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Halogen Perchlorates. Additions to Perhaloolefins

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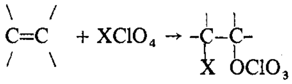
The recently discovered halogen perchlorates, Cl_2O_4 and $BrClO_4$, have been found to react with perhaloolefins by adding across the carbon-carbon double bond. These reactions proceeded quickly at low temperatures, in the absence of a solvent, to furnish the previously unknown perhaloalkyl perchlorates in high yield. Compounds prepared in this manner were $ClCF_2CF_2ClO_4$, $ClCF_2CFClClO_4$, $Cl_2CFCFClClO_4$, $CF_3CFClCF_2ClO_4$, $BrCF_2CFClClO_4$, and $CF_3CFBrCF_2ClO_4$. Characteristic data for these surprisingly stable compounds are reported. All the new perchlorates reacted with alkali metal fluorides to form the corresponding acid fluorides and either $FClO_3$ or mixtures of $FClO_3$, Cl_2, and O_2.

Introduction

Compounds which contain terminal halogen-oxygen single bonds have been reported to add to olefin double bonds through cleavage of the X-O single bond. For example, halogen fluorosulfates ($X\text{-}OSO_2F$),[1,2] chlorine nitrate ($Cl\text{-}ONO_2$),[3] and haloxyperfluoromethanes ($X\text{-}OCF_3$)[4-6] all participate in such reactions. As part of a systematic investigation of the recently discovered halogen perchlorates, Cl_2O_4 ($ClOClO_3$)[7] and $BrClO_4$ ($BrOClO_3$),[8] their reaction with perhaloolefins was examined. Rapid and generally smooth reaction was found which produced the new class of compounds, perhaloalkyl perchlorates



$$\gt C{=}C\lt + XClO_4 \rightarrow -\underset{X}{\overset{|}{C}}-\underset{OClO_3}{\overset{|}{C}}-$$

(X = Cl, Br)

These reactions occurred in high yield (~90%) at low temperatures and have been used to prepare $ClCF_2CF_2ClO_4$, $ClCF_2CFClClO_4$, $Cl_2CFCFClClO_4$, $CF_3CFClCF_2ClO_4$, $BrCF_2CFClClO_4$, and $CF_3CFBrCF_2ClO_4$. Although thermally stable at ambient temperature, the alkyl perchlorates were susceptible to catalytic decomposition with alkali metal fluorides at these same temperatures. Catalyzed decompositions gave quantitative yields of the respective acid fluorides and provided a useful procedure for their identification.

Experimental Section

Apparatus and Materials. The equipment used in this work has been described.[9] Chlorine perchlorate and bromine perchlorate were prepared as reported.[7,8] The haloolefins used were purchased and purified by fractional condensation except tetrafluoroethylene which was prepared by pyrolyzing Teflon. Cesium fluoride and potassium fluoride were fused and then powdered in a drybox prior to use.

Halogen Perchlorate Additions. General Method. In general the reactions of the halogen perchlorates and haloolefins were conducted in a Teflon U trap on the vacuum line. A known quantity of the halogen perchlorate was maintained in the trap at −78°. At this temperature these perchlorates are liquid and have little vapor pressure. An excess of the gaseous olefin was added to this trap incrementally or at a continuous rate such that a pressure of 20-30 mm was not exceeded. The rate of the observed pressure drop was appreciably increased if the liquid phase was agitated. Some reactions were run by condensing all the reactants in a Pyrex bulb at −196° and then warming first to −78° and finally to room temperature. No problems were encountered with this method for the $CF_3CF{=}CF_2\text{-}Cl_2O_4$ system on a 4-mmol scale. However, using this method with the $CF_2{=}CFCl\text{-}Cl_2O_4$ system on the same scale resulted in an explosion. Therefore additional reactions were not conducted in this manner. Product work-up was easily accomplished by fractional condensation since the perhaloalkyl perchlorates were considerably less volatile than any unreacted material present or any byproducts formed. All the perhaloalkyl perchlorates prepared were colorless, mobile liquids which did not freeze down to −78°. The compounds were stable and storable at ambient temperature in clean and dry Pyrex or stainless steel containers. Purity, as determined by gas chromatography, was generally 98+%, even after 1 year at ambient temperature. Details of the synthesis and characterizations follow. The ^{19}nmr data are shown in Table II and the infrared bands of the perchlorate compounds in Table I.

Perfluoropropene-Halogen Perchlorate Reactions. According to the general procedure described above, $CF_3CF{=}CF_2$ (4.20 mmol) was added to Cl_2O_4 (3.56 mmol) over a 20-min period. On fractionation, the product $CF_3CFClCF_2ClO_4$ (3.48 mmol, 97.6% yield) was retained at −78°. The purity of the product was indicated by tensiometric homogeneity, 44 mm at 20.1° and 18 mm at 0.0°. The observed vapor density was 280 g/mol; calculated 285 g/mol. Prominent peaks were noted in the mass spectrum for the m/e values corresponding to the ions $C_3F_6Cl^+$, $C_2F_4Cl^+$, CF_2Cl^+, ClO_3^+, CF_3^+ (base peak), ClO_2^+, CF_2O^+, ClO^+, and COF^+. The densities measured in a Pyrex pycnometer at −77.2, 0.0, and 20.0° were 2.01, 1.84, and 1.80 g/ml. For this temperature range, the density, ρ, is given by the equation $\rho = 1.84 - 2.18 \times 10^{-3}t°C$.

Perfluoropropene (4.46 mmol) was added to $BrClO_4$ (4.28 mmol) over 30 min. Pure $CF_3CFBrCF_2ClO_4$ (3.78 mmol, 88.4% yield) was retained at −64° and exhibited vapor pressures of 7 mm at 0.0° and 22 mm at 20.0°. The observed vapor density was 331 g/mol; calculated 329.3 g/mol. Major peaks in the mass spectrum corresponded to the ions $C_3F_6Br^+$, $C_3F_5BrO^+$, $C_2F_4Br^+$, $C_2F_3Br^+$, CF_2Br^+, ClO_3^+, CF_3^+ (base peak), ClO_2^+, CF_2O^+, ClO^+, CF_2^+, and COF^+. The measured densities at −77.4, 0.0, and 21.0° were 2.25, 2.09, and 2.05 g/ml giving a density-temperature relation for this temperature range: $\rho = 2.09 - 2.05 \times 10^{-3}t°C$.

Chlorotrifluoroethylene-Halogen Perchlorate Reactions. During a 4-hr period, $CF_2{=}CFCl$ (8.05 mmol) was added to Cl_2O_4 (7.70 mmol) forming $ClCF_2CFClClO_4$ (7.19 mmol, 93.5% yield) which was retained at −64° on fractionation. Measured vapor pressures were 10 mm at 0.0° and 25 mm at 22.9° and the vapor density was 249 g/mol; calculated 251.5 g/mol. The mass spectrum showed strong peaks for the ions $C_2F_3Cl^+$, $CFCl_2^+$, $C_2F_3O^+$, CF_2Cl^+ (base peak), ClO_3^+, CF_3^+, ClO_2^+, $CFCl^+$, ClO^+, CF_2^+, and COF^+. Densities observed at −77.4, 0.0, and 20.1° were 1.98, 1.83, and 1.79 g/ml. The density-temperature relation for this temperature range is given by the equation $\rho = 1.83 - 1.96 \times 10^{-3}t°C$.

Chlorotrifluoroethylene (2.64 mmol) was allowed to react with $BrClO_4$ (2.45 mmol) over a 1-hr period and furnished $BrCF_2CFClClO_4$ (2.08 mmol, 85% yield) which was trapped at −54° during fractional condensation. The purified material showed vapor pressures of 3 mm at 0.0° and 11 mm at 20.4°.

Tetrafluoroethylene-Chlorine Perchlorate Reaction. The reaction of C_2F_4 (3.16 mmol) and Cl_2O_4 (3.12 mmol) at −78° was quite slow, even with a C_2F_4 pressure of 100 mm, and was allowed to proceed overnight prior to work-up. Fractional condensation at −95° gave $ClCF_2CF_2ClO_4$ (2.86 mmol, 91.5% yield) with an observed vapor density of 233 g/mol; calculated 235 g/mol. The following tempera-

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Table I. Infrared Spectra of Fluorocarbon Perchlorates (4000–400-cm^{-1} Range)

$Cl_2CFCFClClO_4$	$ClCF_2CFClClO_4$	$BrCF_2CFClClO_4$	$ClCF_2CF_2ClO_4$	$CF_3CFClCF_2ClO_4$	$CF_3CFBrCF_2ClO_4$	Tentative assignments
1307 s	1310 s	1311 s	1320 s	1318 s	1318 s	Asym Cl=O str
1296 s	1297 s	1299 s	1295 s	1300 s	1302 s	Asym Cl=O str
1178 m	1232 wm	1224 wm	1198 s	1260 sh	1290 sh	C–F str Region
1130 m	1189 ms	1190 ms	1163 s	1242 s	1255 sh	
1090 m	1140 m	1141 m	1115 s	1182 w	1240 s	
1050 m	1091 m	1088 m		1149 m	1187 vw	
	1054 m	1047 m		1128 m	1170 vw	
					1148 w	
					1123 m	
997 s	1008 s	1004 s	1032 s	1036 s	1033 s	Sym Cl=O str
908 ms	918 m	892 m	970 s	976 s	960 m	
879 m	855 m	820 m	958 s	955 s	924 m	C–O str
818 ms	752 w	749 w	815 w	811 w	805 w	
	660 sh	650 sh	672 m	739 m	737 m	
				670 m	670 sh	
632 s	630 s	630 s	647 ms	653 ms	652 m	Cl–O str
610 sh	580 w	582 w	610 m	620 ms	620 m	
575 w				598 vw	595 vw	
					545 w	

Table II. ^{19}F Nmr Data[a]

Compound	$CF_{3-n}X_n$ (X = Cl)	CFX (X = Cl, Br)	$CFXClO_4$ (X = F, Cl)	COF
$Cl_2CFCFClClO_4$	69.8 [1][b]		76.0 [1]	
$ClCF_2CFClClO_4$	69.0 [2]		79.0 [1]	
$ClCF_2CF_2ClO_4$	72.7 [1]		92.5 [1]	
$CF_3CFClCF_2ClO_4$	78.4 [3]	139.2 [1]	85.8 [2]	
$CF_3CFBrCF_2ClO_4$	76.5 [3]	141.5 [1]	84.7 [2]	
$CFCl_2COF$	65.9 [1]			−7.5 [1]
CF_2ClCOF	65.1 [2]			−10.0 [1]
$CF_3CFClCOF$	80.5 [3]	132.3 [1]		−20.6 [1]
$CF_3CFBrCOF$	78.7 [3]	137.1 [1]		−20.3 [1]

[a] Chemical shift in ppm relative to internal $CFCl_3$. [b] Values in brackets are approximate relative area ratios.

ture–vapor pressure data were noted (°C, mm): −24.1, 10; 0.0, 42; 10.3, 71; 20.4, 113. The vapor pressure–temperature relation is described by the equation $\log p_{\mathrm{mm}} = 7.968 - (1735/T\,°\mathrm{K})$. The extrapolated normal boiling point is 67.8°, with a heat of vaporization of 7.93 kcal/mol and a Trouton constant of 23.3. Intense peaks in the mass spectrum were found for the ions $C_2F_4Cl^+$, CF_2Cl^+ (base peak), ClO_3^+, CF_3^+, ClO_2^+, $CFCl^+$, CF_2O^+, ClO^+, CF_2^+, and COF^+. The density at −76.5, 0.0, and 20.1° was 1.98, 1.80, and 1.75 g/ml. The derived density–temperature equation is $\rho = 1.80 - 2.43 \times 10^{-3}t\,°C$.

1,2-Dichlorodifluoroethylene–Chlorine Perchlorate Reaction. Chlorine perchlorate (5.75 mmol) was maintained at −35° for its addition to ClCF=CFCl (6.03 mmol) so that the reaction could be followed manometrically. Initially the reaction appeared rapid but it soon became sluggish, requiring 10 hr to complete the addition using 40 mm as the maximum reaction pressure. Vacuum fractionation at −35° gave pure $Cl_2CFCFClClO_4$ (5.04 mmol, 87.6% yield). Prominent mass spectral peaks were found for the ions $C_2F_2ClO^+$, $CFCl_2^+$ (base peak), ClO_3^+, ClO_2^+, $CFCl^+$, ClO^+, CCl^+, and COF^+. The vapor pressure was 2 mm at 0.0° and 5 mm at 20.2°. Density measurements at −77.6, 0.0, and 20.0° were 2.06, 1.92, and 1.89 g/ml. The density–temperature relation is given by the equation $\rho = 1.92 - 1.77 \times 10^{-3}t\,°C$.

Perfluorobutadiene–Chlorine Perchlorate Reaction. An attempt was made to prepare a monoperchlorate-substituted product from a diolefin by treating CF_2=CFCF=CF_2 (2.28 mmol) with Cl_2O_4 (2.34 mmol). The addition proceeded smoothly and less than 0.1 mmol of unreacted material was recovered by pumping on the reaction mixture at −64°. However, when the product was warmed to near room temperature it exploded.

Perhaloalkyl Perchlorate. Alkali Metal Fluoride Reactions. The perhaloalkyl perchlorates were treated with CsF or KF in Pyrex at slightly elevated temperatures. Products of these reactions were separated by fractional condensation and identified by spectral and chromatographic analysis. For the compounds $ClCF_2CF_2ClO_4$, $CF_3CFClCF_2ClO_4$, and $CF_3CFBrCF_2ClO_4$; nearly quantitative yields of $FClO_3$ and the acyl fluorides $ClCF_2COF$, $CF_3CFClCOF$, and $CF_3CFBrCOF$ were obtained on heating overnight at 60°. Chlorodifluoroacetyl fluoride was identified by its infrared spectrum and vapor pressure which agreed with the reported[10] data and that of an authentic sample prepared from $ClCF_2COCl$ and KF.

2-Chlorotetrafluoropiopionyl fluoride has not been reported but was identified by its vapor density: observed, 184 g/mol; calculated, 182.5 g/mol. The vapor pressure was measured over the range −78 to 0° and the equation describing the vapor pressure–temperature relation is $\log p_{\mathrm{mm}} = 7.281 - (1248/T\,°\mathrm{K})$. The calculated normal boiling point is 10.4° with a heat of vaporization of 5.71 kcal/mol. Infrared bands were found at 1860 (s), 1298 (m), 1245 (vs, multiplet), 1142 (s), 968 (s), 760 (w), 700 (m), and 674 (w) cm^{-1}. Together with a weak parent peak, $C_3F_5ClO^+$, the mass spectrum contained intense peaks for $C_2F_4Cl^+$, C_2FClO^+, CF_2Cl^+, CF_3^+ (base peak), $CFCl^+$, CF_2^+, and COF^+.

The corresponding bromine compound $CF_3CFBrCOF$ was identified by its vapor density (observed, 231 g/mol; calculated, 229 g/mol) and the reasonable comparison of its infrared spectrum and boiling point with that reported.[11] Vapor pressure–temperature values were obtained for the range −48.3 to +8.7° (°C, mm): −48.3, 12; −32.0, 36; −18.1, 85; 0.0, 224; 8.7, 328. The derived vapor pressure–temperature equation is $\log p_{\mathrm{mm}} = 8.224 - (1607/T\,°\mathrm{K})$ with a calculated normal boiling point of 27.5° (lit.[11] bp 32°) and a heat of vaporization of 7.35 kcal/mol. Strong mass spectral peaks were found for the ions $C_3F_5BrO^+$ (parent peak), $C_2F_4Br^+$, C_2FBrO^+, CF_2Br^+, $C_2F_4^+$, Br^+, CF_3^+ (base peak), CF_2^+, and COF^+.

For the compounds $ClCF_2CFClClO_4$, $Cl_2CFCFClClO_4$, and $BrCF_2CFClClO_4$ the cesium fluoride catalyzed degradation also produced nearly quantitative yields of the corresponding acid fluorides, $ClCF_2COF$, Cl_2CFCOF, and $BrCF_2COF$. However, the other products were variable amounts of $FClO_3$, Cl_2, and O_2. In addition, the susceptibility of these perchlorates to this reaction varied with $ClCF_2CFClClO_4$ requiring 2 days at 90° for complete decomposition while $BrCF_2CFClClO_4$ was approximately 50% reacted after overnight at room temperature. Chlorodifluoroacetyl fluoride was identified as noted above. Bromodifluoroacetyl fluoride was identified by its infrared spectrum: 1875 (vs), 1267 (m), 1198 (s), 1105 (vs), 940 (s), 768 (w), 670 (m), and 555 (w) cm^{-1}, compared to that of an authentic sample.[12]

Dichlorofluoroacetyl fluoride was identified by its vapor density: observed, 148 g/mol; calculated, 149 g/mol. Observed vapor pressure–temperature data were (°C, mm): −65.1, 11; −47.1, 29; −31.7, 60; −24.0, 85; −10.2, 147; 0.0, 212. The equation describing the vapor pressure–temperature relation is $\log p_{\mathrm{mm}} = 6.440 - (1124/T\,°\mathrm{K})$ leading to a calculated normal boiling point of 42.6° and a heat of vaporization of 5.14 kcal/mol. A boiling point of 38–42° (720 mm) has been reported[13] which compares well with the 40° (710 mm) calculated from the equation. Major mass spectral peaks were found for the ions $C_2F_2ClO^+$, $CFCl_2^+$ (base peak), CF_2Cl^+, $CFCl^+$, CCl^+, and COF^+.

Discussion

Caution! The halogen perchlorates and the alkyl perchlo-

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[12] C. J. Schack, unpublished work.

[13] W. Fink, U. S. Patent 3,261,864 (1966).

rates are potentially explosive. Safety precautions should be taken in handling and using these materials.

The new class of compounds, perhaloalkyl perchlorates, have been prepared by the reaction of Cl_2O_4 or $BrClO_4$ with perhaloolefins. Excellent yields, good material balances, and molecular weight data served to establish the 1:1 addition stoichiometry. Two modes of addition were considered possible for this interaction. Further, with each mode of reaction, isomeric products could result using unsymmetrical olefins. For example, in addition to rupture of the terminal X-O bond, the possibility existed for rupture of the central XO-Cl single bond thereby producing $XO\text{-}C\text{-}C\text{-}ClO_3$ adducts. However, all the evidence obtained indicated that only one addition isomer was formed from each olefin, that isomer being a perchlorate. This evidence consisted of ^{19}F nmr, infrared, and mass spectra not only of the perchlorates but also of their respective derivatives, acid fluorides.

The infrared spectra of the perhaloalkyl perchlorates (Table I) are quite characteristic with respect to showing definitive bands for a covalent $OClO_3$ group. All the compounds exhibit strong bands at 1295-1320 (doublet), 997-1036, and 630-652 cm^{-1}. These are assigned respectively to the Cl=O antisymmetric and symmetric stretching vibrations and Cl–O stretching vibration. Other covalent perchlorates, $HOClO_3$,[14] $O_3ClOClO_3$,[15] $FOClO_3$,[16] and the parent perchlorates,[7,8] show bands of very similar position, shape, and relative intensity. Hydrocarbon perchlorates have also been shown[17] to have comparable bands associated with the infrared absorption of the perchlorate group. Formulation of the addition compounds as $XO\text{-}C\text{-}C\text{-}ClO_3$ species was precluded by the absence of the very strong band at ~ 1200 cm^{-1} which has been ascribed[18] to the ClO_3 group directly bonded to carbon.

Although the perchlorate spectra shown in Table I represent only a limited group, it is noteworthy that distinct differences are apparent for vibrations of the $OClO_3$ group when bonded to a CF_2 as opposed to a CFCl unit. With CF_2 the antisymmetric Cl=O stretches are split further (16-25 cm^{-1}) than with CFCl (11-13 cm^{-1}) and are shifted to slightly higher frequencies. The Cl=O symmetric stretches are shifted even further apart occurring at 1032-1036 cm^{-1} for CF_2 compounds and at 997-1004 cm^{-1} for CFCl species. Bands assigned to the singly bonded Cl–O stretch are also shifted, 647-653 cm^{-1} for CF_2 and 630-632 cm^{-1} for CFCl. These correlations indicate the sensitivity of the ClO_4 group to the nature of the group directly bonded to it.

Fluorine nmr data are given in Table II. The peaks were slightly broadened with indications of multiplet structure but were not resolvable owing to small coupling constants. The chemical shifts, area ratios, and number of peaks observed for the acid fluoride derivatives readily defined the structures of those compounds. For the perchlorates, comparison of the chemical shifts and area ratios of the series together with values reported for similar compounds permitted assignment of the peaks. In the case of the ethyl compounds with equal numbers of fluorine substituents on each carbon, $ClCF_2CF_2ClO_4$ and $Cl_2CFCFClClO_4$, the $ClCF_2$ (72.7 ppm) and Cl_2CF (69.8 ppm) assignments were made which are comparable to the known values for these groups in $ClCF_2CF_2OF$ (69.4 ppm) and Cl_2CFCF_2OF (71.8 ppm)[19] and in $ClCF_2CF_2NF_2$ (69.7 ppm) and $Cl_2CFCF_2NF_2$ (72.8 ppm).[20] The remaining peaks are then assigned to the fluorine resonances of the groups CF_2ClO_4 (92.5 ppm) and $CFClClO_4$ (76.0 ppm). For $ClCF_2CFClClO_4$ these considerations led to the assignments $ClCF_2$ (69.0 ppm) and $CFClClO_4$ (79.0 ppm). The alternate formulation, $Cl_2CFCF_2ClO_4$, would require the assignments Cl_2CF (79.0 ppm) and CF_2ClO_4 (69.0 ppm) which are unjustifiably different from established trends. Unequivocal support for the assignments was obtained from the spectra of the decomposition products. Thus $ClCF_2CFClClO_4$ gave exclusively $ClCF_2COF$ whereas $Cl_2CFCF_2ClO_4$ would have produced Cl_2CFCOF. Similar comparisons and observations regarding the propyl perchlorates and their derivatives resulted in the assignments shown in Table II.

The mass spectra of the perchlorates did not show ions for the parent molecules. Ion fragment assignments were corroborated by the presence of isotopic species in the correct abundance. The highest *m/e* values found generally corresponded to loss of the ClO_4 or ClO_3 groups. Base peaks corresponded to and verified the respective terminal units $CFCl_2$, CF_2Cl, and CF_3. The appearance of these ions as base peaks is typical of simple perhaloalkyl compounds in which they are present.[21] Also typical of such compounds is the appearance of fairly intense peaks for recombination or rearranged ion fragments. This phenomenon was observed as with $ClCF_2CFClClO_4$, where Cl_2CF^+ ($\sim$15%) and CF_2Cl^+ (100%) peaks were found. Perchlorate ions were absent from the spectra as they are also absent in the spectrum of Cl_2O_4.[7] Ion fragments corresponding to ClO_3^+, ClO_2^+, and ClO^+ were of appreciable magnitude.

Mass spectra of three of the acid fluorides were obtained. The two propyl compounds, $CF_3CFXCOF$, gave spectra consistent with formulations deduced from infrared and ^{19}F nmr data. Prominent peaks corresponded to the ions, $C_2F_4X^+$, CFX^+, and CF_3^+, with the latter being the base peak. Again appreciable peaks were noted for the rearranged ions, CF_2X^+, particularly in the case of the bromine compound. In addition both compounds exhibited parent peaks corresponding to $C_3F_5XO^+$. The remaining acid fluoride, Cl_2CFCOF, did not give a parent ion peak. The largest *m/e* number fitted the ion $C_2F_2ClO^+$. Other features of its spectrum were analogous to the other halocarbons.

The addition of $XClO_4$ compounds to perhaloolefins is undoubtedly directed since in each case only one product was formed. This would not be expected if the reaction involved a free-radical mechanism. The polar nature of the reactants could be expected to effect a directed addition and such an explanation is adequate for the perfluoropropene reactions

$$CF_3CF{=}CF_2 + XOClO_3 \rightarrow CF_3CFXCF_2ClO_4$$

However, the adducts of chlorotrifluoroethylene are not in keeping with this rationale. Here the only product that was isolated, observed by ^{19}F nmr or indicated by derivative formation, was the opposite of that predicted by polarity considerations. Numerous examples of polar additions to $ClCF{=}CF_2$ have been documented.[22] Usually a mixture of isomers results with the relative amounts dependent on specific reaction conditions. Lacking radical conditions the major and sometimes only product is that expected from a

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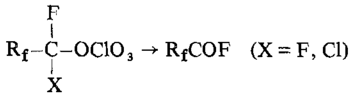
simple polar addition. No examples are known to us in which the alternate adduct is the sole product. Obviously a dominant control is operating but its explanation at this point would be purely speculative.

The overall stability of the perhaloalkyl perchlorates is much superior to that of analogous -OCl compounds.[23] Qualitative tests showed that no decomposition of $CF_3CFClCF_2ClO_4$ occurred on heating in stainless steel at 100° for 72 hr after an initial passivating effect. At 180° complete decomposition in 24 hr produced mainly $CF_3CFClCOF$ with a small amount of COF_2, indicating little carbon–carbon rupture. No decomposition of $ClCF_2CFClClO_4$ was observed after 24 hr at 70° but complete decomposition was found after 72 hr at 100° giving $ClCF_2COF$, $FClO_3$, Cl_2, and O_2. The compound $CF_3CFClCF_2ClO_4$ was insoluble and unaffected by water at ambient temperature.

Alkali metal fluoride catalyzed decomposition of the perchlorates paralleled reported[2,24] reactions of similar fluorosulfate materials. The fluorosulfates produce carbonyl compounds and SO_2F_2 while the perchlorates gave carbonyl compounds and $FClO_3$ or mixtures of $FClO_3$, Cl_2, and O_2. Perchlorates containing $R_fCF_2ClO_4$ structures generated essentially quantitative amounts of $FClO_3$. Perchlorates with $R_fCFClClO_4$ structures gave variable mixtures of $FClO_3$, Cl_2, and O_2. Either type of perchlorate was completely degraded to the respective acid fluoride and was of great assistance in characterizing the perchlorates



$$R_f-\overset{F}{\underset{X}{C}}-OClO_3 \rightarrow R_fCOF \quad (X = F, Cl)$$

Reactions of the $R_fCFClClO_4$ compounds did not yield any acid chlorides and therefore some fluorination by the metal fluoride must have occurred before or after the elimination of ClO_3.

Registry No. $CF_3CF{=}CF_2$, 116-15-4; Cl_2O_4, 27218-16-2; $CF_3CFClCF_2ClO_4$, 38126-25-9; $BrClO_4$, 32707-10-1; $CF_3CFBrCF_2ClO_4$, 38126-26-0; $CF_2{=}CFCl$, 79-38-9; $ClCF_2CFClClO_4$, 38126-27-1; $BrCF_2CFClClO_4$, 38217-36-6; C_2F_4, 116-14-3; $ClCF_2CF_2ClO_4$, 38126-28-2; $ClCF{=}CFCl$, 598-88-9; $Cl_2CFCFClClO_4$, 38126-29-3; $CF_2{=}CFCF{=}CF_2$, 685-63-2; 2-chlorotetrafluoropropionyl fluoride, 28627-00-1; $CF_3CFBrCOF$, 6129-62-0; dichlorofluoroacetyl fluoride, 354-18-7; $ClCF_2COF$, 354-27-8; $BrCF_2COF$, 38126-07-7.

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Nuclear Quadrupole Resonance Study of Heavy Transition Metal Pentahalide Dimers, M_2X_{10} [1a]

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Halogen and metal nqr transitions have been measured in a series of heavy transition metal pentahalide dimers M_2X_{10} (M = ^{93}Nb, ^{181}Ta, W, Re; X = ^{35}Cl, ^{81}Br, ^{127}I), in which each molecule contains eight terminal and two bridging halogen atoms. The ^{181}Ta nqr resonances are believed to be the first such resonances detected. From the ^{181}Ta and ^{93}Nb resonances detected in Ta_2X_{10} (X = Cl, Br, I) and Nb_2X_{10} (X = Cl, Br) it was concluded that the coordination about the metal atoms more closely approaches octahedral symmetry as the halogen is varied from Cl to Br to I. In general, terminal halogen atom resonances were found to exhibit small asymmetry parameters and/or positive temperature coefficients ($d\nu/dT$) indicative of M–X π bonding, while bridging halogen atom resonances were found to have large asymmetry parameters and/or negative temperature coefficients. The bridging halogen resonances in these compounds occurred consistently at higher frequencies than the terminal halogen resonances. A trend of increasing halogen resonance frequencies accompanied the increasing covalent character of the M–X bonds as the metal atoms varied from members of group Vb to VIb to VIIb.

Introduction

An important application of nuclear quadrupole resonance (nqr) spectroscopy to the study of the structure of transition metal halide compounds resides in the ability to distinguish between bridging and terminal halogen atom resonances. Buslaev and coworkers have suggested that the sign of the temperature coefficient ($d\nu/dT$) of an nqr transition can be used as a criterion for assigning resonances in the nqr spectrum of a transition metal compound containing both bridging and terminal halogen atoms.[2] Their argument is based in part on their study of the Br nqr spectra of Nb_2Br_{10}, Ta_2Br_{10}, and $NbOBr_3$, in which the terminal Br atoms exhibited positive values, and the bridging Br atoms negative values of $d\nu/dT$. This argument should be applicable to any compound in which one type of halogen atom has the ability to donate electron density, *via* a π interaction, to another atom in the molecule, while the other type of

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