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Novel Onium Salts. Synthesis and Characterization of $SH_3^+SbF_6^-$

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The synthesis and properties of $SH_3^+SbF_6^-$, the first known example of a stable salt containing the sulfonium cation, are reported. The SH_3^+ cation was characterized by vibrational spectroscopy and a normal-coordinate analysis was carried out. Attempts to prepare $SH_3^+AsF_6^-$ resulted in the formation of As_2S_5. Protonation of HCl in HF–SbF_5 solution yields an unstable white solid, but no evidence was obtained for adduct formation in the HF–SbF_5–Xe system at temperatures as low as −78°.

Introduction

Recent studies[1] in our laboratory showed that the protonation of H_2O in HF–MF_5 (M = Sb and As) solutions produces the surprisingly stable oxonium salts $OH_3^+MF_6^-$. This prompted us to investigate the synthesis of other onium salts. In this paper we report on the protonation of H_2S, HCl, and Xe. Results on the protonation of HNF_2 and NF_3 will be given elsewhere.[2]

Whereas a huge number of alkyl- or aryl-substituted sulfonium salts are known, we could not find any literature reports on the isolation of a salt containing the SH_3^+ cation, although Olah and coworkers had observed[3] the SH_3^+ cation at low temperature in HSO_3F–SbF_5–SO_2 solution by proton NMR spectroscopy (singlet at δ −6.60). In addition, the formation of gaseous SH_3^+ was studied[5-7] in mass spectrometers (ion–molecule and electron-impact studies). Similarly, the protonation of HCl has been studied only in HSO_3F–SbF_5 solution at low temperature by NMR spectroscopy, but no direct evidence for the formation of a ClH_2^+ cation was reported.[8] For xenon, protonation in HF–SbF_5 solution was postulated[9] based on its ability to suppress isotopic hydrogen–deuterium exchange; protonation in ion–molecule reactions has been also reported.[10,11]

Experimental Section

The experimental techniques used in this study were essentially the same as those previously described.[1]

Preparation of $SH_3^+SbF_6^-$. In a typical experiment, SbF_5 (5.38 mmol) and anhydrous HF (10 ml of liquid) were combined at −196° in a Teflon–FEP ampoule. The mixture was warmed to 25° to give a homogenous solution. Hydrogen sulfide (7.10 mmol) was added to the ampoule at −196°. The mixture was warmed first to −78° and then slowly to 25°. During warmup was formed a white solid, which was only partially soluble in the excess of HF. Volatile products were removed at 25° in vacuo, leaving behind 1.452 g of a white, stable solid (weight calcd for 5.38 mmol of $SH_3^+SbF_6^-$ 1.457 g). Anal. Calcd for SH_3SbF_6: Sb, 44.95; S, 11.84. Found: Sb, 44.8; S, 11.9. The $SH_3^+SbF_6^-$ product can be stored at 25° without noticeable decomposition in Teflon or Kel-F containers, but it attacks quartz.

The HF–AsF_5–H_2S System. Anhydrous HF (10 ml of liquid) and AsF_5 (3.54 mmol) were combined at −196° in a Teflon–FEP ampoule. The mixture was warmed to 25° and then recooled to −196°. Hydrogen sulfide (3.54 mmol) was added to the ampoule at −196°. During slow warmup of the mixture to 0° a white to yellow solid formed. The ampoule was recooled to −78° and volatile material was pumped off during warmup to 25° leaving behind 221 mg of a stable yellow solid (weight calcd for 0.708 mmol of As_2S_5 220 mg). Vibrational spectroscopy showed that the solid did not contain bands characteristic for either SH_3^+ (see below) or AsF_6^-. It was insoluble in water but slowly dissolved in boiling concentrated HNO_3. Anal. Calcd for As_2S_5: As, 48.3; S, 51.7. Found: As, 48.5; S, 51.6.

The HF–SbF_5–HCl System. To a homogenized mixture (see above) of SbF_5 (2.57 mmol) and anhydrous HF (5 ml of liquid) in a Teflon–FEP ampoule, HCl (6.81 mmol) was added at −196°. The mixture was warmed to −78° and then cycled several times between −78 and 0°. A white solid was formed upon melting of the starting materials. Volatile material was pumped off at −45°, resulting in 711 mg of an unstable, white solid melting below room temperature to a pale yellow, clear liquid (weight calcd for 2.57 mmol $ClH_2^+SbF_6^-$ 702 mg). The vapor phase above the liquid at 26° was shown by infrared spectroscopy to consist essentially of HF and HCl. The Raman spectrum of the HF solution showed the bands characteristic of SbF_6^- (see below).

The HF–SbF_5–Xe System. To a homogenized (see above) mixture of SbF_5 (3.07 mmol) and anhydrous HF (10 ml of liquid) in a Teflon–FEP ampoule, Xe (7.04 mmol) was added at −196°. The mixture was slowly warmed to 0° and then kept at −78° for 16 hr. No evidence for adduct formation between Xe and HF–SbF_5 at −78° was detected, and the xenon starting material was quantitatively

Table I. X-Ray Powder Data for $H_3S^+SbF_6^-$ [a]

d_{obsd}, Å	d_{calcd}, Å	Intens	*hkl*
5.96	5.94	vw	200
5.26	5.26	vs	002
3.94	3.94	vs	202, 300
3.56	3.54	vs	311
3.16	3.16	m	302
2.619	2.623	mw	303, 004
2.456	2.471	w	332
2.257	2.265	m	403
2.176	2.165	ms	502
2.069	2.068	w	105
1.963	1.966	w	503, 404
1.839	1.833	w	315
1.769	1.771	w	630
1.750	1.750	w	006
1.720		w	
1.616		mw	
1.572		w	
1.535		w	
1.484		mw	
1.461		mw	
1.401		w	
1.308		w	
1.251		w	
1.239		w	
1.212		w	

[a] Tetragonal, $a = 11.89$ Å, $c = 10.51$ Å, $V = 1484.0$ Å^3, $Z = 8$, $\rho_{calcd} = 2.43$ g cm^{-3}, Cu K$_\alpha$ radiation, and Ni filter.

recovered from the reaction mixture at −78°.

Results and Discussion

Synthesis and Properties of SH_3^+ Salts. Protonation of H_2S in HF–SbF_5 solution produced the white, stable solid $SH_3^+SbF_6^-$ in quantitative yield according to

$$H_2S + HF + SbF_5 \rightarrow SH_3^+SbF_6^-$$

To our knowledge this is the first reported example of a stable salt containing the sulfonium cation.

According to the DSC data, $SH_3^+SbF_6^-$ starts to decompose at 90° with the onset of an exotherm which rapidly changes into a large endotherm. The salt is moderately soluble in anhydrous HF. Attempts were unsuccessful to dissolve it in organic solvents, such as $CH_3SO_2CH_3$, which were found[1] suitable for $OH_3^+SbF_6^-$. When the solvent was added, gas evolution and the formation of a cinnabar solid (probably Sb_2S_5) and a yellow solution were observed. Attempts to dissolve the sulfonium salt in SbF_5 caused oxidation of SH_3^+ as indicated by gas evolution and the appearance of a strong blue color, similar to that previously reported[12] for polysulfur radical cations. When exposed to atmospheric moisture, the solid turns yellow first and then cinnabar accompanied by the evolution of H_2S. Obviously, H_2S is displaced from its salt by the more basic water. This displacement reaction might be used as a convenient way to generate gaseous H_2S from the storable solid $SH_3^+SbF_6^-$ by the simple addition of water. Vibrational spectroscopy (see below) showed that some samples contained some sulfur in the form of S_8, as was also indicated by their faint yellow color.

The X-ray powder pattern of $SH_3^+SbF_6^-$ is listed in Table I. The tetragonal unit cell with a = 11.89 Å, c = 10.51 Å, and Z = 8 is in good agreement with those found for $OH_3^+SbF_6^-$ and the related $M^+XF_6^-$ salts.[13-15] As expected, $SH_3^+SbF_6^-$ has a larger unit cell and a lower density than $OH_3^+SbF_6^-$ owing to SH_3^+ having a significantly larger radius than OH_3^+.

Attempts to synthesize $SH_3^+AsF_6^-$ from the HF–AsF_5–H_2S system were unsuccessful and resulted in the quantitative conversion of AsF_5 to As_2S_5 according to

$$2AsF_5 + 5H_2S \rightarrow As_2S_5\downarrow + 10HF$$

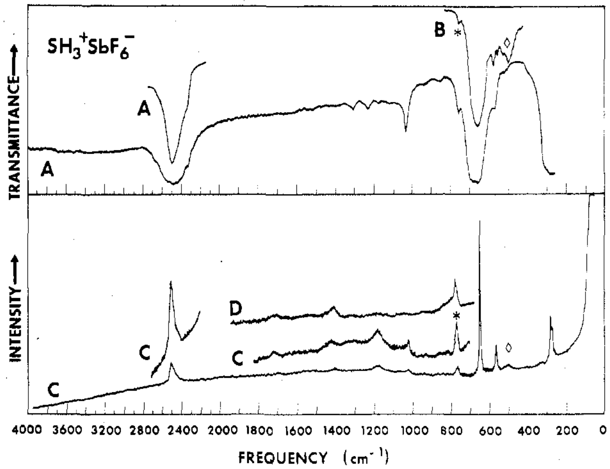

Figure 1. Vibrational spectrum of $SH_3^+SbF_6^-$. For clarity, bands due to sulfur (S_8) were deleted: trace A, infrared spectra of the solid as dry powders between AgBr disks at two different concentrations; part of the intensity of the 270-cm^{-1} band is due to absorption by the thin AgBr windows; trace B, spectrum of a different sample shown to demonstrate the variable relative intensities of the impurity bands marked by an asterisk and a diamond (see text); trace C, Raman spectra of solid $SH_3^+SbF_6^-$ recorded at two different recorder voltages and spectral slit widths of 4 (lower) and 8 cm^{-1} (upper traces); sample container was a quartz tube; trace D, background spectrum recorded after complete decomposition of $SH_3^+SbF_6^-$ had occurred.

This difference in behavior between SbF_5 and AsF_5 is not surprising since it is well known[16] that in the presence of fluoride ions H_2S will precipitate only arsenate, but not antimonate, as the corresponding pentasulfide.

Protonation of HCl and Xe. Since the protonation of H_2O and of the more acidic H_2S had resulted in the formation of novel stable MF_6^- salts, we decided to examine the protonation of the even more acidic species HCl and of Xe. For both, previous studies[8,9] had indicated protonation in solution.

The protonation of HCl in HF–SbF_5 solution produced a white solid product stable at −45° but melting below room temperature with decomposition. From the observed material balance, the composition of the adduct was found to be approximately 1:1:1 and the more volatile decomposition products were shown to be HCl and HF. By analogy with the OH_3^+ and SH_3^+ salts and on the basis of the Raman spectrum of an HF solution showing the presence of SbF_6^-, this adduct is likely to be $ClH_2^+SbF_6^-$. For xenon, no evidence for the formation of a stable adduct was found at temperatures as low as −78°. Our studies indicate that compounds more basic than HCl stand a good chance of forming a reasonably stable protonated SbF_6^- salt. NMR evidence for the existence of such protonated species in superacid solutions at low temperature has already been reported[17] for several species, and the isolation of these and other novel simple protonated cations in form of their stable MF_6^- salts can be predicted. Obviously, the parent species are not limited to nonmetal hydrides but can include many other moieties.

Vibrational Spectrum of $SH_3^+SbF_6^-$. Since $SH_3^+SbF_6^-$ decomposes in organic solvents, such as $CH_3SO_2CH_3$, and its proton NMR spectrum in HSO_3F–SbF_5–SO_2 solution (singlet at δ 6.60)[3] yields little structural information, we have used vibrational spectroscopy to characterize the SH_3^+ cation. The vibrational spectrum of solid $SH_3^+SbF_6^-$ is shown in Figure 1. Attempts to record the Raman spectrum of an HF solution were unsuccessful owing to the moderate solubility of the salt in HF. When exposed to the blue 4880-Å line of an Ar ion laser, the sample tended to decompose rapidly even at −120°. However, this problem could be overcome by defocusing the laser beam. In general, the Raman spectra showed bands[18,19]

Table II. Vibrational Spectrum of $SH_3^+SbF_6^-$ and Its Assignment Compared to That of PH_3[a]

	Obsd freq, cm^{-1}, and rel intens[b]		Assignment (point group)	
	$SH_3^+SbF_6^-$ solid			
PH_3	Ir	Raman	XH_3 (C_{3v})	SbF_6^- (O_h)
2328		2520 (1.3)	ν_3(E)	
	2520 vs			
2323		2490 sh	$\nu_1(A_1)$	
	2360 sh		$2\nu_4(A_1 + E + F_2)$	
	1308 w			$\nu_1 + \nu_3(F_{1u})$
	1222 w			$\nu_1 + \nu_2(E_g)$
1122	1180 vw	1180 (0.4)	ν_4(E)	
992	1028 mw	1025 (0.3)	$\nu_2(A_1)$	
	848 vw			$\nu_1 + \nu_6(F_{2u})$
	660 vs			$\nu_3(F_{1u})$
		650 (10)		$\nu_1(A_{1g})$
	569 m	556 (1.6)		$\nu_2(E_g)$
		282 (2.8)		$\nu_5(F_{2g})$
		275 sh		
	270 s			$\nu_4(F_{1u})$

[a] Reference 23. [b] Uncorrected Raman intensities; bands due to decomposition products have not been listed.

due to varying amounts of sulfur (S_8) as was also indicated by the yellowish color of these samples. In addition, the spectra showed a band at 760 cm^{-1} (marked in Figure 1 by an asterisk) which based on literature data[18,19] does not belong to S_8. Decomposition studies showed that, contrary to the $SH_3^+SbF_6^-$ bands, this band was stable toward decomposition in the focused laser beam and, therefore, cannot belong to $SH_3^+SbF_6^-$ (see trace D, Figure 1). The Raman spectrum contains also a weak band at about 500 cm^{-1} (marked by a diamond) which is definitely due to a decomposition product. This band becomes the most intense band in the spectrum, when most of the $SH_3^+SbF_6^-$ has decomposed. The remainder of the spectrum (see Table II) is in excellent agreement with our expectations for ionic $SH_3^+SbF_6^-$ and is discussed below.

The general appearance of the vibrational spectrum of $SH_3^+SbF_6^-$ (see Figure 1) strongly deviates from that[1] of $OH_3^+SbF_6^-$ recorded at room temperature. Contrary to $OH_3^+SbF_6^-$, the bands due to $SH_3^+SbF_6^-$ are sharp and narrow and show little or no splittings indicating for SbF_6^- and SH_3^+ no appreciable deviation from symmetry O_h and C_{3v}, respectively. In particular, the Raman bands due to SbF_6^- are very narrow and exhibit the frequencies and relative intensities expected[20-22] for octahedral SbF_6^-. This indicates that, contrary to $OH_3^+SbF_6^-$, either the cation–anion coupling in $SH_3^+SbF_6^-$ is relatively weak or the crystal lattice becomes rigid at a higher temperature. Since $OH_3^+SbF_6^-$ and $SH_3^+SbF_6^-$ have similar tetragonal unit cells with $Z = 8$ (see above), it is unlikely that crystal effects are the main reason for this pronounced difference. A better explanation for the observed difference is the lower electronegativity of sulfur when compared to oxygen. This should markedly decrease the polarity of the X–H bond and thereby decrease the positive charge on the hydrogen ligands. This in turn should result in a much weaker coulombic interaction between the positively polarized hydrogen ligands of the cation and the negatively polarized fluorine ligands of the anion, hence substantially reducing the cation–anion coupling.

The assignments for the SH_3^+ cation in point group C_{3v} were made by comparison with those[23] of isoelectronic PH_3 (see Table II). Pyramidal XY_3 of symmetry C_{3v} has four fundamentals which are classified as 2 A_1 + 2 E, all being active in both the infrared and the Raman spectra. Of these, each symmetry species contains one stretching and one bending mode. By comparison with PH_3, the two stretching modes of SH_3^+ are expected to have very similar frequencies and, indeed, only one intensive band is observed in the S–H stretching region at 2520 cm^{-1}. Since the symmetric SH_3 stretch should be of much higher Raman intensity than the antisymmetric one, the maximum of the Raman band at 2520 cm^{-1} must be due to $\nu_1(A_1)$. This band shows a shoulder at 2490 cm^{-1}, which might represent the antisymmetric stretch ν_3(E). However, we prefer to assume a complete coincidence of ν_1 and ν_3, since ν_3 should be more intense in the infrared spectrum[24] and the infrared band has its maximum at about 2520 cm^{-1}. The weak shoulder observed at 2360 cm^{-1} in the infrared spectrum is due to the overtone $2\nu_4(A_1 + E + F_2)$ in Fermi resonance with ν_1 and ν_3.

Of the two deformation modes of SH_3^+, one obviously is represented by the 1028-cm^{-1} infrared band. For the other deformation, we had originally considered the 760-cm^{-1} infrared band. However, a normal-coordinate analysis, carried out with this assignment, resulted in unreasonable force constants. Whereas the stretching force constant in SH_3^+ was larger than in PH_3, the deformation constant was significantly lower. This is not plausible since any H···F bridging possible in such a solid should decrease the value of the stretching and increase the value of the deformation force constant. A careful reexamination of the spectra established that the 760-cm^{-1} band is not part of the $SH_3^+SbF_6^-$ spectrum and that the Raman spectrum exhibits a band of moderate intensity at 1180 cm^{-1}, a frequency value quite reasonable for the missing SH_3^+ deformation. The assignment of this band to ν_4(E) of SH_3^+ is further supported by the observation of its overtone in the infrared spectrum (see above) and the results from a normal-coordinate analysis (see below). Direct observation of ν_4 in the infrared spectrum is complicated by its relatively low infrared intensity and interference by SbF_6^- combination bands. This leaves the 1028-cm^{-1} infrared band for assignment to $\nu_2(A_1)$, in excellent agreement with the frequencies[23] of PH_3.

Table III. Symmetry and Internal Force Constants[a] of SH_3^+ Compared to Those of Isoelectronic PH_3

	SH_3^+							PH_3[b]
Bond angle, deg	90	95	95	95	100	105	110	93
Force field	DFF	DFF	F_{22} and F_{44} = min	PH_3 TR	DFF	DFF	DFF	GVFF
A_1 $F_{11} = f_r + 2f_{rr}$	3.6535	3.6730	3.6764	3.6797	3.6930	3.7130	3.7320	3.1222
$F_{22} = f_\alpha + 2f_{\alpha\alpha}$	0.2958	0.3252	0.3252	0.3263	0.3705	0.4472	0.6030	0.2938
$F_{12} = 2f_{r\alpha} + f_{r\alpha}'$	0	0	0.0180	0.0784	0	0	0	0.0784
E $F_{33} = f_r - f_{rr}$	3.6543	3.6445	3.6467	3.6469	3.6350	3.625	3.6158	3.1087
$F_{44} = f_\alpha - f_{\alpha\alpha}$	0.4071	0.3872	0.3873	0.3874	0.3658	0.3426	0.3178	0.3548
$F_{34} = -f_{r\alpha} + f_{r\alpha}'$	0	0	−0.0140	−0.0392	0	0	0	−0.0392
f_r	3.6540	3.6540	3.6566	3.6578	3.6543	3.6543	3.6545	3.1132
f_{rr}	−0.0003	0.0095	0.0099	0.0109	0.0193	0.0293	0.0387	0.0045
f_α	0.3700	0.3665	0.3666	0.3670	0.3674	0.3775	0.4129	0.3345
$f_{\alpha\alpha}$	−0.0371	−0.0207	−0.0207	−0.0204	0.0016	0.0349	0.0951	−0.0203
$f_{r\alpha}$			0.0107	0.0392				0.0392
$f_{r\alpha}'$			−0.0033	0				0

[a] All force constants have units of mdyn/Å. Frequency values used: $\nu_1 = \nu_3 = 2520$, $\nu_2 = 1028$, and $\nu_4 = 1180$ cm^{-1}. [b] Values from ref 23.

Normal-Coordinate Analysis. To support the above assignments for SH_3^+, a normal-coordinate analysis was carried out, the results of which are given in Table III. Since the geometry of SH_3^+ is unknown, we have computed force fields for different bond angles ranging from 90 to 110° (the bond angle in isoelectronic PH_3 is 93.345°).[25] For the bond length in SH_3^+ an estimated value of 1.33 Å was used. The force constants were computed by trial and error with the help of a computer to obtain an exact fit between observed and calculated frequencies. Three different force fields were used to show that for a vibrationally weakly coupled (heavy central atom, light ligands) species, such as SH_3^+, the choice of a particular force field is less important than other variables, such as the bond angle. To demonstrate the small variation in the computed force fields, insignificant decimals are carried in Table III. Of the three different force fields used, the diagonal force field (DFF) and the force field requiring the deformation symmetry force constants to have minimal values were selected for their established[26] usefulness for vibrationally weakly coupled species. The third force field (PH_3,TR) was computed by using the general valence force field (GVFF) off-diagonal symmetry force constants of isoelectronic PH_3 for SH_3^+. As can be seen from Table III, all three force fields yield very similar force constants. Therefore, the given force fields are likely to be good approximations of a GVFF. By comparison with the known bond angles of H_2O, CH_3^+, NH_3, H_2S, and PH_3, a bond angle of about 95° appears to be most likely for SH_3^+, although the choice of the bond angle is not very critical as can be seen from the small variation of the force constants within the most probable bond angle range of 90–100°. As expected for a vibrationally weakly coupled species containing only one stretching and one deformation vibration of very different frequency in each symmetry block, the potential energy distribution showed all fundamentals to be highly characteristic. Thus, ν_1 and ν_3 were 100% pure stretching modes and ν_2 and ν_4 were 97–99% pure deformations. Comparison of the force constants of SH_3^+ with those[23] of PH_3 shows excellent agreement thus supporting the above given assignments for SH_3^+.

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Registry No. $SH_3^+SbF_6^-$, 55590-58-4; SbF_5, 7783-70-2; HF, 7664-39-3; hydrogen sulfide, 7783-06-4; $ClH_2^+SbF_6^-$, 55590-57-3.

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Hexafluoroiodine(VII) Hexafluoroantimonate(V) ($IF_6^+SbF_6^-$)[1]

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The 1:1 complex of iodine heptafluoride and antimony pentafluoride has been prepared and has been shown to have the ionic structure $IF_6^+SbF_6^-$ by Raman and infrared spectral analysis. The X-ray powder pattern has been indexed for a cubic unit cell with $a_0 = 6.069$ Å. The complex reacts rapidly with radon gas at ambient temperature, forming a nonvolatile radon compound; hence it can be used for purification of radon-contaminated air and for analysis of radon in air. In reactions with carbon monoxide, sulfur dioxide, nitric oxide, and nitrogen dioxide, it forms COF_2, SO_2F_2, $NO^+SbF_6^-$, and $NO_2^+SbF_6^-$, respectively.

Introduction

Solid oxidants have been shown to be useful for collecting radioactive noble gases, such as ^{222}Rn and ^{133}Xe.[3–5] Among the compounds that have been used for this purpose are halogen fluoride–metal fluoride complexes, such as $ClF_2^+SbF_6^-$, $BrF_2^+BiF_6^-$, and $BrF_4^+Sb_2F_{11}^-$, the fluoronitrogen salts $N_2F^+SbF_6^-$ and $N_2F_3^+Sb_2F_{11}^-$, and the dioxygenyl salt $O_2^+SbF_6^-$. The dioxygenyl salt is the most suitable oxidant for collecting ^{222}Rn in uranium mines, since it has negligible dissociation pressure at ambient temperature and releases oxygen as the gaseous reduction product. Reactions of this salt with radon and components of diesel exhausts (CO, CO_2, CH_4, SO_2, NO, and NO_2) have therefore been studied in some detail.[4,6] In this article, we report some properties of a new oxidant, $IF_6^+SbF_6^-$, which may also be suitable for applications in mines.

Seel and Detmer[7,8] have previously reported that two complexes are formed in the IF_7–SbF_5 system, one containing iodine and antimony in the ratio 1:3 and the other containing a higher proportion of iodine. The first complex was postulated to have the ionic structure $IF_4^{3+}(SbF_6^-)_3$; the second complex was postulated to be $IF_7 \cdot SbF_5$, although the solid actually