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Preparation of Fluorothiosulfonium Salts $CF_3SSCF_3(F)^+MF_6^-$, $CF_3SSCH_3(F)^+MF_6^-$, and $CH_3SSCH_3(F)^+MF_6^-$ (M = As, Sb)[1]

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The monofluorothiosulfonium salts $CF_3SS(F)CF_3^+MF_6^-$, $CF_3SS(F)CH_3^+MF_6^-$, and $CH_3SS(F)CH_3^+MF_6^-$ are formed by oxidative fluorination of the corresponding disulfanes with $XeF^+MF_6^-$ (M = As, Sb). The regioselective fluorination of CH_3SSCF_3 by XeF^+ at the SCH_3 fragment of the molecule is remarkable and can be rationalized on the basis of the Pearson concept. All salts have been characterized by IR, Raman, and NMR spectroscopic methods. They are stable below 245 ($CH_3SSCF_3(F)^+MF_6^-$) and 255 K ($CH_3SSCH_3(F)^+MF_6^-$) and decompose above these temperatures to give $S_8^{2+}(MF_6^-)_2$.

Introduction

Organosulfonium salts $R_3S^+A^-$ represent a very large class of compounds with a wide variety of substituents R and an even larger range of preparative methods.[2–4] In contrast, only a few examples of organothiosulfonium salts of the type $R_{3-n}S(SR)_n{}^+X^-$ with $n = 1$, 2 and R = alkyl are known;[2–8] they are formed by treating either alkyloxonium salts or alkyl halides with alkyldisulfanes.[2–4]

The related halosulfonium salts $(CH_3)_2SSSCl^+SbF_6^-$, $(CH_3)_2SSCl^+SbF_6^-$, and the isomeric $CH_3(Cl)SSCH_3{}^+SbCl_6^-$ have been prepared recently for the first time.[9] The latter compound was characterized by an X-ray structure analysis and can be obtained by the following condensation reactions.

$$(CH_3)_2SH^+SbF_6^- + ClS_nCl \xrightarrow[-HCl]{} (CH_3)_2S{-}S_nCl^+SbF_6^- \tag{1}$$

$$n = 1, 2$$

$$SCl_3{}^+SbCl_6^- + 2CH_3SH \xrightarrow[-2HCl]{} (CH_3S)_2SCl^+SbCl_6^- \rightarrow (CH_3S)(Cl)S{-}SCH_3{}^+SbCl_6^- \tag{2}$$

Oxidative chlorination of CF_3SSCF_3 with Cl_2/AsF_5 or Cl_2/SbF_5 leads to splitting of the SS bond with formation of the corresponding dichlorosulfonium salts (eq 3[10]).

$$CF_3SSCF_3 + 2Cl_2 + 3AsF_5 \rightarrow 2CF_3SCl_2{}^+AsF_6^- + AsF_3 \tag{3}$$

In this context the question of reactivity and regioselectivity in reactions of monofluoroxenonium salts with disulfanes has to be discussed. We have been able to carry out oxidative fluorination of sulfanes[11–13] and oxanes[14,15] using the soft "Pearson cation" XeF^+.

Experimental Section

Materials and Apparatus. Literature methods were used for the synthesis of $XeF^+MF_6^-$ (M = As, Sb),[16] CF_3SSCF_3,[17] CF_3SSCH_3,[18] and CF_3SSH.[19] CH_3SSCH_3 (Merck) was used without further purification. HF (Bayer) was treated with F_2 and SO_2 (Hoechst) stored over CaH_2.

All reactions were carried out in KEL-F reactors with valves made of the same material. For the work with HF, a stainless-steel high-vacuum apparatus with valves (Fa. Hoke) was used. Nonvolatile compounds were handled in a dry N_2 atmosphere by using Schlenk techniques.

IR spectra were recorded on a Bruker IFS 113 v spectrometer in a low-temperature cell[20] between NaCl and polyethylene plates. Raman spectra were run on a Coderg T 800 spectrometer equipped with an Ar^+ laser (Spectra Physics) operating at 514.5 nm. The maximum resolution was 5 cm^{-1}.

The NMR spectra in HF or SO_2 solution at 213 K were recorded with a Bruker AM 300 spectrometer (^1H NMR, 10-mm tubes, standard TMS, 300.0 MHz from +15 ppm to −1 ppm; ^{13}C NMR, 10-mm tubes, standard TMS, 75.5 MHz from +210 ppm to −10 ppm; ^{19}F NMR, 5 mm-tubes, standard CF_3Cl, 282.5 MHz from +200 ppm to −200 ppm); shifts to low field of the external standards are defined as positive. The pulse widths were 1.8 μs (^1H), 2.5 μs (^{13}C), and 2.0 μs (^{19}F), and 2048 scans were run for each spectrum; the digital resolution was 3.4 Hz/data point.

For the sulfur analysis of $CF_3SSCF_3(F)^+AsF_6^-$, a sample was hydrolyzed by a mixture of bromine in water so that all sulfur was completely oxidized to sulfate(VI), which could be detected gravimetrically. For the arsenic determination a complexometric titration of a hydrolyzed sample with Titriplex III was carried out. Both analytical methods are reproducibly in the range ±5%.

Preparation of $RSSR'(F)^+MF_6^-$ (R, R' = CH_3, CF_3; M = As, Sb). A 5-mL aliquot of dry HF was condensed in a KEL-F reactor with 1 mmol of $XeF^+MF_6^-$. At 77 K, an equimolar amount of the disulfane was condensed into the reactor, and the reaction mixtures were stirred for 4 h ($CH_3SSCH_3(F)^+$ and $CH_3(F)SSCF_3{}^+$) and 6 h ($CF_3SSCF_3(F)^+$) at 213 K. After the solvent was removed by pumping at 213 K, yellowish white solids remained, which were stable up to 245 K ($CF_3SSCF_3(F)^+$), 250 K ($CH_3(F)SSCF_3{}^+$), and 255 K ($CH_3SSCH_3(F)^+$).

The relative proportions of sulfur and arsenic for $CF_3SSCF_3(F)^+AsF_6^-$ were reproducibly 2:1 with a deviation of 5% from the theoretical values.

Results and Discussion

The reaction of RSSR' (R, R' = CH_3, CF_3) with $XeF^+MF_6^-$ (M = As, Sb) in anhydrous HF at 213 K leads to formation of yellowish fluorothiosulfonium salts $RSSR'(F)^+MF_6^-$ (eq 4).

$$RSSR' + XeF^+MF_6^- \rightarrow RSSR'(F)^+MF_6^- + Xe \tag{4}$$

$$R, R' = CH_3, CF_3; M = As, Sb$$

These salts are sensitive to hydrolysis and can be kept without decomposition up to 243 K. They are only slightly soluble in HF;

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Table I. Vibrational Frequencies (cm^{-1}) for $RSS(F)R'^{+}MF_6^-$ (R, R' = CF_3, CH_3; M = As, Sb)

$CF_3SS(F)CF_3^+$				$CF_3SS(F)CH_3^+$				$CH_3SS(F)CH_3^+$				
AsF_6^-		SbF_6^-		AsF_6^-		SbF_6^-		AsF_6^-		SbF_6^-		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	assgnt
				3040 s	3044 w	3042 s	3043 w	3039 ms	3040 w	3040 ms	3038 w	$\nu_{as}(CH_3)$
				2940 ms	2938 mw	3928 ms	2938 mw	2944 ms	2940 w	2945 m	2945 w	$\nu_s(CH_3)$
				1440 m	1445 w	1440 m	1442 w	1426 w	1412 w	1428 m	1411 w	$\delta_{as}(CH_3)$
				1335 m	1330 w	1334 m	1330 w	1379 m	1382 vw	1382 vw	1380 m	$\delta_s(CH_3)$
								1330 m			1330 m	
1129 s		1128 s		1175 s	1172 w	1174 s	1169 w					$\nu(CF_3)$
	1069 mw		1083 mw									
1040 s	1032 mw	1043 s	1035 mw	1108 s	*a*	1108 s	*a*					
				998 s	*a*	1002 s	*a*	1007 vs	1005 w	1009 vs	1006 w	$\delta(CH_3)$
								989 vs	993 w	987 vw	990 w	$\delta(CH_3)$
825 vs	825 m	822 vs	821 m	830 s	824 m	830 s	827 m	834 vs	835 w	834 vs	835 w	$\nu(SF)$
755 m	766 s	*a*	770 s	760 ms	766 ms	760 m	767 ms					$\delta_{as}(CF_3)$
				689 m	690 ms	689 m	688 m	681 m	683 mw	684 m	685 mw	$\nu(H_3CS)$
566 mw	566 mw	*a*	567 mw	580 mw	575 m	580 mw	575 m					$\delta(CF_3)$
596 m	592 m	594 m	597 m	528 m	522 m	522 m	528 m	511 m	505 m	511 m	502 m	$\nu(SS)$
								646 m	643 m	646 m	650 m	$\nu(S{-}CH_3)$
530 m	531 ms	530 m	532 ms	460 m	460 m	461 m	460 m					$\nu(S{-}CF_3)$
474 w	474 ms	476 w	467 ms									
320 w	325 mw	318 w	321 mw	340 w	345 m	340 w	344 m					$\delta(CF_3)$
258 m	258 m	259 m	261 m	266 m	267 m	264 m	264 m	330 m	327 mw	332 m	330 mw	$\delta(SSF)$
238 m	240 mw	240 m	235 mw	232 m	233 ww	230 m	230 mw	248 mw	250 vs	250 mw	248 vs	$\delta(CSF)$
290 w	289 m	290 w	295 m									$\delta(CF_3)$
				250 m	250 m	245 m	250 m					$\delta(SSC)$
a	160 s	*a*	159 s	*a*	180 m	*a*	178 m					$\delta(SSC)$
a	115 m	*a*	115 m	*a*	155 w	*a*	163 mw	*a*	175 mw			τ
700 s		671 s		700 s		669 s		698 s		670 s		$\nu_3(MF_6^-)$
	690 s		652 s		682 s		650 s		680 s		650 s	$\nu_1(MF_6^-)$
	585 w		590 w		585 w		588 w		585 w		586 w	$\nu_2(MF_6^-)$
400 s		280 s		400 s		285 s		395 s		280 s		$\nu_4(MF_6^-)$
	380 m		280 m		380 m		285 m		375 m		290 m	$\nu_5(MF_6^-)$

[a] Not observed.

SO_2 is a convenient solvent for $CF_3SSCF_3(F)^+MF_6^-$. At higher temperatures, decomposition is observed both in solution and in the solid state with formation of an intensely blue solid, $S_8^{2+}(MF_6^-)_2$. Under these conditions, the following stability series for the new salts with increasing decomposition point can be quoted: $CF_3SSCF_3(F)^+MF_6^-$ (245 K) < $CF_3SSCH_3(F)^+MF_6^-$ (250 K) < $CH_3SSCH_3(F)^+MF_6^-$ (253 K). The comparison of the stabilities of the thiosulfonium salts with the corresponding sulfonium salts $RSR'(F)^+MF_6^-$ shows a lower thermal stability for $RSSR'(F)^+MF_6^-$.[11,12,22] No difference in stability was observed between the AsF_6^- and the SbF_6^- salts.

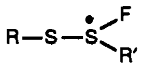
One disulfane that could not be fluorinated oxidatively by $XeF^+MF_6^-$ is CF_3SSH. All reactions, including those carried out at 195 K, yielded a mixture of orange yellowish and blue solids. The first was identified by Raman spectroscopy to be antimony sulfides.[31] The IR spectrum of the whole mixture showed additional bands that are identical with those recorded from a sample of isolated $S_8^{2+}(SbF_6^-)_2$ (688 cm^{-1} vs (br), 640 cm^{-1} sh, 605 cm^{-1} w, 560 cm^{-1} m (br), 525 cm^{-1} w, 485 cm^{-1} vw, 470 cm^{-1} m, 340 cm^{-1} mw, 290 cm^{-1} vs (br)).[32]

The impossibility of preparation of $CF_3SSH(F)^+MF_6^-$ and the already mentioned difference in the thermal stabilities of monofluorinated thiosulfonium salts agree well with the HSAB concept.[23,24] Because of the variable ligand influences, the basic centers in the disulfanes are different in agreement with the hardness of the groups CH_3 < CF_3 < H. The monofluoroxenonium cation as a soft acid favors attack at the softer nucleophile in the disulfane to form the more stable product. These considerations also explain the regioselectivity of the reaction of XeF^+ with the mixed substituted methyl(trifluoromethyl)disulfane, where electrophilic attack in the first step of the reaction occurs exclusively at the softer methylthio group, followed by oxidative fluorination with elimination of xenon.

Table II. Selected SS Vibrational Frequencies (cm^{-1}) of Disulfanes and Thiosulfonium Cations

SSF_2[27]	718	SSF^+[30]	676
FSSF[27]	623		
CF_3SSCF_3[17]	536	$CF_3SSCF_3(F)^+$	594
CF_3SSCH_3[18]	536	$CF_3SSCH_3(F)^+$	525
CH_3SSCH_3[28]	517	$CH_3SSCH_3(F)^+$	507
CF_3SSH[19]	621		
HSSH[29]	510		

Vibrational Spectra. Table I shows the vibrational frequencies of the new thiosulfonium salts. Because of the C_1 symmetry of the cation skeleton



nine Raman and IR active vibrations are expected. In the spectra of the investigated salts seven to nine of these are observed in addition to vibrations arising from the methyl- and trifluoromethyl groups.

In all monofluorothiosulfonium cations the SF valence vibration is found in the expected range.[25] The position of $\nu(CH_3S)$ or $\nu(CF_3S)$ is only a little influenced by the transition from the disulfanes to the fluorinated species. The value of $\nu(SS)$ changes only a little on fluorination for $CH_3SSCH_3(F)^+MF_6^-$ and $CF_3SSCH_3(F)^+MF_6^-$ while for $CF_3SSCF_3(F)^+MF_6^-$ a significant shift toward higher frequencies is observed (Table II). A possible explanation is given by the dependence of the frequency shift on the SS bond force constant. Investigations by Saethre[26] show that

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Table III. NMR Data (ppm) for $RSS(F)R'^{+}MF_6^{-}$ and $RS(F)R'^{+}MF_6^{-}$ (R, R' = CF_3, CH_3; M = As, Sb)

	R, R' = CF_3	R = CF_3, R' = CH_3	R, R' = CH_3
		^{19}F NMR	
$RSS(F)R'^{+}$	$\delta(SF) = -117.0$	$\delta(SF) = -123.5$ q	$\delta(SF) = -132.0$
		$^{3}J(HF) = 16.3$ Hz	
	$\delta(CF_3S) = -48.35$	$\delta(CF_3S) = -36.09$	
	$\delta(CF_3S^{+}) = -31.90$ q		
$RS(F)R'^{+}$	$\delta(SF) = -159.4$[21]	$\delta(SF) = -189.4$[11]	$\delta(SF) = -190.7$[22]
	$^{3}J(FF) = -7.2$ Hz		
	$\delta(CF_3S) = -43.2$ d	$\delta(CF_3S) = -56.4$	
		^{13}C NMR	
$RSS(F)R'^{+}$	$\delta(CF_3S) = 125.4$ q	$\delta(CF_3S) = 127.6$ q	$\delta(CH_3S) = 22.4$
	$^{1}J(CF) = 342.8$ Hz	$^{1}J(CF) = 305.0$ Hz	
	$\delta(CF_3S^{+}) = 124.7$ dq	$\delta(CH_3S) = 37.9$ d	$\delta(CH_3S^{+}) = 31.3$ d
	$^{1}J(CF) = 335$ Hz	$^{3}J(CF) = 13$ Hz	$^{3}J(CF) = 14.7$ Hz
	$^{2}J(CF) = 15$ Hz		
$RS(F)R'$	$\delta(CF_3S) = 128.8$ qdq[21]	$\delta(CF_3S) = 123.5$ qdq[11]	[a]
	$^{1}J(CF) = 341.7$ Hz	$^{1}J(CF) = 330$ Hz	
	$^{2}J(CF) = 16.7$ Hz	$^{2}J(CF) = 17.2$ Hz	
	$^{3}J(FF) = 4$ Hz	$^{3}J(FF) = 1.9$ Hz	
		^{1}H NMR	
$RSS(F)R'^{+}$		$\delta(CH_3) = 3.9$ d	$\delta(CH_3S^{+}) = 2.92$
		$^{3}J(HF) = 15.6$ Hz	
			$\delta(CH_3S) = 3.17$
$RS(F)R'$		$\delta(CH_3) = 4.3$ d[11]	$\delta(CH_3) = 3.73$[22]
		$^{3}J(HF) = 22.3$ Hz	

[a] Not measured.

the bond distance is influenced by the nature of the substituents. The increasing electronegativity of bonded substituents causes a strengthening of the (p–p) π bonds by delocalization of the "lone pair" electrons and a shortening of the bond. For the salts in this work the above-mentioned effect can be observed for $CF_3SSCF_3(F)^{+}$. By introduction of an additional electronegative substituent (F), the bond strength increases, and this is revealed by a shift toward higher frequencies. In the case of $CH_3SSCH_3(F)^{+}$ and $CF_3SSCH_3(F)^{+}$ cations, the influence of the electronegative fluorine atom is compensated by the $+I$ effect of the methyl groups, so that the position of the vibrational frequency remains uninfluenced.

NMR Spectra. The chemical shifts of the ^{19}F, ^{13}C, and ^{1}H NMR nuclei in monofluorothiosulfonium salts are compared in Table III with the values for the corresponding sulfonium compounds.

Within the series $CH_3SSCH_3(F)^{+}$, $CF_3SSCH_3(F)^{+}$, and $(CF_3)_2S_2F^{+}$, a downfield shift for the ^{19}F resonances with increasing CH_3/CF_3 substitution is observed. The same effect due to the decreasing influence of the $+I$ effect of the methyl group on the SF bond can also be noted for the fluorosulfonium cations $(CH_3)_2SF^{+}$, $CH_3S(CF_3)F^{+}$, and $(CF_3)_2SF^{+}$. The comparison of each single pair shows a downfield shift from the sulfonium to the homologous thiosulfonium cation. This can also be explained on the basis of decrease of the inductive effect onto the SF group with increasing number of sulfur atoms, which leads to a decrease of electron density at the fluorine atom.

The ^{19}F signal in $CF_3SSCH_3(F)^{+}$ shows a quartet splitting with a coupling constant of $^{3}J(HF) = 16.3$ Hz, which demonstrates the localization of the fluorine atom at the CH_3S group. This is confirmed by ^{13}C and ^{1}H couplings.

The differentiation between the nonequivalent CF_3 groups in $CF_3SSCF_3(F)^{+}$ followed from the coupling constants in ^{19}F and the shifts in the ^{13}C NMR spectra.

The observed differences in the ^{13}C shifts for the CF_3 groups in all of the compounds studied are only marginal. For the methyl groups, however, a significant downfield shift of the CH_3S^{+} group in comparison to the CH_3S group is distinguishable; this shift is largest for the mixed substituted thiosulfonium salt.

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Registry No. $CF_3SS(F)CF_3^{+}AsF_6^{-}$, 135823-54-0; $CF_3SS(F)CF_3^{+}\cdot SbF_6^{-}$, 135823-61-9; $CF_3SS(F)CH_3^{+}AsF_6^{-}$, 135823-56-2; $CF_3SS(F)CH_3^{+}SbF_6^{-}$, 135823-62-0; $CH_3SS(F)CH_3^{+}AsF_6^{-}$, 135823-58-4; $CH_3SS(F)CH_3^{+}SbF_6^{-}$, 135823-63-1; CF_3SSCF_3, 372-64-5; CF_3SSCH_3, 14410-21-0; CH_3SSCH_3, 624-92-0; CF_3SSH, 55860-39-4; SSF^{+}, 43431-44-3; $CF_3SSCF_3(F)^{+}$, 135823-53-9; $CF_3SSCH_3(F)^{+}$, 135823-55-1; $CH_3SSCH_3(F)^{+}$, 135823-57-3; $XeF^{+}AsF_6^{-}$, 135823-60-8; $XeF^{+}SbF_6^{-}$, 36539-18-1.

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