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Thermochemical Study of Gaseous Salts of Oxygen-Containing Acids: XXVIII.[1] Gallium Borates

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Abstract—Reactions of the gas-phase synthesis of gallium borate from oxides and its dimerization were studied. It was found that the molecules Ga_2O, B_2O_3, $GaBO_2$, and $(GaBO_2)_2$ are present in the vapor above the Ga_2O_3–B_2O_3 system. Enthalpies of formation and atomization of gaseous gallium borates were determined.

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At present an extensive experimental material on the determination of thermodynamic and structural characteristics of gaseous salts of oxygen-containing acids formed by oxides of elements of the first and second groups of the periodic system and also of the first transition series has been accumulated. Salts formed by oxides of the elements of 13th and 14th groups of the periodic system are poorly studied.

Metaborates represent one of the most numerous and most studied groups among gaseous salts of oxygen-containing acids [2]. Gaseous metaborates are formed either on the evaporation of condensed metaborates or as a result of the gas-phase synthesis from oxides in high-temperature vapors. Results of works dedicated to the problem of vapor formation by metaborates of alkaline metals point to the presence of monomer MBO_2, dimer $(MBO_2)_2$, and in some cases trimer $(MBO_2)_3$ molecules in vapor.

Elements of the 13th group, according to their position in the periodic system, can form two kinds of oxides: M_2O_3 and M_2O. Boron oxide B_2O_3 evaporates on heating congruently without dissociation. Gallium and indium oxides Ga_2O_3 and In_2O_3 at temperatures about 1600 and 1400 K, respectively, pass in vapor in the form of M_2O and oxygen [3], the degree of gallium and indium oxidation in the condensed phase equal to +3 is retained in this case. At temperatures about 2100 K and higher Al_2O_3 passes in vapor in the form of atomic aluminum, Al_2O, AlO, and oxygen. Tl_2O_3 loses oxygen at rather low temperatures (650−700 K) and turns into Tl_2O, which evaporates on the further heating congruently without decomposition. Gaseous gallium(I), indium(I), and thallium(I) oxides react with acid oxides to form salts similar to salts of alkaline metals [4].

The authors of [5] have detected molecules AlBO and $AlBO_2$ in the vapor formed on heating the system Al_2O_3–B_2O_3 in reducing conditions and have measured equilibrium constants and enthalpies of gas-phase reactions (1) and (2) at 1500 K.

$$1/2\ Al_2O + 1/2\ B_2O_3 = AlBO_2, \qquad (1)$$

$$Li + AlBO_2 = LiBO_2 + Al. \qquad (2)$$

Authors of the handbook [6] have reduced the values of enthalpies of reactions (1) and (2) found in [5] to standard conditions and have determined the standard enthalpy of the $AlBO_2$(gas) formation of –541.4±17 kJ mol^{-1} at 298 K.

It has been confirmed in [7−10] that the composition of vapor above indium and thallium metaborates is similar to the composition of vapor above metaborates of alkaline metals except that polymers have not been found in the vapor above $InBO_2$. The enthalpies of formation of gaseous $InBO_2$ and $TlBO_2$ at 0 K are –520.5±24.3 and –528.4±22 kJ mol^{-1}, respectively. The appearance energies of In^+ and Tl^+ ions measured by the electron impact method in mass spectra of vapor above $InBO_2$ and $TlBO_2$ in combination with the ionization energies of indium and thallium have allowed energies of M–BO_2 bonds

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

Table 1. Partial pressures of molecular forms of vapor above the system $Ga_2O{-}B_2O_3$ and values of reaction (3) enthalpy

T, K	p_i, atm			$-\Delta_rH^0(0)$, kJ
	Ga_2O, $\times 10^8$	B_2O_3, $\times 10^6$	$GaBO_2$, $\times 10^5$	
1493	2.7	21.1	1.1	−5.6
1488	2.1	14.9	1.0	−0.3
1525	3.8	28.7	1.9	−0.5
1523	2.9	28.7	1.8	2.4
1513	1.5	5.8	1.1	18.1
1506	2.2	2.8	0.9	16.7
1473	7.0	6.0	1.6	7.8
1463	1.8	4.5	1.0	17.0
1477	2.2	1.3	0.4	7.5
1474	0.6	0.8	0.2	10.1
1491	2.1	4.7	1.0	14.8
1488	1.8	5.3	1.1	17.1
1487	2.1	5.1	0.9	9.9
1485	1.2	5.0	0.8	14.5
1478	1.2	4.5	0.7	13.7
1479	0.9	4.5	0.7	16.1
1499	1.8	7.4	1.0	11.2
1502	1.5	7.4	1.0	12.0
1500	1.5	4.9	0.4	4.3
1502	0.6	4.5	0.4	4.8
1526	2.0	9.6	0.9	2.7
1528	1.6	9.1	0.8	3.9
1528	1.2	2.7	0.6	13.3
1524	1.2	1.3	0.3	10.2
			Average value:	8.9±7.0

(here M = In, Tl) to be found. Combinations of the bond energies with formation enthalpies of gaseous indium, thallium, and BO_2 radical have made it possible to calculate the formation enthalpies of gaseous indium and thallium metaborates. It is necessary to note that the values of the formation enthalpies of gaseous metaborates of alkaline metals determined in [11] in a similar way substantially differed from the values found by measuring sublimation enthalpies of corresponding crystal salts. Later on the practice of the determination of thermochemical values by measuring appearance energies was rejected, and these values were assumed to be incorrect.

Owing to its high basicity, Ga_2O acts as a cation-forming oxide in gas-phase synthesis of salts from oxides. At present gaseous gallium phosphates [12], molybdates, and tungstates [13] are known.

Peaks of the ions Ga^+, Ga_2^+, $B_2O_3^+$, Ga_2O^+, MoO_2^+, MoO_3^+, $GaBO_2^+$, $Ga_2BO_2^+$, and $Ga_2B_2O_4^+$ were recorded in the mass spectra of vapor above the system $Ga_2O_3{-}B_2O_3$ in the temperature range of 1450–1550 K. To determine molecular predecessors of the above-mentioned ions, we have measured their appearance energies, which comprise (eV, ±0.3): Ga^+ 10.9, Ga_2^+ 12.8, Ga_2O^+ 7.6, MoO_2^+ 9.5, MoO_3^+ 12.1, $B_2O_3^+$ 14.0, and $GaBO_2^+$ 10.1. We failed to measure appearance energies of $Ga_2BO_2^+$ and $Ga_2B_2O_4^+$ ions because of low intensities of the corresponding ionic currents.

The analysis of the mass spectrum of vapor above the system under study and the values of appearance energy of ions have shown that the molecules Ga_2O, MoO_2, MoO_3, B_2O_3, $GaBO_2$, and $(GaBO_2)_2$ are present in the vapor. The appearance energies of the ions Ga_2O^+, MoO_2^+, MoO_3^+, and $B_2O_3^+$ coincide with the ionization energies of corresponding molecules [14], and the appearance energy of the ion $GaBO_2^+$ is comparable with ionization energies of metaborates of alkaline metals [15]. The nature of $M_2BO_2^+$ ions, which are the products of dissociative ionization of $(MBO_2)_2$ molecules, has been studied in detail in [16]. The appearance energies of Ga^+ and Ga_2^+ ions, which exceed the ionization energies of atomic gallium and Ga_2 dimer, respectively [14], and also the constancy of the ratios of intensities of ionic currents $Ga^+/GaBO_2^+$ and Ga_2^+/Ga_2O^+ point to the fact that the ions Ga^+ and Ga_2^+ are the products of dissociative ionization of $GaBO_2$ and Ga_2O molecules, respectively. The ions MoO_2^+ and MoO_3^+ are the products of the direct ionization of molybdenum oxides, which are formed in the reaction of Ga_2O_3 with a cell material.

Partial pressures of molecular vapor species were determined by the method of comparing ionic currents, using gold [17] and silver [18] as external pressure standards. To determine the partial pressures, we calculated ionization cross-sections of molecules by the additivity method, using atomic cross-sections [19]. The results of the measurements of partial pressures of molecular vapor forms are presented in Tables 1 and 2.

To determine standard enthalpies of formation of gallium borates, we measured equilibrium constants of gas-phase reactions (3) and (4) and calculated their enthalpies using Eq. (5).

$$Ga_2O + B_2O_3 = 2\ GaBO_2, \tag{3}$$

$$2\ GaBO_2 = (GaBO_2)_2, \tag{4}$$

$$\Delta_r H^0(0) = T[\Delta_r\Phi^0(T) - R\ln K_e(T)]. \tag{5}$$

Here $\Delta_r H^0(0)$ and $\Delta_r\Phi^0(T)$ are changes in the enthalpy and reduced Gibbs potential of a reaction at 0 and T K, respectively, R is the gas constant, K_e is equilibrium constant of the reaction. Thermodynamic functions of gaseous gallium and boron oxides were taken from the handbook [20], and thermodynamic functions of gallium borate and its dimer were calculated by statistical thermodynamics methods in the approximation “rigid rotator–harmonic oscillator.”

Structural parameters and normal vibration frequencies of gaseous molecules $GaBO_2$ and $(GaBO_2)_2$ were calculated by quantum-chemistry methods using the PC GAMESS version [20] of the GAMESS(US) quantum-chemical package [21]. All the calculations were carried out without imposing restrictions on symmetry.

It was found by gas electron-diffraction methods [22, 23] and IR spectroscopy of molecules isolated in inert matrixes [24, 25] that MBO_2 molecules of metaborate of alkaline metals have a planar trigonal configuration with a linear OBO group and MOB angle ~130° (C_s symmetry group). A linear configure-tion ($C_{\infty v}$ symmetry group) of these molecules was established by the quantum-chemical studies [26–28]. To check a hypothesis on the possible existence of cyclic groups in gaseous salts of indium and thallium metaborates, the IR absorption spectra of vapors above these compounds were studied [29]. A conclusion on the bidentate nature of the metal-oxygen bonds was drawn on the basis of the spectral data.

Above-mentioned MBO_2 structures presented in Figs. 1a–1c were optimized by the B3LYP/6-31G method. Structure (b) with multiplicity 1 has the minimal energy among the considered structures; the same structure with multiplicity 3 is located higher by 405.0 kJ mol^{-1}. Structure (a) reduces to structure (b) in the course of the optimization. Structure (c) has appeared to be a transition state with a higher energy (by 107.6 kJ mol^{-1}) than minimum (b). It is necessary to pay attention to the calculated multiplicities of B−O bonds in anions with linear (b) and cyclic (c) structures: the multiplicity of the B−O bond of 1.615 in the cyclic structure is close to the arithmetic mean of the B−O$_t$ (2.156) and B−O$_\mu$(1.167) multiplicities in the linear structure.

Table 2. Partial pressures of monomer and dimer of gallium borate and values of reaction reaction (4) enthalpy

T, K	p_i, atm		$-\Delta_r H^0(0)$, kJ
	$GaBO_2$, $\times10^4$	$(GaBO_2)_2$, $\times10^7$	
1425	2.5	1.1	231.5
1422	1.9	1.0	235.6
1443	2.9	2.0	237.4
1451	3.1	2.1	237.5
1448	3.0	1.9	236.8
1454	2.8	1.7	238.1
1482	4.3	3.8	241.1
1486	2.4	3.2	254.4
1520	4.3	4.4	248.6
1519	3.3	4.3	254.8
1533	2.9	2.2	252.2
1529	1.4	0.91	259.5
1576	1.4	0.76	263.6
1581	0.84	0.46	271.0
1586	0.73	0.46	275.5
		Average value: 249.2±13.7	

Later on structures (a) and (b) were considered by the B3LYP method in wider bases: the full-electron basic set cc-pVQZ [30] was used for atoms B and O, and the same full-electron basic set [31] or the cc-pVQZ (PP) basis [32] with the corresponding pseudo-potential [33], for atom Ga.

Passing from the trigonal structure to the linear structure with changing the GaOB angle from 173° (calculated without pseudo-potential) or 176° (calculation with pseudo-potential) up to 180° results in the energy change less than 1 kJ mol^{-1}, the linear structure in all cases having a higher energy. Moreover, in the case of the calculation without pseudo-potential the

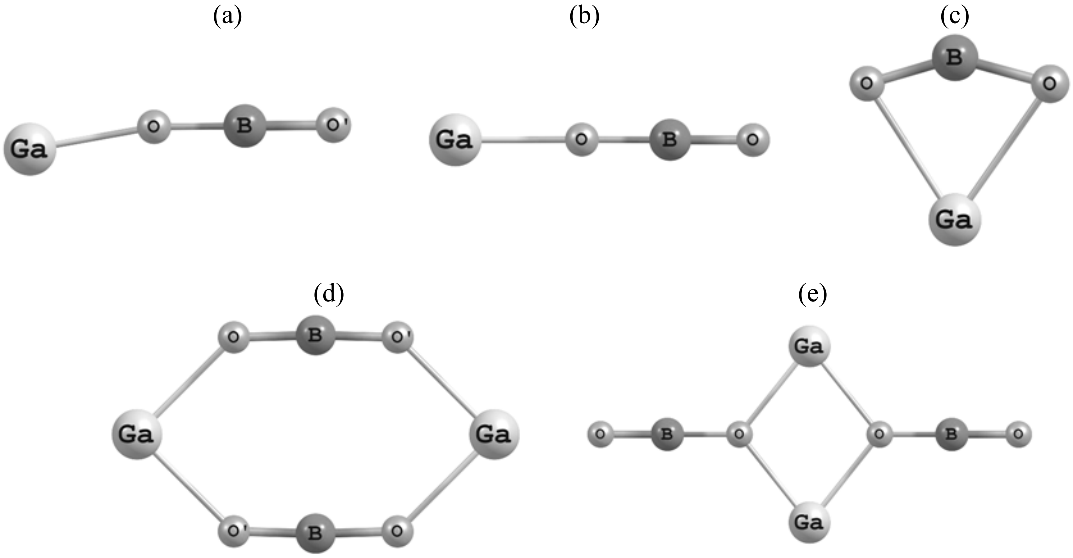

Fig. 1. Structures of gaseous molecules (a–c) $GaBO_2$ and (d, e) $Ga_2B_2O_4$.

linear structure turned out to correspond to a minimum on the potential energy surface, whereas in the case of the calculation with a pseudo-potential – to a transition state, in which an imaginary frequency corresponds to a change in the GaOB angle. The problem of mixing frequencies corresponding to the rotation of a molecule as a whole with the lowest vibration frequencies corresponding to a change in the GaOB angle was revealed. As even such small difference in the energy and geometry leads to an essential difference in thermodynamic functions (for example, Φ^0 values differ at 1500 K by 15 J mol^{-1} K^{-1}), on the one hand, and the variation of calculation parameters, on the other hand, strongly affects the result, the choice of calculation parameters is a matter of principle.

In connection with the above-stated we refused the use of a pseudo-potential, fulfilled the calculation with the *5d/7f* set of spherical *d* and *f* orbitals (the option d5 =.t. in the $CONTRL group), activated projection of the Hessian matrix by the algorithm described in [34] (the option projct =.t. in the $FORCE group), and increased accuracy of the stationary point localization by a factor of three (reduced the parameter opttol in the $STATPT group by a factor of three as compared with a default value). As a result we obtained structure (a) and used its parameters in the calculation of thermodynamic functions [bond lengths: *r*(Ga−O) 1.861, *r*(O−B) 1.299, *r*(B−O') 1.219 Å; angles: GaOB and OBO' 170.26° and 179.96°, respectively]. The frequencies corresponding to translation and rotation of a molecule as a whole are strictly equal to 0, and the frequencies of normal fluctuations, to 34, 384, 533, 534, 1143, and 2045 cm^{-1}.

Total energies of structures of the dimer molecule $(GaBO_2)_2$ (Fig. 1) found by the B3LYP/6-31G method differed by 76.1 kJ mol^{-1} in favor of structure (d). By the results of the calculations, the both structures appeared to correspond to minima on the potential energy surface. The structure (d) was reoptimized by the B3LYP/cc-pVQZ method. To make calculations uniform, we used the same additional parameters as in the optimization of $GaBO_2$ by a similar method [bond lengths: *r*(Ga−O) 2.105, *r*(Ga−O') 2.104, *r*(B−O) = *r*(B−O') 1.257 A, angles OBO', OGaO', GaO'B, and GaOB are 177.04°, 90.10°, 136.42°, and 136.44°, respectively]. Frequencies of vibrations: 30, 40, 51, 79, 134, 196, 204, 214, 251, 305, 547, 563, 565, 600, 1121, 1129, 1944, and 2009 cm^{-1}. It is seen from the values of the equilibrium parameters that, first, the structure appeared to be a little distorted in relation of the D_{2h} symmetry, and, second, the B−O bond length in the dimer is equal to the arithmetic mean of the B−O bond lengths in the monomer within 2×10^{-3} Å.

The values of enthalpies of reactions (3) and (4) are presented in Tables 1 and 2. Combinations of these values recalculated to the temperature 298 K and the heats of formation of Ga_2O and B_2O_3 gaseous oxide [35] allowed us to calculate the standard enthalpies of formation and atomization of gaseous $GaBO_2$ and $(GaBO_2)_2$: −469±8 and 1084±10, −1186±18 and 3585±21 kJ mol^{-1}, respectively.

The values of total energies and energies of zero-point vibrations of the molecules Ga_2O, B_2O_3, $GaBO_2$, and $(GaBO_2)_2$ obtained by the B3LYP/CC-PVQZ method allowed us to calculate enthalpies of reactions (3) and (4) at 0 K (−100.2 and −139.6 kJ, respecttively). These values considerably differ from the experimental values. It is necessary to note that gallium borate acts in reaction (3) as a product and in reaction (4) as a reagent, and as the calculated value of the reaction (3) enthalpy is less than the experimental value, whereas in reaction (4) it is greater, it is not improbable that the disagreement is connected with a complicated structure of the potential energy surface of the molecule $GaBO_2$ near to a minimum.

To check this assumption, we calculated the enthalpy of gas-phase reaction (6) passing without participation of gallium borate monomer.

$$Ga_2O + B_2O_3 = (GaBO_2)_2. \qquad (6)$$

The value obtained with the use of quantum-chemical calculations is −240 kJ. The same value determined on the basis of reference values of the formation enthalpies of oxides [35] and our value of the standard enthalpy of the dimeric gallium borate formation is equal to −255±23 kJ. The fact that the values of reaction (6) enthalpy determined both experimentally and with the use of quantum-chemical calculations coincide within the limits of the measurement error suggests that it is necessary to apply quantum-chemical calculations of a higher level for the calculation of enthalpies of reactions involving gallium borate monomer, which require essential resource and time expenses.

Measured partial pressures of the gallium borate monomer and dimer allow us to estimate relative contents of these molecules in the vapor above the studied system. The relative content of the dimer was calculated by Eq. (7).

$$x = \frac{p_{\mathrm{dim}}}{p_{\mathrm{mon}} + p_{\mathrm{dim}}} \times 100\%. \qquad (7)$$

Here x is a relative content of the dimer (%) in a mixture, p_{mon} and p_{dim} are partial pressures of vapor of gallium borate monomer and dimer, respectively. In the temperature range 1450−1550 K the content of dimer is ~0.04%, which is much less than the contents of dimers in vapors above the borates of alkaline metals [16].

Enthalpies of atomization of gaseous salts of oxygen-containing acids with equal cations linearly depend on the enthalpies of atomization of gaseous anion-forming oxides [4]. The dependence is described by Eq. (8).

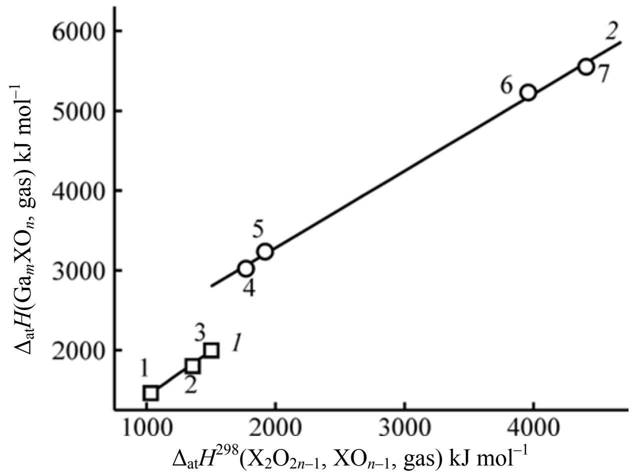

Fig. 2. Dependence of atomization enthalpies of gaseous gallium(I) salts on atomization enthalpies of anion-forming oxides: (*1*) $GaBO_2$, (*2*) $GaPO_2$, (*3*) $GaPO_3$, (*4*) Ga_2MoO_4, (*5*) Ga_2WO_4, (*6*) $Ga_2Mo_2O_7$, (*7*) $Ga_2W_2O_7$. (*1*) $m = 1$, (*2*) $m = 2$.

$$\Delta_{\mathrm{at}}H^0(\text{salt, gas, 298}) = k\Delta_{\mathrm{at}}H^0(\text{anion-forming oxide, gas, 298}) + b, \qquad (8)$$

The values of the $GaBO_2$(gas) atomization enthalpy found in the present work in combination with the known values of atomization enthalpies of gaseous phosphates [12], molybdates, and tungstates [13] allow us to calculate similar dependences for the isocation series Ga_mXO_n of gallium(I) salts (Fig. 2). For $m = 1$ (Fig. 2a) coefficients k and b in Eq. (8) are equal to 1.128±0.072 and 288.5±95.1, respectively, and regression coefficient is 0.998. For $m = 2$ (Fig. 2b) regression coefficient is 0.999, coefficients k and b, 0.963±0.027 and 1355.7±89.0. Thus obtained equations allow rather reliable estimating of atomization enthalpies of gaseous gallium(I) salts, which still were not studied.

Complication of a quantum-chemical calculation method can affect values of vibration frequencies of the $GaBO_2$ molecule and, as a consequence, the thermodynamic functions. Nevertheless, closeness of coefficient k in Eq. (8) to unity and the high correlation factor point to the fact that $\Phi^0(T)$ values used in this work resulted in obtaining correct values of the formation and atomization enthalpies of gallium borate.

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 V. A mixture of gallium and boron oxides was evaporated from a dual one-temperature cell; a sample was placed in one of its sections and the pressure standard, gold or silver, into another. Temperature was measured by an EOP-66 optical pyrometer accurate to ±5 K. The equipment was calibrated against vapor pressure of CaF_2 [35].

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