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Novel Onium Salts. Synthesis and Characterization of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$

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The novel oxonium salts $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ were isolated as well-defined crystalline solids from the H_2O–HF–SbF_5 and the H_2O–HF–AsF_5 system, respectively. These salts are the most stable oxonium salts presently known. It was shown by DSC studies that $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ decompose at about 357 and 193°, respectively. Their ionic nature in both the solid state and polar solvents was established by vibrational and ^{19}F and ^1H NMR spectroscopy. The infrared spectra of these adducts closely resemble those recently attributed to H_2F^+ salts, suggesting that the latter may have been incorrectly identified. Furthermore, the frequencies of the OH_3^+ fundamentals in these salts are very similar to those of isoelectronic NH_3, but significantly different from those previously observed for OH_3^+ in mineral acid monohydrates. This indicates that in the MF_6^- salts the hydrogen bridges are considerably weaker, although similar phenomena are observed for the low-temperature spectra suggesting rigidity of the lattice at low temperature. The assignments for OH_3^+ were examined by force field computations. On the basis of its X-ray powder diffraction pattern, $OH_3^+AsF_6^-$ is cubic with $a = 8.015$ Å, $Z = 4$. From the H_2O–HF–BF_3 system a solid adduct was isolated at low temperature but was not further characterized owing to its thermal instability. A new method for drying HF based on oxonium salts is proposed.

Introduction

During a study of the controlled hydrolysis of $BrF_4^+Sb_2F_{11}^-$ in HF, a stable white solid was obtained in high yields. Elemental analysis of this solid showed that it did not contain detectable amounts of bromine. Its infrared spectrum closely resembled that recently reported[1] by Couzi et al. for H_2F^+. However, attempts to prepare a stable product from HF and SbF_5 alone failed. This agrees with a DTA study[2] of the HF–SbF_5 system which showed no evidence for any high-melting adduct. Surprisingly, the addition of small amounts of water to HF–SbF_5 mixtures produced the same stable solid which, as shown in this paper, was identified as $OH_3^+SbF_6^-$.

A literature search did not reveal any reports on the isolation of $OH_3^+MF_6^-$ salts, in spite of many papers dealing with the relatively unstable mineral acid monohydrates and Commeyras and Olah's proton NMR (singlet at δ 10.25) evidence[3] for the existence of the oxonium ion in SbF_5–$HOSO_2F$ solution. Recently, Bonnet and coworkers studied[4] solutions of SbF_5 in H_2O and HF by DTA and identified the crystalline phases $SbF_5{\cdot}2H_2O$, $4SbF_5{\cdot}5H_2O$, $SbF_5{\cdot}H_2O$, $3SbF_5{\cdot}2H_2O$, and $SbF_5{\cdot}HF{\cdot}2H_2O$. Surprisingly, no evidence for $OH_3^+SbF_6^-$ was reported, although the infrared spectra attributed to $SbF_5{\cdot}H_2O$ and $4SbF_5{\cdot}5H_2O$ closely resemble those obtained by us for $OH_3^+SbF_6^-$.

The general interest in oxonium salts and superacid systems,[5,6] in which, unless rigorously dried, these salts are bound to be formed, prompted us to study these simple oxonium salts in more detail. Their unexpected high thermal stability also induced us to study the protonation of other compounds, such as H_2S, HCl, Xe, HNF_2, NF_3, etc. Details on novel salts containing the SH_3^+ and the $NH_2F_2^+$ cations will be reported elsewhere.[7]

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3 and HF) Monel Teflon–FEP vacuum system. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Hydrogen fluoride (The Matheson Co.) was first electrolytically dried[8] followed by treatment with either fluorine or SbF_5. In the latter case, the HF was added to a Teflon–FEP ampoule containing SbF_5. Any water present formed nonvolatile $OH_3^+SbF_6^-$ and the anhydrous HF was pumped off at −40°. Antimony pentafluoride and AsF_5 (Ozark Mahoning Co.) and BF_3 (The Matheson Co.) were purified by distillation and fractional condensation, respectively, prior to their use.

The infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer Model 457 infrared spectrophotometer. The spectra of gases were obtained using Monel cells of 5-cm path length fitted with AgCl windows. Spectra of dry powders at room temperature were recorded as pressed (Wilks minipellet press) disks between AgCl windows. Low-temperature spectra were obtained as dry powders between CsI plates using a technique similar to one previously reported.[9]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[10] for the elimination of plasma lines. Sealed quartz or Teflon–FEP tubes were used as sample containers in the transverse-viewing, transverse–excitation technique. The low-temperature spectra were recorded using a previously described[11] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[10]

Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.).

The ^{19}F and ^1H NMR spectra were recorded at 56.4 and 60 MHz, respectively, on a Varian Model DA60 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique relative to external $CFCl_3$ and TMS, respectively.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used for the determination of the thermal stability of the compounds. The samples were sealed in aluminum pans, and heating rates of 2.5 and 10°/min in N_2 were used.

The H_2O content in the OH_3^+ salts was determined by dissolving a known amount of sample in pyridine and titrating the evolved H_2O with Karl Fischer reagent using a Labindustries Aquametry apparatus. Antimony and arsenic were determined by X-ray fluorescence spectroscopy of basic aqueous solutions.

Preparation of $OH_3^+SbF_6^-$. In a typical experiment, SbF_5 (8.305 mmol) was placed in a Teflon–FEP ampoule and 8 ml of liquid anhydrous HF was added at −196°. The mixture was warmed to 25° to give a homogenous solution. Distilled water (8.30 mmol) was added to the ampoule at −196° and the mixture was warmed to 25°. Removal of all volatile material in vacuo at 25° resulted in 2.116 g of a white solid residue (weight calcd for 8.30 mmol of $OH_3^+SbF_6^-$ 2.115 g). Anal. Calcd for OH_3SbF_6: H_2O, 7.07; Sb, 47.8. Found: H_2O, 6.93; Sb, 48.0.

Preparation of $OH_3^+AsF_6^-$. In a typical experiment, H_2O (5.421 mmol) and anhydrous HF (8 ml of liquid) were combined at −196° in a Teflon–FEP ampoule, followed by warm-up to 25°. Arsenic pentafluoride (5.427 mmol) was added to this mixture at −196° and the contents of the ampoule were allowed to warm slowly to room temperature. Removal of volatile material at 25° in vacuo resulted in 1.128 g of a white solid residue (weight calcd for 5.421 mmol of $OH_3^+AsF_6^-$ 1.127 g). Anal. Calcd for OH_3AsF_6: H_2O, 8.66; As, 36.0. Found: H_2O, 8.26; As, 35.7.

The H_2O–HF–BF_3 System. To a mixture of H_2O (3.66 mmol) and anhydrous HF (10 ml of liquid), prepared as described above, BF_3 (7.4 mmol) was added at −196°. This mixture was kept at −78° for 10 min and then slowly warmed until a clear solution resulted. Removal of volatile material at −70° in vacuo produced a white solid residue melting at around 0° to a colorless liquid having a dissociation pressure of about 4 mm at 22°. The weight of the adduct, after being pumped on at 0° for several minutes, was 376 mg (calcd for 3.66 mmol OH_3BF_4 387 mg).

Results and Discussion

Syntheses. Addition of water to mixtures of HF with the strong Lewis acids SbF_5 and AsF_5 produces stable 1:1:1 adducts in quantitative yield according to

$$HF + H_2O + MF_5 \xrightarrow{HF} H_3O^+MF_6^-$$

The formation of these adducts is not surprising in view of the previous evidence[12-14] showing that in HF solution the following equilibrium exists

$$SbF_5 + 2HF \rightleftarrows H_2F^+SbF_6^-$$

and that the stronger base H_2O can displace[3,15] H_2F^+ with formation of the OH_3^+ cation

$$H_2F^+ + SbF_6^- + H_2O \rightarrow OH_3^+ + SbF_6^- + HF$$

However, in view of the several hundred recent publications dealing with superacid chemistry, the well-known difficulties in obtaining completely anhydrous systems, and the general interest in oxonium salts, we were extremely surprised to find that these stable adducts had not previously been isolated.

It appears that the low-temperature infrared spectra of these adducts have been observed[1] previously by Couzi and coworkers in the course of their study of the binary HF–Lewis acid systems but were mistaken for H_2F^+ salts. Although not impossible, it is highly unlikely that OH_3^+ and H_2F^+ would show such similar vibrational spectra. Furthermore, comparison of the observed frequencies and computed force constants of "H_2F^+" with those of isoelectronic H_2O show poor agreement (H_2O, $f_r = 8.45$, $f_\alpha = 0.76$; "H_2F^+", $f_r = 5.71$, $f_\alpha = 1.36$ mdyn/Å).[1]

The failure of Bonnet et al. to isolate $OH_3^+SbF_6^-$ from the SbF_5–H_2O–HF system[4] may be explained by their unfortunate choice of reaction conditions. They combined H_2O with SbF_5 in the absence of a solvent. This can result in partial hydrolysis of SbF_5 with HF formation, thus making it very difficult to obtain well-defined products.

We have established the 1:1:1 composition of the $HF \cdot H_2O \cdot SbF_5$ and the $HF \cdot H_2O \cdot AsF_5$ adducts by the observed material balances, elemental analyses, and vibrational and NMR spectroscopy. With the weaker Lewis acid BF_3, an unstable 1:1:1 adduct is formed at lower temperature. It melts at about 0° to a colorless liquid having a dissociation pressure of about 4 mm at 22°.

The quantitative formation of a stable nonvolatile OH_3^+ salt is an effective way to remove small amounts of water from HF by treating it with a strong Lewis acid. Bismuth pentafluoride, although not used in this study, should be the most convenient drying reagent, since it is nonvolatile at room temperature. Thus, its use would permit the removal of the dry HF from $OH_3^+BiF_6^-$ and the excess of BiF_5 at ambient temperature. This method appears more convenient than previously reported methods, such as pyrolysis of dried $NaHF_2$,[16] electrolytic drying,[8] or fluorine treatment.[17] Furthermore, the stable solid $OH_3^+MF_6^-$ salts could find applications in systems requiring catalytic amounts of strong acids. Owing to their physical properties (see below), these solids should be easier to store, ship, and handle then highly corrosive liquids.

Properties. The $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ salts are white crystalline solids. They are highly soluble in HF and moderately soluble in polar solvents, such as $CH_3SO_2CH_3$. With stronger bases such as pyridine or acetonitrile, water is evolved and the nitrogen atom is protonated. The quantitative displacement of OH_3^+ by pyridine was successfully used for the determination of the H_2O content with Karl Fischer reagent. Evidence for the protonation of acetonitrile was obtained by proton NMR spectroscopy (see below). The oxonium ion is surprisingly inactive as a hydrolyzing agent. In addition to its compatibility with the SbF_6^- and AsF_6^- ions in HF solution, it does not cause BrF_5, BrF_4^+ salts,[7] and NF_4^+ salts[18] to hydrolyze to a significant extent.

Table I. X-Ray Powder Data for $OH_3^+AsF_6^-$ [a]

d_{obsd}, Å	d_{calcd}, Å	Intens	h	k	l
4.64	4.62	vs	1	1	1
4.01	4.00	vs	2	0	0
2.82	2.83	s	2	2	0
2.420	2.414	w	3	1	1
2.315	2.312	w	2	2	2
1.999	2.002	w	4	0	0
1.833	1.837	w	3	3	1
1.785	1.791	mw	4	2	0
1.636	1.634	m	4	2	2
1.542	1.541	mw	5 3	1 3	1 3
1.414	1.416	vw	4	4	0
1.355	1.353	w	5	3	1
1.336	1.335	w	6 4	0 4	0 2
1.267	1.266	vw	6	2	0

[a] Cubic, $a = 8.015$ Å, $V = 514.9$ Å^3, $Z = 4$, $\rho_{calcd} = 2.890$ g cm^{-3}, Cu Kα radiation, and Ni filter.

The thermal stability of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ was determined by DSC. The SbF_6^- salt exhibited reversible endotherms at 89 and 209° (probably phase changes), followed by some small irreproducible endotherms from about 230 to 357° and a large irreversible endotherm at 357°. The occurrence of complete decomposition at 357° was also confirmed by the observation of white fumes escaping from the sample cup at this temperature. Heating the salt to 150° under a static vacuum resulted in the buildup of only a little pressure over a period of several hours. The $OH_3^+AsF_6^-$ salt exhibited no endo- or exotherms prior to the onset of its strongly endothermic decomposition at 193° indicating the absence of any phase change between 25 and 193°.

The thermal stability of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ is unusually high, when compared to the previously reported OH_3^+ salts. Most of these salts are stable only at low temperature, and the more stable $OH_3^+CF_3SO_3^-$, $OH_3^+ClO_4^-$, and $OH_3^+CH_3C_6H_4SO_3^-$ melt at 35, 50, and 105°, respectively.[19-21]

X-Ray Powder Diffraction Data. The powder diffraction patterns of $OH_3^+AsF_6^-$ and $OH_3^+SbF_6^-$ are listed in Tables I and II, respectively. The $OH_3^+AsF_6^-$ salt is cubic with $a = 8.015$ Å and $Z = 4$. As previously pointed out,[22] it is very difficult to distinguish from the powder pattern alone for this type of compound whether it has the face-centered cubic $NaSbF_6$ or the primitive cubic $CsPF_6$ structure. The intensities observed for $OH_3^+AsF_6^-$ seem to agree somewhat better with the primitive cubic $CsPF_6$ type. Since the size of the OH_3^+ cation[23] is roughly comparable to that of K^+, Ag^+, or NH_4^+, it is not surprising that $OH_3^+AsF_6^-$ should be isotypic with $Ag^+AsF_6^-$ ($a = 7.74$ Å) and $NH_4^+PF_6^-$ ($a = 7.90$ Å).

The $OH_3^+SbF_6^-$ pattern was indexed for a tetragonal cell with $a = 11.48$ Å, $c = 8.78$ Å, and $Z = 8$. By comparison with the known[22,24] structures of similar MXF_6 compounds, it might be considered as a tetragonally distorted cubic $KSbF_6$ structure. Tetragonal unit cells with $Z = 8$ have previously been reported[25] for $KReF_6$, KWF_6, and $KMoF_6$, although their deviation from a cubic cell is much smaller. This might be explained by the fact that OH_3^+ is not spherical.[23] In addition to the cubic phase ($Z = 8$), a high-temperature tetragonal phase ($Z = 2$) has been reported[22,24] for $AgSbF_6$ and $KSbF_6$ containing one-fourth of the cubic superlattice.

In summary, the structures observed for the $OH_3^+MF_6^-$ salts agree well with those reported[22,24] for related MF_6^- salts. This comparison also suggests the possibility of different phases as was indicated for $OH_3^+SbF_6^-$ by the DSC data (see above).

Table II. X-Ray Powder Data for $OH_3^+SbF_6^-$ [a]

d_{obsd}, Å	d_{calcd}, Å	Intens	*h*	*k*	*l*
8.75	8.77	m	0	0	1
4.78	4.80	m	2	0	1
4.38	4.39	s	0	0	2
3.47	3.49	m	2	0	2
3.32	3.34	vs	2	1	2
2.868	2.869	mw	4	0	0
2.785	2.784	m	4	1	0
2.241	2.251	m	5	1	0
2.199	2.194	s	0	0	4
2.053	2.049	mw	4 2	0 0	3 4
2.021	2.017	m	2	1	4
1.901	1.903	mw	3	0	4
1.877	1.877	m	3	1	4
1.779	1.777	mw	6	2	1
1.760	1.756	m	5	4	1
1.680	1.679	mw	6	3	1
1.663		m			
1.595		mw			
1.578		m			
1.515		vw			
1.505		w			
1.401		mw			
1.392		m			
1.347		mw			
1.341		m			
1.258		mw			
1.220		m			
1.187		mw			
1.155		mw			
1.100		mw			
1.075		mw			
1.052		mw			
1.030		mw			
1.010		m			
0.990		m			
0.972		w			
0.963		vw			
0.937		m			
0.922		m			
0.9072		mw			
0.8925		m			
0.8793		m			
0.8663		m			
0.8538		m			
0.8365		vw			
0.8306		m			
0.8251		w			
0.8195		m			
0.8144		w			
0.8091		w			
0.8037		w			
0.7988		m			
0.7890		m			
0.7880		w			
0.7794		m			
0.7786		w			

[a] Tetragonal, $a = 11.48$ Å, $c = 8.78$ Å, $V = 1157.1$ Å^3, $Z = 8$, $\rho_{calcd} = 2.93$ g cm^{-3}, Cu Kα radiation, and Ni filter.

Contrary to $OH_3^+SbF_6^-$, cubic $OH_3^+AsF_6^-$ did not exhibit a phase change between room temperature and its decomposition point. This is not surprising since $OH_3^+AsF_6^-$ appears to be isotypic with KPF_6 which has a rhombohedral low-temperature and a cubic high-temperature phase.[26]

Nuclear Magnetic Resonance Spectra. The NMR spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ were recorded in $CD_3SO_2CD_3$, CH_3CN, and CD_3CN solutions. The ^{19}F NMR spectra of $OH_3^+AsF_6^-$ in $CD_3SO_2CD_3$ and CH_3CN solution showed a quartet of equal intensity at ϕ 60.9 and 65.4 with $J_{AsF} = 915$ and 930 Hz, respectively, in good agreement with the values previously reported,[27] for octahedral AsF_6^-. Similarly, the $OH_3^+SbF_6^-$ samples showed a sextet ($J_{^{121}SbF} = 1946$ Hz) and octet ($J_{^{123}SbF} = 1053$ Hz) of equal intensities at ϕ 120.1, characteristic[27,28] of octahedral SbF_6^-. In agreement with the vibrational spectra (see below), no evidence was found for the presence of $MF_5{\cdot}OH_2$[29] or $MF_5{\cdot}NCCH_3$[30,31] molecular adducts in these systems.

The proton NMR spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ in $CD_3SO_2CD_3$ solution showed only a singlet at δ −9.49 and −10.58, respectively. These values agree well with that of δ −10.2 previously attributed[3] to OH_3^+ in superacid solutions. In CH_3CN or CD_3CN solutions, however, the spectra were more complex. The strongest resonances for the SbF_6^- and AsF_6^- salts were observed at δ −10.92 and −11.34, respectively. In addition, a very broad resonance at δ −8.8 and a triplet of equal intensity ($J_{NH} = 53.5$ Hz) at δ −6.3 were observed. The latter is characteristic for NH_4^+.[32] The observation of NH_4^+ together with the fact that the proton resonance in CH_3CN solutions is significantly shifted to lower field, when compared to $CD_3SO_2CD_3$ solutions, indicate that this resonance is due to a $\equiv NH^+$ type species and not to OH_3^+. The CH_3 resonance consisted of a single peak at δ −2.21 indicating rapid exchange between CH_3CN and its protonated form. The ready protonation of CH_3CN in $HSO_3F-SbF_5-SO_2$ solution has previously been established.[33] The difference between the reported spectrum[33] and our spectrum can be explained by the fact that in one case small amounts of CH_3CN were dissolved in large amounts of acid, whereas in our case small amounts of $OH_3^+SbF_6^-$ were added to large amounts of CH_3CN. Since the NMR spectrum of OH_3^+ in superacids has previously been reported[3] and agrees with our data for the $CD_3SO_2CD_3$ solution, we have not studied superacid or HF solutions.

Vibrational Spectra. Figures 1 and 2 show the vibrational spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$, respectively. The observed frequencies are listed in Table III. Whereas no difficulty was encountered in obtaining reproducible infrared spectra of $OH_3^+SbF_6^-$ as a dry powder between AgCl disks at room temperature, for $OH_3^+AsF_6^-$ low-temperature conditions were required. At room temperature, the band centered at about 900 cm^{-1} would rapidly become broad and shift to higher frequency (~1020 cm^{-1}). Similarly, the broad band centered at about 3200 cm^{-1} became less symmetric with its maximum being shifted to ~3500 cm^{-1}, and the 1630-cm^{-1} band was shifted to about 1680 cm^{-1}. In the Raman spectra, except for that of $OH_3^+SbF_6^-$ in HF solution, the bands due to OH_3^+ were not observed owing to their very low intensity and broadness.

The anion bands, both in HF and $CD_3SO_2CD_3$ solution, were in excellent agreement with those previously observed for octahedral AsF_6^- [34-36] and SbF_6^-.[35-37] In the room-temperature spectra of the solids, $\nu_2(E_g)$ showed a splitting into two bands which is not uncommon for octahedral MF_6^- ions in solids.[35,37-40] For $OH_3^+SbF_6^-$, the intensities of the infrared bands at about 490 and 570 cm^{-1} varied from sample to sample (see traces A and B of Figure 1). Although one might be tempted to attribute the 490-cm^{-1} band to the presence of some $Sb_2F_{11}^-$ polyanion[35,41-43] or to an OH_3^+ libration mode (see below), we prefer to assign it to SbF_6^- for the following reasons. The $OH_3^+AsF_6^-$ spectra show similar bands and AsF_6^- is unlikely to form stable polyanions,[44] the observed material balances and elemental analyses gave no indication of polyanion formation, and an OH_3^+ libration should be of very low Raman intensity. Whereas in the room-temperature spectra of the solids, $\nu_3(F_{1u})$ and $\nu_1(A_{1g})$ appear as single bands, these bands become doublets in the low-temperature spectra. Furthermore, four relatively sharp bands were observed in the low-temperature infrared spectrum of $OH_3^+AsF_6^-$ (trace B, Figure 2) in the region of $\nu_2(E_g)$ of AsF_6^-.

The most plausible explanation for these additional low-

Table III. Vibrational Spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ and Their Assignments Compared to that of NH_3[a]

	Obsd freq, cm^{-1}, and rel intens[b]										Assignment (point group)	
	$OH_3^+SbF_6^-$					$OH_3^+AsF_6^-$						
		Raman						Raman				
		Solid		Soln		Ir, solid		Solid				
NH_3	Ir, solid, 25°	25°	−120°	$CD_3SO_2CD_3$	HF	25°	−196°	25°	−120°	$CD_3SO_2CD_3$ soln	XH_3 (C_{3v})	MF_6 (O_h)
					3300 (0.2) br, p	3600–2800 vs, vbr	3250 sh				$\nu_1(A_1)$, $\nu_3(E)$	
3336	3330 vs, br						3080 vs					
3444	3150 vs, br											
1626	1615 s				1630 (0.1) br, dp	1630 s, br	1615 s				$\nu_4(E)$	
950	900 s, br					800–1050 s, br	912 s				$\nu_2(A_1)$	
	670 vs, br		674 (10)			720 vs, br	715 vs		715 (10)			$\nu_3(F_{1u})$
		663 (10)						698 (10)				
			640 (5.3)	650 (10)	658 (10) p		676 s		677 (7.4)	680 (10)		$\nu_1(A_{1g})$
	588 sh	590 sh, br	590 (0.3)				586 s					
	(551)[c]	558 (0.8)	559 (1.2)					580 (1) br	566 (4.1)			
				568 (1)	568 (0.9) dp	550 s, br	560 s			573 (0.5)		$\nu_2(E_g)$
							511 s					
	(484)[c]	490 (0.6) br	498 (0.6)					500 (1) br	480 (1)			
		450 sh	450 (0+)									
							467 s					
						392 s, br	392 vs					
							371 w					$\nu_4(F_{1u})$
		287 s	288 (0.5)									
		280 (4.1)	280 (3.4)	274 (3)	273 (2.8) dp		367 w	378 (4)	369 (8)	368 (1.8)		$\nu_5(F_{2g})$
		265 sh	263 (0.4)				361 vw					
							255 s				Lattice vib or XH· · ·FM str	

[a] W. S. Benedict and E. K. Plyler, *Can. J. Phys.*, 35, 1235 (1957). [b] Uncorrected Raman intensities. [c] These infrared bands were of variable intensity from sample to sample (see traces A and B of Figure 1), but the relative intensities of their Raman counterparts were similar.

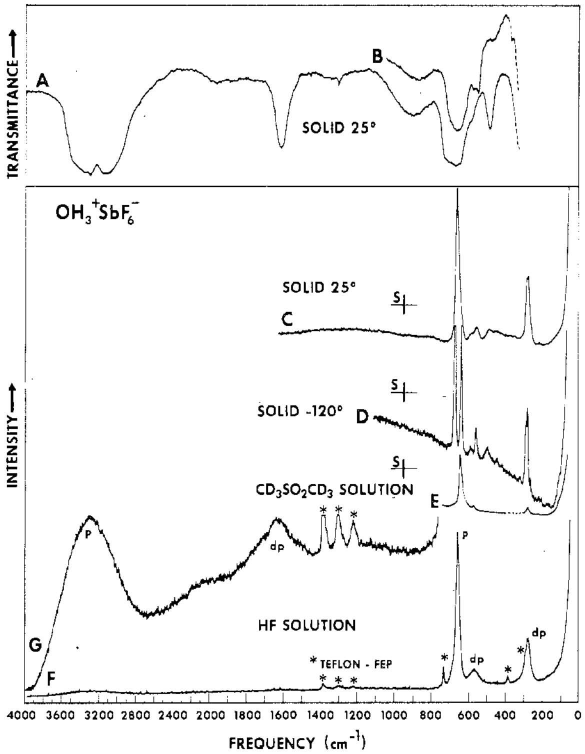

Figure 1. Vibrational spectra of $OH_3^+SbF_6^-$: traces A and B, infrared spectra of two different samples as dry powder between AgCl disks; traces C and D, Raman spectra of the solid contained in a quartz tube at +25 and −120°, respectively; trace E, Raman spectrum of a $CD_3SO_2CD_3$ solution (the broken lines indicate regions obscured by solvent bands); traces F and G, Raman spectra of an HF solution contained in a Teflon–FEP tube at two different recorder voltages. P and dp indicate polarized and depolarized bands, respectively, and S indicates the spectral slit width.

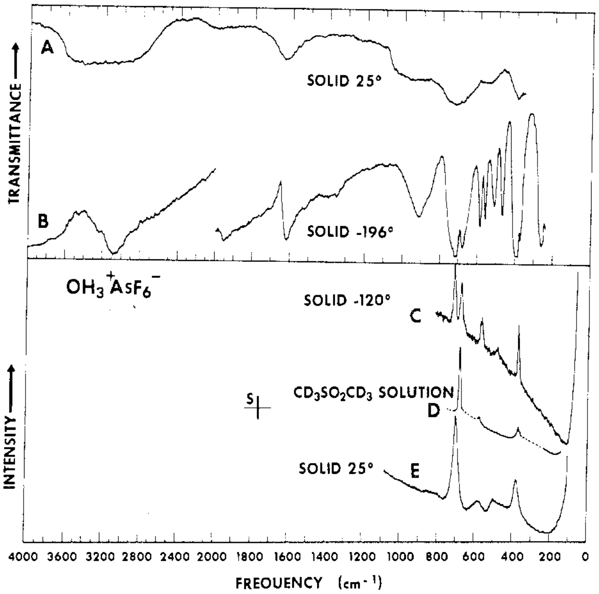

Figure 2. Vibrational spectra of $OH_3^+AsF_6^-$: trace A, infrared spectrum of the solid as a dry powder between AgCl disks at 25°; trace B, infrared spectrum of the solid as a dry powder between CsI disks at −196°; traces C and E, Raman spectra of the solid in a quartz tube recorded at +25 and −120°, respectively; trace D, Raman spectrum of a $CD_3SO_2CD_3$ solution. S indicates the spectral slit width.

temperature splittings is the assumption that at low temperature OH_3^+ and the lattice become rigid. This should result in site symmetry splittings[36] and in a large distortion of the MF_6^- octahedrons owing to cation–anion interaction (H···F bridging), particularly, since the MF_6^- ions are in a field of forces of nonoctahedral symmetry. Similar effects were observed for $OH_3^+ClO_4^-$ by broad-line proton NMR[45,46] and vibrational spectroscopy.[47] However, some of the bands observed in the region of the MF_6^- fundamentals could be of different origin, as was shown[47] by Savoie and Giguere for $OH_3^+NO_3^-$, $OH_3^+ClO_4^-$, and $OH_3^+HSO_4^-$. They established that libration and translation modes of polar OH_3^+ are of relatively high frequency and infrared intensity. Since the OH_3^+ modes are only of very low intensity in the Raman spectrum, the observed Raman bands are very likely due to the anion. However, some of the infrared bands, which have no Raman counterpart, could be due to OH_3^+ libration or translation modes. Spectra of the deuterated species would be helpful to distinguish between these possibilities. In addition, extensive low-temperature vibrational and wide-line NMR spectroscopic studies combined with X-ray and DTA data are desirable to correlate all the observed phenomena. However, this was beyond the scope of the present study.

Assignments for the fundamentals of the OH_3^+ cation were made by comparison with isoelectronic NH_3 (see Table III). Pyramidal XY_3 of symmetry C_{3v} has four fundamentals which are classified as $2A_1 + 2E$, all being active in both the infrared and Raman spectra. Of these, each symmetry species contains one stretching and one bending mode. The frequencies of the two bending modes are sufficiently separated and present no assignment problem. Of the two stretching modes, the symmetric stretch $\nu_1(A_1)$ is obviously represented by the polarized Raman band at 3300 cm^{-1} observed for $OH_3^+SbF_6^-$ in HF solution. This Raman band has an intense counterpart in the infrared spectrum of the solid. Assuming that no significant frequency shift occurred for ν_1 on going from the solution spectrum to that of the solid, the second intense infrared band in this region (~3150 cm^{-1}) should be due to the antisymmetric stretch $\nu_3(E)$. These assignments are supported by the low-temperature infrared spectrum of $OH_3^+AsF_6^-$ which shows a strong band at about 3080 cm^{-1} with a strong shoulder at about 3250 cm^{-1} in agreement with the higher ir intensity expected[48] for ν_3 in an ideal, rather oblique XY_3 pyramid. The agreement between the frequencies of isoelectronic NH_3 and OH_3^+ is excellent. The only difference in their assignments results from a reversal of ν_1 and ν_3 for OH_3^+. Whereas force field arguments (see below) do not support such a reversal, it must be kept in mind that we are comparing a free molecule with a poorly understood solid exhibiting relatively strong anion–cation coupling.

In our spectra two relatively weak broad infrared bands were frequently observed at about 1950 and 1350 cm^{-1}, respectively. Their relative intensities varied and they cannot readily be assigned to an overtone or combination band. Their origin is at the present not fully understood.

In summary, the vibrational spectra unambiguously establish that the $HF{\cdot}H_2O{\cdot}MF_5$ adducts are ionic both in the solid state and in solution and contain octahedral MF_6^- anions and pyramidal OH_3^+ cations, although some of the details of the spectra are still poorly understood. The fundamentals of OH_3^+ in its MF_6^- salts significantly differ from those found for OH_3^+ in mineral acid monohydrates,[21] such as $OH_3^+ClO_4^-$, and resemble more closely those of isoelectronic NH_3. The fact that in $OH_3^+MF_6^-$ the OH stretches have higher and the deformations have lower frequencies than in the mineral acid hydrates strongly indicates that the hydrogen bridging in $OH_3^+MF_6^-$ is significantly weaker, i.e., that these compounds are more ionic.

Force Constants. To support the above assignments, force fields were computed for OH_3^+ (see Table IV) using the vibrational frequency values from this study and the geometry

Table IV. Symmetry and Internal Force Constants[a] of OH_3^+ Compared to Those[b] of NH_3

	OH_3^+					NH_3
Bond angle, deg	110	110	110	110	100	107
Force field	DFF	F_{22} and $F_{44} \equiv$ min	NH_3 TR	$\nu_3 \to \nu_1$ $\nu_1 \to \nu_3$ F_{22} and $F_{44} \equiv$ min	F_{22} and $F_{44} \equiv$ min	GVFF
A_1 $F_{11} = f_r + 2f_{rr}$	6.3369	6.3398	6.3565	5.7783	6.2128	6.4540
$F_{22} = f_\alpha + 2f_{\alpha\alpha}$	0.4296	0.4295	0.4448	0.4295	0.1942	0.4049
$F_{12} = 2f_{r\alpha} + f_{r\alpha}'$	0	0.02395	0.3244	0.02395	0.0183	0.3244
E $F_{33} = f_r - f_{rr}$	5.4213	5.4398	5.4542	5.9696	5.4908	6.4732
$F_{44} = f_\alpha - f_{\alpha\alpha}$	0.5826	0.5817	0.5840	0.5817	0.6752	0.6161
$F_{34} = -f_{r\alpha} + f_{r\alpha}'$	0	−0.0648	−0.1622	−0.0648	−0.0554	−0.1622
f_r	5.7265	5.7398	5.7550	5.9058	5.7315	6.4668
f_{rr}	0.3050	0.3000	0.3008	−0.0638	0.2407	−0.0064
f_α	0.5316	0.5310	0.5376	0.5310	0.5149	0.5457
$f_{\alpha\alpha}$	−0.0510	−0.0507	−0.0464	−0.0507	−0.1603	−0.0704
$f_{r\alpha}$	0	0.0296	0.1622	0.0296	0.0246	0.1622
$f_{r\alpha\alpha}$	0	−0.0352	0	−0.0352	−0.0308	0

[a] All force constants have units of mdyn/Å. Frequency values used: $\nu_1 = 3300$, $\nu_2 = 900$, $\nu_3 = 3150$, and $\nu_4 = 1620$ cm^{-1}, except for column 5 where the frequencies of ν_1 and ν_3 were exchanged. [b] Values from ref 50.

($\angle = 110°$, $r = 1.01$ Å) previously established[23] for the $OH_3^+CH_3C_6H_4SO_3^-$ salt. 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 computed to demonstrate that the choice of the force field has little influence on its values for a vibrationally weakly coupled species, such as OH_3^+, in which the central atom is much heavier than the ligands. To demonstrate the small variation in the force constant values, four decimals are listed in Table IV, in spite of the rather large uncertainties in the given force constant values. These are caused by the broadness of the bands and the unknown bond angle of OH_3^+ in its MF_6^- salts. Two of the three force fields used, the diagonal force field and the force field requiring the deformation symmetry force constants to have minimal values, were selected owing to their established[49] usefulness for weakly coupled systems. For the third force field, the off-diagonal symmetry force constants were borrowed from the known[50] general valence force field of isoelectronic NH_3. Since the antisymmetric OH_3^+ stretch has a significantly lower frequency than the symmetric one and since their frequency separation is a function of the bond angle,[51] this might be taken as some evidence for the OH_3^+ bond angle being smaller than that in isoelectronic NH_3. Consequently, we have also computed the three force fields for OH_3^+ assuming a bond angle of 100°. Whereas the stretching force constants show little angle dependence, F_{22} becomes unreasonably small for $\alpha = 100°$, thus arguing against such a small bond angle for OH_3^+. As expected for a 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. The two high-frequency fundamentals were in all cases pure stretches and the two low-frequency fundamentals were 95–100% deformation modes depending upon the values of the chosen off-diagonal symmetry force constants.

Comparison of the OH_3^+ force fields with that[50] of isoelectronic NH_3 shows good agreement. The only major divergence is found for the stretch–stretch interaction constant f_{rr} which is caused by ν_3(E) of OH_3^+ having a lower frequency value than $\nu_1(A_1)$. This discrepancy could be eliminated either by reversing their assignment (see Table IV) or by assuming very similar frequency values for them and explaining the observed splitting of the broad band at ~3300 cm^{-1} in the infrared spectrum of $OH_3^+SbF_6^-$ by Fermi resonance between $2\nu_4(A_1 + E + F_2)$ and $\nu_1(A_1)$ or ν_3(E). Clearly, the force field computations for OH_3^+ and comparison with those for NH_3,[50] PH_3,[50] and SH_3^+[7] favor $\nu_3 > \nu_1$. However, the experimental data (see above) seem to suggest $\nu_1 > \nu_3$. Obviously, additional experimental data are required to resolve this remaining ambiguity.

Several papers[20,21,52,53] have previously been published dealing with force fields of OH_3^+. Owing to the great variance of the frequencies used, the values reported, for example, for f_r range from 3.93 to 6.31 mdyn/Å. The variance of the frequencies is due partially to the different degree of hydrogen bridging in the different OH_3^+ salts studied[21] and partially to the broadness of the bands rendering their assignments extremely difficult and uncertain.

Conclusion

The novel oxonium salts $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ were synthesized and partially characterized. They possess unusual thermal stability, are easy to prepare, are well defined, appear to be highly ionic and, therefore, should be ideally suited for the study of the oxonium cation.

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Registry No. $OH_3^+SbF_6^-$, 55649-03-1; $OH_3^+AsF_6^-$, 21501-81-5; SbF_5, 7783-70-2; HF, 7664-39-3; H_2O, 7732-18-5; OH_3BF_4, 14219-41-1; BF_3, 7637-07-2; arsenic pentafluoride, 7784-36-3.

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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