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Articles

Monofluorosulfonium Hexafluoroantimonate, $H_2SF^+SbF_6^-$ [1]

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Monofluorosulfonium hexafluoroantimonate was prepared by oxidative fluorination of H_2S with $XeF^+SbF_6^-$ in anhydrous HF at 195 K. The slightly yellow thermolabile salt was characterized by vibrational and NMR spectroscopy. Isotopically substituted H/D and $^{32/34}S$ species were also investigated. On the basis of the observed frequency shifts and the geometric parameters $r_{SH} = 134.0$ pm, $r_{SF} = 157.1$ pm, $\angle SH_2 = 95.1°$, and $\angle HSF = 99°$, obtained by ab initio methods, a force field calculation was carried out. This calculation resulted in the values $f(SF) = 5.38$ N/cm and $f(SH) = 3.52$ N/cm.

Introduction

Monofluoroxenonium hexafluorometalates represent a class of extremely selective fluorinating agents with a high oxidation potential which are reactive even at low temperatures. Their use for the preparation of monofluorinated salts of different nonmetal compounds has recently been reported in a series of articles.[2-12] Arsenic[2] compounds (eq 1) as well as oxygen[3] and differently substituted sulfur[4-11] compounds (eq 2) were used as nucleophilic educts.

$$AsCl_3 + XeF^+AsF_6^- \rightarrow AsCl_3F^+AsF_6^- + Xe \qquad (1)$$

$$RSR' + XeF^+MF_6^- \rightarrow RS(R')F^+MF_6^- + Xe \qquad (2)$$

$$R = Cl, CF_3, CH_3, C_6F_5, CN;\ R' = Cl, H, C_6F_5, CH_3, CF_3, CN;\ M = As, Sb$$

The selectivity of the mild fluorinating agent $XeF^+MF_6^-$ (M = As, Sb) is confirmed by its reaction with disulfanes of the type RSSR′ (R = CH_3, CF_3),[12] which can be fluorinated without cleavage of the SS bond. The regioselectivity of this reaction is demonstrated by the mixed substituted disulfane CH_3SSCF_3 (eq 3). In this case only the CH_3-substituted sulfur atom is attacked by the monofluoroxenonium cation, as demonstrated by NMR spectroscopy.

$$CF_3SSCH_3 + XeF^+MF_6^- \rightarrow CF_3SS(F)CH_3{}^+MF_6^- + Xe \qquad (3)$$

$$M = As, Sb$$

The high oxidation potential of $XeF^+MF_6^-$ can be shown by the synthesis of the recently isolated monofluoroxonium hexafluorometalates $H_2OF^+MF_6^-$ (M = As, Sb)[3] (eq 4). In spite of the very high ionization potential of H_2O with 12.6 eV[13] the formally protonated hypofluorous acid salts were obtained in high yield and could be handled without any problems.

$$H_2O + XeF^+MF_6^- \rightarrow H_2OF^+MF_6^- \qquad (4)$$

$$M = As, Sb$$

In view of these results it seemed logical to attempt the synthesis of the H_2SF^+ cation, the only still missing link within the series of monofluorosulfonium cations. In analogy to the thermolysis of $H_2OF^+SbF_6^-$,[3] during which HOF was isolated in an inert-gas matrix, the new $H_2SF^+SbF_6^-$ salt could be a precursor for the hitherto unknown thiohypofluorous acid HSF.

In this paper we report the reactions of H_2S with monofluoroxenonium hexafluorometalates.

Experimental Section

Materials and Apparatus. Literature methods were used for the synthesis of $XeF^+MF_6^-$ (M = As, Sb)[14] and SCl_2.[15] Commercial Cl_2 (Bayer) and CH_3Cl were used without further purification. C_6F_5SCl was made available to us by Prof. A. Haas, University of Bochum. SbF_5 (Merck) was distilled three times, and HF (Bayer) was treated with F_2 and stored over SbF_5. H_2S was purified by distillation.

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 of the solids were recorded on a Bruker IFS 113v spectrometer in a low-temperature cell[16] between silicon plates, and IR spectra of gases were measured in a stainless steel gas cell equipped with silicon windows. Raman spectra were recorded on a Coderg T 800 spectrometer equipped with an Ar^+ laser (Spectra Physics) operating at $\lambda = 514.5$ nm. The maximum resolution was 5 cm^{-1}.

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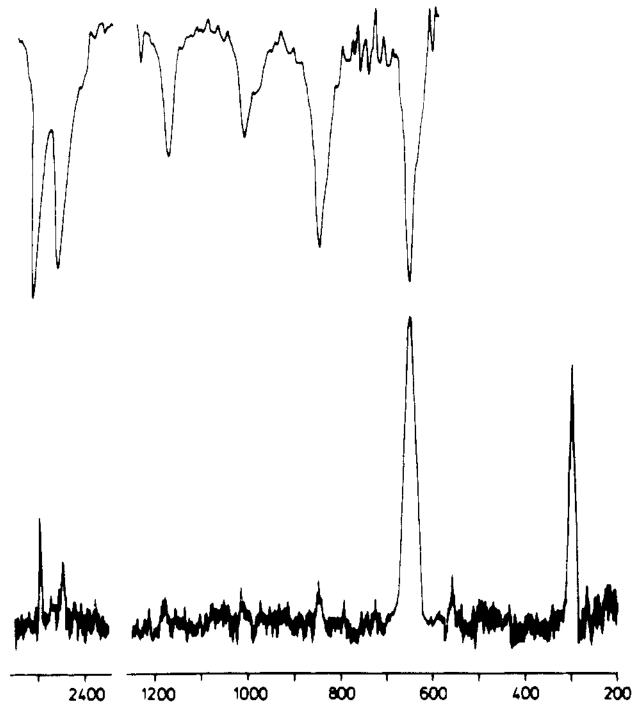

Figure 1. IR and Raman spectra of $H_2SF^+SbF_6^-$.

The NMR spectra in HF solution at 213 K were recorded with a Bruker Am 300 spectrometer (^{1}H-NMR, 10-mm tubes, standard TMS; 300.0 MHz from +15 ppm to −1 ppm; ^{19}F-NMR, 5-mm tubes, standard $CFCl_3$, 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 (^{1}H) and 2.0 μs (^{19}F).

Mass spectra were recorded on a Finnigan MAT spectrometer with IE = 70 eV.

Estimation of the sulfur/antimony ratio was performed gravimetrically for sulfur[17] and complexometrically for antimony.[18]

The amount of xenon formed during the reaction was determined by its weight.

Preparation of $H_2SF^+SbF_6^-$. Dry HF (5 mL) was condensed into a KEL-F reactor containing $XeF^+SbF_6^-$ (0.75 mmol). At 77 K an equimolar amount of H_2S was condensed into the reactor, and the mixture was kept at 195 K for 6 h. After removal of the solvent and the evolved xenon at 195 K, a yellowish solid, which is stable up to 195 K for 1–2 d, remained.

It is necessary to work with exact stoichiometries, because any excess of H_2S or $XeF^+SbF_6^-$ catalyzes the decomposition into $S_8^{2+}(SbF_6^-)_2$.

Results and Discussion

The reaction of H_2S with an exactly equimolar amount of $XeF^+SbF_6^-$ at 195 K in HF solution leads to the formation of the slightly yellow colored monofluorosulfonium hexafluoroantimonate, $H_2SF^+SbF_6^-$, in high yield (eq 5). Xenon, eliminated

$$H_2S + XeF^+SbF_6^- \rightarrow H_2SF^+SbF_6^- + Xe \qquad (5)$$

during the reaction, can be collected nearly quantitatively (89–91%) and identified by mass spectroscopy. On average, the sulfur/antimony ratio in the salt—determined by chemical analysis—amounts to 1:1 with a deviation of 10%.

The quality of the solvent is critical for a successful synthesis. In solution, traces of H_2O catalyze the decomposition of $H_2SF^+SbF_6^-$ with HF elimination, followed by oxidation of S_8 by SbF_5 to blue $S_8^{2+}(SbF_6^-)_2$ (eqs 6 and 7). In the solid state at 195 K, the extremely thermolabile $H_2SF^+SbF_6^-$ remains stable for 2 or 3 days and, in contrast to its behavior in solution, it

$$3H_2SF^+SbF_6^- \longrightarrow 6HF + {}^3/_8S_8 + 3SbF_5 \qquad (6)$$

$$\downarrow$$

$${}^3/_8S_8^{2+}(SbF_6^-)_2 + SbF_3 \qquad (7)$$

decomposes under formation of $S_4^{2+}(SbF_6^-)_2$ and S_8.[11] Decomposition products analogous to those in eqs 6 and 7 are observed when the synthesis of $H_2SF^+AsF_6^-$ is attempted, which indicates that the hexafluoroarsenate exists only below the melting point of HF, at 189 K.

The following reactions were carried out to verify the existence of $H_2SF^+SbF_6^-$ by chemical means (eqs 8–11).

$$H_2SF^+SbF_6^- + 2Cl_2 \rightarrow SCl_2F^+SbF_6^-{}^{8} + 2HCl \qquad (8)$$

$$H_2SF^+SbF_6^- + 2CH_3Cl \rightarrow (CH_3)_2SF^+SbF_6^-{}^{19} + 2HCl \qquad (9)$$

$$H_2SF^+SbF_6^- SCl_2 \rightarrow S_2F^+SbF_6^-{}^{11} + 2HCl \qquad (10)$$

$$H_2SF^+SbF_6^- + 2C_6F_5SCl \xrightarrow[213\ K]{SO_2} (C_6F_5)_2SF^+SbF_6^-{}^{6} + 2HCl + {}^1/_4S_8 \qquad (11)$$

The high tendency toward formation of hydrogen chloride can be regarded as the driving force of the observed reaction pathways. The formed HCl was identified in all cases by IR spectroscopy of the gaseous phase. The already known compounds, resulting from the reactions in eqs 8–11 were characterized by vibrational as well as by NMR spectroscopy. In addition to our spectroscopic measurements, the reaction in eq 10 was proven to be quantitative by weighting the educt SCl_2 and both products.

Further investigations of the synthetic potential of $H_2SF^+SbF_6^-$ are the subject of our ongoing research.

Vibrational Spectra and Force Field Calculations. To characterize the salt by vibrational spectroscopy (Figure 1) ^{34}S derivatives have been used besides the deuterated compounds. The vibrations of the SbF_6^- anion can be unequivocally assigned due to their mutual exclusiveness in the infrared and Raman spectra. All other bands appear in the infrared as well as in the Raman spectra and can be assigned to a pyramidal H_2SF^+ cation of C_s symmetry.

The most outstanding features are a pair of bands in the 2440–2500-cm^{-1} and 1720–1750-cm^{-1} regions (SH/SD stretching vibrations), respectively, and a very intense infrared band at 820–850 cm^{-1} attributed to the SF stretching. The deformation modes are much weaker, especially in the Raman spectra, and cannot always be clearly localized.

Surprisingly, the observed frequencies of the cation do not obey the Teller–Redlich product rule.[20] Moreover, the deviation is opposite to the direction expected for anharmonicity effects (Table II). This cannot be remedied by a change of the assignment of the deformation modes, as the main part of the discrepancy arises from the SH and SD stretchings, which can be clearly observed and unequivocally assigned. Although these infrared bands are rather sharp, the only plausible explanation is the assumption of hydrogen bridges between the cation and the fluorine atoms in the anion. It is known that such bridges are stronger with deuterium.[21,22] Thus substitution of H by D will

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Table I. Vibrational Frequencies (cm^{-1}) of $H_2{}^nSF^+SbF_6^-$ (X = H, D; *n* = 32, 34)^a

$H_2{}^{32}SF^+$		$H_2{}^{34}SF^+$		$D_2{}^{32}SF^+$		$D_2{}^{34}SF^+$		
IR	RA	IR	RA	IR	RA	IR	RA	assgnt
2500 s	2500 (39)	2496 s	2498 (37)	1745 s	1744 (36)	1742 s	1742 (36)	$\nu_1(a')$, $\nu_s(SX_2)$
2447 s	2446 (23)	2445 s	2444 (22)	1725 s	1725 (22)	1724 s	1724 (22)	$\nu_5(a'')$, $\nu_{as}(SX_2)$
1181 s	1181 (16)	1180 mw	1180 (14)	844 mw	844 (17)	844 mw	843 (15)	$\nu_2(a')$, $\delta(SX_2)$
1020 mw	1019 (16)	1015 mw	1016 (14)	728 mw	729 (17)	726 mw	726 (14)	$\nu_3(a'')$, $\delta(XSF)$
987 w	n.o.	986 w	n.o.	n.o.	n.o.	705 sh	n.o.	$\nu_6(a')$, $\omega(SX_2)$
853 s	856 (24)	850 s	850 (22)	827 s	825 (23)	821 s	820 (23)	$\nu_4(a')$, $\nu(SF)$
	650 (100)		640 (100)		650 (100)		650 (100)	$\nu_1(SbF_6^-)$
655 s		660 s		658 s		660 s		$\nu_3(SbF_6^-)$
	575 (16)		562 (18)		569 (17)		570 (17)	$\nu_2(SbF_6^-)$
280 s		281 s		280 s		280 s		$\nu_4(SbF_6^-)$
	281 (51)		284 (63)		275 (59)		280 (61)	$\nu_5(SbF_6^-)$

^{a} n.o. = not observed.

Table II. Teller–Redlich Product Rule of H_2SF^+ and D_2SF^+

	A′ $32_S/34_S$	A″ $32_S/34_S$
theoretically calcd	2.5948	1.8807
from force field calculations	2.6200/2.6280	1.9005/1.9032
experimental	2.8736/2.8729	1.9397/1.9468

Table III. Force Constants of H_2SF^+ ^{a}

		ab initio	diagonal iteration of H/D	diagonal iteration of H freqs only	free iteration of H/D
A′	*F*11	6.449	5.307	5.376	5.333
	*F*22	4.502	3.420	3.458	3.422
	*F*33	1.252	1.002	1.029	1.008
	*F*44	0.961	0.714	0.725	0.717
	*F*12	−0.013	−0.013	−0.013	0.051
	*F*13	0.451	0.451	0.451	0.516
	*F*14	−0.036	−0.036	−0.036	−0.058
	*F*23	0.021	0.021	0.021	0.083
	*F*24	0.095	0.095	0.095	0.174
	*F*34	0.079	0.079	0.079	0.069
A″	*F*55	4.478	3.508	3.583	3.516
	*F*66	1.148	0.972	0.966	0.948
	*F*56	−0.056	−0.056	−0.056	0.044

^{a} Stretching force constants in N cm^{-1}. Deformation constants in a J. Stretch–bend interaction force constants in 10 mN.

Table IV. Calculated Frequencies (cm^{-1}) of $X_2{}^nSF^+SbF_6^-$ (X = H, D; *n* = 32, 34)

		ab initio	diagonal iteration of H/D	diagonal iteration of H freqs only	free iteration of H/D	exptl freqs
				A′		
$H_2{}^{32}SF^+$	1	2792	2433	2477	2434	2500
	2	1364	1171	1181	1173	1181
	3	1121	1006	1019	1009	1020
	4	945	851	857	845	853
$H_2{}^{34}SF^+$	1	2790	2431	2445	2432	2497
	2	1363	1170	1180	1172	1180
	3	1120	1005	1017	1007	1015
	4	935	841	848	835	850
$D_2{}^{32}SF^+$	1	2002	1744	1754	1743	1745
	2	978	853	859	858	844
	3	935	840	847	837	728
	4	833	745	755	742	826
$D_2{}^{34}SF^+$	1	1999	1741	1751	1740	1742
	2	977	845	851	853	844
	3	935	838	845	833	726
	4	831	742	752	739	821
				A″		
$H_2{}^{32}SF^+$	5	2755	2474	2500	2474	2447
	6	1076	980	987	979	987
$H_2{}^{34}SF^+$	5	2792	2471	2497	2472	2445
	6	1075	989	986	978	986
$D_2{}^{32}SF^+$	5	2011	1780	1799	1799	1725
	6	787	724	722	716	n.o.
$D_2{}^{34}SF^+$	5	2007	1776	1795	1776	1724
	6	786	723	721	715	705

Table V. Stretching Force Constants of SH and SF Compounds (N cm^{-1})

	f_{SH}	f_{SF}
H_2SF^+	3.52	5.38
SH_3^+ [28]	3.70	
H_2S [29]	3.95	
H_2S_2 [30]	4.07	
SF_3^+ [31]		5.67
SF_4 [32]		5.36/3.25
OSF_2 [33]		4.07
SSF_2 [34]		3.46

give a larger frequency shift than expected and predicted by the Teller–Redlich rule. This explanation is further corroborated by the low-frequency values of the SH/SD stretchings, which are normally found above 2500 and 1780 cm^{-1}, respectively.

Though the postulated hydrogen bridges will cause perturbations, which have to be considered in the analysis of the results, force constant calculations were performed for the isolated cation H_2SF^+. An ab initio force field was calculated by the force method,[23,24] using a 432-1G basis with an additional d function (exponent 0.8) for the sulfur atom.[25] The geometric data obtained for minimal energy of H_2SF^+ (r_{SH} = 134.0 pm, r_{SF} = 157.1 pm, ∠SH_2 = 95.1°, ∠HSF = 99°) agree well with previously published values.[26] Calculated force constants are reported in Table III, and the corresponding frequencies, in Table IV.

As usual, the ab initio force constant matrix was fitted to the observed frequencies by a diagonal iteration. For the reasons discussed above, a good fit could not be achieved. Even an iteration of the whole force field including all coupling terms did not improve the frequency fit, and all diagonal terms of the force constant matrix remained almost unchanged. Of course, the calculated frequencies match the Teller–Redlich rule (see Table II). Thus, the calculations confirm the too large H/D shifts measured and the explanation given for this observation. As for the H compound, the hydrogen bridges are weaker, and we iterated the force field using only the hydrogen frequencies, to keep the bridging effect as small as possible. But even this calculation gave only a maximum increase for the diagonal force constants of less than 2%. Thus, one may consider these values as quite reliable, though the SH stretching constant should be lower than for an isolated H_2SF^+ ion.

Comparing the H_2SF^+ stretching force constants with those of similar molecules (Table V), f_{SH} in H_2SF^+ is lower than those in uncharged sulfanes and even lower than that found for SH_3^+. This might be due to changes in the bond polarities. Thus, going from the sulfanes to the sulfonium cations, an increase of the bond polarity $S^{\delta-}$–$H^{\delta+}$ can be assumed, which results in a lower

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stretching force constant. This effect may override the strengthening of the bonds, which is normally observed if the oxidation state of the central atom is increased (e.g. for the phosphonium ions compared with the phosphanes[27]). However, there might also be a contribution of the hydrogen bridges to this lowering of force constants indicated by the spectroscopic findings for the sulfonium cations.

The effect of the positive charge is reverse for the $S^{\delta+}–F^{\delta-}$ bonds, which become less polar. Thus, the SF stretching force constants for the fluorosulfonium cations are considerably higher than those of uncharged $S^{IV}F$ compounds. The lower value found for H_2SF^+ relative to SF_3^+ is due to the well-known effect of substituting F ligands by the less electronegative H.[27]

NMR Spectra. In the ^{19}F-NMR spectrum of $H_2SF^+SbF_6^-$, besides the resonance for the anion ($\delta(SbF_6^-) = -110.9$ ppm),[35] one additional unsplit signal ($\delta(SF) = -169.9$ ppm) is observed for the cation fitting well into the series of $(CH_3)_nSH_{2-n}F^+$ cations ($n = 1, 2$) (Table VI). The expected downfield shift of the SF resonances with increasing substitution of the methyl groups by the H atoms is caused by the decreasing electron density at the observed F atom. The smaller screening effect of the nuclei is in good correlation with the decrease of the diagmagnetic part of the chemical shift.

Table VI. NMR Data (ppm) for $(CH_3)_nS(H_{2-n})F^+$ Salts ($n = 1, 2$)

	H_2SF^+	$CH_3S(H)F^+$ [9]	$(CH_3)_2SF^+$ [19]
^{19}F	−169.9	−177.0	−190.7
^{1}H	4.59	4.27	
^2J(HF)	15 Hz		

In the ^{1}H-NMR spectrum of $H_2SF^+SbF_6^-$ the signal of the cation at ($\delta(SH) = 4.59$ ppm) is split into a doublet with $^2J(HF) = 15$ Hz. Also in this case a downfield shift can be observed relative to the methylated and trifluormethylated sulfonium salts.

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