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Thermochemical Study of Gaseous Salts of Oxygen-Containing Acids: XXVII.[1] Antimonites of Alkali Metals

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Abstract—Vaporization of sodium, potassium, rubidium, and cesium antimonates was studied. Vapors above the studied antimonates contain dimeric $(MSbO_2)_2$ molecules in addition to monomeric antimonites $MSbO_2$. Standard enthalpies of formation of these gaseous molecules were determined.

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The vaporization of antimonates of alkali metals was studied in detail in [2]. Heating antimonates in neutral conditions (vaporization from platinum cells) in the range of 1115–1305 K results in high-temperature redox reaction (1) yielding antimonites.

$$MSbO_3(cr.) = MSbO_2(gas) + 0.5O_2\ (gas). \tag{1}$$

Hereinafter M = Na, K, Rb, Cs. Reaction (1) describes the vaporization of all antimonates of alkali metals, except for lithium antimonate, which suffers a deeper dissociation. When $LiSbO_3$ is heated, antimony oxide Sb_4O_6 passes into vapor and forms the dominating vapor component in the above-mentioned temperature range, whereas poorly volatile lithium oxide is accumulated in a condensed phase. Enthalpies of reactions (1) have been determined in [2] using Eqs. (2) and (3) alongside the standard enthalpies of formation of gaseous molecules $MSbO_2$, which are presented in Table 1.

$$\Delta_r H^0(T) = -R\{[\partial \ln K_e(T)]/(\partial T^{-1})\}, \tag{2}$$

$$\Delta_r H^0 H^0(0) = T[\Delta_r \Phi_0(T) - R\ln K_e(T)]. \tag{3}$$

Here $\Delta_r H^0 H^0(0)$, $\Delta_r H^0(T)$, and $\Delta_r \Phi_0(T)$ are changes in the enthalpy and reduced Gibbs energy of the reaction at temperature 0 and T (K), respectively, R is the gas constant, and K_e is the reaction equilibrium constant.

In vapor above sodium, potassium, rubidium, and cesium antimonates molecules of dimers $(MSbO_2)_2$ were also detected. Their enthalpies of formation were not determined because of the absence of published thermodynamic functions of these molecules.

The present work is a prolongation of the study of polymerization of gaseous salts of oxygen-containing acids. Earlier we have studied polymerization processes of gaseous phosphates [3], perrhenates [4], and iodates of [1] alkali metals.

In the mass spectra of vapor above antimonates of sodium (1170–1374 K), potassium (1121–1237 K), rubidium (1093–1197 K), and cesium (1092–1224 K) peaks of M^+, $MSbO_2^+$, $M_2SbO_2^+$, and $M_2Sb_2O_4^+$ ions were recorded, ratios of their intensities depending on temperature and the metal nature. The temperature range of measurements is shown in parentheses. Molecular precursors of all ions were identified by the procedure proposed in [2], where it was shown that the ions $MSbO_2^+$ and $M_2Sb_2O_4^+$ correspond to the direct ionization processes, and M^+ and $M_2SbO_2^+$, to the dissociative ionization of the molecules $MSbO_2$ and $M_2Sb_2O_4$, respectively. The complete coincidence of our mass spectra of vapor above the studied antimonates and those obtained in [2] indicates that the molecules $MSbO_2$ and $M_2Sb_2O_4$ pass into vapor.

To determine standard enthalpies of formation of monomeric and dimeric gaseous antimonites, we have measured temperature dependences of intensities of

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[1] For communication XXVI, see [1].

Table 1. Values of enthalpies of reactions (1), (4), and (5)

Compound	$\Delta_r H^0(298)$, kJ			$-\Delta_f H^0(298)$, kJ mol^{-1}		References
	reaction (1)	reaction (4)	reaction (5)	$MSbO_2$ (gas)	$M_2Sb_2O_4$ (gas)	
$NaSbO_3$	609±19	–	–	236	–	[2]
	547±45	756±80	339±20	298	934	This work
$KSbO_3$	585±24	–	–	269	–	[2]
	533±19	776±30	326±23	321	950	This work
$RbSbO_3$	552±26	–	–	306	–	[2]
	506±12	684±25	308±11	352	1022	This work
$CsSbO_3$	533±19	–	–	329	–	[2]
	476±27	727±35	303±22	386	1036	This work

M^+, $MSbO_2^+$, $M_2SbO_2^+$, and $M_2Sb_2O_4^+$ ionic currents, which have allowed us to calculate enthalpies of reactions (1), (4), and (5) for the midpoints of temperature ranges of measurements by Eq. (2).

$$2MSbO_3(cr.) = M_2Sb_2O_4(gas) + O_2(gas), \quad (4)$$

$$M_2Sb_2O_4(gas) = 2MSbO_2(gas). \quad (5)$$

The resulting values were reduced to the standard temperature 298 K. Temperature dependences of heat capacities of condensed antimonates were calculated by the Landiya method [5]. Values of standard entropies necessary for the calculations were found by the method described in [2], and melting points were determined experimentally on a high-temperature microscope developed in Grebenshchikov Institute of silicates chemistry. The instrument is intended for observation of melting, crystallization, and polymorphic transformation processes in crystalline substances at high temperatures, and also for studying phenomena of wetting of metals by non-metallic melts. The measured melting points of sodium, potassium, rubidium, and cesium antimonates were 1598, 1425, 1305, and 1487 K, respectively. The total error of their determination did not exceed ±20 K.

Thermodynamic functions of gaseous molecules were calculated by the statistical thermodynamics method in the approximation "rigid rotator–harmonic oscillator" using molecular parameters determined by quantum-chemical studying $MSbO_2$ and $M_2Sb_2O_4$ molecules. The scheme of the calculations is described in detail in [1]. The results obtained are presented in Tables 2 and 3.

For monomeric molecules a planar structure *a* of the C_{2v} symmetry with the alkali metal atom bound in the bidentate mode with two oxygen atoms (see the figure) corresponds to a global minimum on a potential energy surfaces (PES).

Values of internuclear distances and angles, and also of effective charges on atoms, bond orders, and dipole moments in $MSbO_2$ molecules found by the quantum-chemical calculations are presented in Table 2. In [6, 7] internuclear distances and angles in the SbO_2^- anion and also normal vibration frequencies of the anionic group SbO_2 were determined experimentally. Satisfactory agreement of the values of internuclear *r*(Sb–O) distance and OSbO angle in $MSbO_2$ molecules determined experimentally [6] and calculated in this work point to the validity of our calculations.

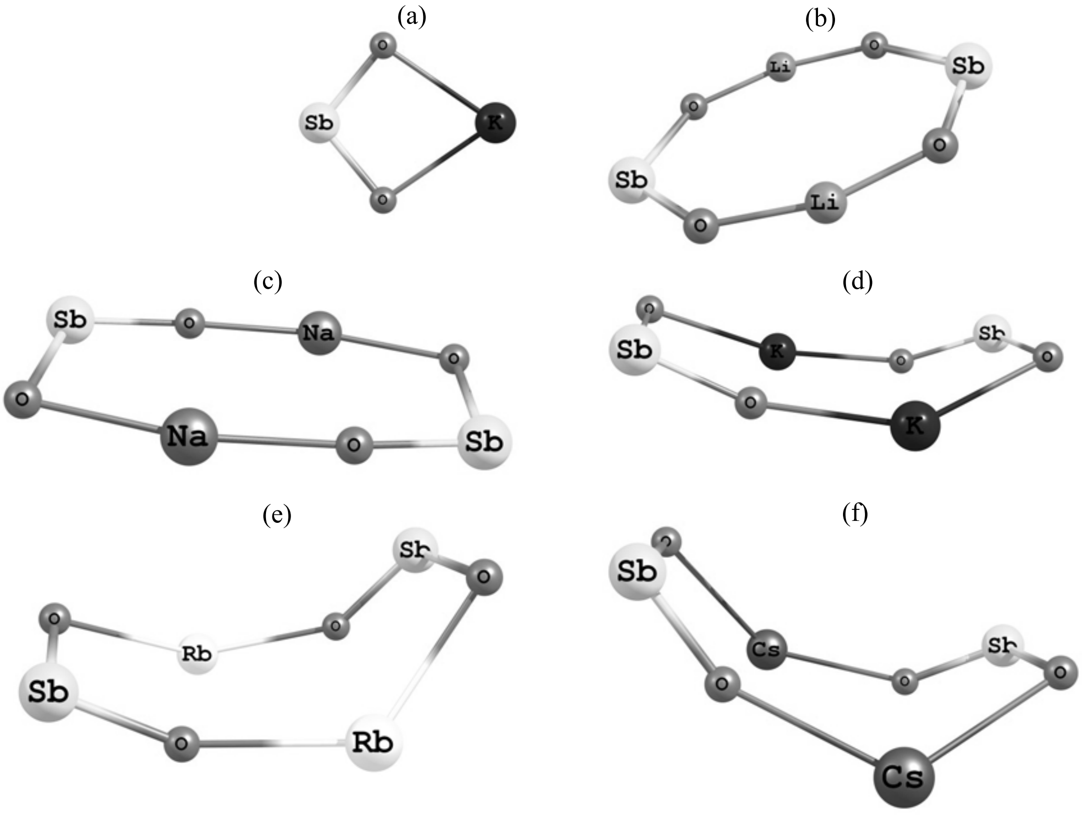
Structures (b)–(f) presented in the figure have minimal energies of dimeric molecules of gaseous antimonites. Structures containing a planar or slightly distorted cycle $(M–O–X–O)_2$, where M is an alkali metal, X is an anion-forming element, are characteristic of the majority of polymeric salts of alkali metals, the dimer symmetry being preserved irrespective of the alkali metal nature [1, 3, 4]. The symmetry of gaseous molecules $M_2Sb_2O_4$ significantly varies on passing from lithium salts to cesium salts, but the $(M–O–X–O)_2$ cycle is retained. Planar bidentate D_{2h} structures (b) and (c) are characteristic of gaseous dimers of lithium and sodium antimonates. Nonplanar structures (d)–(f) of C_1 symmetry correspond to a minimum on the potential energy

Table 2. Values of molecular parameters, effective charges on atoms, bond orders, and dipole moments of molecules of gaseous antimonites of alkali metals calculated by the density functional method

Parameter	$LiSbO_2$	$NaSbO_2$	$KSbO_2$	$RbSbO_2$	$CsSbO_2$
r(M–O), Å	1.872	2.211	2.521	2.602	2.757
r(Sb–O), Å	1.861	1.856	1.852	1.850	1.852
r(Sb–M), Å	2.555	2.916	3.255	3.354	3.520
∠OSbO, deg	94.0	98.6	101.0	101.0	101.7
Effective charge on atom (e^- charge units)					
M	0.52	0.54	0.63	0.77	0.72
O	–0.82	–0.83	–0.85	–0.90	–0.88
Sb	1.12	1.11	1.07	1.04	1.04
Bond order					
M–O	0.44	0.40	0.29	0.16	0.22
O–Sb	1.26	1.29	1.34	1.36	1.35
Dipole moment, D	0.58	3.10	4.92	5.70	5.25

Table 3. Values of molecular parameters, effective charges on atoms, bond orders, and dipole moments of molecules of dimers of antimonites of alkali metals calculated by the density functional method

Parameter	$(LiSbO_2)_2$	$(NaSbO_2)_2$	$(KSbO_3)_2$	$(RbSbO_3)_2$	$(CsSbO_3)_2$
r(M–O), Å	1.774	2.161	2.510	2.611	2.744
r(M–O'), Å	1.774	2.240	2.600	2.670	2.801
r(Sb–O), Å	1.847	1.861	1.862	1.860	1.857
r(Sb–O'), Å	1.847	1.841	1.837	1.837	1.837
r(Sb–Sb), Å	5.710	6.415	6.577	6.040	6.162
r(M–M), Å	3.609	3.173	3.830	4.033	4.388
$\angle_{tors}$OSbO, deg	179.9	179.3	155.9	135.5	135.1
∠OSbO', deg	106.1	100.1	102.5	102.7	103.4
Effective charge on atom (e^- charge units)					
M	0.52	0.56	0.61	0.75	0.84
O	–0.88	–0.91	–0.88	–0.96	–0.97
O'	–0.88	–0.82	–0.83	–0.87	–0.90
Sb	1.25	1.17	1.10	1.07	1.04
Bond order					
M–O	0.44	0.32	0.23	0.11	0.06
M–O'	0.44	0.38	0.25	0.16	0.07
O–Sb	1.23	1.16	1.22	1.24	1.29
O'–Sb	1.23	1.38	1.43	1.45	1.45
Dipole moment, D	0.006	0.03	2.15	4.47	4.95



Structures of (a) monomeric and (b–f) dimeric molecules of gaseous antimonites of alkali metals.

surface of dimers of potassium, rubidium, and cesium antimonates, a distortion of a plane increasing on passing from the potassium antimonite dimer to the cesium antimonite dimer. Planar structures correspond to local minima on the potential energy surface. Differences in energy between planar and distorted structures are equal to 14, 17, and 10 kJ mol^{-1} for potassium, rubidium, and cesium antimonites, respectively. For the dimer of lithium antimonite the local minima on the potential energy surface were not found. The obtained values of enthalpies of reactions reduced to the standard temperature are presented in Table 1.

Total energies of gaseous antimonates and their dimers found by quantum-chemical calculations allow us to calculate enthalpies of dimerization reactions (5) of lithium, sodium, potassium, rubidium, and cesium antimonates, which are equal to –221, –180, –145, –140, and –700 kJ, respectively. The values obtained for sodium potassium, and rubidium antimonates are underestimated as compared with our experimental data, and the value for cesium antimonite is essentially overestimated, which is attributable to the fact that the more narrow basis (3-21G) was used for the cesium atom in the calculations, as compared to the other alkali metals [6-311G(df)]. The wide scatter of the cited values does not allow us to recommend that the value of enthalpy of reaction (5) be used for lithium antimonite.

Values of enthalpies of reaction (1) found in the present work and in [2] differ from each other by 40–60 kJ. The difference in the values is defined by differences in used thermodynamic functions of gaseous antimonites calculated in this work by modern quantum-chemical methods and those accepted in [2] as a result of a number of estimates and approximations. In particular, in [2] the distance *r*(Sb–O) and the angle OSbO for the SbO_2 anionic group are taken from [6] where they were obtained on the basis of moments of inertia with a high inaccuracy and were averaged for all antimonites of alkali metals. The rest of vibration frequencies and also internuclear alkali metal-oxygen distances were taken from molecules of nitrites of alkali metals with similar structures [8].

According to our estimation, the inaccuracy in enthalpies of reactions (1), (4), and (5) involving sodium antimonite is greater than analogous values for reactions involving potassium, rubidium, and cesium antimonites. It can be due to a partial dissociation of sodium antimonite accompanied by passing monatomic sodium in vapor. It is rather complicated to separate contributions of $Na^+(Na)$ and $Na^+(NaSbO_2)$ ionic currents to the total intensity of the Na^+ ionic current, therefore our values of enthalpies of reactions (1), (4), and (5) involving sodium antimonite and its dimer should be considered as estimates.

As there are no published values of standard enthalpies of formation of alkali metals crystalline antimonates, to calculate values of standard enthalpies of formation of gaseous monomeric and dimeric antimonites by Eqs. (1) and (4), we used the data of [2] where enthalpies of formation of crystalline antimonates have been calculated by the Yudin's method [9]. The same values were also estimated in [10] as follows. The handbook [11] contains the values of enthalpies of formation of crystalline Na_3AsO_4 (–1535.5 kJ mol^{-1}) and Na_3SbO_4 (–1485.3 kJ mol^{-1}). The ratio of these values gives a coefficient, which can be multiplied by standard enthalpies of formation of arsenates $MAsO_3$ of alkali metals to estimate enthalpies of formation of corresponding crystalline antimonates $MSbO_3$ of alkali metals. According to [2] and [10], the values of enthalpies of formation of crystalline antimonates of alkali metals differ on the average by 16 kJ mol^{-1} (~2%).

The defined values of enthalpies of formation of gaseous antimonites of alkali metals and their dimers are given in Table 1. Errors of the determination of standard enthalpies of gaseous antimonites formation are not given, because the enthalpies of formation of crystalline antimonates of alkali metals appearing in Eqs. (1) and (4) are only estimated.

It was assumed in [12] that the tendency of gaseous salts of oxygen-containing acids to polymerization is due to the fact that molecules of gaseous monomers have dipole moments. Quantum-chemical calculations have shown that the dipole moment increases on passing from lithium antimonite to rubidium antimonite and slightly decreases on passing from rubidium antimonite to cesium antimonite. Content of dimers in vapor above antimonates of alkali metals vary in the same way as in the case of phosphates of alkali metals [3]: it is maximal for potassium antimonite (3%) and minimal for cesium antimonite (0.2%). Relative content of dimers in vapor above sodium and rubidium antimonates are approximately the same (1%). Analogous results have been obtained in [2]. The same trend in the variation of relative content of dimers in vapor was observed earlier for phosphates [3], perrhenates [4], and iodates [1] of alkali metals. No correlation between the values of dipole moments of monomer molecules and relative content of dimers in vapor is observed, which points to the fact that the value of dipole moment does not influence the ability of gaseous salts to polymerization.

The presence of dipole moments in the monomeric molecules of salts of oxygen-containing acids not always results in the formation of polymeric compounds, in particular, polymeric compounds were detected in a vapor above metaborates [13], nitrites [14, 15], and bismuthites [16, 17] of alkali metals, whereas the data on the dimerization of molecules MPO_2 [18] and MVO_2 [19] in vapor were absent.

It was found in [20] that the atomization enthalpy of gaseous salts in isocation series of gaseous salts linearly depends on the atomization enthalpy of the corresponding gaseous anion-forming oxides. The dependence can be expressed by Eq. (6).

$$\Delta_{at}H^0(\text{salt, gas, 298}) = k\Delta_{at}H^0\,(\text{anion-forming oxide, gas, 298}) + b. \qquad (6)$$

The absence of published values of standard enthalpies of formation of gaseous Sb_2O_3 does not allow us to estimate the degree of reliability of our data. The value of $\Delta_fH^0(Sb_2O_3\text{, gas, 298})$ can be calculated, using values of atomization enthalpies of gaseous sodium, potassium, rubidium, and cesium antimonites determined in the present work and also of coefficients k and b in Eq. (6) found earlier for isocation series of these alkali metals [20]. The enthalpies of atomization and formation of the gaseous antimony oxide Sb_2O_3 equal to 1574±18 and –(114±18) kJ mol^{-1}, respectively, in turn enable us to estimate the enthalpy of formation of gaseous lithium antimonite $LiSbO_2$ equal to –309 kJ mol^{-1}. This value and the enthalpies of formation of sodium, potassium, rubidium, and cesium antimonites agree with the trend in the variation of enthalpies of formation of gaseous salts of alkali metals.

EXPERIMENTAL

The work was fulfilled by the method of high-temperature mass spectrometry on an MS-1301 mass spectrometer at the ionizing voltage of 25 and 70 V.

Antimonates of alkali metals were synthesized by the procedure described in [2]. The samples were evaporated from platinum cells, which were heated by a resistance furnace. The temperature was measured by a platinum, platinum-rhodium thermocouple accurate to ±1 K. The instrumentation was calibrated against vapor pressure of KPO_3 [21].

Quantum-chemical calculations were carried out using the GAMESS program complex [22] by the density functional DFT method in the B3LYP approximation [23]. The 3-21G(3d) basis was selected for rubidium and cesium atoms, calculations for the antimony atom were carried out using the LANL2DZ effective core potential [24] and the 6-311G(df) potential for atoms of the other elements.

When determining melting points of antimonates on a high-temperature microscope we applied iridium as a heater, which allowed us to carry out experiments starting from room temperature up to 2200°C. To plot a calibration graph "current voltage on the heater–melting point," we used compounds with precisely known melting points, which are given in parentheses (°C): K_2SO_4 (1070), FeO (1360), CaF_2 (1402), $CaSO_4$ (1450), WO_3 (1470), Nb_2O_5 (1490), $CaAl_2O_4$ (1600), CoO (1935), TiO_2 (1850), NiO (1955), and γ-Ca_2SiO_4 (2130). Determination of melting points involved two stages. The first stage consists in measuring of a current voltage on the heater, at which complete melting-down of a microscopic object (sample) occurred. The second stage is the determination of a melting point (liquidus temperature) by the calibration graph "current voltage on the heater–melting point."

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