ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 6, pp. 871–874. © Pleiades Publishing, Inc., 2006.
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Thermochemical Study of Gaseous Salts of Oxygen-containing Acids: XX.[1] Phosphates of Beryllium and Beryllates of Alkaline-Earth Metals

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Received January 26, 2006

Abstract—Gas-phase reactions involving beryllium phosphates and calcium, strontium, and barium beryllates were studied. The standard enthalpies of gaseous formation and atomization of $BePO_3$, $BePO_2$, $CaBeO_2$, $SrBeO_2$, and $BaBeO_2$ salts were determined.

DOI: 10.1134/S1070363206060053

Beryllium oxide passes into vapor as $(BeO)_n$ (n = 1–5), atomic beryllium, and oxygen at sufficiently high temperatures (2100–2200 K) [2]. When studying BeO vaporization from molybdenum and tungsten effusion cameras [3] we showed that, along with the above-mentioned compounds, $BeMoO_3$, $BeWO_3$, $BeWO_4$, and Be_2WO_4 are present in the vapor. On joint vaporization of beryllium oxide with boron, niobium, and tantalum oxides B_2O_3, Nb_2O_5, and Ta_2O_5, gaseous BeB_2O_4 [4], $BeNbO_3$ [5], and $BeTaO_3$ [6], respectively, are formed. In all these cases BeO exhibits basic properties and participates in the synthesis of gaseous salts as a cation-forming oxide. In [7] we found that heating of beryllium in the 1250–1850 K range results in consecutive vaporization of phosphorus oxides P_4O_{10}, PO_2, and PO; simultaneously beryllium oxide is accumulated in the condensed phase. No coexistence of phosphorus and beryllium oxides was observed in the gas phase. According to the reactivity criterion of gaseous oxides [8], beryllium oxide can exhibit amphoteric properties, participating in gas-phase synthesis of salts both as a cation- and an anion-forming oxide.

We created conditions for coexistence of beryllium oxides with phosphorus and alkaline-earth metal oxides in vapor and obtained gaseous phosphates $BePO_2$ and $BePO_3$, as well as calcium, strontium, and barium beryllates, respectively. For this purpose, mixtures of beryllium oxide with calcium or strontium oxide were evaporated from a single one-temperature tungsten chamber, and mixtures of beryllium oxide with barium oxide or magnesium diphosphate, from a double two-temperature molybdenum chamber [9]. The low-volatile beryllium oxide was loaded in the upper compartment of the double two-temperature chamber, and barium oxide or magnesium diphosphate, which dissociated on heating to form PO and PO_2 in the vapor [10, 11], were loaded in the lower compartment. Ion currents of $Be_nO_n^+$ (hereinafter n = 1–5), Ba^+, BaO^+, and $BaBeO_2^+$ were detected in the mass spectra of the vapor over the BaO–BeO system at 2150–2300 K. With magnesium diphosphate instead barium oxide in the lower compartment of the two-temperature chamber and at 2200–2300 K in the upper compartment, $Be_3O_3^+$, PO^+, PO_2^+, $BePO_2^+$ and $BePO_3^+$ ion peaks were detected in the vapor mass spectra. When mixtures of beryllium oxide with calcium or strontium oxides were evaporated from the single camera in the range 2140–2425 K, Ca^+, CaO^+, and $CaBeO_2^+$ or Sr^+, SrO^+, and $SrBeO_2^+$ ion peaks, respectively, were observed in the mass spectra along with $Be_nO_n^+$ ion peaks. The ratio of ion currents in all the cases depended on the temperature and time of evaporation. Ions resulted from ionization of molecules formed by the reactions of alkalineearth metal and beryllium oxides with the materials of effusion chambers [3, 12] were also detected in the vapor mass spectra.

To identify molecular precursors of the recorded ions, we measured the appearance energies of the latter (eV, +0.5): $Be_2O_2^+$ 11.0, $Be_3O_3^+$ 10.6, $Be_4O_4^+$ 11.0, $Be_5O_5^+$ 11.0, PO_2^+ 11.7, PO^+ 9.2, Ca^+ 6.0, CaO^+

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

6.5, Sr^+ 5.5, SrO^+ 6.0, Ba^+ 5.5, and BaO^+ 6.5. These ions all are formed by direct ionization of the corresponding molecules [13]. The appearance energy of $BaBeO_2^+$ is rather low (8.0 eV), which allows us to identify this ion as molecular. We failed to measure appearance energies for $BePO_2^+$, $BePO_3^+$, $CaBeO_2^+$, and $SrBeO_2^+$ because of the low intensity of their ion currents. However, by analogy with chromium [14], manganese [15], and iron [16] phosphates and barium beryllate, it is safe to assign them to direct ionization of $BePO_2$, $BePO_3$, $CaBeO_2$, and $SrBeO_2$ molecules.

Analysis of the vapor mass spectra and appearance energies of ions provide evidence to show that beryllium oxides Be_nO_n, atomic calcium, strontium, barium, and their oxides, phosphorus oxides PO and PO_2, beryllium phosphates $BePO_2$ and $BePO_3$, and calcium, strontium, and barium beryllates are present in the gas phase over the systems studied. To find standard enthalpies of formation for gaseous salts identified for the first time, we determined the equilibrium constants of gas-phase reactions (1)–(6) and calculated the enthalpies of these reactions by Eq. (7).

$$1/3Be_3O_3 + PO_2 \rightleftarrows BePO_3, \qquad (1)$$

$$1/3Be_3O_3 + PO \rightleftarrows BePO_2, \qquad (2)$$

$$MO + 1/3Be_3O_3 \rightleftarrows MBeO_2, \qquad (3)$$

$$MO + 1/4Be_4O_4 \rightleftarrows MBeO_2, \qquad (4)$$

$$CaO + 1/2Be_2O_2 \rightleftarrows MBeO_2, \qquad (5)$$

$$CaO + 1/5Be_5O_5 \rightleftarrows MBeO_2, \qquad (6)$$

$$\Delta_r H^0(0) = T[\Delta_r \Phi^0(T) - R\ln K_e(T)]. \qquad (7)$$

Hereinafter M = Ca, Sr, Ba; $\Delta_r H^0(0)$, $\Delta_r \Phi^0(T)$ are the reaction enthalpy and reduced Gibbs energy at 0 and T, K, respectively, R is the gas constant, K_e is equilibrium constant of the reaction.

The thermodynamic functions of gaseous oxides necessary for calculating the reaction enthalpies and their reducing to the standard temperature (298 K) were taken from [17]. The thermodynamic functions of gaseous salts formed by beryllium oxide, that were obtained for the first time, were calculated by statistical thermodynamics methods in the rigid rotor–harmonic oscillator approximation. The interatomic distances and normal mode frequencies were calculated using the GAMESS program complex [18] by the ab initio SCF method and by the DFT method in the B3LYP approximation [19]. For beryllium, oxygen, phosphorus, and calcium atoms, the 6-31G* basis was taken, and for strontium and calcium atoms, the Basch–Stevens–Krauss effective potential [20] was used. The results of the ab initio calculations were further used as the initial approximation in the DFT calculations. The B3LYP method makes it possible to account for electron correlation effects in molecular systems and is widely used for calculation of energy effects in chemical processes.

For beryllium phosphates, a C_{2v} structure with the beryllium atom bound to oxygen atoms in a bidentate mode, is minimal in energy. The DFT interatomic distances were as follows: $BePO_3$: r(P–O) 1.54, r(P=O) 1.45, and r(Be–O) 1.64 Å, OPO angle 98°; $BePO_2$: r(P–O) 1.70, r(Be–O) 1.47 Å, OPO angle 89°. The normal vibration modes were as follows, cm^{-1}: $BePO_3$: 1409, 1081, 942, 726, 593, 588, 400, 353, and 120; and $BePO_2$: 1147, 1055, 721, 698, 569, and 376. The calculated molecular parameters of $BePO_3$, namely, the P–O distances and normal vibration frequencies in the anionic PO_3 group, agree well with those calculated earlier for $BaPO_3$, $CrPO_3$ [14], $MnPO_3$ [15], and $FePO_3$ [16], as well as with the experimental frequencies determined by the matrix isolation method for alkali metal phosphates [21]. The Be–O distance is equal to the sum of beryllium and oxygen ionic radii [3]. The calculated molecular parameters of the PO_2 group in $BePO_2$ differ considerably from those of $CrPO_2$ [13], $MnPO_2$ [14], $FePO_2$ [15] molecules and from the experimental data in [21, 22]. Since the reason for such discrepancy is not clear at present, in the calculations of the thermodynamic functions of $BePO_2$ we took for the molecular parameters of the PO_2 group those in alkali metal phosphites [21, 22] and for the interatomic distance and normal mode frequencies of the BeO group, those in $BePO_3$.

For beryllates of alkaline-earth metals, too, a C_{2v} structure is minimal in energy. The interatomic distances and normal vibration modes are given in Table 1. According to the calculated data, the Be–O distances and the OBeO angle are practically independent of the nature of the alkaline-earth metal. The Be–O distance is shorter than in $BePO_3$, which points to a higher oxidation state of beryllium in beryllates and to different oxidation states of beryllium in gaseous salts, where beryllium plays the role of a cation- or an anion-forming element.

The enthalpies of reactions (1)–(6), calculated by Eq. (7), the standard enthalpies of formation and atomization of gaseous beryllium gaseous phosphates and alkaline-earth metal beryllates at 298 K, and as well as the calculated standard entropies of first-prepared salts are given in Table 2.

As shown in [23, 24], the atomization enthalpy of a gaseous salt in isocationic series of gaseous salts of oxygen-containing acids linearly depends on the

Table 1. Molecular parameters of gaseous alkaline-earth metal beryllates, calculated by quantum-chemical methods

Parameter	Method	$CaBeO_2$	$SrBeO_2$	$BaBeO_2$
r(Be–O), Å	HF	1.433	1.425	1.415
	MP2	1.465	1.454	1.443
	DFT	1.451	1.442	1.432
r(M–O), Å	HF	2.184	2.217	2.214
	MP2	2.242	2.254	2.257
	DFT	2.196	2.255	2.240
OBeO angle, deg	HF	130.5	130.9	128.5
	MP2	132.2	131.1	127.7
	DFT	129.9	130.7	127.8
Vibration modes, cm^{-1}	HF	1349, 1011, 682, 541, 506, 454	1391, 1025, 815, 661, 557, 519	1424, 1051, 657, 530, 317, 290
	MP2	1237, 924, 621, 514, 438, 417	1263, 947, 635, 454, 409, 366	1311, 979, 605, 469, 305, 273
	DFT	1245, 965, 678, 506, 473, 455	1248, 977, 703, 483, 402, 400	1299, 1002, 682, 481, 326, 296

Table 2. Reaction enthalpies and standard entropies and enthalpies of formation and atomization of gaseous salts formed by beryllium oxide

Molecule	Temperature range, K	Reaction	$-\Delta_r H^0(0)$, kJ	$-\Delta_f H^0(298)$, kJ mol^{-1}	$\Delta_{at} H^0(298)$, kJ mol^{-1}	$S^0(298)$, J mol^{-1} K^{-1}
$BePO_3$	2213–2328	1	149 ± 14	777 ± 22	2165 ± 23	290.2
$BePO_2$	2213–2328	2	60 ± 13	433 ± 21	1572 ± 22	274.3
$CaBeO_2$	2196–2354	3	118 ± 3	415 ± 24	1415 ± 25	297.9
	2196–2354	4	49 ± 4			
	2347–2354	5	260 ± 2			
	2349–2354	6	27 ± 2			
$SrBeO_2$	2138–2424	3	81 ± 3	436 ± 24	1419 ± 25	323.1
	2138–2424	4	14 ± 3			
$BaBeO_2$	2154–2298	3	17 ± 4	485 ± 21	1486 ± 22	337.2
	2154–2298	4	–50 ± 4			

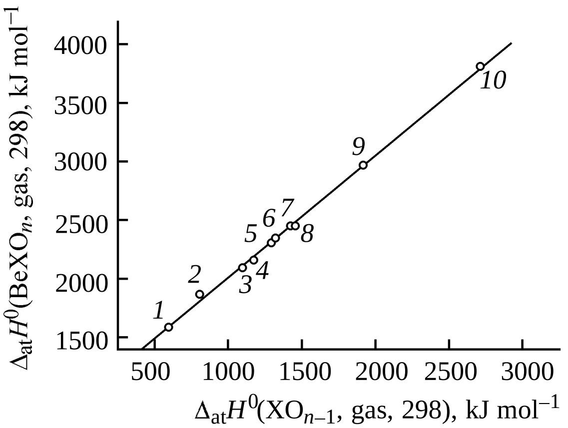
atomization enthalpy of the corresponding gaseous anion-forming oxide. This dependence has Eq. (8).

$$\begin{aligned}&\Delta_{at}H^0(M_mXO_n,\ \text{gas},\ 298)\\ &k\Delta_{at}H^0(XO_{n-1},\ \text{gas},\ 298) + b. \qquad (8)\end{aligned}$$

Our present results together with data in [3, 4] allowed us to obtain a similar dependence for the isocationic series of gaseous beryllium salts (see figure). The high correlation coefficient (0.9987) and small standard deviation (34.6) point to the reliability of the data obtained. The coefficients k and b are equal to 1.036 ± 0.019 and 981 ± 28, respectively. The resulting dependence makes it possible to estimate atomization enthalpies for previously unexplored gaseous beryllium salts. It is also necessary to note that the resulting atomization enthalpies of gaseous beryllates of alkaline-earth metals also agree well with those for isocationic series of gaseous calcium, strontium, and barium salts [12].

EXPERIMENTAL

The work was carried out on an MS-1301 mass spectrometer at an electron ionizing energy of 25 eV. Samples were evaporated from single tungsten effusion chambers and from a double two-temperature molybdenum chamber. The chambers were heated by electron bombardment, the temperature was measured by an EOP-66 optical pyrometer. The partial pressures of vapor components were measured using gold as a pressure standard [25]. The ionization cross sections were calculated by the additivity method [26], and the ionization cross sections of gaseous salts were multiplied by 0.7 [27]. The molecular compositions of vapor was determined from the appearance energies of ions in the mass spectra, measured by the method



Atomization enthalpies of gaseous beryllium salts vs. atomization enthalpies of gaseous anion-forming oxides. (*1*) $BePO_2$, (*2*) $BeBO_2$, (*3*) $BePO_3$, (*4*) $BeMoO_3$, (*5*) $BeWO_3$, (*6*) $BeMoO_4$, (*7*) $BeWO_4$, (*8*) and BeB_2O_4.

of vanishing ion current, against the ionization energy of gold [13]. The instrument was calibrated by the vapor pressure of CaF_2 [17].

ACKNOWLEDGMENTS

The work was financially supported by the *Universities of Russia* Program (grant no. UR.05.01.312).

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