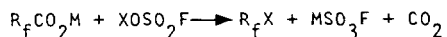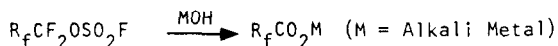# HALOGEN FLUOROSULFATE REACTIONS WITH FLUOROCARBONS

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ABSTRACT

The scope of the reaction of simple fluorocarbon halides with chlorine fluorosulfate and mixtures of chlorine and bromine fluorosulfate to produce R_fOSO_2F compounds has been investigated. It is shown that in many cases even primary chlorine in $-CF_2Cl$ groups can be replaced by $-OSO_2F$. Primary bromine or iodine in $-CF_2X$ are more readily replaced. The mechanism of this replacement reaction has been established by the isolation of the metastable iodine III intermediate $R_fI(OSO_2F)_2$. Neither secondary chlorine nor bromine in $-CFX-$ groups is affected. With the secondary iodide, $i-C_3F_7I$, the salt $[(i-C_3F_7)_2I]^+ [I(OSO_2F)_4]^-$ is formed. Furthermore, it has been found that $ClOSO_2F$ is capable of converting fluorocarbon acids or their derivatives into fluorocarbon halides. A combination of these two $ClOSO_2F$ reactions with the known conversion of $R_fCF_2OSO_2F$ to the corresponding fluorocarbon acid offers a novel, high yield chain shortening reaction for the otherwise unreactive fluorocarbon halides according to:

$$R_fCF_2Hal + XOSO_2F \longrightarrow R_fCF_2OSO_2F + HalX$$

$$R_fCF_2OSO_2F \xrightarrow{\text{MOH}} R_fCO_2M \quad (M = \text{Alkali Metal})$$

$$R_fCO_2M + XOSO_2F \longrightarrow R_fX + MSO_3F + CO_2$$

INTRODUCTION

Shortly after the discovery by Cady and coworkers [1-4] of the halogen fluorosulfates and peroxydisulfuryl difluoride, their reactivity with select fluorocarbon compounds was noted. This activity included addition to olefins [3,4], displacement of chlorine, bromine, or iodine from methyl compounds [5,6] and a few others [7] to give $ROSO_2F$ (commonly written RSO_3F), as well as cleavage of anhydrides [8]. Iodofluorocarbons were also converted successfully to fluorocarbon fluorosulfates by treatment with fluorosulfonic acid at elevated temperature [9]. However, the scope of these reactions, particularly the displacement of halogen by fluorosulfate was not defined. Since many fluorocarbon halides would be more useful if the halide could be replaced by a more reactive group such as the fluorosulfate, it was the goal of this work to determine the practical extent of this displacement reaction. In addition, the utility of chlorine fluorosulfate in decarboxylating fluorocarbon acids was discovered. The combination of the displacement of -X by $-OSO_2F$, followed by conversion to an acyl fluoride or acid salt [9] and decarboxylation, opens a path for stepwise fluorocarbon chain shortening.

EXPERIMENTAL

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube-type pressure gauge. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an EAI Quad 300 quadrupole spectrometer and ^{19}F nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 MHz, using $CFCl_3$ as an internal standard. Chlorine fluorosulfate was prepared from ClF and SO_3 [10]. Literature methods were used to synthesize $i-C_3F_7X$ (X=Cl, Br, I) [11], $ClCF_2CF_2Cl$ and $CF_3CFClCF_2Cl$ [12], $BrCF_2CF_2CF_2Br$ [13], and $CF_3CFClCF_2SO_3F$ [14]. Other fluorocarbon materials were purchased from PCR Research Chemicals, Inc.

R_fX Reactions. These reactions were carried out by loading measured quantities of the reactants, R_fX, chlorine fluorosulfate, and Br_2 (where noted in Table 1) into a precooled stainless steel cylinder. The reactions were allowed to proceed by warming the cylinder to a given temperature. Products were separated by fractional condensation and residual reactive impurities, such as XSO_3F or the halogens, were chemically removed by treatment with Hg. Table I summarizes the results from the reactions. Comparison to reported spectroscopic data served to identify most of the materials. Only new data and those for new compounds are presented herein.

$FO_3SCF_2CF_2CF_2SO_3F$. This compound was obtained from the reaction of $BrCF_2CF_2CF_2Br$ with $ClOSO_2F$. Its ^{19}F nmr spectrum consisted of three peaks with an area ratio of 2:4:2 which are assigned to $-SO_3F$ (-50.8), terminal $-CF_2-$ (83.7), and internal $-CF_2-$ (128 ppm). The following infrared spectrum was observed (cm^{-1}) 1500(S), 1320(M), 1258(VS), 1220(S), 1150(S), 1127(S), 992(VS), 865(M), 843(VS), 752(M), 608(W), 570(M), and 548(M) which is similar to that of $FO_3SCF_2CF_2SO_3F$ [3]. Ions found in the mass spectrum were m/e (assign. rel. intens.) $249(C_3F_6SO_3F$, 1), $199(C_2F_4SO_3F$, 0.5), $169(C_3F_7$, 2), $150(C_3F_6$, 1), $149(CF_2SO_3F$, 8), $147(C_3F_5O$, 7), $119(C_2F_5$, 48), $100(C_2F_4$, 14), $97(C_2F_3O$, 2), $83(SO_2F$, 100), $69(CF_3$, 15), $67(SOF$, 6), $66(CF_2O$, 1), $50(CF_2$, 1), $48(SO,4)$, $47(CFO$, 27). In addition, this compound was characterized by its CsF catalyzed decomposition to 2 equivalents of SO_2F_2 and the corresponding acyl fluoride, $OFCCF_2CFO$. The latter was identified by comparison of its ^{19}F nmr, infrared, and mass spectra with literature values [15].

A by-product of the reaction of the dibromide with $ClSO_3F$ was identified as $ClCF_2CF_2CF_2SO_3F$, based on its infrared spectrum (cm^{-1}) 1498(S), 1320(M), 1255(VS), 1233(S), 1190(S), 1118(M), 1078(S), 1024(S), 965(S), 843(S), 756(W), 595(W) and 560(W); and mass spectrum m/e (assign. rel. intens.) $249(C_3F_6SO_3F$, 0.3), $199(C_2F_4SO_3F$, 11), $185(C_3F_6Cl$, 3), $169(C_3F_7$, 25), $150(C_3F_6$, 20), $149(CF_2SO_3F$, 8) $147(C_3F_5O$, 3), $135(C_2F_4Cl$, 7), $131(C_3F_5$, 3), $119(C_2F_5$, 49), $100(C_2F_4$, 62), $97(C_2F_3O$, 4), $85(CF_2Cl$, 28), $83(SO_2F$, 70), $69(CF_3$, 100), $67(SOF$, 10), $64(SO_2$, 4), $51(SF$, 2), $50(CF_2$, 4), $48(SO$, 4), and $47(CFO$, 35). Assignments for Cl containing ions were confirmed by the presence of ^{37}Cl isotope ions of the expected one third intensity.

$n\text{-}C_7F_{15}SO_3F$. The reaction of $n\text{-}C_7F_{15}I$ with a twofold excess of $ClSO_3F$ was conducted at $-45°$ because of the ease of oxidation of iodine by related hypochlorites [16]. At that temperature, one mole of Cl_2 was formed for each mole of R_fI and a white solid was produced. On warming to ambient temperature, the solid gradually decomposed furnishing the colorless liquid product, $n\text{-}C_7F_{15}SO_3F$ and non-volatile ISO_3F. The infrared spectrum of $n\text{-}C_7F_{15}SO_3F$ (cm^{-1}) 1505(S), 1336(W), 1258(VS), 1233(S), 1162(M), 1150(M), 1115(W), 1054(W), 1030(W), 868(M), 842(M), 760(W), 740(W), 730(W), 665(W) and 550(MW); and mass spectrum, m/e (assign. rel. intens.) 449($C_7F_{14}SO_3F$ 0.3), 399($C_6F_{12}SO_3F$, 0.1), 369(C_7F_{15}, 2), 347($C_7F_{13}O$, 1), 319(C_6F_{13}, 1), 300(C_6F_{12}, 0.1), 281(C_6F_{11}, 2), 269(C_5F_{11},0.3) 247(C_5F_9O, 0.1), 231(C_5F_9, 2), 199($C_2F_4SO_3F$, 0.1), 197(C_4F_7O, 0.3) 181 (C_4F_7, 2), 169(C_3F_7, 9), 149(CF_2SO_3F, 13), 131(C_3F_5, 10), 119(C_2F_5, 18), 100(C_2F_4, 9), 97(C_2F_3O, 3), 83(SO_2F, 65), 80(SO_3,4), 78(C_2F_2O, 1), 69 (CF_3, 100), 67(SOF, 11), 64(SO_2, 8), 50(CF_2, 10), 48(SO, 9) and 47(CFO, 35) were used to identify the product. Additional proof was obtained by catalytically decomposing the fluorosulfate with CsF to furnish SO_2F_2 and $C_6F_{13}CFO$. The acyl fluoride was identified by infrared and mass spectra which included a parent ion.

$[(i\text{-}C_3F_7)_2I]^+[I(SO_3F)_4]^-$. Perfluoroisopropyl iodide and chlorine fluorosulfate reacted in a 1:2 mole ratio at $-45°$ liberating one mole of Cl_2. The white, thermally stable, solid product of composition, $i\text{-}C_3F_7I(SO_3F)_2$, was formed in quantitative yield; from 2.36 mmol $i\text{-}C_3F_7I$ was obtained 1.170 g solid (theory, 1.167 g), m.p. 101° (sealed tube). The Raman spectrum of the solid is shown in Figure 1.

R_fCO_2M. Prepassivated stainless steel cylinders were loaded in the drybox with measured amounts of R_fCO_2M (M=H, Na, Ag, or $CF_3C=O$). The halogen fluorosulfate XSO_3F (X=Cl or Br) was loaded into the cooled ($-196°$), evacuated cylinder from the vacuum line. After warming to a temperature of 25-50° for a given period, the products were separated by fractional condensation. Acid impurities, halogens, XSO_3F, and CO_2 when necessary, were removed from the products by treatment with aqueous base. All the products were identified spectroscopically and the data for new moieties are listed.

$C_7F_{15}Cl$. Sodium perfluorooctanoate was reacted with $ClSO_3F$ for 2 days. In addition to CO_2 and solid $NaSO_3F$, the principal product was the colorless liquid $C_7F_{15}Cl$ whose identity was established from infrared (cm^{-1}) 1365(W), 1320(W), 1252(VS), 1223(S), 1160(M), 1121(W), 1072(W), 994(W), 780(W), 745(W), 706(W), 678(W), 650(W), 565(W), and 530(W); and mass spectra which did not exhibit a parent ion but had numerous peaks corresponding to $C_nF_{2n}^+$, $C_nF_{2n\pm1}^+$, and $C_nF_{2n}Cl^+$ with (n=1-7). A lesser quantity of the by-product $C_6F_{13}CFO$ was also formed and identified spectroscopically as noted earlier.

RESULTS AND DISCUSSION

As shown in Table I, the displacement of halogen by fluorosulfate can be carried out in high yields for Hal being Cl, Br, or I. The reactivity of the halogen decreases in the order I > Br > Cl and is reflected by the necessary reaction temperatures. Whereas iodides react readily at temperatures as low as -45°, the chlorides require heating to about 130°. Furthermore, iodides react regardless of their position in the fluorocarbon molecules, i.e. as primary or secondary iodides. In the case of bromides and chlorides, only the primary halides were found to react, and in the case of the chlorides, even some of the primary chlorides were found to be unreactive. These unreactive chlorides included C_2F_5Cl, $C_7F_{15}Cl$, $CF_3CFClCF_3$, $CF_3CFClCF_2Cl$, $ClCF_2CF_2SO_3F$, and $CF_3CFClCF_2SO_3F$.

The reactivity of $ClSO_3F$ can be enhanced by the addition of catalytic amounts of Br_2, as demonstrated by examples 1, 3 and 4 of Table 1. In the absence of bromine, only one chlorine atom is replaced by $-SO_3F$ in 1,2-dichloro-tetrafluoroethane, whereas in the presence of about 10% of Br_2 a significant amount of disubstitution was observed.

Additional cases showing the catalytic effect of Br_2 are examples 2 and 5 of Table 1. However, the secondary halides in $CF_3CFBrCF_3$ and $CF_3CFClCF_2SO_3F$ were found to be unreactive even in the presence of Br_2. An isolated example of the displacement of secondary Br with $S_2O_6F_2$ is known [17], but in that instance it was adjacent to a carbonyl group, $CF_3CFBrC(O)CF_3$. Interestingly, Fokin [7] reported that one of the chlorines of the $CFCl_2$ group in $ClCF_2CFCl_2$ is replaced by SO_3F using $ClSO_3F$, but that the reaction requires HSO_3F catalysis. While we

Table 1.

Fluorocarbon Halide Displacement Reactions

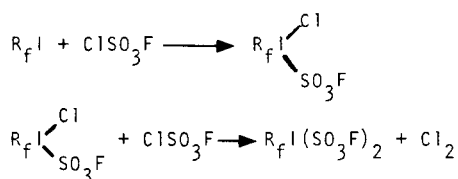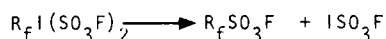| No.	Reactant	mmol			Temp. °C	Time Days	Products (%)
		$ClSO_3F$	Br_2	Reactant			
1	$ClCF_2CF_2Cl$	6.42	-	3.10	130	5	$ClCF_2CF_2SO_3F$ (90) [a]
2	CF_3CF_2Cl	2.36	0.2	2.16	130	3	$CF_3CF_2SO_3F$ (22) [a]
3	$ClCF_2CF_2Cl$	11.8	0.6	5.94	140	1	$ClCF_2CF_2SO_3F$ (89) $FO_3SCF_2CF_2SO_3F$ (6) [b]
4	$ClCF_2CF_2SO_3F$	4.64	0.9	4.24	140	14	$FO_3SCF_2CF_2SO_3F$ (31)
5	$CF_3CFClCF_2Cl$	5.10	0.6	2.35	25	15	$CF_3CFClCF_2SO_3F$ (76) [c]
6	CF_3CF_2Br	5.31	-	4.98	25	21	$CF_3CF_2SO_3F$ (96)
7	$BrCF_2CF_2Br$	8.20	-	3.97	25	24	$BrCF_2CF_2SO_3F$ (40) [a] $ClCF_2CF_2SO_3F$ (5)
8	$BrCF_2CF_2Br$	4.75	-	2.18	65	2	$FO_3SCF_2CF_2SO_3F$ (64) $ClCF_2CF_2SO_3F$ (31)
9	$Br(CF_2)_3Br$	5.16	-	2.04	50	11	$FO_3SCF_2CF_2CF_2SO_3F$ (5) [b] $ClCF_2CF_2CF_2SO_3F$ (10)
10	$CF_3CFBrCF_2Br$	4.78	-	2.15	25	21	$CF_3CFBrCF_2SO_3F$ (70) [c]
11	$n\text{-}C_7F_{15}I$	6.05	-	2.73	25	7	$n\text{-}C_7F_{15}SO_3F$ (85)
12	CF_3CFICF_3	5.20	-	2.34	-45	10	$[(i\text{-}C_3F_7)_2I]^+$ $[I(SO_3F)_4]^-$
							100

a) Ref. 4
b) Ref. 3
c) Ref. 14

cannot be absolutely certain that no HSO_3F was present in our system, all efforts were made to exclude moisture. In addition it should be noted that the above fluorosulfate substitution reactions do not result in any C-C bond breakage and also that ether functions are not affected [18].

The catalytic effect of bromine is best explained by the in situ generation of the more reactive $BrSO_3F$ from Br_2 and $ClSO_3F$. Since the generated HalBr species are generally unstable and decompose back to Br_2, only catalytic amounts of bromine are required.
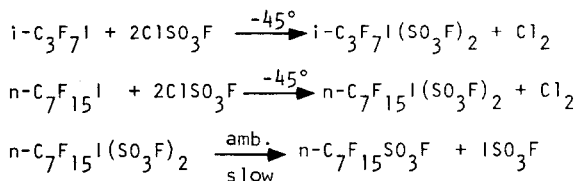
By analogy with the known reaction chemistry of other positive halogen compounds [16], fluorocarbon iodides and $ClSO_3F$ were expected to undergo an oxidative addition, followed by $-SO_3F$ substitution

$$R_fI + ClSO_3F \longrightarrow R_fI\begin{smallmatrix}Cl\\ \\SO_3F\end{smallmatrix}$$

$$R_fI\begin{smallmatrix}Cl\\ \\SO_3F\end{smallmatrix} + ClSO_3F \longrightarrow R_fI(SO_3F)_2 + Cl_2$$

This iodine III compound may then undergo ISO_3F elimination

$$R_fI(SO_3F)_2 \longrightarrow R_fSO_3F + ISO_3F$$

Depending on the thermal stability of the $R_fI(SO_3F)_2$ intermediate, either this intermediate or the final R_fSO_3F product was obtained. The formation of R_fSO_3F from this reaction had already previously been established for CF_3I [6,7]. The fact that this reaction indeed proceeds through the above intermediate has now been demonstrated for both n-perfluoroheptyl iodide and perfluoroisopropyl iodide:

$$i-C_3F_7I + 2ClSO_3F \xrightarrow{-45°} i-C_3F_7I(SO_3F)_2 + Cl_2$$

$$n-C_7F_{15}I + 2ClSO_3F \xrightarrow{-45°} n-C_7F_{15}I(SO_3F)_2 + Cl_2$$

$$n-C_7F_{15}I(SO_3F)_2 \xrightarrow[slow]{amb.} n-C_7F_{15}SO_3F + ISO_3F$$

Thus for the heptyl case, a clearly defined two-step substitution process was noted. For the isopropyl case, the oxidative addition product was stable even at its melting point, 101°. Examination of its Raman spectrum (Figure 1) showed that this solid adduct is not a covalent iodine (III) compound, but has instead the ionic structure $[(i-C_3F_7)_2I]^+[I(SO_3F)_4]^-$. Thus, these $R_fI-ClSO_3F$ reactions and products are analogous to those previously reported for $R_fI - ClOClO_3$ systems [19].

With carboxylic acids their salts, or anhydrides, $ClSO_3F$ or $BrSO_3F$ acted at ambient temperature or slightly above as a most facile decarboxylating agent (Table 2).

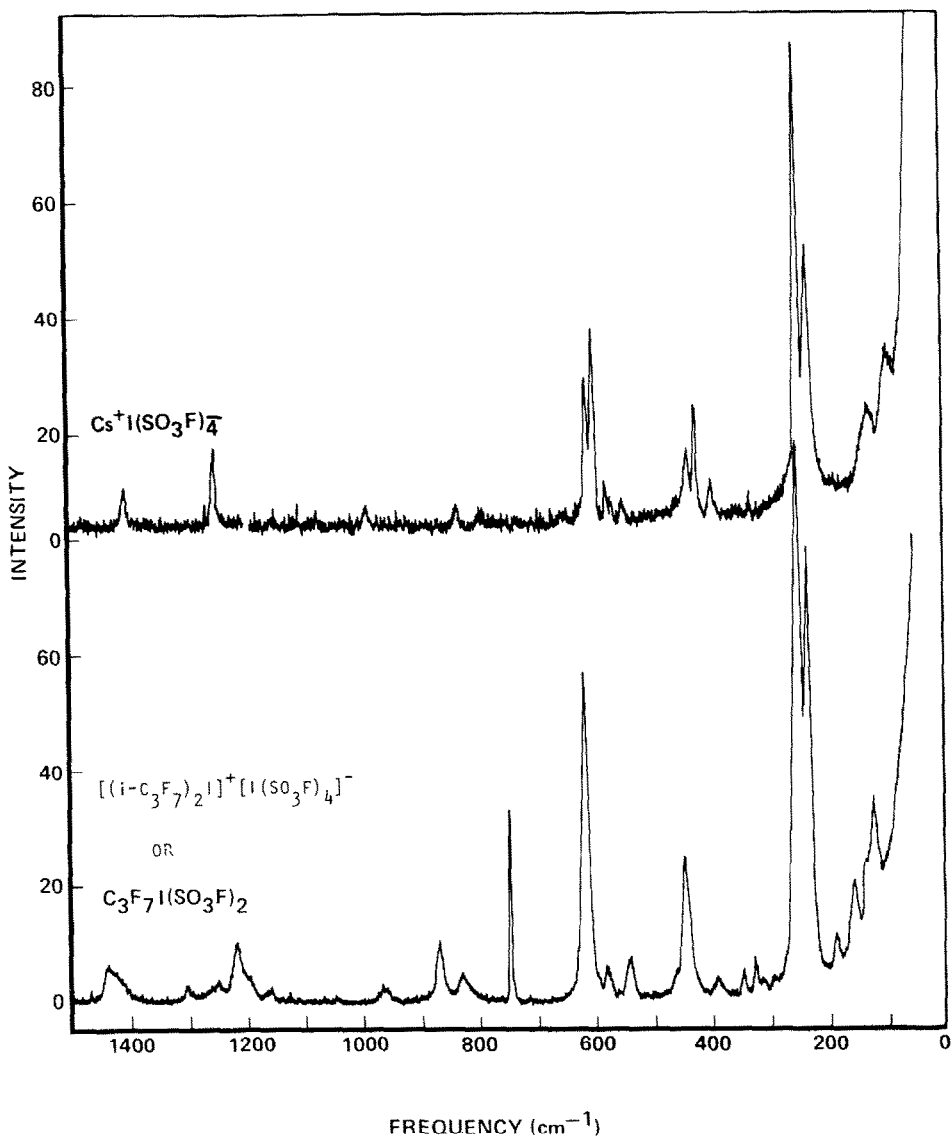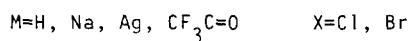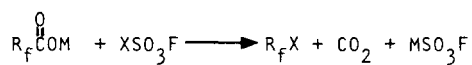Fig. 1. Raman Spectra of $Cs^+I(SO_3F)_4^-$ and $[(i-C_3F_7)_2I]^+[I(SO_3F)_4]^-$ Demonstrating the presence of the $I(SO_3F)_4^-$ anion in the latter compound.

$$R_f\overset{\overset{O}{\|}}{C}OM \; + \; XSO_3F \longrightarrow R_fX \; + \; CO_2 \; + \; MSO_3F$$

M=H, Na, Ag, $CF_3C=O$ X=Cl, Br

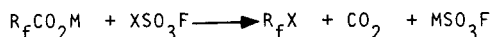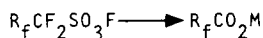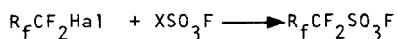High yields of R_fX were generally encountered. Where lower, the observed decrease was probably caused by either a lower purity starting material (used as received) or a side reaction such as the decarboxylation giving CF_2Cl_2 which reacted further to furnish $ClCF_2SO_3F$, a known interaction [20]. The R_fCO_2M + XSO_3F reactions probably proceed through the intermediate formation of R_fCO_2X. When the R_fCO_2M -$ClSO_3F$ system is moderated sufficiently, i.e. by lowering the temperature to $-45°$ or lower, then the intermediate acyl hypochlorite, R_fCO_2Cl, may be isolated [21].

$$R_f\overset{\overset{O}{\|}}{C}OM \; + \; ClSO_3F \longrightarrow R_f\overset{\overset{O}{\|}}{C}OCl \; + \; MSO_3F$$

SUMMARY

The above results show that $ClSO_3F$ and $BrSO_3F$ are useful reagents for introducing a functional -SO_3F group into the generally unreactive class of fluorocarbon halides and to convert fluorocarbon carboxylic acids to the corresponding fluorocarbon halides. A combination of both reactions offers a unique, high yield method to carry out a chain shortening reaction for the otherwise highly "inert" fluorocarbon halides according to

$$R_fCF_2Hal \; + \; XSO_3F \longrightarrow R_fCF_2SO_3F$$

$$R_fCF_2SO_3F \longrightarrow R_fCO_2M$$

$$R_fCO_2M \; + \; XSO_3F \longrightarrow R_fX \; + \; CO_2 \; + \; MSO_3F$$

Since the chain shortening product is a fluorocarbon halide, the shortening cycle can be repeated as often as desired.

Table 2.

Fluorocarbon Acid and Derivative Reactions[a]

Reactant	mmol	X-SO$_3$F	mmol	Time(hr)	Products(%)
CF$_3$CO$_2$H	4.30	Cl	4.30	5	CF$_3$Cl(90)
CF$_3$CO$_2$H	2.46	Br	2.31	2	CF$_3$Br(88)
ClCF$_2$CO$_2$H	2.80	Cl	2.91	3	CF$_2$Cl$_2$(85)
CF$_2$(CF$_2$CO$_2$H)$_2$	2.29	Cl	4.86	18	CF$_2$(CF$_2$Cl)$_2$(86)[b], ClCF$_2$CF$_2$CFO(11), ClCF$_2$CF$_2$CF$_2$SO$_3$F(1)
CF$_3$CF$_2$CO$_2$Na	2.82	Cl	2.66	24	CF$_3$CF$_2$Cl(79), CF$_3$CF$_2$SO$_3$F(2)
CF$_3$CF$_2$CO$_2$Na	2.54	Br	2.76	5	CF$_3$CF$_2$Br(83)
C$_7$F$_{15}$CO$_2$Na	2.26	Cl	2.19	48	C$_7$F$_{15}$Cl(78), C$_6$F$_{13}$CFO(18)
CF$_2$(CF$_2$CO$_2$Ag)$_2$	2.38	Cl	4.94	48	CF$_2$(CF$_2$Cl)$_2$(53), ClCF$_2$CF$_2$CFO(8), CF$_3$CF$_3$CF$_2$Cl(3)
ClCF$_2$CO$_2$Na	2.11	Cl	2.59	48	CF$_2$Cl$_2$(28), ClCF$_2$SO$_3$F(39)[c], ClCF$_2$CFO(1)
(CF$_3$CO)$_2$O	2.43	Cl	2.42	24	CF$_3$Cl(80), CF$_3$C(O)SO$_3$F(85)[d]

a) Reactions generally run at ambient temperature although some were also heated at 50° for a short period.

b) Ref. 12.

c) Ref. 20.

d) Ref. 8.

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