied chlorine perchlorate. This compound was purified immediately prior to use by fractionation through U-traps kept at -80, -112, and -196°C. The chlorine perchlorate was retained at -112°C. The yield was usually 90 to 95 percent (~9 millimoles).

BROMINE PERCHLORATE

Bromine (1.82 millimoles) was loaded into a prepassivated 30-milliliter stainless-steel cylinder at -196°C followed by Cl_2O_4 (3.69 millimoles). After several days at -45°C, the byproduct Cl_2 and excess Cl_2O_4 were removed by first pumping on the cylinder at -80°C for one hour, then at -64°C for 10 minutes. The total amount of Cl_2 produced (1.74 millimoles) indicated a nearly quantitative conversion to $BrClO_4$ which was retained in the cylinder.

IODINE tris-PERCHLORATE

A prepassivated Teflon tube fitted with a stainless-steel valve was loaded with I_2 (0.698 millimole) in the dry box. To this was added Cl_2O_4 (6.06 millimoles) at -196°C from the vacuum line. The reaction was completed by warming first to -80°C, then -45°C for several days. Keeping the tube at -45°C, excess Cl_2O_4 (1.70 millimoles) and byproduct Cl_2 (2.14 millimoles) were pumped away. The nearly white, fluffy, solid $I(ClO_4)_3$ was stored at -45°C pending use.

FLUOROCARBON HALIDES FROM OLEFIN-HALOGEN REACTIONS

Perfluoropropene (8.30 millimoles) and Cl_2 (9.55 millimoles) were successively condensed at -196°C into a 250-milliliter Pyrex ampoule fitted with a Fischer-Porter Teflon valve. After warming to ambient temperature, the ampoule was irradiated with a 100-watt Hanovia Utility Lamp for four hours. Vacuum fractionation through traps cooled to -80 and -196°C furnished $CF_3CFClCF_2Cl$ (7.50 millimoles), 90-percent yield. The product was identified by its infrared (Reference 14) and mass spectrum which did not include a parent ion but did exhibit a strong peak corresponding to the ion $C_3F_5Cl^+$.

Perfluoropropene and Br_2 (8.30 millimoles each) were reacted in a similar manner to produce a 98-percent yield of $CF_3CFBrCF_2Br$. Identification of the product was again made based on its infrared spectrum (Reference 14) and mass spectrum where again no parent ion was detected, but a strong $C_3F_6Br^+$ ion fragment was observed.

Perfluorobutadiene (5.11 millimoles) and Br_2 (11 millimoles in a Pyrex ampoule) were irradiated with the Hanovia Utility Lamp overnight at about 60°C (Reference 15). The excess Br_2 was distilled away leaving a clear colorless liquid having very little vapor pressure at ambient temperature. A chromatograph showed the material to be better than 98 percent pure. Its identity as $BrCF_2CFBrCFBrCF_2Br$ was confirmed by its infrared, mass, and ^{19}F nmr spectra. The yield was 95 percent of theory. Interestingly, the mass spectrum of this compound shows a weak parent ion, $C_4F_6Br_4^+$, readily identifiable due to the ^{79}Br-^{81}Br isotopic distributions. The nmr consisted of two peaks: 52.6 ppm relative to external $CFCl_3$ for $BrCF_2$- and 114.6 ppm for $\geq CFBr$ with the appropriate 2:1 area ratios.

Tetrafluorethylene was prepared by pyrolyzing shredded Teflon under vacuum at approximately 600°C. A 7.90-millimole sample of C_2F_4 was reacted with I_2 (~13 millimoles) at 175°C overnight in a 75-milliliter stainless-steel cylinder. After removing material volatile at -80°C, the remaining IC_2F_4I/I_2 mixture was treated with Hg to remove I_2. On refractionating past -80°C, a colorless liquid product was acquired, 6.57 millimoles, 83-percent yield. Infrared, mass, and ^{19}F nmr confirmed the identity of the product. The mass cracking pattern was quite characteristic, including a prominent parent ion, $C_2F_4I_2^+$. The single fluorine nmr resonance occurred at 52.9 ppm.

Employing the essentially literature procedure (Reference 16), the preparation of CF_3CFICF_3 was carried out. Thus, perfluoropropene (14.0 millimoles) and IF_5 (3.96 millimoles) were successfully condensed into a prepassivated 30-milliliter stainless-steel cylinder at -196°C. Previously, I_2 (4.92 millimoles) had been loaded into the cylinder in a dry box. After warming to room temperature, the reactor was subsequently heated to 150°C for 16 hours. Cooling and fractionation through traps maintained at -95 and -196°C furnished the product contaminated with I_2. The latter was removed by treatment with Hg giving the desired clear, colorless liquid (11.6 millimoles) in 83-percent yield. The ^{19}F nmr spectrum (75.5 ppm for CF_3 and 148.8 ppm for $\geq CFI$) was as expected, as was the infrared spectrum (Reference 16). A quite intense (42 percent of the base peak) parent ion, $C_3F_7I^+$, was noted in the mass spectrum.

FLUOROCARBON HALIDES FROM HUNSDIECKER REACTIONS

Perfluoroglutaric acid was converted to the di-silver salt by reaction with excess silver carbonate in aqueous solution. After filtration to remove the unreacted Ag_2CO_3, the salt was stripped to dryness on a rotary evaporator and dried in an oven. Upon powdering in a dry box, 8.91 millimoles of the salt was placed in a 30-milliliter stainless-steel cylinder. To this was added 20.8 millimoles of Br_2 at -196°C. The reaction was conducted at 90°C overnight. Purification of the product was effected by fractional condensation to remove CO_2 and other volatile byproducts, whereas Hg was used to react excess Br_2. Significant amounts of $BrCF_2CF_2Br$ were encountered, perhaps due to perfluorosuccinic acid impurity in the perfluoroglutaric acid starting materials. Separation of this byproduct by distillation at -64°C yielded pure $BrCF_2CF_2CF_2Br$ (4.88 millimoles), 55 percent. Infrared (Reference 18) and mass spectral data, including a very weak parent ion, confirmed the identity of the product.

Silver perfluoroglutarate (33 millimoles) and I_2 (67 millimoles) were loaded into a prepassivated 150-milliliter cylinder in the dry box. Formation of $ICF_2CF_2CF_2I$ was accomplished by heating at 120°C for 24 hours. Carbon dioxide was removed at -80°C followed by the main product, perfluorobutyrylactone (Reference 18). Later warming volatilized the $ICF_2CF_2CF_2I$ which was trapped at -45°C. After Hg treatment for I_2 removal, several additional vacuum fractionations resulted in the best purity product obtainable. However, there was still about 10 percent ICF_2CF_2I impurity present despite the use of a new, different, and fresh batch of perfluoroglutaric acid for the preparation of the silver salt. The mass spectrum of this sample of $ICF_2CF_2CF_2I$ exhibited a strong parent ion, and its infrared spectrum was consistent with that reported (Reference 18).

PREPARATION OF $CF_3CFBrCF_2ClO_4$

Perfluoropropene (1.45 millimoles) was added slowly at -80°C to $BrClO_4$ (1.43 millimoles) contained in a 10-milliliter cylinder. Rapid addition occurred and the colorless product was purified by fractionation, being retained at -80°C. The characteristic spectral properties noted for this material were in agreement with earlier results (Reference 5).

PREPARATION OF $O_4ClCF_2CFBrCFBrCF_2ClO_4$

Perfluorobutadiene (2.58 millimoles) was added at -196°C to $BrClO_4$ (5.80 millimoles) in a 30-milliliter stainless-steel cylinder that was then maintained at -80°C for several days. A deficiency of the olefin was used to ensure its complete reaction since in an earlier program (Reference 5) a monoperchlorate adduct of C_4F_6 had exploded on warming to room temperature. Gradual warming to -10°C, followed by pumping, allowed separation of excess $BrClO_4$ plus minor amounts of an unidentified fluorocarbon acyl fluoride species. On opening the cylinder in the dry box, a clear, colorless, mobile liquid was found (2.25 millimoles, 87 percent). The infrared spectrum of this liquid showed very intense ClO_4 group vibrations and no C=O or C=C bands. Its ^{19}F nmr spectrum showed only two types of C-F, 82 ppm attributable to $-CF_2ClO_4$ and 132 ppm due to $>CFBr$, with approximately a 2:1 area ratio. The mass spectrum of the liquid was complex, and the parent ion was beyond the range of the instrument (m/e=500) negating any possibility of detecting it. No ion containing more than 2 Br atoms was found. Several $C\text{-}ClO_4^+$ containing ion fragments were noted as well as intense ClO_3^+, ClO_2^+, and ClO^+ ions. No ClO_4^+ was present, which is typical of the mass spectra of perchlorates.

PREPARATION OF $C_4F_6Cl_2(ClO_4)_2$

Chlorine perchlorate (4.98 millimoles) was condensed at -196°C into a 30-milliliter cylinder followed by perfluorobutadiene (2.24 millimoles). The reactor was gradually allowed to warm to ambient temperature by the evaporation of the liquid nitrogen/dry ice slush from the dewar in which it was contained. Purification by removal of O_2, Cl, and other volatiles at -10°C gave 0.913 g $C_4F_6Cl_2(ClO_4)_2$, 96 percent. The product on examination in the dry box was found to be a colorless mobile liquid. Its infrared spectrum gave very strong, characteristic bands attributable to covalent perchlorate groups (the strongest in the spectrum). No unreacted C=C groups of C=O decomposition product was evident on examination of the spectrum. The ^{19}F nmr spectrum was complex, with three basic types of C-F, all of which were well separated and easily distinguished: (1) 63 ppm, $-CF_2Cl$; (2) 84 ppm, CF_2ClO_4; (3) 133 ppm, $>CFZ$ (Z = Cl or ClO_4). The approximate total area of (1) and (2) compared to (3) was nearly 2:1. More than one peak occurred for each type, but within each group all peaks were quite close. These slight shifts may be due to various conformations for this rotationally hindered molecule. Basically the nmr spectrum shows this liquid to be a mixture of isomers resulting from 1, 4, and 1, 2 addition to the diolefin. The mass spectrum was much less structurally informative. Fragmentation to lighter ions predominated, but intense ClO_3^+, ClO_2^+, and ClO^+ ions corroborated the presence of ClO_4 groups.

PREPARATION OF $C_4F_6Cl_2(SO_3F)_2$

In the manner indicated above for the Cl_2O_4 adduct, perfluorobutadiene (3.15 millimoles) and $ClSO_3F$ (6.50 millimoles) were reacted. Pumping away excess $ClSO_3F$ and other volatile byproducts at 0°C left behind colorless, liquid $C_4F_6Cl_2(SO_3F)_2$ (2.49 millimoles, 79 percent). The infrared spectrum was consistent with straightforward addition of $ClSO_3F$ across the C=C bands. No C=C or C=O type unsaturation was detected. Discounting SO_3F and ClO_4 vibrations, the spectrum was much like that of $C_4F_6Cl_2(ClO_4)_2$. The ^{19}F nmr spectrum revealed three types of C-F: (1) 67 ppm, $-CF_2Cl$; (2) 82 ppm, $-CF_2SO_3F$; (3) 135 ppm, $>CFZ$ (Z = Cl, SO_3F). More than one peak of types (2) and (3) again indicated possible different rotational conformers. There were also present two S-F peaks at -51.4 and -50.5 ppm. Thus, both 1,4 and 1,2 addition to the diolefin occurred to give a mixture of isomeric products. The mass spectrum contained numerous large m/e valued fragments. The highest of these were assignable to the parent molecule less an SO_3F group, $C_4F_6Cl_2(SO_3F)^+$ and the parent less CF_2Cl, $C_3F_4Cl(SO_3F)_2^+$. These assignments were confirmed by the appropriate Cl isotopes.

CHLOROFLUOROCARBON-CHLORINE PERCHLORATE REACTIONS

$CFCl_3$

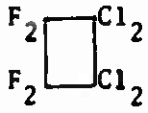
Fluorotrichloromethane, Freon 11 (1.10 millimoles) and Cl_2O_4 (3.80 millimoles) were successively condensed into a prepassivated 30-milliliter cylinder at -196°C. The reactor was maintained at -25°C for three weeks before recooling to -196°C and measuring noncondensable gases, i.e., O_2. Only 0.07 millimoles of O_2 was observed. Vacuum fractionation was carried out while warming the reactor to ambient temperature using U-traps cooled to -80, -112, and -196°C. The latter (3.86 millimoles) was primarily COFCl and Cl_2 together with much smaller amounts of COF_2, CO_2, CF_2Cl_2, and $FClO_3$ as indicated by infrared and GC analysis. The yield of COFCl was 85 percent, and no $CFCl_3$ was recovered. Excess Cl_2O_4 (1.43 millimoles) and byproduct Cl_2O_7 (0.98 millimole) were contained in the other traps. No evidence for a $C-ClO_4$ derivative was obtained.

$ClCF_2CFCl_2$

Freon 113 (2.04 millimoles) and Cl_2O_4 (3.14 millimoles) were separately added to a 30-milliliter cylinder at -196°C. Placed in an ice bath, the cylinder was allowed to warm over several days from 0°C to room temperature. Oxygen generated by the reaction was separated from the other products at -196°C and measured (6.08 millimoles). Vacuum fractionation through traps cooled to -80, -112, and -196°C showed no material was retained in the cylinder or at -80°C. The -112°C fraction was $ClCF_2CFCl_2$ (2.05 millimoles) and the -196°C fraction was Cl_2 (2.99 millimoles). Reaction other than decomposition of the Cl_2O_4 to the elements had not occurred. A three-week reaction of this kind at -15°C also produced only Cl_2O_4 decomposition, although it was only partially lost.

Other Chlorofluorocarbons

Wholly analogous reactions of Cl_2O_4 and several primary and secondary R_fCl species were carried out. These were CF_3Cl, $ClCF_2CF_2Cl$, $CF_3CFClCF_2Cl$, $CF_3CFClCF_2ClO_4$, $C_4F_5Cl_2(ClO_4)_2$, and



These reactions lasted for from several weeks at -25°C to months. Periodic monitoring for evolved byproduct Cl_2 (by pumping past -112°C) served as an efficient and simple way to monitor the extent of any possible reactions. Because little or no Cl_2 was formed at -25°C, the reactions were then kept at -15°C for three to four weeks. Here approximately 5 percent of the Cl_2O_4 decomposed per week, but no evidence for reaction of any of the R_fCl substrates was observed. Whenever complete workup was conducted, the fluorocarbon starting material was recovered unchanged. Finally, at 0°C to room temperature, the Cl_2O_4 was completely decomposed to elements in a day or so, but again these R_fCl compounds did not react. The $C_4F_6Cl_2(ClO_4)_2$ reaction was kept, in all, several months at -25°C with large excesses of Cl_2O_4. Upon removal of all volatile components, the remaining colorless liquid was checked by infrared and ^{19}F nmr. It was identical to the starting material and thus had not reacted in any manner.

BROMOFLUOROCARBON-HALOGEN PERCHLORATE REACTIONS

CF_2Br_2

Dibromodifluoromethane (2.02 millimoles) and Cl_2O_4 (5.12 millimoles) were added to a 30-milliliter stainless-steel cylinder at -196°C before allowing the reaction to proceed at -45°C for three weeks. Several vacuum fractionations in a series of U-traps kept at -80, -112, -142, and -196°C served to separate the products. Analysis by infrared and GC showed COF_2 (~1.9 millimoles) and COFCl (~0.1 millimole) had formed together with Cl_2, Cl_2O_7, and $BrClO_4$. Thus, all of the CF_2Br_2 had been converted to $>C=O$ species.

CF_2CF_2Br

Bromopentafluoroethane (3.95 millimoles) was condensed into a 30-milliliter cylinder at -196°C followed by Cl_2O_4 (5.37 millimoles). The reaction was first kept at -25°C. Periodic monitoring over the next several weeks showed that all of the C_2F_5Br remained unreacted. Some gradual and moderate decomposition of the Cl_2O_4 occurred apparently to Cl_2, O_2, and Cl_2O_6. Finally, the reaction was maintained at +5°C for several weeks. Recooling to -196°C showed that considerable O_2 had formed. This was pumped away, and the condensable products were separated by fractional condensation. The only materials found were C_2F_5Br and Cl_2 (8.80 millimoles total). No new species were observed, and only the decomposition of Cl_2O_4 to the elements occurred without reaction of the C_2F_5Br.

$BrCF_2CF_2Br$ - Synthesis of $BrCF_2CF_2ClO_4$

Sym-dibromotetrafluoroethane (2.01 millimoles) and Cl_2O_4 (4.60 millimoles) were successively condensed into a 30-milliliter cylinder. The cylinder was then gradually warmed to -25°C, at which temperature it was maintained for six weeks. Separation of the products was accomplished by fractional condensation at -80, -112, and -196°C. The -80°C fraction contained some apparent $BrCF_2CF_2ClO_4$ by comparison with the known infrared spectrum of $ClCF_2CF_2ClO_4$ (Reference 5). The fractions were recombined and warmed slowly to ambient temperature. Repetition of the fractionation then produced a purer product but in not much greater yield than originally (0.23 millimole, 11-percent yield). The infrared spectrum compared to that of the related Cl and I compounds served to identify the material. This conclusion was supported by the ^{19}F nmr data, which showed two types of C-F: (1) 68.2 ppm, $-CF_2Br$; and (2) 91.4 ppm, $-CF_2ClO_4$. Nearly all of the unreacted $BrCF_2CF_2Br$ was recovered, but a small amount was converted to $BrCF_2CF_2Cl$.

$BrCF_2CF_2CF_2Br$

A clean, prepassivated 30-milliliter cylinder was charged with $BrCF_2CF_2CF_2Br$ (1.26 millimoles) and Cl_2O_4 (4.87 millimoles) at -196°C. Over several hours, the reactor was warmed to -45°C and then maintained at 0°C for three days. Finally, the reactor was warmed to ambient temperature for four days. Oxygen (7.51 millimoles) was removed at -196°C. Further fractionation separated $BrCF_2CF_2CF_2Br$ (1.16 millimoles), Cl_2 (3.84 millimoles) and ClO_2 (1.56 millimoles). The distinctive infrared bands of R_fClO_4 compounds were completely absent from all fractions.

In a similar manner, $BrCF_2CF_2CF_2Br$ (1.14 millimoles) was added to purified $BrClO_4$ (3.39 millimoles) in a 30-milliliter cylinder. The reaction was carried out at 0°C for five days and room temperature for three days. On workup, the products obtained were O_2 (6.20 millimoles) and Cl_2-BrCl-Br_2 (3.25 millimoles) together with a trace of ClO_2. The bromofluorocarbon was recovered unchanged (1.10 millimoles).

$CF_3CFBrCF_2Br$ - Synthesis of $CF_3CFBrCF_2ClO_4$

1,2 dibromo perfluoropropane (2.01 millimoles) and Cl_2O_4 (2.68 millimoles) were condensed into a 30-milliliter stainless-steel cylinder at -196°C. For three days, the reactor was maintained at 0°C, and for four days at room temperature. Several fractional condensations were carried out after O_2 (3.49 millimoles) was removed by pumping. At -80°C, pure $CF_3CFBrCF_2ClO_4$ (0.903 millimole) was obtained; the yield was 45 percent. This product was identified by comparison of its infrared, mass, and ^{19}F nmr spectra to that of an authentic sample (Reference 5). In addition, only a trace of $C_3F_6Br_2$ was recovered; the main fluorocarbon was $CF_3CFBrCF_3$ (55 percent) as determined by infrared and mass spectral analysis. Chlorine, bromine, and bromine monochloride were the only other products.

Several related experiments were carried out to better define the characteristics of this reaction. A cylinder passivated with Cl_2O_4 was used under conditions the same as above. This reaction produced a 30- to 35-percent yield

of $CF_3CFBrCF_2ClO_4$ and practically no $CF_3CFBrCF_3$, the $CF_3CFBrCF_3Br$ being recovered. In addition, possible catalysts, $CsClO_4$ and NO_2ClO_4, were tested. The former produced a 35-percent yield of $CF_3CFBrCF_2ClO_4$ in one week at -25°C, which compared favorably with the 31-percent yield obtained after four weeks at -25°C without any added catalyst. Nitronium perchlorate did less well as catalyst since in a reaction at 0°C to room temperature over one week, the yield of $CF_3CFBrCF_2ClO_4$ was still only about 30 to 35 percent. Both tested potential catalysts were recovered and determined to be unchanged by comparison with the starting compounds.

In addition, a reaction of $BrClO_4$ (1.70 millimoles) and $CF_3CFBrCF_2Br$ (1.17 millimoles) was conducted in a 30-milliliter stainless-steel cylinder by warming to room temperature after three days at 0°C. Oxygen (2.16 millimoles) was found, indicating better than one-half of the $BrClO_4$ had decomposed without reacting. The isolated, pure $CF_3CFBrCF_2ClO_4$ (0.27 millimole) was the only fluorocarbon perchlorate observed. The yield was 23 percent. The remaining starting fluorocarbon was recovered together with the halogens, Cl_2, BrCl, Br_2, and some ClO_2.

$CF_3CFBrCF_2ClO_4$

A sample of the title perchlorate compound (1.33 millimoles) was loaded in a 10-milliliter cylinder followed by Cl_2O_4 (2.70 millimoles). After four weeks at -25°C, the reaction products were separated and examined. No evidence of any reaction other than decomposition of some of the Cl_2O_4 was noted. The reaction was then allowed to proceed at 0°C and then at room temperature for more than a week. Separation of the products lead to recovery of the $CF_3CFBrCF_2ClO_4$ and Cl_2 (2.64 millimoles). Much O_2 was present, but it was not measured. No new perchlorate was observed.

$BrCF_2CFBrCFBrCF_2Br$ - Synthesis of $O_4ClCF_2CFBrCFBrCF_2ClO_4$

Sym-tetrabromo perfluorobutane (1.29 millimoles) was loaded in a 30-milliliter stainless-steel cylinder in the dry box. From the vacuum line Cl_2O_4 (7.37 millimoles) was added at -196°C. The reactor was stored at -25°C for four weeks before workup. Very little O_2 was observed at that time, and vacuum fractionation was used to remove and separate the volatile byproducts from the mixture while keeping the cylinder at 0°C. In all, 2.67 millimoles of Cl_2 (contaminated with a little $FClO_3$), 2.42 millimoles of unreacted Cl_2O_4, and a large, but unmeasured amount of $BrClO_4$ were obtained. Thus, from the recovered Cl_2O_4 and formed Cl_2, very nearly 2 Br of the starting $C_4F_6Br_4$ should have been replaced by ClO_4. Spectral data confirmed this conclusion since the infrared, mass, and ^{19}F nmr were virtually identical to that of $O_4ClCF_2CFBrCFBrCF_2ClO_4$ prepared earlier from $BrClO_4$ and $CF_2{=}CFCF{=}CF_2$. Further proof of the presence of covalent ClO_4 in the product was obtained by its partial and qualitative decomposition over CsF. This led to the formation of $FClO_3$ and R_fCFO, the typical products generated from fluorocarbon perchlorates under these conditions. In a second example of this reaction between $C_4F_6Br_4$ and Cl_2O_4 carried out for three months at -25°C, the same results were obtained. Thus, two of the bromine atoms were replaced only, and these were the primary ones.

$O_4ClCF_2CFBrCFBrCF_2ClO_4$

A sample of the title perchlorate (1.34 millimoles) and Cl_2O_4 (2.00 millimoles were reacted in a 30-milliliter cylinder at -45°C for three weeks. The Cl_2 (0.19 millimole) evolved at that time indicated a very slow reaction. More Cl_2O_4 was added, and the temperature was raised to -25°C for four weeks. Byproduct analysis of that time showed more Cl_2 had been formed, but this was accompanied by some $FClO_3$ and a fluorocarbon acyl fluoride which were indicative of decomposition. Hence, accurate Cl_2 monitoring was not possible, but the degree of reaction overall appeared to be about 35 to 45 percent. Examination of the nonvolatile liquid perchlorate remaining after removal of all gaseous species showed it to still be a clear, colorless, mobile liquid. An infrared spectrum of the liquid showed some differences relative to the starting material, but these were not great. Covalent perchlorate and C-F absorptions still dominated the spectrum. The ^{19}F nmr of the liquid was significantly different than the starting perchlorate. Three types of C-F resonance were noted: (1) 81 ppm, $-CF_2ClO_4$; (2) 125 ppm, $>CFBr$; and (3) 134 ppm $>CFClO_4$. The approximate areas for these types were 4:1.4: 0.6, indicating about 30 percent of the secondary bromine had been replaced by perchlorate. Each type of C-F resonance found was present as a distorted pair of peaks, perhaps indicative of more than one preferred conformation.

IODOFLUORCARBON-CHLORINE PERCHLORATE REACTIONS

CF_3I - Synthesis of CF_3ClO_4

Trifluoromethyl iodide (2.02 millimoles) and Cl_2O_4 (4.24 millimoles) were successively condensed at -196°C into a 30-milliliter stainless-steel cylinder that was slowly warmed to -45°C and stored for three weeks. Recooling to -196°C showed no noncondensable products had formed. While warming to room temperature for one hour, the volatile materials evolved were separated by fractional condensation. These consisted essentially of Cl_2 (0.57 millimole) trapped at -196°C and CF_3ClO_4 (2.01 millimoles) trapped at -112°C; the yield was 99 percent. Trifluoromethyl perchlorate was identified by its infrared spectrum which showed typical CF_3 and $OClO_3$ vibrations and its mass spectrum which included a weak parent ion and very intense ClO_3^+ and CF_3^+ fragments. The ^{19}F nmr spectrum showed one absorption only at 60.4 ppm with area 3.00 relative to the measured amount of $CFCl_3$ at 0.97. There were three fluorines per molecule compared to one in the $CFCl_3$. The observed molecule weight based on vapor density measurements was 167 versus a calculated value of 168.4 g/mole for CF_3ClO_4. The vapor pressure of the liquid was determined at various temperatures over the range of -78 to 0°C: (C, mm): -77.7, 7; -62.3, 20; -45.8, 56; -32.0, 121; -24.3, 180; -16.2, 268; 0.0, 535. The vapor pressure-temperature relation is described by the equation $\log p_{mm} = 7.4828 - (1301.0/T°K)$. The extrapolated normal boiling point is 9.5°C, with a heat of vaporization of 5.95 kcal $mole^{-1}$ and a Trouton constant of 23.3.

Despite the excellent CF_3ClO_4 yield, much I, Cl, and ClO_4 material was unaccounted for. After several days at room temperature, the reactor was again pumped. This produced more Cl_2 (1.56 millimoles) and a minor amount of O_2 and Cl=O species. The weight of the material left in the reactor was 0.424. For

2.02 millimoles of $IClO_4$ (the approximate composition of the still unobserved material) a weight of 0.458 g was calculated. Opening the bomb in the dry box showed that a pale yellow solid was present throughout, coating most of the wall and the bottom. An infrared spectrum of this solid pressed as a powder between AgCl disks showed it to be identical with the solid obtained from the decomposition of $I(ClO_4)_3$ (Reference 10) which has an indefinite composition, $IO_x(ClO_4)_y$.

An earlier reaction of CF_3I (2.42 millimoles) and Cl_2O_4 (6.00 millimoles) had been found to have deflagrated. This was evidenced by the finding of much O_2 (9.4 millimoles), CO_2, COF_2, 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 millimole) was loaded into a 10-milliliter cylinder containing ~1 g of CsF at -196°C. The closed cylinder was heated at 100°C for 18 hours prior to fractionation of the products. Most of the CF_3ClO_4 (0.321 millimole) was recovered. The decomposition products were COF_2 and $FClO_3$ (0.134 millimole each).

CF_3CF_2I - Synthesis of $CF_3CF_2ClO_4$

Pentafluoroethyl iodide (1.97 millimoles) and Cl_2O_4 (4.65 millimoles) were condensed at -196°C into a 30-milliliter cylinder which was then gradually warmed to -45°C, where it was maintained for two weeks. Recooling to -196°C showed no noncondensable gas was present. Fractionation was carried out for 1.5 hours through U-traps cooled to -80, -112, and -196°C, while the reactor was kept at -64°C. The two high-temperature traps contained nothing, and the -196°C trap had 2.03 millimoles of Cl_2 only. The cylinder was then warmed to -25°C for three days before completing the workup. Warming to room temperature and then fractionating produced $C_2F_5ClO_4$ (1.84 millimoles, 94-percent yield) plus a small additional amount of Cl_2 and a little unreacted C_2F_5I.

The identification of $C_2F_5ClO_4$ was based in part on its infrared spectrum which contained only bands typical of C_2F_5 compounds (Reference 2) and the $-OClO_3$ group. In addition, the mass spectrum of the compound was very simple and distinctive although lacking in a parent ion. Strong ClO_3^+ and CF_3^+ m/e values and a weak parent $-CF_3$ fragment, $CF_2ClO_4^+$, were noted. The ^{19}F nmr spectrum showed two resonances: (1) 84.6 ppm, $-CF_3$; and (2) 93.2 ppm, $-CF_2ClO_4$; with the expected 3:2 area ratio for the peaks. The observed molecular weight by vapor density measurement was 216 g/mole, compared to the calculated value of 218.4 g/mole for $C_2F_5ClO_4$.

Vapor-pressure-temperature measurements were made over the range of -78 to 0°C: (C, mm): -77.9, 2; -45.5, 23; -31.1, 54; -23.7, 81; -14.3, 127; 0.0, 244. The vapor-pressure-temperature relation is described by the equation $\log p_{mm} = 7.6356 - (1430.8/T\ K)$ giving an extrapolated normal boiling point of 27.7°C. The heat of vaporization is 6.54 kcal $mole^{-1}$ and the Trouton constant is 21.8.

The solid remaining in the reactor after the workup was again identified as $IO_x(ClO_4)_y$ by its infrared spectrum (Reference 10). Other examples of these reactions which were worked up somewhat differently gave the same final

result as the present case. However, at the intermediate stages there was even more definite evidence for the formation of an intermediate complex, $C_2F_5I(ClO_4)_2$. Thus, in one instance, at the completion of the -45°C reaction, the cylinder was warmed directly to room temperature while pumping and fractionating as before. After one and one-half hours the cylinder was closed and the fractions obtained were examined. From 2.04 millimoles of C_2F_5I and 4.92 millimoles of Cl_2O_4 was obtained 0.59 millimole of Cl_2O_4, 2.17 millimoles of Cl_2, and a little $FClO_3$ in good agreement with the reaction of 2 Cl_2O_4 with 1 C_2F_5I. No R_f species were obtained. Upon standing for two hours at ambient temperature, the reactor was reopened and was now found to contain free $C_2F_5ClO_4$ in approximately 95-percent yield, together with small quantities of Cl_2 and Cl_2O_7. The weight of solid remaining approximated that expected for ICl_4. In yet another example, the volatile byproduct Cl_2 and excess Cl_2O_4 were removed at -45°C, and the complex was stored at -25°C for three weeks. Re-examination at that time with the temperature maintained at -25°C showed dissociation of the complex to $C_2F_5ClO_4$ and ICl_4 had occurred. Thus, the complex $C_2F_5I(ClO_4)_2$ is stable indefinitely at -45°C but decomposes slowly at -25°C and fairly rapid (although not instantaneously) at room temperature.

As part of the characterization of $CF_3CF_2ClO_4$, a sample (0.598 millimoles) was reacted with 1.6 g CsF for one week at ambient temperature in a 30-milliliter stainless-steel cylinder. Reaction did not occur, and the sample was fully recovered. However, heating the mixture at 120°C for 12 hours completely decomposed the perchlorate, furnishing 0.60 millimole of $FClO_3$ only. Subsequent pyrolysis of the bomb contents under vacuum liberated 0.60 millimole of CF_3CFO. Thus, a quantitative decomposition to these products was accomplished.

ICF_2CF_2I - Synthesis of $ICF_2CF_2ClO_4$

1,2 diodotetrafluoroethane (1.34 millimoles) and Cl_2O_4 (8.35 millimoles) were successively condensed at -196°C into a 30-milliliter cylinder. This was placed in liquid nitrogen/dry ice slush and allowed to warm slowly to -80°C over a two-day period. The temperature was then raised to -45°C for a week before fractionation. Noncondensable gases were not generated and the fractionation was performed while keeping the reactor at -30°C. This liberated Cl_2 (1.89 millimoles), Cl_2O_4 (4.15 millimoles), and very little R_fClO_4. Warming to room temperature with resumed fractionation produced ICF_2CF_2Cl (0.29 millimole, 22 percent of theory) which was identified by its infrared and mass spectra, which included a parent ion. Also obtained was $ICF_2CF_2ClO_4$ (0.85 millimole) contaminated with Cl_2O_7. A completely pure sample of $ICF_2CF_2ClO_4$ was difficult to obtain by fractional condensation. However, small amounts of good material were secured, sufficient to unequivocally identify the compound. The infrared spectrum was quite characteristic for a R_fClO_4 compound and more particularly $ICF_2CF_2ClO_4$ when compared to the known $ClCF_2CF_2ClO_4$ and $BrCF_2CF_2ClO_4$ analogs. The mass cracking pattern was also noteworthy, showing a good parent ion, $IC_2F_4ClO_4^+$ and predictable ion fragments. Finally, the ^{19}F nmr spectrum showed only two types of C-F in the compound and these in a 1:1 ratio: (1) 63.3 ppm, $-CF_2I$; and (2) 90.4 ppm, $-CF_2ClO_4$. The compound is a clear, colorless liquid with about 15 mm vapor pressure at 20°C, and it slowly pumps through taps cooled to -45°C. It is stable in metal and metal-Teflon equipment at ambient temperature. However, it is reactive, being decomposed by water with which a sample was treated to remove Cl_2O_7.

Other attempts to prepare $ICF_2CF_2ClO_4/O_4CF_2CF_2ClO_4$ were made. In one case, the byproducts of the synthesis were removed at -45°C, and since there was much unreacted Cl_2O_4 it was re-added to the reaction in which the temperature was then raised to -25°C. After one week, it was found that the sample had deflagrated giving copious amounts of O_2, CO_2, Cl_2, and some COF_2. All of the iodine from the starting material was converted to I_2-IF_5. No nonvolatile products were formed.

In addition, the solvent FC-78 (MMM) was used to help moderate the reaction. This attempt was conducted in a Kel-F cylinder. The FC-78/ICF_2CF_2I solution was kept at -80 to -35°C, and Cl_2O_4 vapor was added in increments. At the very first addition, a voluminous white precipitate formed. After standing overnight at -80°C, the reaction was worked by removing Cl_2 and the solvent at -64°C. Finally, at -45°C and above, the last of the solvent was stripped off together with some Cl_2O_7 and the crude $ICF_2CF_2ClO_4$ was obtained. Again, the compound was not pure, being mixed with some Cl_2O_7. Retained at -45°C after this fractionation was a quite small amount (~0.1 millimole) of an R_fClO_4 compound. This was tentatively identified as $O_4ClCF_2CF_2ClO_4$, based on its infrared spectrum which closely resembled that of $FO_3SCF_2CF_2SO_3F$ (Reference 13) for absorptions other than the $-OSO_2F$ and $OClO_3$ groups. Furthermore, the ^{19}F nmr spectrum of this material mixed with $ICF_2CF_2ClO_4$ showed, other than the two $ICF_2CF_2ClO_4$ fluorine resonances (64.0 ppm for $-CF_2I$ and 90.7 ppm for $-CF_2ClO_4$), only one sharp peak at 92.2 ppm, which was readily assignable to $-CF_2ClO_4$ groups and which compared well with that of $-CF_2SO_3F$ (90.4 in $FO_3SCF_1CF_2SO_3F$).

$ICF_2CF_2CF_2I$-Cl_2O_4 Reaction

A 30-milliliter stainless-steel cylinder was charged with $ICF_2CF_2CF_2I$ (1.29 millimoles) followed by Cl_2O_4 (5.63 millimoles) at -196°C. The closed cylinder was placed in a liquid nitrogen/dry ice slush and slowly warmed to -80°C. Finally, it was warmed to and maintained at -45°C for three weeks. Recooling to -196°C showed no O_2 had been formed. While warming to room temperature, the volatile material was pumped from the reactor through traps cooled to -45, -112, and -196°C for two hours. The cylinder was closed and the volatile species were analyzed. These were Cl_2O_4 (0.47 millimole) and Cl_2 (2.61 millimoles) which agreed extremely well with the formation of the complex, $(O_4Cl)_2ICF_2CF_2CF_2I(ClO_4)_2$. Four hours later the reactor was reopened. It now contained very large amounts of O_2 (~7 millimoles), Cl_2, CO_2, COF_2, and some CF_4 and C_2F_6 (total ~6 millimoles). Once again, all of the iodine from the starting material was recovered as I_2-IF_5, and essentially no nonvolatile residue remained in the cylinder.

CF_3CFICF_3 - Synthesis of $(CF_3)_2CFI(ClO_4)_2$

Using a 30-milliliter cylinder, CF_3CFICF_3 (1.53 millimoles) and Cl_2O_4 (3.31 millimoles) were condensed in separately at -196°C. The mixture was gradually warmed from -196 to -80°C with liquid nitrogen/dry ice bath and then to -45°C for four days. At that point, no O_2 was observed and the products were separated by fractional condensation on warming to room temperature for two hours. Recovered were Cl_2 (1.55 millimoles) contaminated with a little

$FClO_3$, Cl_2O_4 (0.36 millimole), and CF_3CFICF_3 (0.09 millimole). After two hours, the cylinder was reopened and pumped again for hours at room temperature without obtaining additional material. The weight of the nonvolatile product was 0.703 g. For the 1.44 millimoles of CF_3CFICF_3 which had reacted, the weight calculated for $(CF_3)_2CFI(ClO_4)_2$ was 0.711 g. Opening the cylinder in the dry box showed a loose, finely powdered, white solid was present. An infrared spectrum of the solid was run as a neat powder between pressed AgCl disks. Typical C-F bands (1100 to 1250 cm^{-1}) and covalent ClO_4 group bonds (~1300 and 1020 cm^{-1}) dominated the spectrum. The solid fumed vigorously in air and liberated some I_2 on treatment with water together with some oily droplets.

A sample of this complex solid (305 mg, 0.617 millimole) was heated at 105°C for 16 hours in a 10-milliliter cylinder. Oxygen was generated (1.13 millimoles), and the condensable species were partially separated by fractionation. These were mainly CO_2 and Cl_2 with some COF_2 and small amounts of CF_4 and C_2F_6. In all, these totalled 2.42 millimoles. Iodine was found exclusively as I_2-IF_5. All of the solid was converted to gaseous compounds.

Another sample of the complex was heated at 60 to 90°C for four hours with continuous pumping and trapping at -196°C. No evidence of sublimation was found, and only Cl_2 was detected as an evolved gaseous product. An infrared spectrum of the solid after this treatment showed the strongest bands were still present, i.e., C-F and ClO_4, but the spectrum was much more diffuse and some new bands were present. On exposure to air the solid did not fume, but it was deliquescent.

IODINE tris-PERCHLORATE-PERFLUOROPROPENE REACTION

A sample of $I(ClO_4)_3$ (1.40 millimoles) was prepared in a FEP-Teflon tube fitted with a stainless-steel valve. Perfluoropropene (1.85 millimoles) was condensed into the tube at -196°C, and the reaction was allowed to take place at -45°C for one week. Recooling to -196°C showed no noncondensable gas had been generated. Keeping the tube at -45°C, volatile species were pumped out and passed through traps cooled to -80, -112, and -196°C. Two compounds only were recovered: unreacted $CF_2CF=CF_2$ (1.65 millimoles) and $CF_3CFClCF_2ClO_4$ (0.20 millimole), identified by comparison with an authentic sample (Reference 5).

OTHER CHLORINE PERCHLORATE REACTIONS

Reaction With Picryl Chloride

A sample of freshly recrystalized picryl chloride (2.00 millimoles) was placed in a 30-milliliter reactor in the dry box. Chlorine perchlorate (4.56 millimoles) was condensed over it at -196°C, the reactor was warmed to -20°C, and kept for four weeks. The volatile products were separated by vacuum fractionation. Most of the Cl_2O_4 (0.98 millimole) was recovered together with O_2 (3.54 millimoles), Cl_2 (0.70 millimole), and small amounts of ClO_2 and Cl_2O_6. Examination of the solid showed it to be unchanged picryl chloride. There was no discernible weight change for the solid.

In another experiment, picryl chloride (2.00 millimoles) and Cl_2O_4 (2.10 millimoles) were reacted by slowly warming to ambient temperature and then letting the reactor stand for three weeks. At that time, it was found that all of the Cl_2O_4 had decomposed to Cl_2 (2.11 millimoles) and O_2 (4.28 millimoles); the picryl chloride was unchanged.

Using FC-78 (3 milliliters) as a solvent, picryl chloride (0.99 millimole) and Cl_2O_4 (1.48 millimoles) were reacted at -25°C in a FEP-Teflon tube. The picryl chloride was only partially dissolved by the solvent, and most of the crystals remained on the bottom of the tube. During the two-week reaction period, a fluffy, powdery precipitate formed and floated on top of the solvent. Removal of the volatile species showed a little Cl_2 was present, but, mostly, unreacted Cl_2O_4 was reclaimed. The weight of the solid left was within 10 mg of the starting weight; an infrared spectrum of the solid showed it to be unchanged picryl chloride. The fluffy precipitate was apparently just a recrystallized form of the picryl chloride.

Reaction With Cyanuric Chloride

Sublimed cyanuric chloride (1.52 millimoles) was loaded into a 30-milliliter cylinder in the dry box and Cl_2O_4 (5.98 millimoles) was condensed over it at -196°C. The cylinder was warmed to -45°C and stored for six weeks. Partial workup showed no O_2 had formed, but considerable Cl_2 and CO_2 (3.74 millimoles total) were present. Because the presence of appreciable CO_2 indicated extensive degradation had occurred, the remaining products were not analyzed.

Reaction With Trichloroacetonitrile

A 30-milliliter stainless-steel cylinder was charged with CCl_3CN (1.40 millimoles) and Cl_2O_4 (2.82 millimoles) at -196°C. It was put at -20°C for four weeks and warmed to +5°C for two days. Workup showed very little -196°C noncondensable material was formed. The 0°C volatile products were approximately, CO_2 (0.5 millimole), $COCl_2$ (0.2 millimole), Cl_2 (1.0 millimole), and Cl_2O_7 (0.7 millimole). There remained in the cylinder a white, solid product which vacuum sublimation at 50°C revealed to be a mixture. The volatile component formed large, clear, colorless crystal, melting point, 40°C. An infrared spectrum of this solid showed only the characteristic bands of a $CCl_3C(=O)$ material and no ClO_4 bands. The unsublimed solid was a white powder and was identified as NO_2ClO_4 based on comparison of its infrared spectrum with that of an authentic sample.

Repetition of this reaction using the same 1 CCl_3CN: 2 Cl_2O_4 stoichiometry with a 16-hour reaction period over the temperature range -80°C to ambient temperature gave the same basic result. More CO_2 and less $COCl_2$ were found, but no evidence of a stable covalent perchlorate was obtained. The same solid product mixture was produced as previously.

Reaction With Dichlorodinitro Methane

Tetranitromethane and LiCl were used to prepare $Cl_2C(NO_2)_2$ according to Fainzilberg (Reference 19). A 30-milliliter cylinder was charged with 1.49 millimoles of $Cl_2C(NO_2)_2$ and 6.15 millimoles of Cl_2O_4. The reactor was kept

at -20°C for nearly two months. During this period, periodic monitoring of the evolved Cl_2 (and some small amounts of O_2) was conducted by cooling the cylinder to -80°C and fractionating through -112 and -196°C cold traps. Slow, continuous formation of Cl_2 was noted. The Cl_2 was discarded each time and the Cl_2O_4 was recondensed into the reactor. After two months, some CO_2 appeared in the monitored products and a complete workup was undertaken. Recovered Cl_2O_4 (3.80 millimoles) was more than one-half that used while Cl_2 (2.2 millimoles) accounted for the consumed Cl_2O_4, assuming 1 Cl_2 for each Cl_2O_4 reacted. However, the CO_2 (0.3 millimole) and mixed chlorine oxides (ClO_2, Cl_2O_6, and Cl_2O_7) also found showed degradation had occurred. The only detectable C-NO_2 moiety was the starting material. When all volatile species had been pumped from the reactor, it was opened and found to contain a white, powdery solid. This was identified as NO_2ClO_4 through its infrared spectrum.

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APPENDIX I

INFRARED SPECTRA

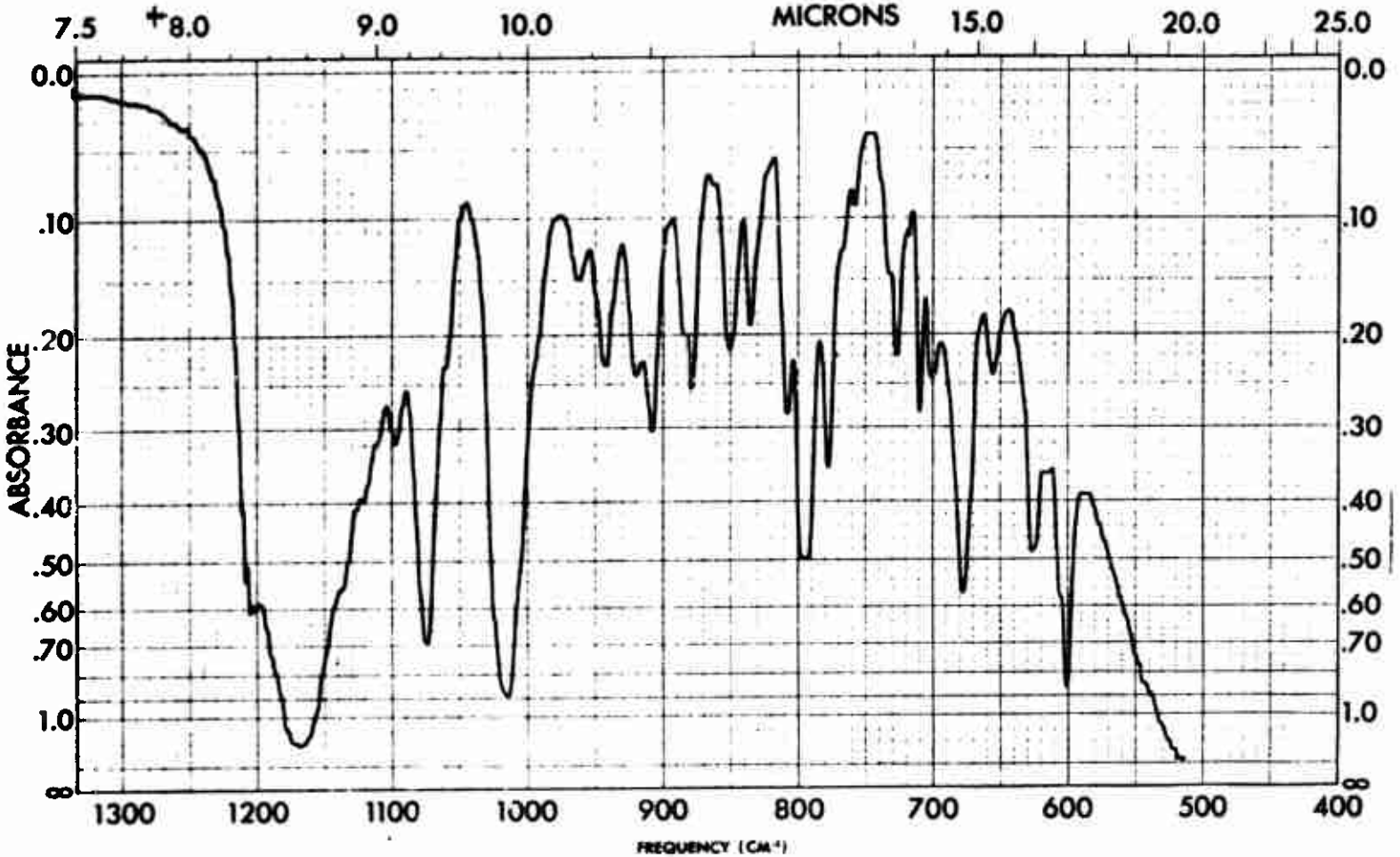

Figure 1-1. $BrCF_2CFBrCFBrCF_2Br$ (Liquid, NaCl Plates)

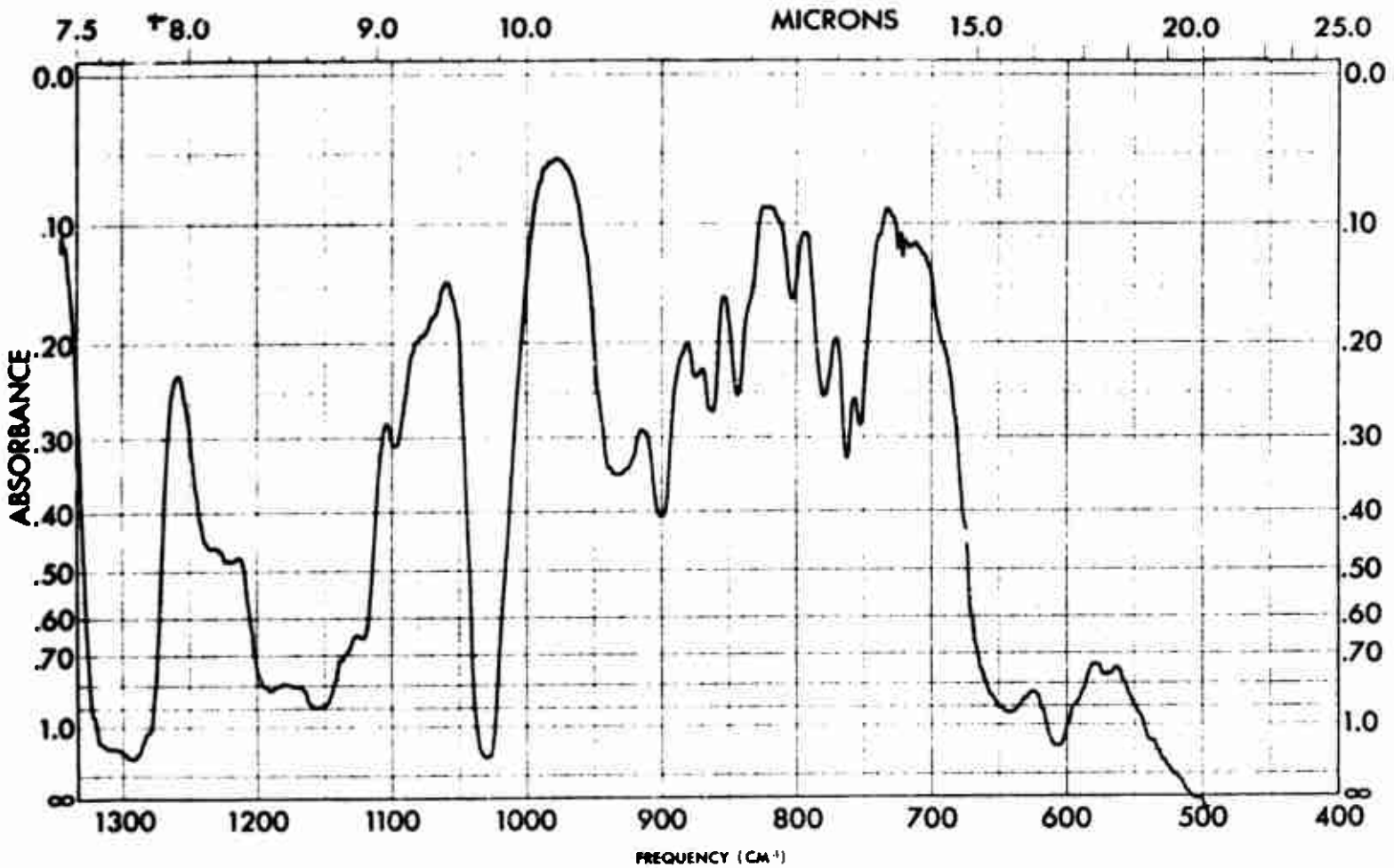

Figure I-2. $O_4ClCF_2CFBrCFBrCF_2ClO_4$ (Liquid, NaCl Plates) Product From $CF{=}CFCF{=}CF_2$ and $2BrClO_4$

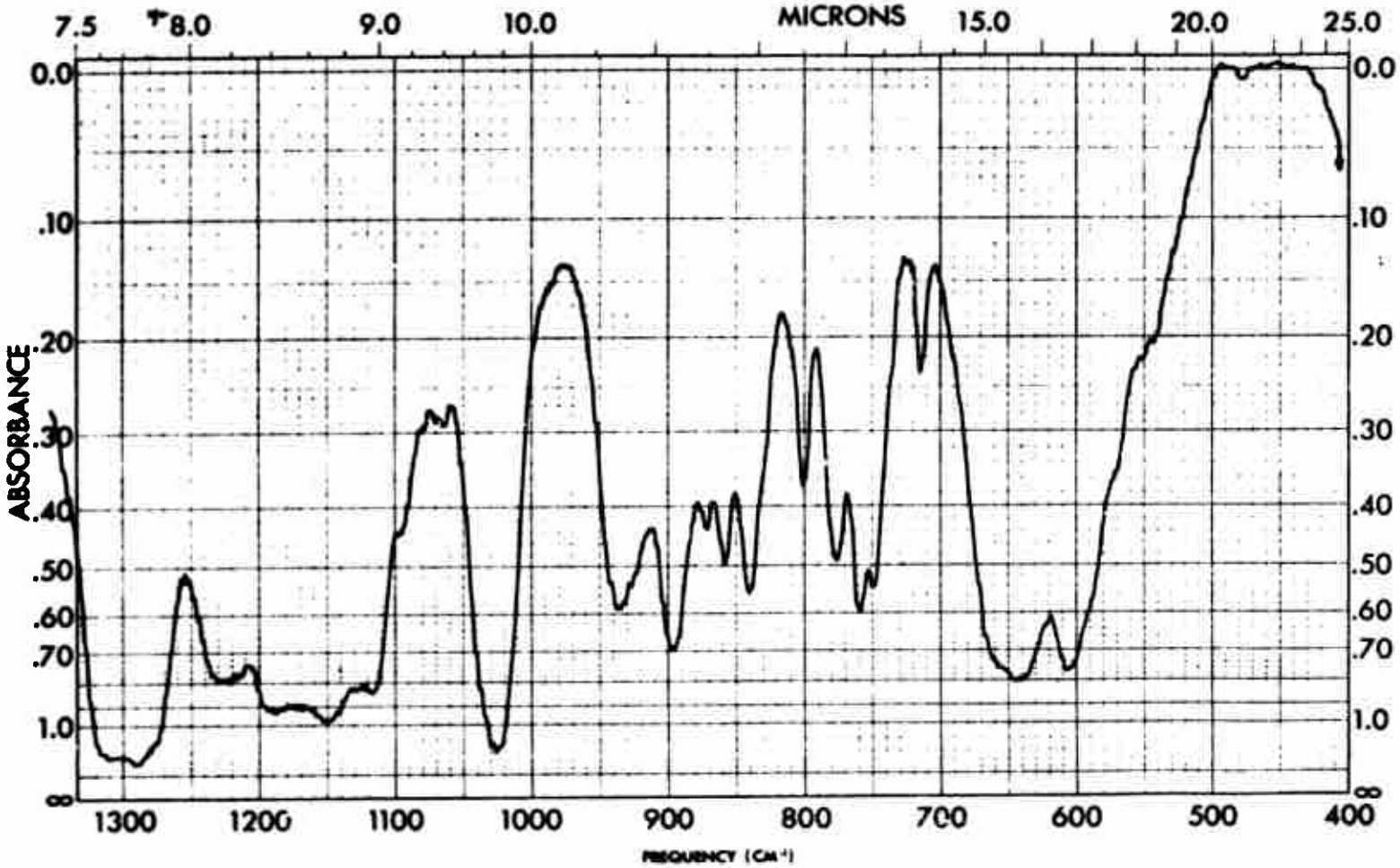

Figure I-3. $O_4ClCF_2CFBrCFBrCF_2ClO_4$ (Liquid, AgCl Plates) Product From $BrCF_2CFBrCFBrCF_2Br$ and Cl_2O_4

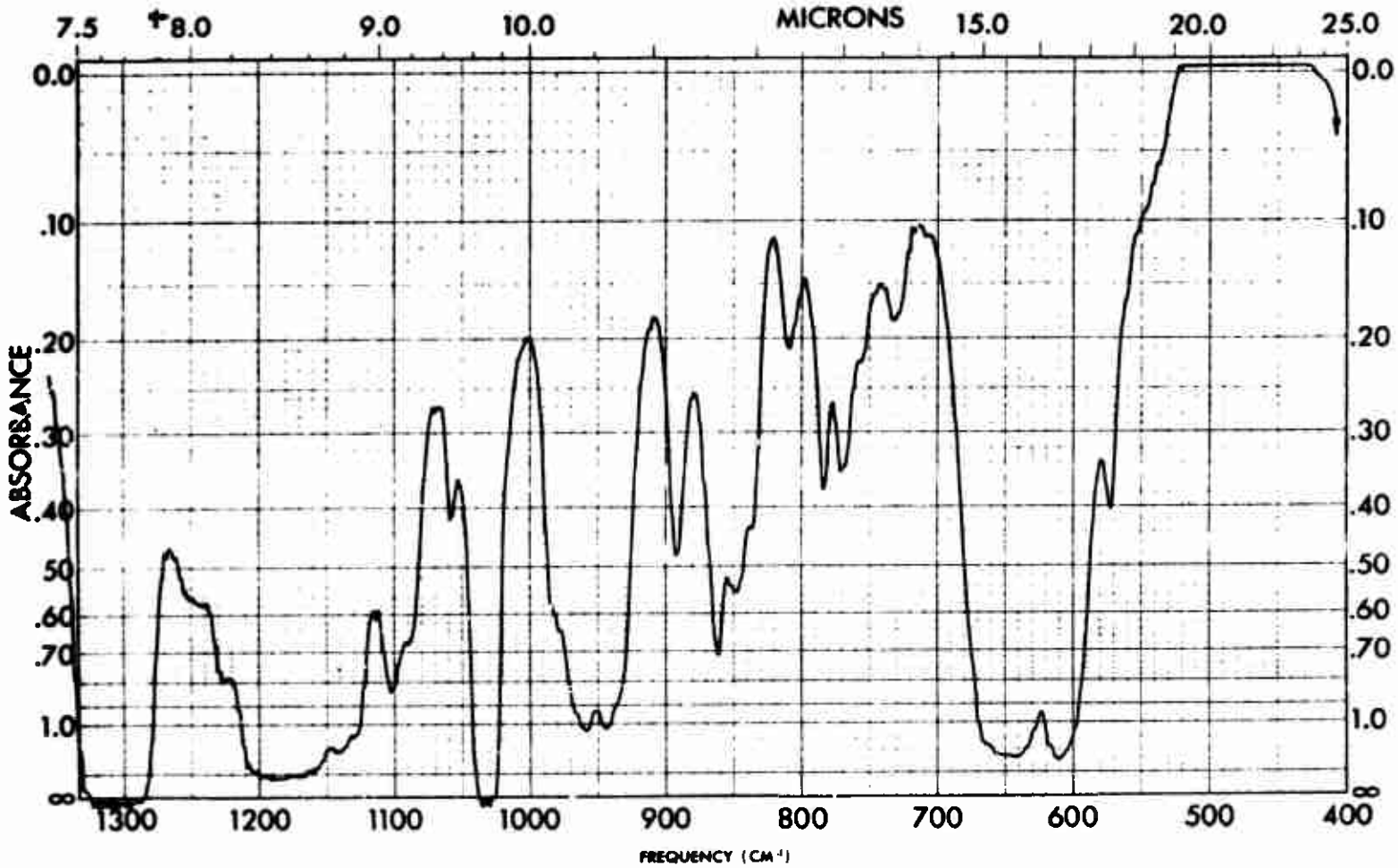

Figure I-4. $C_4F_6Cl_2(ClO_4)_2$ Isomer Mixture (Liquid, AgCl Plates)

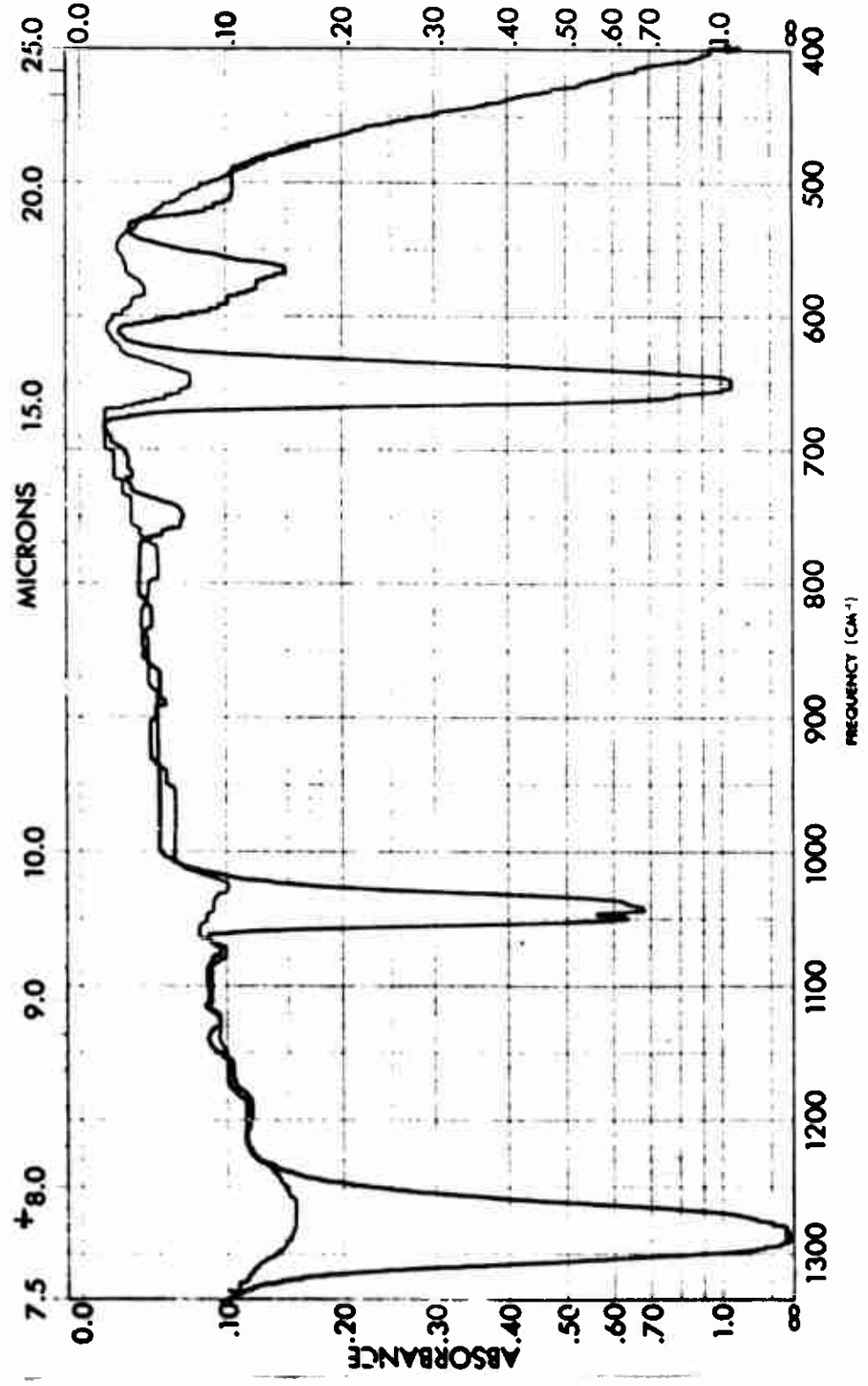

Figure 1-5. Cl_2O_4 (Gas, 8mm)

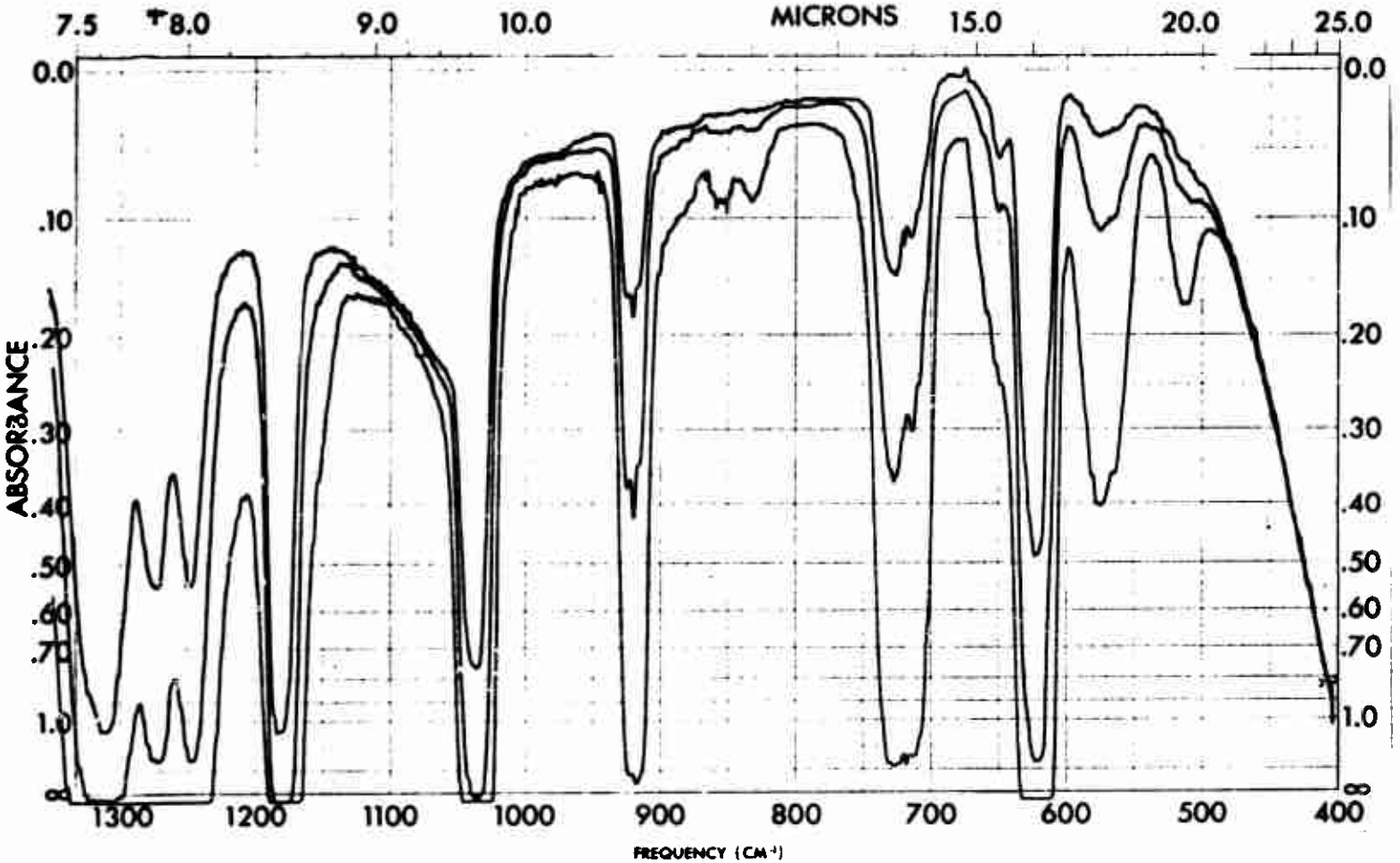

Figure I-6. CF_3ClO_4 (Gas; 50, 13, 5mm)

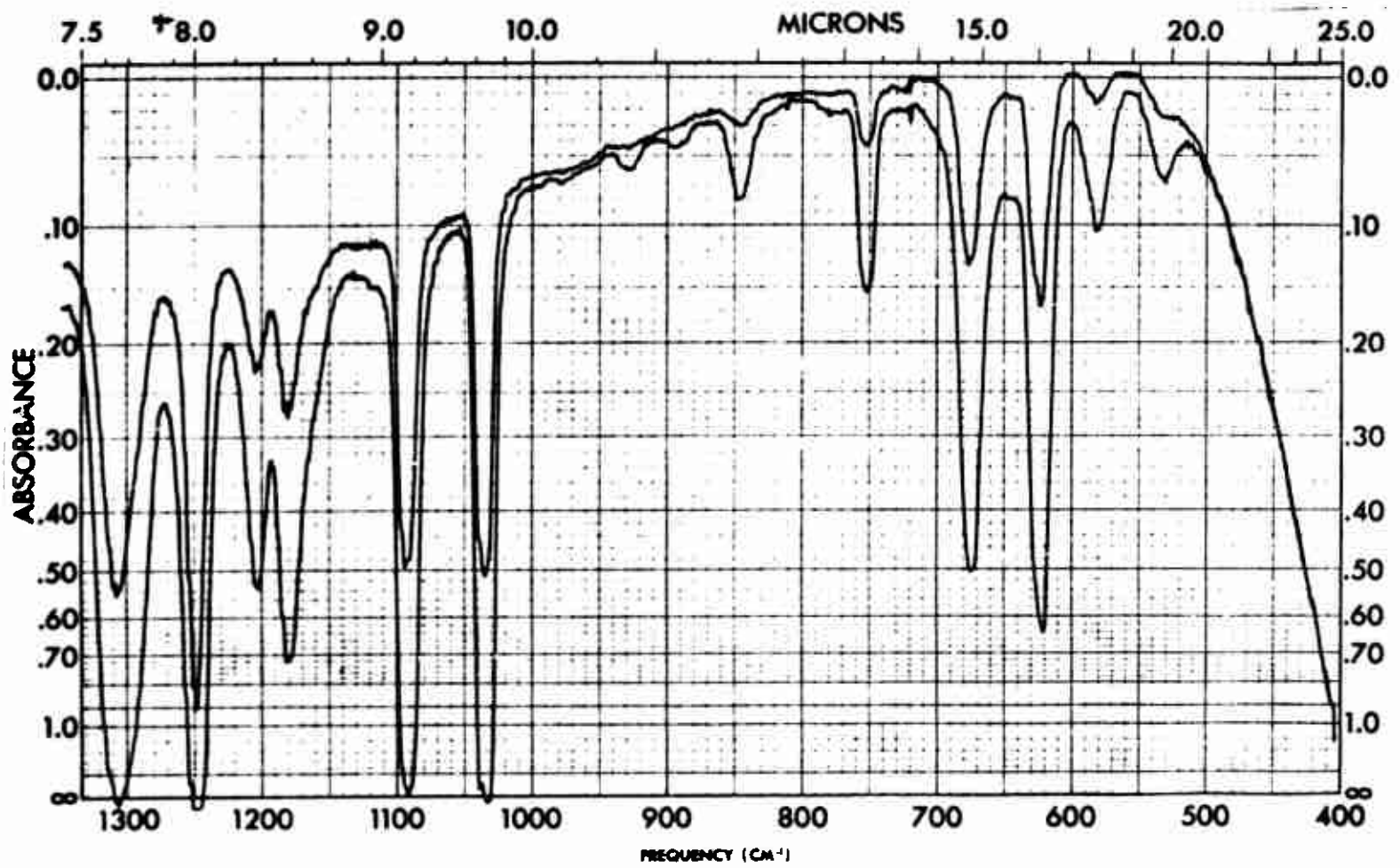

Figure I-7. $CF_3CF_2ClO_4$ (Gas; 7, 2mm)

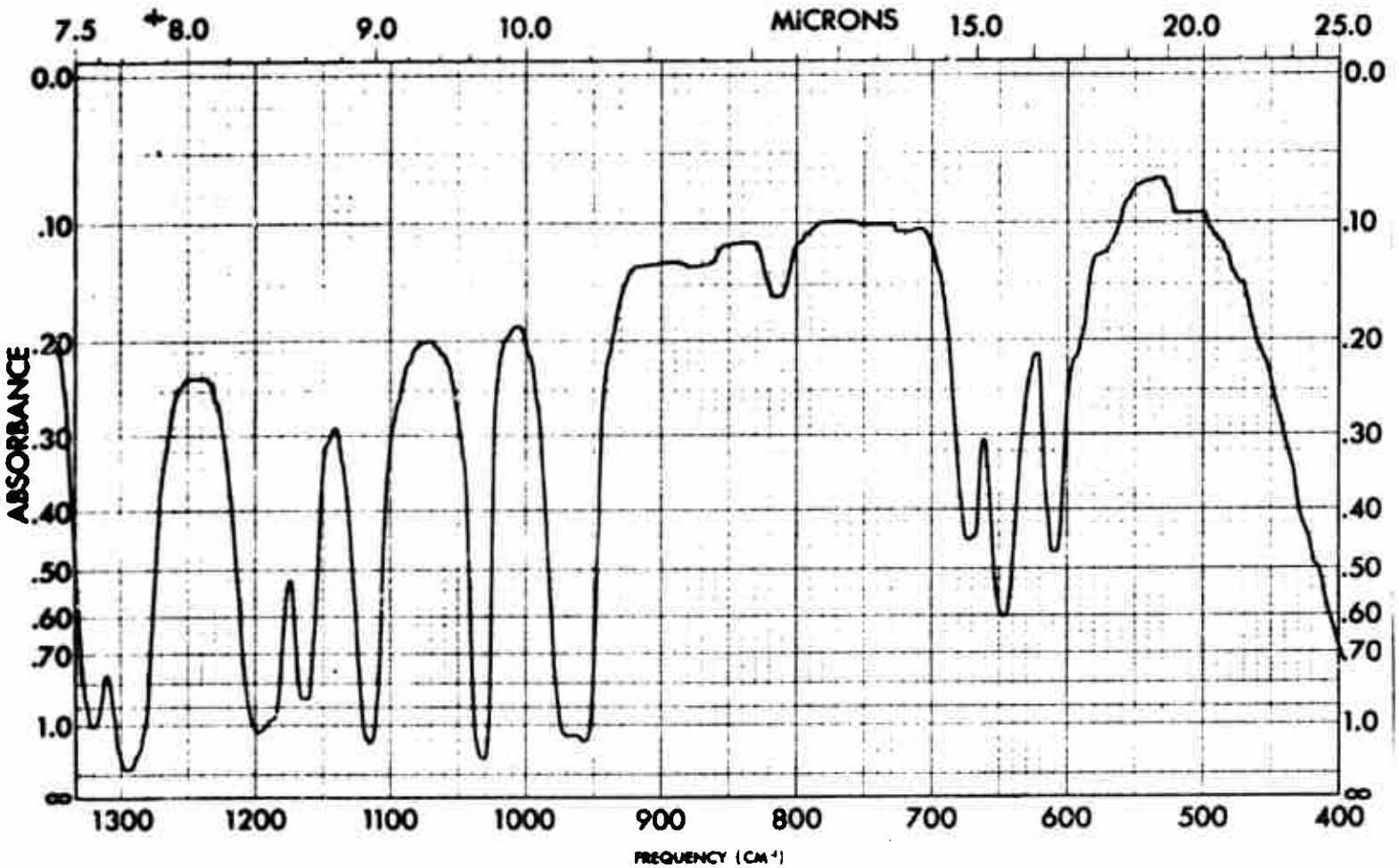

Figure I-8. $ClCF_2CF_2ClO_4$ (Gas, 12mm)

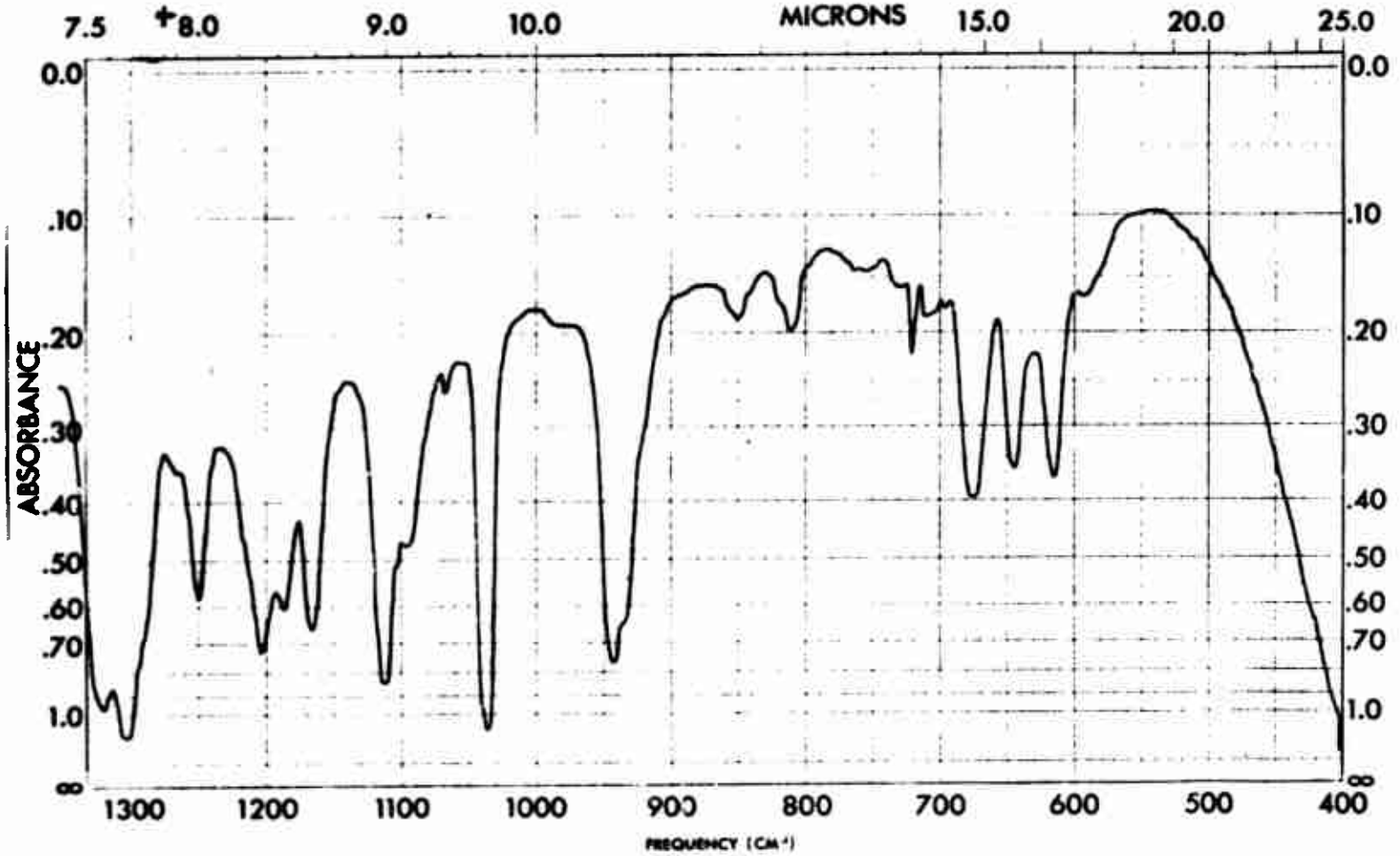

Figure I-9. $BrCF_2CF_2ClO_4$ (Gas, 7mm)

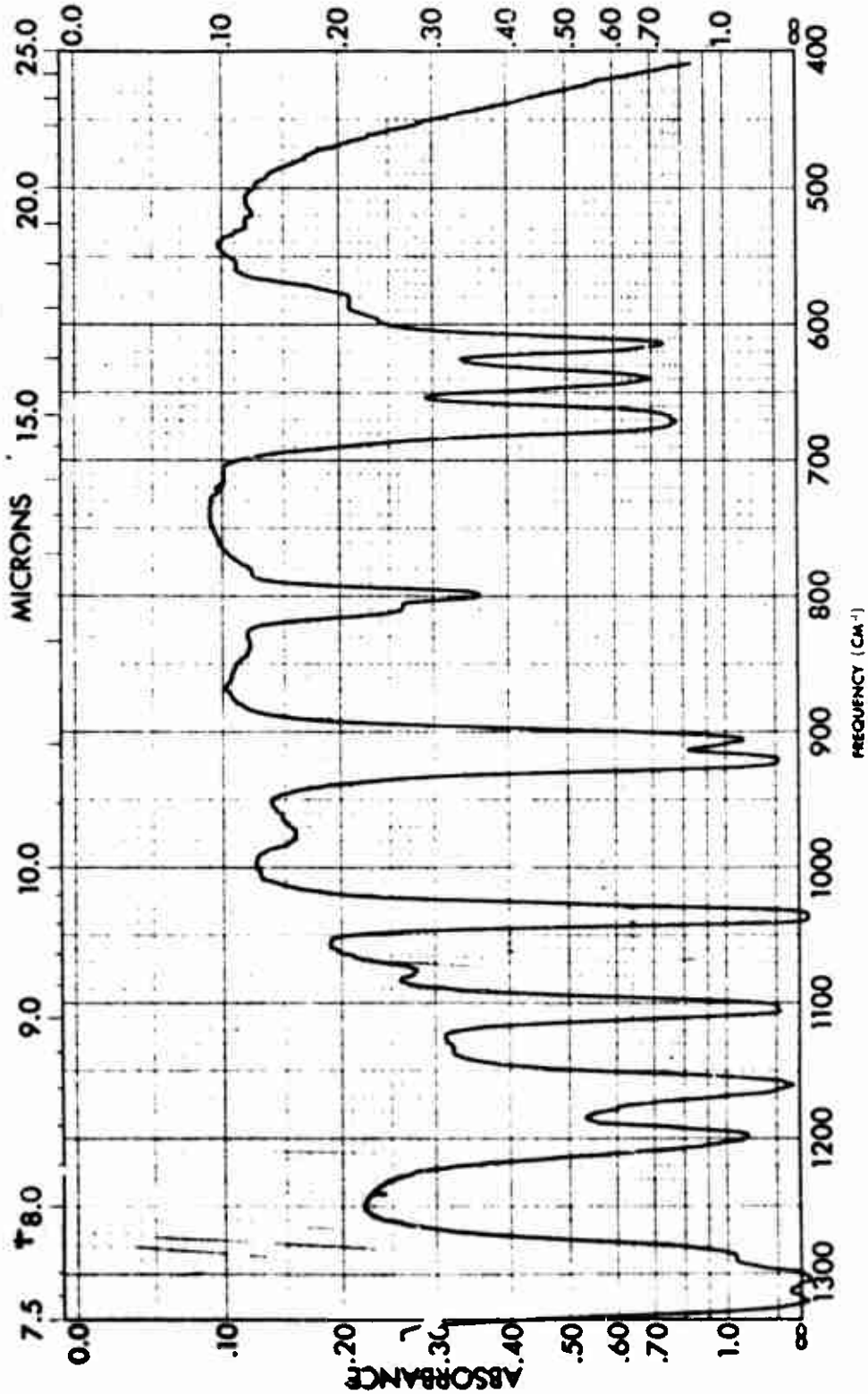

Figure I-10. $ICF_2CF_2ClO_4$ (Gas, 10mm)

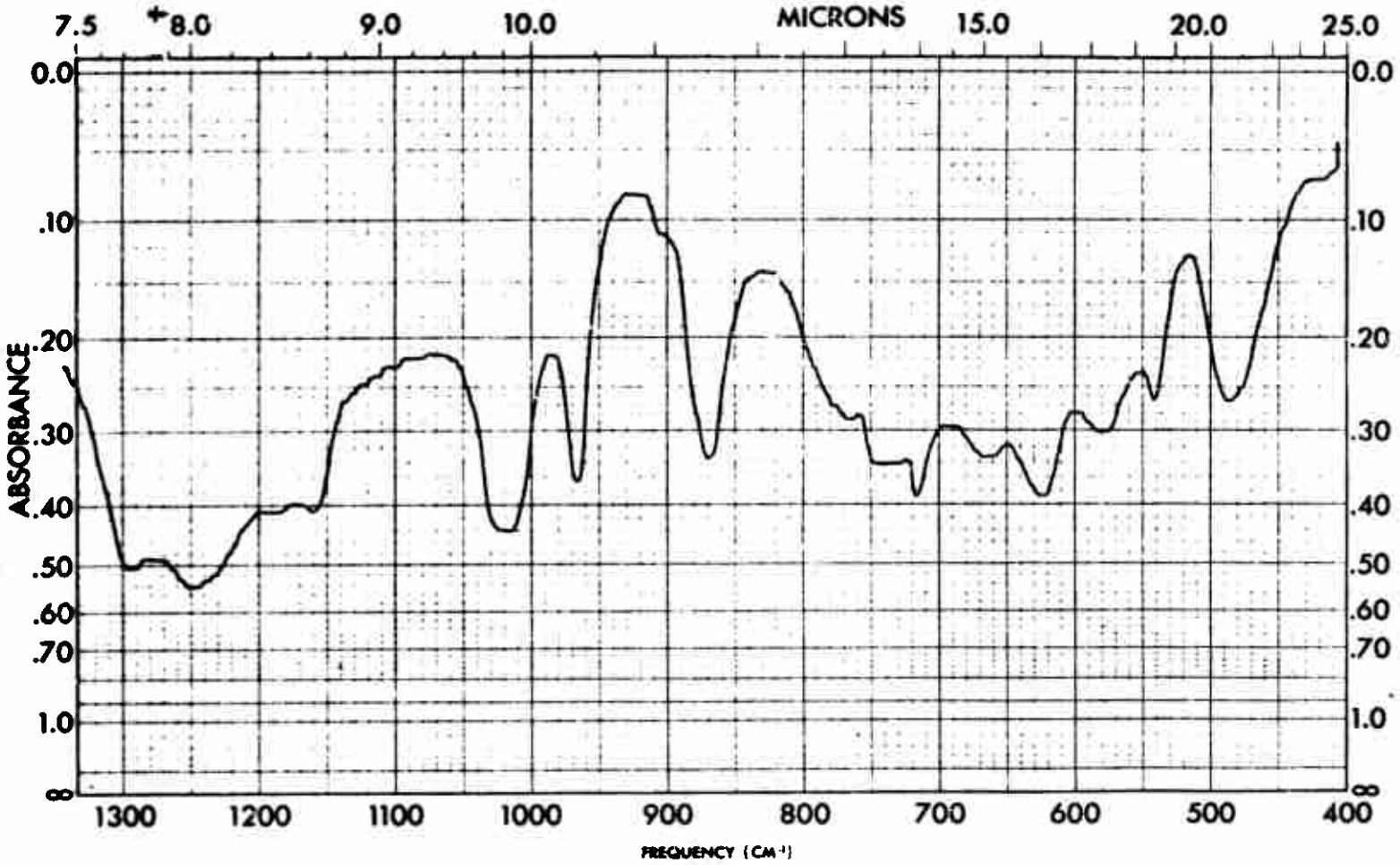

Figure I-11. $(CF_3)_2CFI(ClO_4)_2$ (Solid, pressed AgCl Disks)

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13. ABSTRACT

A variety of new, covalent perchlorates were synthesized, including perfluorinated perchlorates and halofluorocarbon perchlorates. The synthetic approach utilized was a new development and entailed the displacement of halogen from substituted fluorocarbons by the use of chlorine perchlorate.

The objective of this program was the utilization of these new halogen perchlorates in the synthesis of new covalent perchlorates. Of principal concern was the demonstration of model reactions and their subsequent use in preparing a variety of new perchlorates. Structural and physico-chemical characterization of the new materials was sought with the aim of uncovering properties pertinent to explosive end product use.

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