HYDROLYSIS OF ANTIMONY(III) FLUORIDE COMPLEXES

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Vibrational and ^{17}O NMR spectroscopy in combination with quantum chemical calculations are used to investigate the hydrolysis of antimony(III) fluoride complexes. A hydrolytic decomposition of SbF_3 and $[SbF_4]^-$ is accompanied by oligomerization with the formation of edge- and corner-connected dimers ($[Sb_2O_2F_4]^{2-}$, $[Sb_2OF_8]^{4-}$) and trimers ($[Sb_3O_3F_6]^{3-}$, $[Sb_3OF_9]^{2-}$) with bridging oxygen atoms. The hydrolysis of $[SbF_4]^-$ is also characterized by the presence in the solution of a discrete cation of $[SbF_5]^{2-}$ which is least hydrolized. Only a partial isomorphic substitution of fluoride ion by hydroxide one is possible, which is reflected in the composition of $K_2Sb(OH)_xF_{5-x}$ ($x = 0.3$) crystals isolated from the fluoride aqueous solution.

Keywords: antimony trifluoride, fluoroantimonates(III), hydrolysis, oligomerization, vibrational spectra, ^{17}O NMR, quantum chemistry.

INTRODUCTION

Fluoride compounds of antimony(III) are of interest because of their capability to biologically affect various organisms. Their cytotoxic properties are described in [1]. It is noted that the toxicity of aqueous solutions of antimony complexes is lower than that of a SbF_3 solution, which seems to be due to a difference in the nature of hydrolysis of these compounds. According to [2], SbF_3 hydrolizes in aqueous solution. In their work Buslaev and Peshkov [3] make a conclusion based on the identical change in the chemical shift (δ) of SbF_3 in aqueous and alcohol solutions about its insignificant hydrolysis; they also suggest the possibility that different in composition fluoride forms of Sb(III) occur there, but do not specify them (except the discrete $[SbF_4]^-$).

The present work reports the results of investigations on the hydrolysis of Sb(III) fluoride compounds with a different Sb:F ratio, namely SbF_3, $MSbF_4$ (M = Na, K, NH_4), and K_2SbF_5, in order to determine the composition of complex forms in their aqueous solutions.

EXPERIMENTAL

In our work we used crystalline samples of SbF_3 (analytical grade) and of $NaSbF_4$, $KSbF_4$, NH_4SbF_4, and K_2SbF_5 complexes obtained from aqueous solutions of SbF_3 and MF (M = Na, K, NH_4) taken in stoichiometric quantities similarly to [4].

IR spectra of the samples of antimony(III) fluoride compounds and their aqueous solutions in a region from 400 cm^{-1} to 4000 cm^{-1} were recorded on a Shimadzu FTIR Prestige-21 Fourier spectrometer at room temperature. The solutions were measured in a KrS cuvette of 0.0024 cm thick. The IR spectrum of K_2SbF_5 was taken on a sample of plate crystals of this

compound pressed into a pellet with a diameter of 0.3 cm. Raman scattering spectra were obtained in a range from 70 cm^{-1} to 3600 cm^{-1} in back scattering on a RFS100/S Fourier Raman spectrometer. As an excitation source Nd:YAG laser radiation with a wavelength of 1064 nm and power of 350 mW was used.

^{17}O NMR spectra were measured on a MSL-400 Bruker spectrometer at an NMR frequency of 54.24 MHz with a frequency of accumulation of 45 Hz at a temperature of 298-268 K under natural isotopic abundance.

Quantum chemical calculations were carried out by the GAUSSIAN-03 program in the standard LanL2DZ basis set [5] which most precisely reproduces the experimental vibrational spectra of antimony(III) fluoride complexes. The calculation of SbF_5^{2-} in the form of a square pyramid gives the optimal short Sb–F distance of 1.94 Å and the corresponding to it stretching vibration (A_1) at 574 cm^{-1}, which well agrees with the experiment (1.93 Å and 556 cm^{-1} respectively for crystalline K_2SbF_5). In the 321G basis set extended with polarization Slater d-functions of antimony this frequency increases to 668 cm^{-1}, which is far from the experiment. Possible Sb(III) oxofluoride clusters were calculated which simulate the corresponding complexes in solution: $[Sb_2O_2F_4]^{2-}$, $[Sb_2OF_8]^{4-}$ dimmers, and $[Sb_3O_3F_6^{3-}]$, $[Sb_3OF_9]^{2-}$ trimers. A dimer with edge-connected polyhedra of antimony realizes only at a Sb coordination number (c.n.) of 4. The calculation of $[Sb_2OF_8]^{4-}$ was performed with surrounding four sodium atoms to compensate for the high charge of the cluster.

The pH measurements in the solutions of Sb(III) fluoride compounds were conducted by an I-500 ionometer with thermocompensation at 25°C to the accuracy of ±0.02.

RESULTS AND DISCUSSION

Antimony trifluoride SbF$_3$ is extremely well soluble in water (492.4 g per 100 g of H$_2$O at 25°C) [2]; pH of the 4 M solution of this salt equals 1.40, which implies its strong hydrolytic decomposition. Fig. 1 displays the IR spectrum of the 4 M solution of SbF$_3$. A broad band with the minimum at 1782 cm^{-1} corresponding to bending vibrations of hydroxonium ion indicates the presence of this ion in the solution. It is this band situated by 50-100 cm^{-1} above the water absorption band that is usually used as an analytical characteristic of the hydroxonium ion presence [6]. However, it is known that in aqueous solutions of acids a stable proton solvate is $[H_5O_2]^+$ ion for which this frequency is 1710 cm^{-1} [7]. The acidic reaction of the system during the hydrolysis (alkaline hydrolysis) of SbF$_3$ suggests the formation of oxo derivatives in its solution. Indeed, the ^{17}O NMR spectrum of the solution under study, which we managed to visualize by adding C$_2$H$_5$OH at 268 K, shows a single broad signal (Fig. 2) at δ = 258 ppm (here the H$_2$O line is shifted to a high-frequency region due to the acidity of the solution). It should be noted that in ^{19}F NMR spectra of aqueous solutions of numerous fluoride compounds (SbF$_3$, $[Sb_3F_{10}]^-$, $[Sb_2F_7]^-$, $[Sb_4F_{15}]^{3-}$, $[SbF_4]^-$, and $[SbF_5]^{2-}$) also one signal is recorded whose chemical shift naturally depends on the Sb:F ratio, and its value varies in a rather narrow interval from −73.3 ppm to −85.4 ppm relative to CFCl$_3$ [8].
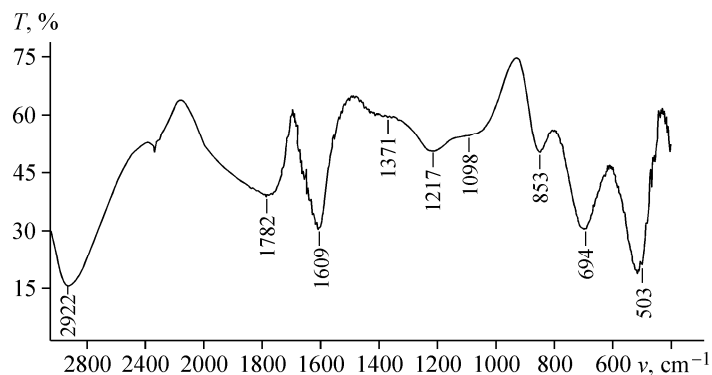

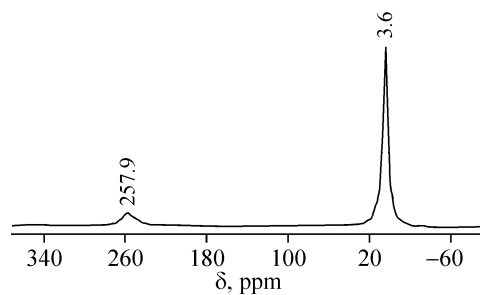**Fig. 1**. IR spectrum of a 4 M SbF$_3$ aqueous solution at room temperature.

Fig. 2. ^{17}O NMR spectrum of the aqueous-alcohol solution of SbF$_3$ at 268 K.

Based on the comparison of chemical shift values in the above series, the authors of [8] make a conclusion about different compositions of Sb(III) fluoride complexes in solutions of the initial complexes without giving any concrete forms.

A solid product of the SbF$_3$ hydrolysis is fine-crystalline oxofluoride Sb$_3$O$_2$F$_5$. Two its modifications α and β are structurally investigated [9]. The basis of both structures consists of dimeric fragments of edge- or corner-connected antimony polyhedra SbX$_4$E (X = O, F; E is the unshared electron pair of antimony atom). In β-Sb$_3$O$_2$F$_5$ a SbX$_5$E polyhedron is found (further we use antimony c.n. without mentioning the electron pair). It is important to note that all the oxygen atoms in oxofluoride structures are bridging ones. In order to clarify the composition of oligomers in solution, the quantum chemical calculations of optimal geometries and vibrational spectra were carried out for the most probable (reasoning from the structural data on oxofluorides) antimony complexes (clusters): [Sb$_2$O$_2$F$_4$]$^{2-}$, [Sb$_2$OF$_8$]$^{4-}$, [Sb$_3$O$_3$F$_6$]$^{3-}$, and [Sb$_3$OF$_9$]$^{2-}$ shown in Fig. 3. The distances of antimony–ligand well correspond in them to those in the oxofluoride structures (Sb–F 1.90-2.10 Å; Sb–O 1.97-2.28 Å). Fig. 4 (curve *2*) displays the experimental Raman spectrum of the 4 M solution of SbF$_3$. It is easily seen that bands in a region from 700 cm^{-1} to 900 cm^{-1} are absent in this spectrum, while there is a band of medium intensity in the experimental IR spectrum (Fig. 1) at 852 cm^{-1}. The calculations show that O-bridging vibrations of corner-connected antimony polyhedra in the dimers reveal themselves in IR spectra and are absent in Raman ones (Fig. 3*b*), whereas the O-bridging vibrations of edge-connected antimony polyhedra are active both in IR and Raman spectra (Fig. 3*a*). Taking into account all the above, it is possible to conclude that [Sb$_2$O$_2$F$_4$]$^{2-}$ and [Sb$_2$OF$_8$]$^{4-}$ dimers are present in the SbF$_3$ aqueous solution. It is worth noting that the frequencies of asymmetric stretching vibrations v_{as} (Sb–O–Sb) and v_{as} (Sb–O$_2$–Sb) rather well correlate with those calculated, but the theoretical symmetric vibration v_s (Sb–O$_2$–Sb) is higher by 100 cm^{-1} than the observed maximum at 580 cm^{-1} (Fig. 4). This means that at least one more form is present in the solution, in which the symmetric vibration of bridging oxygen atoms must be lower than this value. It seems logical that a cyclic trimer with three bridging oxygen atoms corresponds to this variant (Fig. 3*c*), then that is the superposition of its Raman spectrum and the Raman spectrum of the edging dimer (Fig. 3*a*), which results in the actually observed maximum. So, the hydrolysis of SbF$_3$ can be expressed by the following equation:

$$16SbF_3 + 36H_2O = [Sb_2O_2F_4]^{2-} + 2[Sb_3O_3F_6]^{3-} + 4[Sb_2OF_8]^{4-} + 24[H_3O]^+. \qquad (1)$$
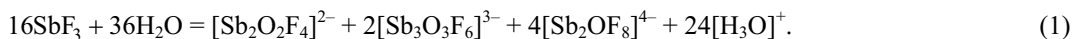
The measured pH in SbF$_3$ solutions (1.40 for 4 M, 1.97 for 1 M, and 2.51 for 0.1 M) mean that in these solutions the equilibrium exists

$$[Sb_xO_yF_z]^{(2y+z-3x)} + n[H_3O]^+ = H_n[Sb_xO_yF_z]^{(2y+z-3x)+n} + nH_2O. \qquad (2)$$
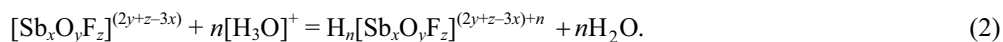
The formation of oxofluoro antimonate acids is supported by v(OH) in a region of 2920 cm^{-1} and by several minima in a region from 1000 cm^{-1} to 1400 cm^{-1} (Fig. 1) which can be related to the dynamics of the hydrogen bond in O$\cdots$H$\cdots$O and O$\cdots$H$\cdots$F fragments. From the data obtained it is difficult, however, to estimate the ratio (and maybe, even the number) of the forms supposed. At least three inflection points were found on the calorimetric curves of the SbF$_3$ aqueous solution titrated by potassium fluoride [10], which the authors, based only on the composition of solid phases isolated in these points, explained by the formation of [Sb$_2$F$_7$]$^-$, [SbF$_4$]$^-$, and [SbF$_5$]$^{2-}$ in the solution. In the work [3], the formation of a discrete [SbF$_4$]$^-$ ion is
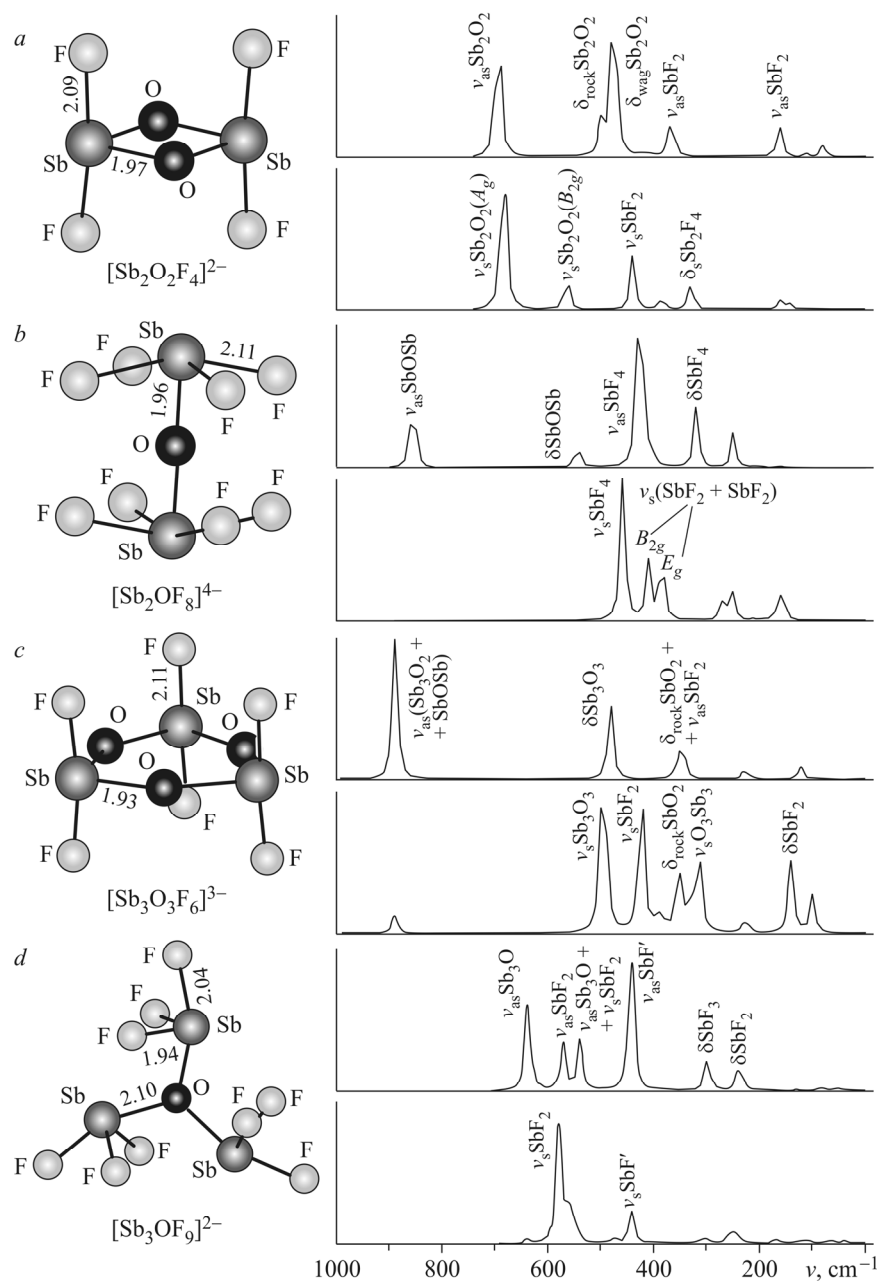
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Fig. 3. Optimal geometry and theoretical vibrational spectra of antimony(III) oxofluoroclusters simulating the presence of possible oligomers in the solution of the initial compounds.

also denoted. The argument for this conclusion was the minimum occurring on the dependence curve of the chemical shift of the ^{19}F NMR signal versus the $NH_4(K)F{:}SbF_3$ ratio equal to 1:1.

It should be noted that all of the $NaSbF_4$, $KSbF_4$, and NH_4SbF_4 aqueous solutions have an acidic reaction which unambiguously indicates the hydrolysis of $[SbF_4]^-$. The most soluble is NH_4SbF_4, and Fig. 4 (curve *1*) displays the Raman spectrum of its 2M aqueous solution. The fact that the spectra of SbF_3 and NH_4SbF_4 solutions look similar attracts attention; the most intense band in a region of 580 cm^{-1} is broadened and slightly shifted to the low-frequency region in the latter case, and in a region from 620 cm^{-1} to 650 cm^{-1} a shoulder is observed. All these quite agree with the Raman spectrum of the $[Sb_3OF_9]^{2-}$ trimer with a triple oxygen bridge (Fig. 3*d*). A substantial difference between the mentioned spectra is in the presence of a broad band in a region from 350 cm^{-1} to 450 cm^{-1} in the case of the $[SbF_4]^-$ solution with maxima at 426 cm^{-1}
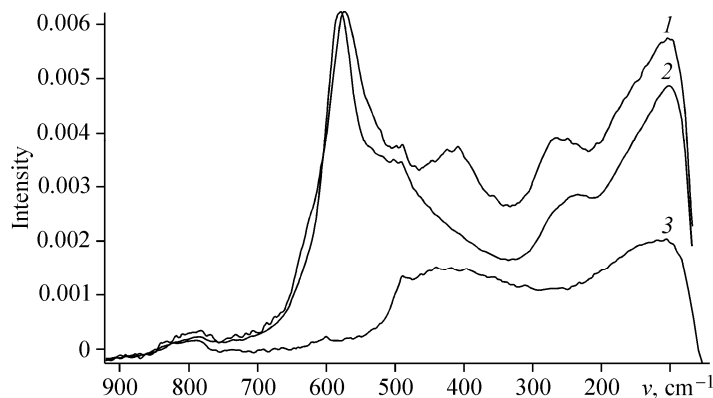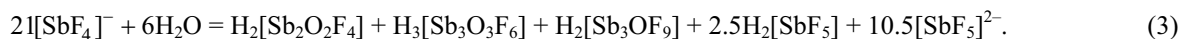
851

Fig. 4. Raman spectra of a 2M aqueous solution of NH$_4$SbF$_4$ (*1*), a 4M aqueous solution of SbF$_3$ (*2*), and H$_2$O (*3*) at room temperature.

and 386 cm^{-1} which, according to [11], may be assigned to $\nu_2(A_1)$ and $\nu_7(E)$ of the $[SbF_5]^{2-}$ discrete ion. The most intense stretching vibration $\nu_1(A_1)$ of this ion at 560 cm^{-1} falls exactly into the region of Sb–O–Sb bridging vibrations, and it is this that results in broadening the band at 580 cm^{-1}. With taking into account the revealed forms, the hydrolysis equation of $[SbF_4]^-$ can be written as follows:

$$21[SbF_4]^- + 6H_2O = H_2[Sb_2O_2F_4] + H_3[Sb_3O_3F_6] + H_2[Sb_3OF_9] + 2.5H_2[SbF_5] + 10.5[SbF_5]^{2-}. \qquad (3)$$
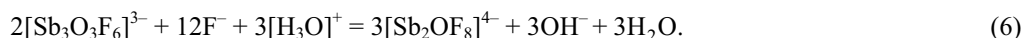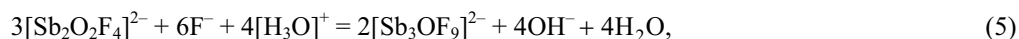
Of course, this is only a scheme because, as in the first case, it is rather difficult to determine the actual ratio of the forms.

The crystal structures of SbF$_3$ and KSbF$_4$ contain SbF$_3$ groups with short (1.92-1.98 Å) and long (2.61 Å and 2.21-2.26 Å respectively) Sb–F bonds [12]. In the SbF$_4$E antimony polyhedra that form the structure of NH$_4$SbF$_4$ [13] three Sb–F distances are short (1.93-1.97 Å), and the fourth one is longer (2.18 Å). The polyhedra are linked in zigzag chains of $[Sb_2F_8]_n^{2n-}$ by bridging fluorine atoms at Sb–F distances of 2.45 Å and 2.66 Å. Long bridging bonds are most likely to be broken in the interaction with water molecules, and hydroxide ions take their place (with protons released). With the assistance of protons the hydroxide-containing forms of antimony rapidly condense with the formation of oligomers (first of all, dimers and trimers) through oxide bridges. A stronger hydrolysis of SbF$_3$ (a substantially lower pH of the solution) in comparison with $[SbF_4]^-$ (pH of a 0.1 M KSbF$_4$ solution is 3.90) appears to be provided by the occurrence in the former of longer bridging bonds and their larger number. The possibility of the presence of discrete $[SbF_4]^-$ in the aqueous solution mentioned in [3, 10] seems unlikely. The regularities of changes in the chemical shift of ^{19}F NMR spectra noticed by the authors of [3] in their study of complex formation in SbF$_3$ solution can be explained by the occurrence of the oxo forms found by us as follows.

1. The chemical shift of the ^{19}F NMR signal moves to the high field (the low-frequency part of the spectrum) as the concentration of SbF$_3$ decreases in solution. The reason is not only a simple decrease in the concentration of hydrogen ions with lowering starting concentration of SbF$_3$, but also a deeper hydrolysis with the formation of a large number of bridging O-bonds per one antimony atom. This weakens the Sb–F bond, and hence, lowers the frequency of the ^{19}F NMR signal.

2. The addition of F$^-$ to the solution of SbF$_3$ shifts the ^{19}F NMR signal to the low field (to the high-frequency region of the spectrum). When F$^-$:SbF$_3$ = 1:1, the titration curve passes through the minimum. Most likely, the addition of F$^-$ causes the rupture of edge bridging bonds or the opening of cyclic trimers producing the oxofluoride forms with corner bridges

$$[Sb_2O_2F_4]^{2-} + 4F^- + [H_3O]^+ = [Sb_2OF_8]^{4-} + OH^- + H_2O, \qquad (4)$$

$$3[Sb_2O_2F_4]^{2-} + 6F^- + 4[H_3O]^+ = 2[Sb_3OF_9]^{2-} + 4OH^- + 4H_2O, \qquad (5)$$

$$2[Sb_3O_3F_6]^{3-} + 12F^- + 3[H_3O]^+ = 3[Sb_2OF_8]^{4-} + 3OH^- + 3H_2O. \qquad (6)$$

The frequency of Sb–F stretching vibrations in the corner-connected forms lies above those in the edge-connected dimers, which is confirmed by calculations. This regularity correlates with the shift of the ^{19}F NMR signal to the high-frequency region in transition from edge- to corner-connected forms.
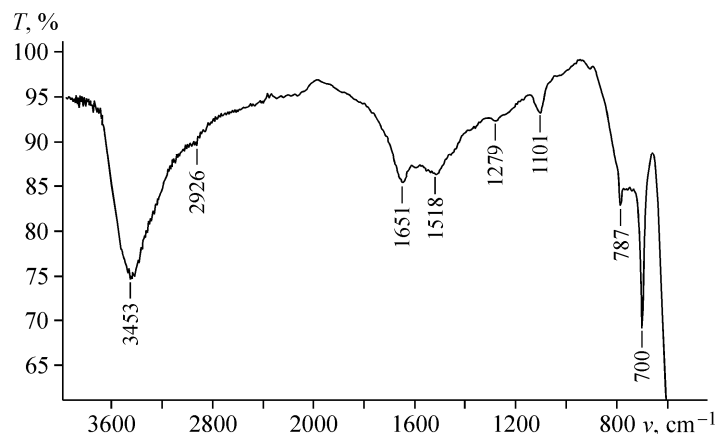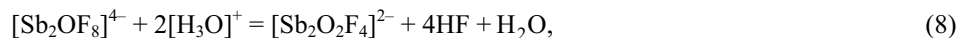
Fig. 5. IR spectrum of $K_2Sb(OH)_xF_{5-x}$ ($x = 0.3$) crystals.

3. When HF is added to $SbF_3 + H_2O$, the minimum is not observed on the titration curve, and an increasing acid concentration shifts the signal to the low-frequency region (the high field). This means that Sb–F bond weakens due to a greater degree of oligomerization (the number of oxygen bridges per one antimony atom grows)

$$[Sb_2OF_8]^{4-} + 4HF + 3H_2O = [Sb_2O_2F_4]^{2-} + 4HF_2^- + 2[H_3O]^+. \tag{7}$$

Possible exchange between $[Sb_2O_2F_4]^{2-}$ and HF_2^- also results in a shift of the signal to the low-frequency region.

4. The addition of KCl or NH_4Cl to the aqueous solution of SbF_3 virtually does not change the situation (an insignificant change in the chemical shift). KCl has a neutral reaction, whereas the hydrolysis of NH_4Cl ($NH_4^+ + 2H_2O = NH_4OH + [H_3O]^+$) is suppressed by the presence of hydroxonium ions in the SbF_3 solution. A stronger displacement of the chemical shift to the low-frequency region for the $HCl–SbF_3–H_2O$ system is explained by a simple shift of the equilibrium in the $SbF_3–H_2O$ system due to the appearance of forms with a higher concentration of bridging oxygen atoms

$$[Sb_2OF_8]^{4-} + 2[H_3O]^+ = [Sb_2O_2F_4]^{2-} + 4HF + H_2O, \tag{8}$$

instead of

$$SbF_3 + HCl = SbF_2Cl + HF\ [3]. \tag{9}$$

Undoubted remains the conclusion of the authors of [3] about a rapid exchange of different forms of antimony(III) because of their short lifetime, which they relate to the ability of antimony to easily change its coordination number. Indeed, single ^{19}F and ^{17}O NMR signals of the SbF_3 aqueous solution absolutely confirm this conclusion. It should be noted that K_2SbF_5 consisting of discrete SbF_5 polyhedra with maximum c.n. is least hydrolysed. The composition of the crystals isolated from the fluoride aqueous solution of this salt corresponds to $K_2Sb(OH)_xF_{5-x}$ ($x = 0.3$). In the IR spectrum of this complex (Fig. 5) a broad absorption band is seen at 3450 cm^{-1} that corresponds to the stretching vibration of hydroxide ion participating in the O–H···F hydrogen bond (νOH of free hydroxide is in the region of 3600 cm^{-1}). Also rather narrow bands are observed in a range from 700 cm^{-1} to 800 cm^{-1} that correspond, in our opinion, to lateral vibrations of the proton from the triple system of O–H···F. Thus, the hydrolysis of $[SbF_5]^{2-}$ relates to isomorphic substitution of fluoride ion with hydroxide

$$[SbF_5]^{2-} + xH_2O = [Sb(OH)_xF_{5-x}]^{2-} + xHF. \tag{10}$$

The hydrolysis of antimony pentafluoride SbF_5 described in [14] occurs similarly.

CONCLUSIONS

So the hydrolytic decomposition of both SbF_3 and fluoroantimonates(III) is accompanied by oligomerization producing oxofluoride forms with bridging oxygen atoms. Based on the IR and Raman spectroscopy data in combination with quantum chemical calculations, an assumption is made about the composition of these forms. In the equilibrium state there

coexist edge- and corner-connected dimers and trimers of Sb(III) with c.n. 4 and 5. The vibrational frequencies of Sb–F bonds well correlate with the frequency shift of the ^{19}F NMR signal in aqueous solutions of the compounds in question. Rapid in the NMR scale exchange processes result in the observation of single signals on ^{19}F and ^{17}O nuclei. The hydrolysis of SbF$_3$ and [SbF$_4$]$^-$ is accompanied by the generation of oxofluoride forms with a higher and lower concentration of fluorine in comparison with the starting compound (as a disproportionation). The same regularity is observed in the case of the hydrolysis of TiF$_4$ and NH$_4$TiO$_x$F$_{5-2x}$ [15]. The data obtained indicate that bridging Sb–O–Sb bonds in the ^{17}O NMR spectra fall in a region of 250 ppm. The ^{17}O NMR signal from hydroxonium ions observed in a range from 95 ppm to 100 ppm in the investigation of AsF$_5$ hydrolysis [14] seems to be assigned to another product of the hydrolysis of this compound.

Higher toxic activity of SbF$_3$ in comparison with fluoroantimonates(III) appears to be due to a strong acidic reaction of its aqueous solutions.

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