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FURTHER REACTIONS OF CHLORINE(I) AND BROMINE(I) TRIFLUOROMETHANESULFONATE AND BROMINE(I)FLUOROSULFATE

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SUMMARY

Substitutive electrophilic dehalogenation reactions of CF_3SO_2OX (X=Cl,Br) are reported with some covalent inorganic chlorides. These reactions result in the formation of XX'(X,X'=Cl,Br) and several new trifluoromethanesulfonate derivatives in excellent yields. Chlorine(I) trifluoromethanesulfonate also oxidatively adds to unsaturated inorganic substrates such as CO, SO_2 and SF_4 forming new compounds. The reactivity of CF_3SO_2OCl is rather similar to that of FSO_2OBr and some comparisons between the two are given.

INTRODUCTION

Chlorine(I) and bromine(I) trifluoromethanesulfonates are very reactive compounds due, in part, to the pronounced electrophilic character of the halogen atoms (1-3). These compounds have previously been shown to undergo substitutive electrophilic dehalogenation reactions with a variety of organic halides (4) to add regio- and stereospecifically to a variety of olefins (5).

$$CF_3SO_2OX + RX' \longrightarrow CF_3SO_2OR + XX'$$

X,X' = Cl,Br; R = alkyl

$$CF_3SO_2OX + \gt\!=\!\lt \longrightarrow CF_3SO_2O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X$$

X = Cl,Br

only one isomer

Bromine(I) fluorosulfate is a closely related compound, which has been known for much longer. It undergoes many reactions analogous to that of CF_3SO_2OX (X=Cl,Br) (6) and it has also been shown to be an effective oxidant for the synthesis of transition metal fluorosulfates and polyhalogen cations (7).

$$3BrOSO_2F + Au \longrightarrow Au(OSO_2F)_3 + 3/2Br_2$$

$$BrOSO_2F + Cl_2 \longrightarrow BrCl_2^+ \, \bar{O}SO_2F$$

As part of a continuing study on the R_fSO_2OX derivatives, we now report some reactions of CF_3SO_2OX (X=Cl,Br) with some covalent inorganic halides and unsaturated compounds. For a comparison on reactivity, certain new reactions of FSO_2OBr are also reported.

EXPERIMENTAL

General

All volatile compounds were manipulated in glass and stainless-steel vacuum systems as previously described (1-5). Routine IR spectra were recorded on a PE-337. IR spectra for assignment were recorded on a PE-180 spectrometer using a glass cell fitted with AgCl windows. NMR spectra were recorded on a Varian XL-100-15 spectrometer using ∿ 15-20 mol% solutions in $CFCl_3$. ^{19}F chemical shifts are reported as $\emptyset^*$ values (δ relative to $CFCl_3$ as a solvent, not at infinit dilution. A negative chemical shift is to higher field of $CFCl_3$ and visa-versa). Molecular weights were calculated by vapor density measurements assuming ideal gas behavior. Melting points and boiling points were determined by methods previously described.

Reagents

CF_3SO_3H, $SiBr_4$, $SiCl_4$, Me_3SiCl, $HOPOF_2$, SF_4, $VOCl_3$, CrO_2Cl_2 and BBr_3 were obtained from commercial sources and were appropriately purified before use. SiF_3Cl (8), SiF_3Br (8), SF_5Cl (9), SF_5Br (10) and POF_2Br (11) were prepared by literature methods.

CF_3SO_2OX (X=Cl,Br) were prepared by methods described in previous papers (1-5). Bromine(I) fluorosulfate was prepared by the method of Roberts and Cady using a slight excess of $S_2O_6F_2$ (12).

General Procedure for the Reactions of CF_3SO_2OX (X=Cl,Br) and FSO_2OBr.

All reactions were carried out in Kel-F reactors (∿15 ml) fitted with stainless steel valves or in 100 ml Pyrex bulbs fitted with glass-Teflon valves. For the reactions of CF_3SO_2OX (X=Cl,Br) in Kel-F, compounds were prepared in the intended reactor and used directly. Some of the CF_3SO_2OCl and all FSO_2OBr reactions were carried out in a glass reactor. For these reactions, the hypohalite was transferred into the glass reactor through a short glass connection. Energetic reactions were moderated by condensing some CF_2Cl_2 between the hypohalite and the other reactant. Care was taken not to let the reaction temperature rise above -50°C, since the hypohalites react with CF_2Cl_2 above -50°C. The reactor (Kel-F or glass) was then placed in a cold bath of desired temperature and allowed to warm slowly (Table I). Completion of reaction was indicated by disappearance of color due to the hypohalites and/or appearance of Br_2,Cl_2 or BrCl. The products were separated by vacuum distillation through cold traps cooled to appropriate temperatures. Some compounds were further purified via GLC on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD and low temperature collection. A 2' x 3/8" column packed with 49% Halocarbon 11-21 polymer oil on acid washed Chromosorb P was used in most cases. For less volatile compounds a similar 1 ft. column was used.

Substitution reactions of CF_3SO_2OX (X=Cl,Br).

SiF_3Br. The products were separated through -60, -111 and -195°C traps. 1.2 mmoles of Cl_2 and unreacted SiF_3Br collected in the -195°C trap. The -60°C trap contained BrCl, Br_2 and the desired product. All the material in the trap was condensed onto Hg and shaken at 22°C for a few minutes to absorb the Br_2 and BrCl. Products were then reseparated via -111 and -195°C traps. The -111°C trap contained pure $CF_3SO_3SiF_3$.

$CF_3SO_3SiF_3$: colorless liquid; mp -75.6°C; Mol. wt. 233.9 (calcd. 234.12); IR 1442 (s) 1250 (sh,s), 1227 (s), 1200 (sh,m), 1150 (s), 1080 (sh,w), 1030 (s), 1015 (sh,s) 987 (s), 890 (m), 833 (m), 773 (w), 690 (m), 620 (s), 562 (w), 551 (w), 512 (w), 460 (s), 429 (m) cm^{-1}; nmr $CF_3{}^ASO_3SiF_3{}^B$ $\phi_A^* = -75.6$ (s), $\phi_B^* = -154.6$ (s).

<u>POF_2Br</u>. The products were separated through traps cooled to -50, -111 and -195°C. The -195°C trap contained 1.16 mmoles of CF_3Cl, Cl_2 and SiF_4. The -50 and -111°C traps contained Br_2, BrCl, $CF_3SO_3POF_2$ and unreacted POF_2Br. The contents of these two traps were combined, condensed onto Hg and shaken at 22°C for ∿ 2 minutes to remove the halogens. Upon reseparation through -20, -65 and -195°C traps, pure $CF_3SO_3POF_2$ collected in the -65°C trap.

$CF_3SO_3POF_2$: colorless liquid; Mol. wt. 231.5 (calcd. 234.03); IR 1460 (s), 1400 (s), 1237 (s), 1200 (sh,w), 1137 (s), 1062 (s), 988 (s), 927 (s), 892 (m), 780 (s), 745 (s), 709 (m), 610 (b,s), 560 (m), 485 (s) cm^{-1}; nmr $CF_3{}^ASO_3POF_2{}^B$ $\phi_A^* = -73.4$ (t), $\phi_B^* = -76.1$ (d,q); ${}^1J_{PF} = 1089$ Hz, $J_{AB} = 1.4$ Hz.

<u>SF_5Br</u>. Products were separated through traps cooled to -40, -111 and -195°C. $CF_3SO_3SF_5$ and BrCl collected in the -111°C trap. BrCl was removed by reaction with Hg. On redistillation through -35, -78 and -195°C traps, pure $CF_3SO_3SF_5$ collected in the -78°C trap.

$CF_3SO_3SF_5$: colorless liquid; Mol. wt. 282.1 (calcd. 276.11); mp -95.2°C; bp 56.5°C; $\Delta H_{vap} = 6.1$ kcal $mole^{-1}$; $\Delta S_{vap} = 18.5$ eu; $\log P\ (torr) = 7.0739 - 1411{\cdot}9/T + 9725.5/T^2$; IR 1660 (w), 1572 (w), 1462 (s), 1335 (w), 1295 (w), 1240 (vs), 1198 (sh,w), 1145 (s), 1100 (sh,w), 1025 (w), 942 (vs), 930 (sh,w) 880 (sh,m), 858 (vs), 785 (m), 745 (m), 720 (m), 665 (m), 626 (m), 578 (vs), 527 (s) cm^{-1}; nmr $CF_3{}^MSO_3SF_4{}^AF^B$; $\phi_M^* = -73.5$ (quintet), $\phi_A^* = 76.7$ (m), $\phi_B^* = 54.0$ (m); $J_{AB} = 156$, $J_{MA} = 2.2$ Hz.

<u>$COCl_2$</u>. The products were separated through -25, -60 and -195°C traps. Pure $(CF_3SO_3)_2CO$ stopped in the -60°C trap.

$(CF_3SO_3)_2CO$: IR 1829 (s), 1462 (s), 1238 (vs), 1205 (sh,w), 1140 (vs), 1015 (vs), 983 (vs), 850 (s), 785 (s), 745 (s), 658 (m), 608 (s), 568 (w), 518 (m), 488 (m) cm^{-1}; nmr $\phi^*_{CF_3} = -72.9$ (s).

$\underline{SiCl_4}$. The products were separated through -45, -78 and -195°C traps. Pure $Cl_2Si(OSO_2CF_3)_2$ stopped in the -45°C trap.
$Cl_2Si(OSO_2CF_3)_2$: m.p -101°C; IR 1452 (m), 1422 (s), 1340 (vw), 1255 (s), 1232 (s), 1222 (s), 1156 (s), 1130 (sh,m), 1080 (vw), 1028 (w), 918 (s), 859 (w), 770 (vw), 620 (s), 570 (w), 505 (w) cm^{-1}; nmr $\phi^*_{CF_3} = -76.2$.

$\underline{SOCl_2}$. The reaction mixture was pumped through traps cooled to -78, -111 and -195°C. The -78°C trap contained $(CF_3SO_2)_2O$ and -195°C trap held SO_2 and Cl_2. No stable substitution product could be isolated.

$\underline{SiMe_3Cl}$. The products were separated through -30, -78 and -195°C traps. The -30°C trap contained the desired product.
$CF_3SO_3SiMe_3$: colorless liquid; physical properties, IR and nmr agreed well with the values reported in the literature (13,14).

$\underline{VOCl_3}$. The reaction products were pumped through traps cooled to -60, -130 and -195°C. 8.5 mmol of Cl_2 was obtained in the -130°C trap. The -195°C trap contained 0.7 mmol of $CFCl_3$ and traces of Cl_2. A dark green solid (1.3588 g) remained in the reactor and was assumed to be $OV(OSO_2CF_3)_3$.

$\underline{CrO_2Cl_2}$. The volatile products were pumped through traps cooled to -60, -130 and -195°C. 6.5 mmol of Cl_2 was collected in the -130°C trap and 0.35 mmol of unreacted CrO_2Cl_2 was also obtained in the -130°C trap. The -195°C contained small amounts of SiF_4. A red-orange solid (1.2685 g) remained in the reactor. The material was assumed to be $CrO_2(OSO_2CF_3)_2$.

Oxidative addition reactions of CF_3SO_2OCl.

SO_2. The reaction mixture was pumped through traps cooled to -60,-111 and -195°C. The -60 and -111°C traps contained an adduct $CF_3SO_2OSO_2Cl$ and small amount of $(CF_3SO_2)_2O$. 1.64 mmol of SO_2 was recovered in the -195°C trap.

$CF_3SO_2OSO_2Cl$: colorless liquid; Mol. wt. 248.3 (calcd. 248.5); IR 1466 (s), 1242 (s), 1216 (sh,m), 1138 (s), 860 (w), 812 (w), 780 (s), 758 (s), 710 (w), 635 (sh,w), 618 (m), 597 (m), 552 (w), 510 (vw), 496 (s), 460 (w), 450 (w) cm^{-1}; nmr $\phi^*_{CF_3} = -72.4$ (s).

CO. The reaction mixture was pumped through traps at -78, -111 and -195°C. 2.6 mmol of CO was recovered. The -78°C trap contained an adduct CF_3SO_3COCl. Small amounts of CO_2, $COCl_2$ and COClF were found in the -195°C trap.

CF_3SO_3COCl: colorless liquid; Mol. wt. 209 (calcd. 212.5); IR 1835 (s), 1460 (s), 1241 (s), 1210 (sh,w), 1140 (s), 1020 (s), 990 (s), 850 (m), 785 (m), 743 (s), 660 (m), 630 (sh,w), 605 (s), 570 (w), 520 (m), 490 (w), 482 (vw) cm^{-1}; nmr $\phi^*_{CF_3} = -73.4$ (s).

SF_4. The reaction mixture was separated through -40, -78 and -195°C traps. Most of the adduct stopped in the -40°C trap with a small amount collected in the -78°C trap. The -195°C trap contained CF_3Cl and SF_4, SOF_2 and other products.

cis-$CF_3SO_3SF_4Cl$: colorless liquid; Mol. wt. 289.2 (calcd. 292.5); mp <-117°C; bp = 74.9°C, $\Delta H_{vap} = 9.4$ kcal $mole^{-1}$; $\Delta S_{vap} = 26.7$ eu; $\log P\ (torr) = 11.5720 - 3688.23/T + 230735/T^2$; IR 1450 (s), 1322 (vw), 1245 (sh,s) 1228 (s), 1197 (w), 1132 (s), 1028 (sh,m), 1022 (m), 983 (m), 900 (s), 855 (s), 830 (s), 805 (s), 762 (m), 722 (m), 665 (m), 618 (m), 585 (br,m), 555 (sh,m), 510 (m), 455 (w) cm^{-1}; nmr ($AA'BCX_3$ or A_2BCX_3 spin system with approximate chemical shifts and coupling constants as follows) $\phi^*_X = -73$, $\phi^*_C = 86.5$, $\phi^*_{A,A',B} \approx 27$, $J_{XC} = 4.0$, $J_{XA} \approx J_{XA'} = 2.5$, $J_{AC} \approx J_{A'C} = 151.5$, $J_{BC} \approx 150$, $J_{AB} \approx J_{A'B} = ?$ Hz.

$\underline{PF_3}$. The products were pumped through traps cooled to -78, -130 and -195°C. The only products identified were Cl_2, POF_3, $(CF_3SO_2)_2O$ and unreacted PF_3. No $CF_3SO_3PF_3Cl$ or $(CF_3SO_3)_2PF_3$ were observed.

Substitution reactions of FSO_2OBr.

$\underline{SiF_3Br}$. The products were separated through -111 and -195°C traps. The contents of the -111°C trap, FSO_3SiF_3 and Br_2, were condensed onto Hg to remove Br_2. Upon reseparation through -60, -111 and -195°C traps, pure FSO_3SiF_3 was obtained in the -111°C trap.

FSO_3SiF_3: mp -78.2°C; Mol. wt. 182.9 (calcd. 184.12); IR 1475 (s), 1399 (s), 1248 (vs) 1138 (m), 1065 (s), 980 (vs), 960 (sh,s), 950 (sh,s) 920 (s), 889 (s), 840 (s), 729 (br,m), 590 (w), 545 (s), 515 (s), 480 (s) cm^{-1}; nmr $F^ASO_3SiF_3{}^B$ $\phi^*_A = 44.8$ (s), $\phi^*_B = +155.9$ (s).

$\underline{POF_2Br}$. The reaction products were separated through -78, -111 and -195°C traps. The contents of the -78°C trap were shaken with Hg to remove Br_2 and reseparated through -111 and -195°C traps. FSO_3POF_2 collected in the -111°C trap.

FSO_3POF_2: mp -62.5 to -61.5°C; bp 61.8°C; Mol. wt. 184.4 (calcd. 184.03); $\Delta H_{vap} = 7.8$ kcal $mole^{-1}$; $\Delta S_{vap} = 23.2$ eu; $\log P\ (torr) \approx 10.303 - 3152.5/T + 223217/T^2$; IR 1498 (s), 1408 (s), 1250 (s), 1140 (m), 1015 (m), 990 (s), 965 (vs), 925 (m), 894 (m), 850 (s), 746 (m), 592 (w), 548 (m), 520 (s), 480 (m), 460 (m) cm^{-1}; nmr $F^ASO_3POF_2{}^B$ $\phi^*_A = 48.3$ (t), $\phi^*_B = -79.3$ (d,t); ${}^1J_{PF} = 1089$, $J_{AB} = 3.0$ Hz.

$\underline{SF_5Br}$. The products were separated through -30, -111 and -195°C traps. Br_2 and FSO_3SF_5 collected in the -111°C trap. Br_2 was removed by condensing the contents of the -111°C trap onto Hg and shaking at 22°C. Upon reseparation through -111 and -195°C traps, pure FSO_3SF_5 was obtained in the -111°C trap.

FSO_3SF_5: colorless liquid; Mol. wt. 223 (calcd. 226.1). The physical properties, IR and NMR corresponded well with the values reported in the literature (15).

$\underline{SiMe_3Cl}$. The reaction products were separated through -50 and -195°C traps. The -50°C trap contained pure FSO_3SiMe_3.

FSO_3SiMe_3: colorless liquid; mp -90.4; IR 2980 (w), 1470 (s), 1238 (s) 1022 (s), 950 (w), 910 (w), 840 (s), 780 (m), 590 (w), 543 (w), 525 (w), 518 (w) cm^{-1}; nmr $\delta_H = 0.48$ (s) ppm (ext. TMS standard), $\phi^*_F = 42.0$ (s). These data agree well with that of related compounds prepared by other methods (16).

RESULTS AND DISCUSSION

The reactions of CF_3SO_2OX presented in this paper further exemplify the versatility of the hypohalites CF_3SO_2OX (X=Cl,Br) for the introduction of the trifluoromethanesulfonate group into a variety of substrates. The reactions summarized in Table I were carried out in part to survey the reactivity of CF_3SO_2OX (X=Cl,Br) with inorganic substrates. As mentioned in the introduction, these hypohalites had previously been used to prepare a variety of carbon trifluoromethanesulfonates by substitutive electrophilic dehalogenation (SED) with carbon halides and by additions to alkenes. It is now clear that related reactions with other non-metal and metal substrates are equally efficient.

SED Reactions

The SED reactions were carried out mainly with CF_3SO_2OCl, because this compound is more easily prepared and handled than CF_3SO_2OBr and it is usually more reactive than the hypobromite. As was observed with carbon halides, element-bromine bonds are more reactive than the respective element-chlorine bonds. This is clearly illustrated with SiF_3X and SF_5X (X=Cl,Br). Similarly for a given halide,electron withdrawing substitutents decrease the reactivity and electron donating groups increase the reactivity. This is clearly illustrated by comparing F_3SiCl and $(CH_3)_3SiCl$. These trends are a consequence of the relative bond energies and polarizability of the halogens. The SED reaction is believed to proceed by the initial attack of the positive halogen of CF_3SO_2OX on a halogen atom of the substrate, followed by a concerted addition-elimination. For SiF_3Br,

TABLE I[a]

Hypohalite	Reactant	Reaction Conditions	Products[b]
$CF_3SO_3Cl(3.0)$	$SiF_3Cl(3.0)$	-130° to 22°C	$CF_3Cl(2.4), SiF_3Cl(3.0), SO_3$
$CF_3SO_3Br(3.0)$	$SiF_3Cl(3.0)$	-130° to 22°C	$CF_3SO_3CF_3(1.3), Br_2(1.3), SiF_3Cl(3.0), SO_3$
$CF_3SO_3Cl(2.5)$	$SiF_3Br(3.2)$	-160° to 111°C (6 hrs) -111° to -60° (overnite)	$CF_3SO_3SiF_3(1.6), Br_2, Cl_2, BrCl(1.6), SiF_3Br(1.5), SiF_4(0.2)$
$CF_3SO_3Cl(3.0)$	$Me_3SiCl(4.0)$	-111° to 0°C	$CF_3SO_3SiMe_3(2.9), Cl_2(3.0)$, trace CF_3Cl
$CF_3SO_3Cl(6.0)$	$SiCl_4(1.5)$	-78° to RT	$(CF_3SO_3)_2SiCl_2, Cl_2(2.9), CF_3Cl(2.5), SO_3$
$CF_3SO_3Cl(10.0)$[c]	$SiBr_4(2.5)$	-100° to -50°C	$(CF_3SO_3)_4Si(2.0), (CF_3SO_3)_nSiBr_{4-n}, BrCl(9.5)$
$CF_3SO_3Cl(2.5)$	$SF_5Cl(3.0)$	-130° to 22°C	No reaction, decomposition products of CF_3SO_3Cl
$CF_3SO_3Cl(5.0)$	$SF_5Br(6.0)$	-130° to -30°C	$CF_3SO_3SF_5(4.6), Br_2, Cl_2, BrCl(4.8)$
$CF_3SO_3Br(\sim 2.5)$	$SF_5Cl(1.5)$	-130° to 22°C	$SF_5Cl(1.5), CF_3SO_3CF_3, Br_2$
$CF_3SO_3Cl(3.0)$	$POF_2Br(3.0)$	-111° to -20°C slow At -20°C for 24 hrs	$CF_3SO_3POF_2(2.1), CF_3Cl(0.6), Br_2Cl_2, BrCl(2.0), SO_3,$ $(CF_3SO_2)_2O$
$CF_3SO_3Cl(8.5)$	$BBr_3(3.0)$	-110° to 22°	$BrCl(8.5), CF_3SO_3CF_3, SO_2$
$CF_3SO_3Cl(6.0)$	$COCl_2(3.0)$	-78° to 22°	$(CF_3SO_3)_2CO$, $Cl_2(5.1), CF_3Cl(0.4), COCl_2(0.8)$
$CF_3SO_3Cl(5.1)$[c]	$SOCl_2(2.5)$	-78° to -60°C	$(CF_3SO_2)_2O, Cl_2, SO_2(5.6)$
$CF_3SO_3Cl(10.0)$	$CrO_2Cl_2(3.34)$	-111° to 0°C	$Cl_2(6.5)$, $CrO_2(OSO_2CF_3)_2$
$CF_3SO_3Cl(10.0)$	$VOCl_3(3.1)$	-111° to 0°C	$Cl_2(8.5), VO(OSO_2CF_3)_3, CF_3Cl(0.7)$

(continued overleaf)

Table I (cont.)

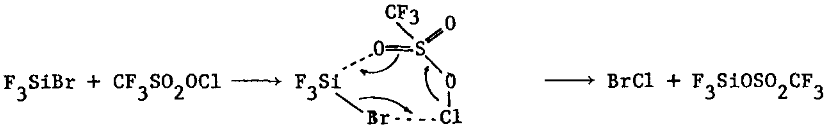
Hypohalite	Reactant	Reaction Conditions	Products[b]
FSO_3Br	SiF_3Cl	-111° to 0°C	No Reaction
$FSO_3Br(\sim 3.0)$	$SiF_3Br(3.0)$	-145° to 22°C	$FSO_3SiF_3(1.5), Br_2(2.8), SiF_4(1.6), SO_3$
$FSO_3Br(4.5)$	$SF_5Cl(3.0)$	-150° to 22°C	$FSO_3SF_5(1.0), SF_5Cl(1.8), Br_2, Cl_2, BrCl(1.0)$
$FSO_3Br(2.5\text{-}3.0)$	$SF_5Br(3.0)$	-111° to 22°C	$FSO_3SF_5(2.8)$, $Br_2(2.8)$
$FSO_3Br(\sim 3.0)$	$POF_2Br(4.0)$	-111° to 22°C	$FSO_3POF_2, Br_2, POF_3, SO_3$
$FSO_3Br(\sim 3.0)$	$SiMe_3Cl(3,0)$	-111° to 22°C	$FSO_3SiMe_3, Br_2, Cl_2, BrCl(3,0)$, trace $FSiMe_3$
$CF_3SO_3Cl(4.5)$	$SF_4(6.0)$	-111° to 22°C	cis-$CF_3SO_3SF_4Cl(2.4), CF_3Cl$, $SF_4(2.5)$
$CF_3SO_3Cl(2.3)$	$CO(5.6)$	-111° to 0°C	$CF_3SO_3COCl(1.88), (CF_3SO_2)_2O, CO_2, COCl_2$
$CF_3SO_2Cl(5.9)$	$SO_2(5.9)$	-78° to 22°C	$CF_3SO_3SO_2Cl(4.0), SO_2(1.6), (CF_3SO_2)_2O(0.4)$
$CF_3SO_3Cl(3.0)$	$PF_3(3.5)$	-130° to 0°C	$OPF_3, (CF_3SO_2)_2O$, Cl_2, PF_3

a) Numbers in parenthesis are amounts in mmols.

b) The amounts of all products were not determined. Other products may also have been formed.

c) CF_2Cl_2 used as solvent.

the following path is envisioned



The concerted nature of the SED reaction seems apparent to us by the fact that other halogen (I) derivatives which cannot react by such a concerted path are ineffective in carrying out related transformations. For example, the hypohalites CF_3OCl and CF_3OOCl are unreactive with F_3SiBr (17). Compounds such as TeF_5OCl and SeF_5OCl, (18) which contain positive Cl, will not attack a substrate such as $CFCl_3$ at 25°C, whereas CF_3SO_2OCl reacts rapidly below -50°C. Many other examples could be given where formal (+1) halogen derivatives will not undergo the SED reaction. On the other hand, $BrOSO_2F$, which could react by an identical mechanism, undergoes the same reactions as CF_3SO_2OCl. Thus, FSO_2OBr undergoes reaction readily with F_3SiBr, $CFCl_3$, SF_5Br and many other substrates found to react with CF_3SO_2OCl.

The reaction of CF_3SO_2OCl and FSO_2OBr with SF_5Br is rather remarkable. To our knowledge, there are no published reactions of a simple substitution of the bromine atom on F_5SBr, although the compound can be readily added to olefins (19) and will undergo nucleophilic substitution of fluorine on sulfur (20). It is absolutely clear that no source of the weak nucleophiles FSO_3^- or $CF_3SO_3^-$ could ever achieve the same result under these conditions and the reactivity of FSO_2OBr and CF_3SO_2OCl is a direct consequence of the very electrophilic halogen atom.

The advantage of the SED reactions for synthesis of trifluoromethanesulfonates and fluorosulfates is illustrated by the high yield synthesis of $(CH_3)_3SiOSO_2CF_3$ and $(CH_3)_3SiOSO_2F$. The reactions are mild and proceed in good yield. Tertiary-butylchloride, on the other hand, reacts explosively with CF_3SO_2OCl and fails to produce the expected ester (21). This difference in reactivity may be attributed to the stability of the silyl ester formed. The t-butyl ester of trifluoromethanesulfonic acid probably decomposes readily by eliminating a molecule of CF_3SO_3H.

Although extension of the SED reaction to other organochlorosilanes has not been demonstrated, it is likely that a variety of related compounds can be prepared by this method. Similarly, earlier attempts to prepare $Si(OSO_2CF_3)_4$ (14) were unsuccessful and $SiF_3OSO_2CF_3$ and SiF_3OSO_2F are novel.

Attempts to extend this reaction to boron derivatives were unsuccessful. With BCl_3 and $BrOSO_2F$, no clear evidence was obtained for a fluorosulfate and only BF_3 and SO_3 could be clearly identified along with an unknown amorphous solid. With BBr_3 and CF_3SO_2OCl, the reaction path is more clear. The tris compound is apparently formed as an unstable liquid, which decomposes as shown in the following equations.

$$BBr_3 + 3CF_3SO_2OCl \longrightarrow B(OSO_2CF_3)_3 + 3BrCl$$

$$B(OSO_2CF_3)_3 \xrightarrow{28°C} (OBOSO_2CF_3)_n + CF_3SO_2OCF_3 + SO_2$$

The solid polymer formed was not characterized but the formula is suggested from the observed stoichiometry.

The reactions of CF_3SO_2OCl and FSO_2OBr with OPF_2Br provide a qualitative check of the relative electronegativities of CF_3SO_3 and FSO_3(22). The difluorophosphoryl fluorosulfate had previously been prepared from the thermal decomposition of $OP(OSO_2F)_3$ (23) but it was not isolated as a pure compound. From a comparison of $^1J_{PF}$ and v(P=O), the relative electronegativities of CF_3SO_3 and FSO_3 appear to be nearly identical with $^1J_{PF}$ = 1089 Hz and ν(P=O) = 1400 and 1408 cm^{-1}, respectively. The thermal stability of $OPF_2OSO_2CF_3$ at 22° was less than that of OPF_2OSO_2F. The former slowly equilibrates to a mixture of the symmetrical anhydrides.

$$2OPF_2OSO_2CF_3 \rightleftarrows P_2O_3F_4 + (CF_3SO_2)_2O$$

The final SED reactions for comment involve those of CF_3SO_2OCl and CrO_2Cl_2 and $VOCl_3$. Essentially stoichiometric quantities of Cl_2 and the appropriate weight changes were observed suggesting the formation of $CrO_2(OSO_2CF_3)_2$ and

$OV(OSO_2CF_3)_3$. The materials were not further characterized but their formation as indicated is reasonable based on the corresponding $OV(OSO_2F)_3$ and $CrO_2(OSO_2F)_2$ (24-26). It is probable that this reaction type can be extended to many covalent transition metal halides.

Oxidative Addition

The oxidative addition reactions of CF_3SO_2OCl were carried out with CO, SO_2, PF_3 and SF_4. Hypochlorites are known to add readily to CO and SO_2 (27) and the reactions with CF_3SO_2OCl gave excellent yields of the expected products. The corresponding reactions of $BrOSO_2F$ with CO and SO_2 give only CO_2 and $S_2O_5F_2$ and Br_2 and $S_3O_8F_2$, respectively (28). This is probably due to the rapid reaction of $BrOSO_2F$ with the initial addition products to give the disubstituted compounds.

$$BrOSO_2F + SO_2 \longrightarrow \text{"}FSO_2OSO_2Br\text{"} \xrightarrow{BrOSO_2F} S_3O_8F_2 + Br_2$$

$$BrOSO_2F + CO \longrightarrow \text{"}BrC(O)OSO_2F\text{"} \xrightarrow{BrOSO_2F} OC(OSO_2F)_2 + Br_2$$

The resultant $OC(OSO_2F)_2$ is unstable and decomposes readily to CO_2 and $S_2O_5F_2$ (6,29). In this respect, it is surprising that $OC(OSO_2CF_3)_2$ is stable at 22°C. It is now clear that fluorosulfates commonly decompose by two routes

$$\text{Type 1} \quad MOSO_2F \longrightarrow MF + SO_3$$

$$\text{Type 2} \quad M(OSO_2F)_2 \longrightarrow MO + (FSO_2)_2O$$

Type 1 decomposition is observed for example with SiF_3OSO_2F and Type 2 with $C(OSO_2F)_4$. While type 1 decomposition is found for CF_3SO_2OCl, no clear example of type 2 decomposition exists for a trifluoromethanesulfonate. While large amounts of anhydride are produced in some reactions, it was shown in the case of $CF_2(OSO_2CF_3)_2$ that the compound did not decompose readily to COF_2 and $(CF_3SO_2)_2O$, even though these are major products in the reaction of CF_2Br_2 with CF_3SO_2OCl. Thus, an alternate transition state was proposed to account for the low yield of $CF_2(OSO_2CF_3)_2$ and the observed products (5).

The reaction of both CF_3SO_2OBr and CF_3SO_2OCl with PF_3 give analogous products. No evidence for the phosphorane is observed and only OPF_3, anhydride, X_2 and unreacted PF_3, are observed in each case. This may be due to a rapid reaction of the intermediate phosphorane with the hypohalite.

$$"PF_3OSO_2A" + ASO_2OX \longrightarrow OPF_3 + (ASO_2)_2O + XCl$$

$A = CF_3$, F X - Cl,Br

Finally, the reaction of CF_3SO_2OCl with SF_4 is extremely interesting. First, it is very surprising that CF_3SO_2OCl will add to SF_4 to give a stable product under the reaction conditions. Chlorine(I) fluorosulfate is reported not to add to SF_4 and the reaction with $BrOSO_2F$ results in the formation of SO_2F_2,$S_2O_5F_2$,SF_6 and Br_2 (30) and none of the addition product. Only cis-$ClSF_4OSO_2CF_3$ is observed and this gives rise to an interesting A_2BXM_3 or an $AA'BXM_3$ spin system in the ^{19}F nmr. The cis product is not surprising in view of the fact that most of the known additions to SF_4 give the cis adduct (31). However, this adduct is the only cis chloro derivative which does not contain a sulfur-carbon bond as the other cis group (32). In this reaction, a white solid is also observed along with some SF_5Cl. The origin of these products is now believed to be due to the initial formation of the $ClSF_4^+$ cation. All the products have been identified and further details of this reaction will be reported separately (33).

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