CONDITIONS FOR THE EXISTENCE OF POTASSIUM ANTIMONATES WITH A M(I):Sb RATIO GREATER THAN ONE

Milan DRÁTOVSKÝ[a] and Jiří KARLÍČEK[b]

[a] *Department of Inorganic Chemistry,*
Charles University, 128 40 Prague 2 and
[b] *Department of Chemistry,*
Pedagogical Faculty, 306 19 Plzeň

Dedicated to Professor Dr S. Škramovský on the occasion of his 80th birthday.

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During a solubility study on the ternary system KOH–$KSbO_3$–H_2O, a method was found for the preparation of the crystallline (X-ray active) compound $KSbO_3.2{\cdot}3\ H_2O$ and a new compound, $K_4Sb_2O_7.(5{\cdot}6—5{\cdot}8)H_2O$, was discovered. Both of these substances and an anhydrous substance with composition $K_4Sb_2O_7$ crystallize in the tetrahedral system. Their constitution was characterized on the basis of their IR spectra.

The position of antimony in the periodic system leads to an analogy to both phosphorus and arsenic, as well as to tellurium and iodine. However, far fewer oxo-compounds with the highest possible oxidation number are known for antimony than for tellurium and iodide or phosphorus and arsenic. This is primarily caused by the fact that only salts with ratio M(I) : Sb $\leqq$ 1, derived from antimonic acid, have mostly been described and study of the conditions for the existence of antimonates with ratio M(I) : Sb > 1 has been carried out in greater detail only for sodium salts[1]. Consequently, also for this reason, far fewer interesting condensation and other products of thermal decomposition derived from antimonates are known compared with phosphates and arsenates[2] or tellurates[3,4] and periodates[5,6]. This work was thus carried out in order to systematically study antimonates formed in contact with aqueous solutions. Results are given for the study of potassium antimonates, which differ from the antimonates of other metals primarily in their high solubility in water.

The following anions exist in aqueous antimonate solutions at various concentrations and pH values: $[SbO(OH)_5]^{2-}$, $[Sb(OH)_6]^-$, $[Sb_6O_{17}]^{4-}$ and $[Sb_9O_{24}]^{3-}$ (ref.[7–18]). The chemical individuality of crystalline antimonates was convincingly demonstrated by X-ray techniques only for compounds with the overall compositions $KSbO_3$ (refs[19–21]), $KSbO_3.0{\cdot}7\ H_2O$ (ref.[21]) and $K_3Sb_5O_{14}$ (refs[19,22]). Variously hydrated products with ratio K : Sb = 1 (refs[23–18]) are precipitated from aqueous solutions; these compounds do not usually yield X-ray interference patterns. Although some of these substances were described as crystalline[26,27], their structures were not studied. Even the structure of the K_3SbO_4 product has not been studied, although it has also been described as crystalline and has been prepared by combusting antimony(III) oxide with potassium hyperoxide[29].

EXPERIMENTAL

Chemicals. The initial substance was the product of the firm Merck (GFR), with the composition $KSbO_3.2{\cdot}5\ H_2O$, of *p.a.* purity, or the substance with the composition $KSbO_3.x\ H_2O$ ($x = 2{\cdot}2$—$2{\cdot}7$), prepared by reaction of antimony(III) oxide *p.a.* with hydrogen peroxide in a medium of potassium hydroxide *p.a.*[7], controlled analytically. The other chemicals used were products of Lachema, of *p.a.* purity.

Analytical methods. Potassium was determined as the sulphate or tetraphenylborate after prior removal of antimony as antimony(III) sulphide. The deviation in the determination was a maximum of 0·8% rel. of the value or the arithmetic mean. Antimony was determined iodimetrically in tartrate medium after prior reduction of Sb(V) to Sb(III) (ref.[30]). The deviation in the measurement was a maximum of 1·3% rel. of the value of the arithmetic mean. The presence of Sb(III) in the substances was not demonstrated, so that the content of Sb(V) equalled the overall antimony content. In orientative analyses, potassium and antimony were determined by atomic absorption spectrophotometry using a Varian-Techtron model AA-5 instrument. The water content was calculated as the difference to 100% and verified by the mass loss on thermal decomposition.

Solubility study. The solubility in the KOH–$KSbO_3$–H_2O system was studied at a temperature of 298 ± 1 K in a nitrogen atmosphere. Samples of heterogeneous mixtures were prepared from a saturated KOH solution and *c.* 20% $KSbO_3$ solution diluted with water so that the concentration of the two components in the individual samples varied countercurrently from saturated solutions to very dilute solutions and so that each sample contained a solution in contact with the precipitated solid phase. Around the eutonic points, the concentration differences between solutions were smaller than in the other regions of the solubility curve. A concentrated $KSbO_3.x\ H_2O$ solution was used for sample preparation because in some cases the reaction of a KOH solution with solid $KSbO_3.x\ H_2O$ did not equilibrate even after two years. Equilibrium formation was indicated by analyses of samples of the solid phase, as analysis of the liquid phase was not conclusive for equilibrium determination.

Thermography. The thermal behaviour of solid samples was studied on a Derivatograph type OD 2 instrument (Hungary). The samples were heated at a rate of 5 K per minute to a temperature of 900 or 1200 K.

X-ray study. A mikrometa 2 instrument (Chirana) was used for the X-ray study of the powder samples, with CuKβ radiation at a voltage of 35 kV and current of 20 mA. The patterns of the substances were either recorded in Lindenmann glass capillaries on a film with an exposure time of 90 min and their diffraction lines measured with a precision of 0·05 mm on a ruler from Hilger (England) or their diffraction patterns were recorded on a NRX (Tesla) evaluation unit for X-ray diffraction and the band positions were read with a precision of 0·5 mm. The intensities of the lines were determined visually on a ten-point scale. The $h\ k\ l$ symbols were assigned to the diffraction lines recorded. The theoretical values of the diffraction angles and interplane distances were calculated on a Hewlett–Packard 9830A calculator using the DTEOROB and DTEORSPEC programs[31].

Infrared spectroscopy. The infrared spectra were recorded in the interval 400—4 000 cm^{-1}, using a UR 20 spectrophotometer (Carl Zeiss, Jena) and the nujol mull technique.

RESULTS

The results of the solubility study in the KOH–$KSbO_3$–H_2O system at a temperature of 298 K are given in Table I, from which it follows that the phases formed can be divided into three groups. A substance with the composition $KSbO_3$.2·3 H_2O is precipitated on the vessel walls in contact with a less concentrated potassium hydroxide solution. Products with a K : Sb ratio increasing from 1 to 2 in dependence on the concentration of potassium hydroxide in the liquid phase are formed in contact with potassium hydroxide solutions of medium concentration. When these products. are decanted with water, adsorbed potassium hydroxide is washed off and $KSbO_3$ .2·3 H_2O is formed. The third group of solid phases is formed in contact with very concentrated potassium hydroxide solutions and the phases have a composition corresponding to $K_4Sb_2O_7$.5·65 H_2O.

Thermal decomposition of the hydrate $KSbO_3$.x H_2O with increasing temperature leads to continuous loss of water and formation of the anhydrous substance $KSbO_3$ at a temperature of 800–900 K. A lower hydrate with composition $K_4Sb_2O_7$.1·5 H_2O is formed by thermal decomposition of the $K_4Sb_2O_7$.5·65 H_2O product, and de-

TABLE I

Analysis of isolated hydrated potassium antimonates and the corresponding liquid phases at a temperature of 298 K

Sample No	Substance in solid phase	Solid phase, wt.%			Liquid phase, wt.%		
		K_2O	Sb_2O_5	H_2O	K_2O	Sb_2O_5	H_2O .
1	$KSbO_3$.2·3 H_2O	18·93	64·47	16·60	9·17	0·52	90·31
2		19·08	64·53	16·39	13·53	0·76	85·71
3		18·84	64·74	16·42	18·45	0·62	80·93
4	1·12 $K_2O.Sb_2O_5$.4·40 H_2O	20·77	63·66	15·58	20·11	2·15	77·74
5	1·21 $K_2O.Sb_2O_5$.5·31 H_2O	21·38	60·69	17·93	24·05	1·67	74·28
6	1·55 $K_2O.Sb_2O_5$.6·36 H_2O	25·43	56·28	18·29	28·19	2·95	68·86
7	1·65 $K_2O.Sb_2O_5$.6·20 H_2O	26·32	54·78	18·90	30·69	1·76	67·55
8	$K_4Sb_2O_7$.5·65 H_2O	30·42	52·79	16·79	32·33	0·97	66·70
9		30·98	52·74	16·28	32·61	0·85	66·54
10		30·79	52·42	16·79	34·58	1·14	64·28
11		30·86	52·47	16·67	35·40	1·22	63·38
12		31·11	52·78	16·11	35·92	1·09	62·99

TABLE II

Crystal systems and lattice parameters (pm) of potassium antimonates

Substance	Crystal system	Lattice[a] parameters
$KSbO_3.2{\cdot}3\ H_2O$ prepared by us[7]	amorphous	
$1{\cdot}12\ K_2O.Sb_2O_5.4{\cdot}4$ H_2O to $1{\cdot}65\ K_2O.SbaO_5.6{\cdot}2\ H_2O$ and $KSbO_3.2{\cdot}3\ H_2O$ obtained by washing these products with water	tetrahedral	a = 1 084 (6) c = 1 381 (7)
$K_4Sb_2O_7.5{\cdot}65\ H_2O$	tetrahedral	a = 1 157 (9) c = 1 370 (8)
$KSbO_3$[b]	rhombohedral	a = 681·4 α = 46·3°
$K_4Sb_2O_7$	tetrahedral	a = 1 161 (7) c = 1 203 (7)

[a] Standard deviations are given in brackets. [b] Literature data (ref.[19]).

TABLE III

X-ray data for $KSbO_3.2{\cdot}3\ H_2O$[a]

I_0	d_0	h	k	l	I_0	d_0	h	k	l
2d	690·0	0	0	2	3	191·4	4	4	0
10	500·0	2	0	1	2	180·5	6	0	0
1	460·0	0	0	3	1	178·4	1	6	0
2	380·0	2	2	0	3d	168·8	4	5	0
3	340·0	2	2	2	2	158·6	1	6	4
8	282·0	1	2	4	1	154·9	7	0	0
4	239·0	1	2	5	2	148·8	7	2	0
1	221·0	1	1	6	1	143·1	3	3	8
5	217·0	5	0	0	2d	131·2	7	2	5
		3	4	0	2d	126·5	7	3	5
1	201·0	2	5	0			5	3	8

[a] Interplanar distances (observed) d_0 in pm, I_0 relative intensity.

hydration to the anhydrous substance $K_4Sb_2O_7$ is complete roughly at a temperature of 1 100 K.

The substances which were studied by the X-ray technique can be divided into 5 groups: *1*) The compound $KSbO_3.2{\cdot}3\ H_2O$, prepared by oxidation of antimony (III) oxide with hydrogen peroxide in a potassium hydroxide medium[7] and compounds with similar composition, obtained in a solubility study on the KOH–$KSbO_3$–H_2O heterogeneous system (Table I, Products 1–3). *2*) Hydrated products with a ratio of $2 < (K : Sb) < 1$, obtained in a solubility study on the same system (Table I, products 4–7), or compounds obtained from these products by decanting with water, with the composition $KSbO_3.\ 2{\cdot}3\ H_2O$. *3*) Compounds with the composition $K_4SbO_7.5{\cdot}65\ H_2O$, obtained in a solubility study on the heterogeneous system (Table I, products 8–12). *4*) The compound $KSbO_3$, obtained by dehydration of the amorphous hydrate $KSbO_3.2{\cdot}3\ H_2O$ at a temperature of 1 100 K. *5*) The compound $K_4Sb_2O_7$, obtained by dehydration of the hydrate $K_4Sb_2O_7.5{\cdot}65\ H_2O$ at a temperature of 1 100 K.

The substances listed under group 1 are X-ray amorphous and the others are crystalline; substances listed in each group have identical diffraction lines. The diffraction lines of compounds in the 2nd, 3rd and 5th groups were indexed in the tetragonal system. The possibility of preparing single crystals of these substances is being studied. Comparison of the observed diffraction angles and interplanar distances of the $KSbO_3$ substance (group 4) with the published data[19–21] confirmed that thermal decomposition of the hydrate $KSbO_3.2{\cdot}3\ H_2O$ yields the rhombohedral modification of $KSbO_3$.

Tables I–V list the results of X-ray study of potassium antimonates.

The character of the IR spectra enables separation of the studied potassium antimonates into three groups. The first includes hydrated substances formed from aqueous solutions and exhibiting absorption bands of the vibrations of the SbO, SbOH, OH and H_2O bonds. This group includes $KSbO_3.2{\cdot}3\ H_2O$ (X-ray amorphous and crystalline), hydrated products with a variable ratio $2 < (K : Sb) < 1$ and the hydrate $K_4Sb_2O_7.5{\cdot}65\ H_2O$. The second group consists of partially dehydrated product $K_4Sb_2O_7.1{\cdot}4\ H_2O$, which exhibits weak bands of the deformation vibrations of the SbOH and valence vibrations of the OH group, while the bands corresponding to the deformation vibrations of water are not visible. The third group consists of the anhydrous compounds $KSbO_3$ and $K_4Sb_2O_7$, whose spectra lack bands corresponding to any bond in which hydrogen atoms participate. The results of the study of the IR spectra of the first two groups are listed in Table VI.

DISCUSSION

The solubility in the KOH–$KSbO_3$–H_2O system was studied for the first time. Except for known[23–28] X-ray amorphous potassium antimonate $KSbO_3.2{\cdot}3\ H_2O$, the exis-

TABLE IV

X-ray data for $K_4Sb_2O_7.5{\cdot}65\ H_2O$

I_0	d_0	h	k	l	I_0	d_0	h	k	l
2	820·0	1	1	0	2	227·0	1	5	0
3	520·0	1	1	2	1	220·0	1	1	6
6	480·0	1	2	1	1	210·0	2	1	6
10	460·0	0	0	3	1	198·8	3	5	0
1	390·0	3	0	0	1	188·1	4	2	5
8	360·0	1	3	1	1	178·5	5	4	1
3	340·0	0	0	4	2	176·2	2	2	7
1	294·0	3	0	3	1	172·2	6	3	0
2	286·0	1	2	4	1	169·6	6	2	3
2	276·0	4	1	1	2	165·6	7	0	0
2	273·0	3	3	0	1	156·8	3	0	8
1	262·0	2	2	4	1	154·9	7	2	2
1	250·0	1	3	4	1	152·6	4	4	6
2	242·0	1	2	5	1	147·7	5	5	4
4	239·0	1	4	3	1	127·9	8	0	5

TABLE V

X-ray data for $K_4Sb_2O_7$

I_0	d_0	h	k	l	I_0	d_0	h	k	l
7	680·0	1	1	1	2d	173·4	5	4	2
5	600·0	0	0	2	3	163·7	4	1	6
2	470·0	1	2	1	3	160·9	6	4	0
2	410·0	2	2	0	6	159·0	6	3	3
2	320·0	3	2	0	4	154·5	7	2	2
10	300·0	0	0	4	2	150·6	6	0	5
1	287·0	2	2	3	3	141·1	8	0	2
1d	284·0	3	2	2	2	137·9	4	3	7
1	279·0	3	0	3	3	135·0	7	5	0
4	266·0	2	0	4	1d	131·5	7	5	2
8	254·0	2	4	1	2	125·8	9	2	0
2	244·0	2	2	4	3	122·9	8	5	0
1	207·0	2	2	5	3	121·4	4	0	9
7	199·9	0	0	6	1d	114·5	3	1	10
1	194·7	4	4	2	1	113·0	6	6	6
8	186·8	2	1	6	4	111·3	7	0	8

tence of the compound $K_4Sb_2O_7$.5·65 H_2O was demonstrated and the stability regions for both compounds were defined. As is confirmed by the literature[23,25,32], the non-stoichiometric water content in the antimonates of the alkali metals is common. There is a third region between the existence regions for $KSbO_3$.2·3 H_2O and

TABLE VI

The infrared spectra of hydrated potassium antimonates[a]. Symbols used: ν valence vibration, δ planar deformation vibration, γ out-of-plane deformation vibration, ν_L H_2O libration vibration of water; relative band intensity: vs — very strong, s — strong, ms — medium strong, w — weak, vw — very weak.

$KSbO_3$. 2·3 H_2O amorphous	1·3 $K_2O.Sb_2O_5$. .6·2 H_2O	$KSbO_3$. .2·3 H_2O (cryst.)	$K_3Sb_2O_7$. 5·65 H_2O	$K_4Sb_2O_7$. .1·4 H_2O	Assignment
	525 (s)	518 (s)	534 (ms)		ν_L H_2O
			425 (vw)	425 (vw)	
450 (s)			480 (w)	477 (ms)	
			564 (s)	549 (vs)	
585 (vs)		590 (vs)	592 (vs)	568 (s)	ν SbO
	605 (vs)	615 (vs)	612 (s)		
			665 (w)	655 (vs)	
720 (s)	720 (ms)	720 (s)	720 (s)		
			760 (s)	760 (s)	
	840 (ms)	840 (s)	830 (ms)		γ SbOH
975 (ms)	985 (w)	980 (w)	990 (w)	975 (w)	δSbOH
1 040 (ms)	1 055 (ms)	1 050 (ms)	1 050 (w)		
	1 118 (ms)	1 114 (s)	1 118 (ms)	1 (120 (w)	
1 165 (ms)	1 160 (ms)	1 161 (ms)	1 150 (w)	1 160 (vw)	
1 660 (w)	1 650 (vw)	1 660 (w)	1 660 (vw)		δ H_2O
	2 170 (vw)	2 150 (w)			2δ SbOH
2 350 (vw)	2 370 (w)	2 340 (w)	2 340 (w)		
3 120 (vs)	3 135 (vs)				
		3 160 (vs)			
3 195 (vs)	3 185 (vs)	3 180 (vs)			
		3 210 (vs)	3 200 (vs)		ν OH
3 230 (vs)	3 220 (vs)	3 220 (s)			
			3 255 (vs)	3 250 (ms)	
				3 310 (ms)	
	3 350 (s)	3 370 (s)		3 370 (ms)	

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[a] Band wavenumbers in cm^{-1}.

$K_4Sb_2O_7.5{\cdot}65\ H_2O$, in which equilibrium was not established even after a long time and in which products with a non-stoichiometric ratio of potassium to antimony were formed. On washing with water, it was possible to prepare crystalline potassium antimonate $KSbO_3.2{\cdot}3\ H_2O$ from these products. This confirms that the products with nonstoichiometric composition are formed by adsorption of various amounts of KOH on the $KSbO_3.2{\cdot}3\ H_2O$ crystals. Its interplanar distances correspond to the literature data[26]. It crystallizes in the tetragonal system, so that the unit cell dimensions could be found from the X-ray powder pattern. The newly prepared compounds, $K_4Sb_2O_7.5{\cdot}65\ H_2O$ and $K_4Sb_2O_7$, were characterized by their interplanar distances and unit cell parameters.

Potassium antimonates with K : Sb ratios greater than 2 are not formed in aqueous solutions. The existence of the potassium antimonate with the composition $[KSb(OH)_6].0{\cdot}5\ H_2O$ was also not confirmed, although the literature states that it crystallizes from aqueous solutions under conditions similar to those used in our study.

In addition to the strong bands of the deformation vibrations of the SbOH group, the IR spectra of the newly isolated compound, $K_4Sb_2O_7.5{\cdot}65\ H_2O$, also contain bands of the deformation vibrations of water. Thus it must be assumed that this substance also contains both constitutional water and water of hydration. Assuming that the coordination number of antimony is 6 in antimonates[23,27], the constitutional formula $K_2[SbO(OH)_5].0{\cdot}33\ H_2O$ can be proposed for this compound. The correctness of this structure is supported by the conclusions drawn by Jander and Ostmann[8], who demonstrated the existence of the anion $[SbO(OH)_5]^{2-}$ in a study of antimonate solutions at $pH > 12$.

The studied substances are thermally exceptionally stable. Complete dehydration to $KSbO_3$ and $K_4Sb_2O_7$ was observed during thermal decomposition without reduction of antimony, which is remarkable stability compared with the instability of hydrated antimony(V) oxide[33] and with that of periodates[5,6] or tellurates[3,4], which lose both water and part of their oxygen at not very high temperatures. The high final dehydration temperature of the $K_4Sb_2O_7$ compound (1 100 K), found by analysis and from the IR spectra of the decomposition products, is also remarkable.

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