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Thermochemical Study of Gaseous Salts of Oxygen-Containing Acids: XXV.[1] Magnesium Borates

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Abstract—Standard enthalpies of formation and atomization of gaseous magnesium borates $MgBO_2$ and MgB_2O_4 were determined.

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Gaseous borates are formed either on the vaporization of condensed borates, or as a result of the synthesis of oxides in a high-temperature vapor. The information on the existence and thermodynamic properties of gaseous borates is systematized in [2]. There are a number of published works [4–15] devoted to the vapor formation in the systems $MO–V_2O_3$ (hereinafter M is an alkaline-earth metal). As a rule, the works are fulfilled by the high-temperature mass-spectrometry method, which makes it possible to determine qualitative and quantitative composition of vapor above samples under study and to obtain thermodynamic characteristics of vaporization processes. The formation of the ions $BeBO_2^+$ and $MgBO_2^+$ was mentioned in [3]. The enthalpy of the BeB_2O_4(gas) formation at 1500 K was determined in [4]. In the handbook [5] this value was reduced to standard conditions. Furthermore the enthalpy of the $BeBO_2$(gas) formation was estimated. Vaporization products in the system $MgO–B_2O_3$ with a molar content of magnesia of 94% were studied in [6]. In the vapor mass spectra the ions Mg^+, $MgBO_2^+$, $B_2O_3^+$, and $MgB_2O_4^+$ were identified. A break of the curve of the effectiveness of $MgBO_2^+$ ionization assigned to the dissociative ionization of MgB_2O_4 [Eq. (1)] was observed.

$$MgB_2O_4 + e^- = MgBO_2^+ + 2BO_2 + 2e^-. \quad (1)$$

The determination of equilibrium constants of reactions (2) and (3) made it possible to calculate standard enthalpies of formation for gaseous MgB_2O_4 and $MgBO_2$ (–1305.4±16.7 and –502±12.6 kJ mol^{-1}, respectively, at 0 K).

$$MgO(cr.) + B_2O_3(gas) = MgB_2O_4(gas), \quad (2)$$

$$1/2\ MgO(cr.) + 1/2\ B_2O_3(gas) + 1/2\ Mg(gas) = MgBO_2(gas). \quad (3)$$

Studying products of barium metaborate BaB_2O_4 vaporization, Il'in et al. [7] determined the enthalpies of formation of gaseous $BaBO_2$ and BaB_2O_4 by measuring energies of $BaBO_2^+$ appearance. The energy of $BaBO_2^+$ appearance (10.8 eV) corresponded to the process of direct ionization of the molecule $BaBO_2$. An inflection in the curve of the ionization effectiveness and the appearance energy of $BaBO_2^+$ (14.7 eV) were assigned to the dissociative ionization of the BaB_2O_4 molecule. The calculated standard enthalpies of formation of gaseous $BaBO_2$ and BaB_2O_4 at 0 K appeared to be –675.3±29.3 and -1344.3±44.8 kJ mol^{-1}, respectively.

Asano et al. [8-12] studied the vaporization processes in the systems $SrO–B_2O_3$ and $BaO–B_2O_3$. In the mass spectra of vapor above the investigated samples ionic currents of M^+, MO^+, $B_2O_3^+$, $B_2O_2^+$, MBO_2^+, and MBO^+ (M = Sr, Ba) were fixed. The appearance energies of M^+, MO^+, and B_2O_3 were equal to the ionization energies of the corresponding molecules, and the appearance energies of $SrBO_2^+$ and $BaBO_2^+$, to 10.8 and 10.5 eV, respectively. The measured appearance energies of the ions in the mass spectrum have allowed the conclusion to be drawn that the ions M^+, MO^+, $B_2O_3^+$, and MBO_2^+ are formed upon the direct ionization of the corresponding molecules, and $B_2O_2^+$ and MBO^+, upon the dissociative ionization. It was

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

found that the vapor above the studied systems consists of a mixture of B_2O_3, M, MO, and MBO_2. Enthalpies of formation of gaseous metaborates $SrBO_2$ and $BaBO_2$ were calculated on the basis of measuring equilibrium constants of reactions (4) in the temperature range of 1390–1535 K.

$$M(gas) + BO_2(gas) = MBO_2(gas). \quad (4)$$

Moreover, the enthalpy of the $CaBO_2$(gas) formation was estimated at –526±46 kJ mol^{-1}. In [13] the ions $B_2O_3^+$, $B_2O_2^+$, B^+, BO^+, BO_2^+, B_2O^+, $CaB_2O_4^+$, $CaB_2O_3^+$, $CaBO_2^+$, $CaBO^+$, CaB^+, and Ca^+ were fixed in the mass spectra of vapor above CaB_2O_4, and it was concluded that the vapor consists of B_2O_3 and CaB_2O_4 molecules.

The composition of vapor above MO–B_2O_3 systems as a function of the condensed phase composition and temperature was studied [14, 15]. In the mass spectra of vapor above the initial compounds CaB_2O_4, SrB_2O_4, and BaB_2O_4 peaks of the ions $B_2O_3^+$, $B_2O_2^+$, BO^+, M^+, MO^+, and MBO_2^+ were fixed. The presence of two noticeably differing appearance energies of MBO_2^+ ions and also breaks in the curves of ionization effectiveness point to a dual nature of the formation of these ions. Higher appearance energies of MBO_2^+ ions correspond to the dissociative ionization of MB_2O_4 molecules by scheme (1) and lower energies, to the direct ionization of MBO_2 molecules [Eq. (5)].

$$MBO_2 + e^- = MBO_2^+ + 2e^-. \quad (5)$$

When CaB_2O_4, SrB_2O_4, and BaB_2O_4 are heated in a molybdenum cell in a temperature range of 1500–1600 K concurrent reactions of vaporization [Eq. (6)] and thermal dissociation [Eq. (7)] occur first.

$$MB_2O_4(l.) = MB_2O_4(gas), \quad (6)$$

$$MB_2O_4(l.) = MO(cr.) + B_2O_3(gas). \quad (7)$$

The extent of the thermal dissociation decreases in the series $CaB_2O_4 > SrB_2O_4 > BaB_2O_4$. As a condensed phase becomes enriched by a metal oxide and as the temperature increases, MBO_2 and MO molecules and monoatomic metal begin to pass into vapor. At a temperature above 2000 K only MBO_2, MO, BO, and M are present in vapor. To determine enthalpies of reaction (6), temperature dependences of the intensity of MBO_2^+ ionic current in the ranges of 1498–1630 K for CaB_2O_4 and SrB_2O_4 and 1498–1630 K for BaB_2O_4 were measured. The reduction of the data obtained to the standard temperature 298 K and the use of the values $\Delta_f H^0$(CaB_2O_4, cr., 298 K) –1972.3±28.0, $\Delta_f H^0$(SrB_2O_4, cr., 298 K) –2016.4, and $\Delta_f H^0$(BaB_2O_4, cr., 298 K) –1972.3±28.0 kJ mol^{-1} have allowed the determination of the standard enthalpies of formation of gaseous CaB_2O_4, SrB_2O_4, and BaB_2O_4 of –1427±19, –1425±18, and –1424±28 kJ mol^{-1}, respectively.

To determine thermodynamic characteristics of MBO_2(gas) molecules, constants of Eq. (8) for the gas-phase reactions were measured, the measurements were carried out in those ranges of temperatures and compositions of a condensed phase where vapor was deliberately free from MB_2O_4 molecules and intensities of MBO_2^+ ionic currents corresponded only to the direct ionization of MBO_2 molecules.

$$MBO_2 = MO + BO. \quad (8)$$

The standard enthalpies of formation and atomization of gaseous $CaBO_2$, $SrBO_2$ and $BaBO_2$ at 298 K are equal to –526.7±4.2, –571.0±5.2, and –594±5 kJ mol^{-1}, respectively.

The aim of the work was to refine values of enthalpies of formation and atomization of gaseous magnesium borates, because, in our opinion, these values were determined in [6] not quite correctly. First of all it is connected with the procedure of separating the total intensity of $MgBO_2^+$ ionic current, which originates from two sources (1) and (5). When determining the enthalpies of reactions involving gaseous magnesium borate the activity of crystalline magnesium oxide was accepted to be equal to 1, though it is known to react with a cell material to form magnesium molybdates or tungstates, and the MgO activity in this case considerably decreases. Furthermore, thermodynamic functions of magnesium borate were only estimated.

In the mass spectra of vapor above samples of the system MgO–B_2O_3 containing from 67 up to 75 mol % of magnesium oxide peaks of Mg^+, BO^+, BO_2^+, $B_2O_3^+$, $MgBO_2^+$, and $MgB_2O_4^+$ ions were fixed in the temperature range of 1869–1965 K. To determine molecular predecessors of the ions in the vapor mass spectra, we measured their energies of appearance by the method of disappearing ionic current (±0.3 eV): Mg^+ (7.6), BO^+ (13.5), BO_2^+ (13.8), $B_2O_3^+$ (14.0), $MgBO_2^+$ (10.5), and $MgB_2O_4^+$ (11.7). At ~1850 K the ratio of ionic currents $MgBO_2^+/MgB_2O_4^+$ was 0.7. Further on this ratio increased with increasing temperature, and an inflection appeared in the curve of the $MgBO_2^+$ ionization effectiveness. Right at the end of the vaporization the ionic current of $MgB_2O_4^+$ was not fixed, and the appearance energy of the $MgBO_2^+$ ion was equal to 8.1 eV. A comparison of the data

obtained with the published data [6, 16] has shown that at 1850 K B_2O_3 and MgB_2O_4 are present in vapor above the system $MgO–B_2O_3$, and at higher temperatures these are boron oxide B_2O_3, the products of its high-temperature disproportionation BO and BO_2, monoatomic magnesium, oxygen, and also magnesium borates $MgBO_2$ and MgB_2O_4. As the ion $MgBO_2^+$ has two sources of formation (1) and (5), we have carried out a separation of the $MgBO_2^+$ ($MgBO_2$) and $MgBO_2^+$ (MgB_2O_4) components. The ratio of the intensities $MgBO_2^+/MgB_2O_4^+$ at ~1850–1900 K was accepted for the ratio of these values in the mass spectrum of the MgB_2O_4 molecule and further it was taken into account when calculating partial pressures of $MgBO_2$ and MgB_2O_4.

To determine standard enthalpies of formation of gaseous magnesium borates, we measured equilibrium constants of gas-phase reactions (9)–(12) and calculated enthalpies of these reactions by Eq. (13).

$$Mg + BO_2 = MgBO_2, \quad (9)$$

$$Mg + 2\ BO_2 = MgB_2O_4, \quad (10)$$

$$MgBO_2 + BO_2 = MgB_2O_4, \quad (11)$$

$$2MgBO_2 = MgB_2O_4 + Mg, \quad (12)$$

$$\Delta_r H^0(0) = T[\Delta_r \Phi^0(T) - R\ln K_e(T)]. \quad (13)$$

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

Partial pressures of the vapor molecular forms were determined by the method of comparing ionic currents, using gold as the interior standard of pressure [17]. Ionization cross-sections of the molecules were calculated by the additivity method using the atomic cross-sections [18]. The ionization cross-section of MgB_2O_4 was multiplied by 0.7 according to [19].

Thermodynamic functions of gaseous oxides necessary for the calculation of enthalpies of reactions (9)–(12) were taken from the handbook [20], and the functions for the gaseous molecules $MgBO_2$ and MgB_2O_4 were calculated by the statistical thermodynamics method in the approximation "rigid rotator–harmonic oscillator." For gaseous molecules $MgBO_2$ and MgB_2O_4 we accepted structures of the symmetry $C_{\infty v}$ and $D_{\infty h}$ similar to the structures of molecules of calcium, strontium, and barium borates [21]. Interatomic distances for $MgBO_2$ are as follows: r(Mg–O) 1.82, r(B–O) 1.28, r(B=O) 1.20 Å; for MgB_2O_4: r(Mg–O) 1.78, r(B–O) 1.28, r(B=O) 1.20 Å.

The values of enthalpies of reactions (9)–(12) involving gaseous $MgBO_2$ and MgB_2O_4 reduced to the standard temperature 298 K were: –444±10 [Eq. (9)], –1021±17 [Eq. (10)], –577±13 [Eq. (11)], and –132±16 [Eq. (12)]. Combining the average values of enthalpies of reactions (9)–(12) at 298 K with enthalpies of formation of gaseous Mg [20], and BO_2 [22] us were able to calculate standard enthalpies of formation of gaseous magnesium borates (see the table). For comparison we also presented in the table enthalpies of formation of borates for remaining elements of the main subgroup II of the periodic system.

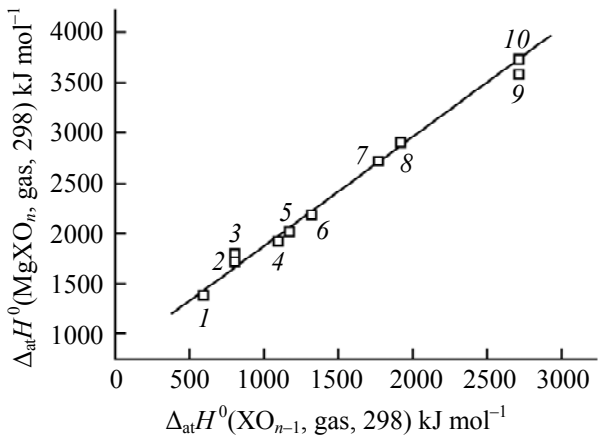
In isocation series of gaseous salts of oxygen-containing acids the enthalpy of gaseous salt atomization linearly depends on the enthalpy of gaseous anion-forming oxide atomization [23]. The dependence can be expressed by Eq. (14).

$$\Delta_{at}H^0(\text{salt, gas, 298}) = k\Delta_{at}H^0(\text{anion-forming oxide, gas, 298}) + b. \quad (14)$$

Using the data of [24] and results of our work, we can construct such dependence for the isocation series of magnesium salts (see figure). Available now data for gaseous magnesium salts were plotted on the graph. In the figure we presented simultaneously both published [6] and our data on the atomization enthalpies of gaseous magnesium borates for comparison. When the data of [6] were replaced by our

Enthalpies of formation of borates of elements of the main subgroup II of the periodic system

Borate MB_2O_4	$-\Delta_f H^0$, kJ mol^{-1}	References	Borate MBO_2	$-\Delta_f H^0$, kJ mol^{-1}	References
BeB_2O_4	1351±42	[4, 5]	$BeBO_2$	482	[5]
MgB_2O_4	1306±17	[6]	$MgBO_2$	502±13	[6]
	1458±22	present work		589±10	present work
CaB_2O_4	1427±18	[15]	$CaBO_2$	527±15	[15]
SrB_2O_4	1425±18	[15]	$SrBO_2$	571±4	[15]
BaB_2O_4	1424±28	[14]	$BaBO_2$	594±5	[14]



Dependence of atomization enthalpies of magnesium gaseous salts on the atomization enthalpies of gaseous anion-forming oxides. (*1*) $MgPO_2$, (*2*) $MgBO_2$ [6], (*3*) $MgBO_2$, our data, (*4*) $MgPO_3$, (*5*) $MgMoO_3$, (*6*) $MgWO_3$, (*7*) $MgMoO_4$, (*8*) $MgWO_4$, (*9*) MgB_2O_4 [6], (*10*) MgB_2O_4, our data.

data we obtained a correlation coefficient of 0.9963; $k = 1.086\pm0.04$; $b = 86.7\pm59.7$.

Our data on the atomization enthalpies of gaseous magnesium borates somewhat worsen the correlation coefficient and seem slightly overestimated. The reasons of uprating the enthalpies of reactions in modulus can be the following.

The standard enthalpy of the BO_2(gas) formation is a key value in the determination of the enthalpies of formation of gaseous magnesium borates. Published data on it fall in the range from –267.8±16.7 [25] up to –324.1 [20] kJ mol^{-1}. To calculate the enthalpies of gaseous $MgBO_2$ and MgB_2O_4 formation, we have chosen the value of –292.1±8.4 kJ mol^{-1} [22], which we believe to result from the most correct determination of enthalpies of several reactions involving BO_2 (gas). In [22] saturated vapors above the systems Bi_2O_3–B_2O_3, PbO–B_2O_3, and ZnO–B_2O_3 in the atmosphere of excessive oxygen were studied, which has allowed us to measure the equilibrium constant of gas-phase reaction (15) at 1200–1400 K.

$$B_2O_3 + 0.5O_2 = 2BO_2. \quad (15)$$

The main problem in measuring the equilibrium constant was the separation of ionic currents of $BO_2^+(BO_2)$ and $BO_2^+(B_2O_3)$. This problem was solved by taking the individual mass spectrum of the B_2O_3 vapor at lower temperatures. The vapor pressure of oxygen was determined by the signal of O_2^+ and by Eq. (16).

$$p_{O_2} = 3/4p\sqrt{M_{O_2}/M_{Bi}}. \quad (16)$$

As all measurements were carried out using a platinum effusion cell inert to oxygen, the oxygen partial pressure under dynamic equilibrium conditions is connected with the pressure of monoatomic bismuth at the dissociation of bismuth oxide by the relationship in stoichiometric Eq. (17).

$$2Bi_2O_3(cr.) = 4Bi(gas) + 3O_2(gas). \quad (17)$$

As the value of the enthalpy of gaseous oxide BO_2 formation was obtained for three studied systems it is possible to consider it as fully reliable.

In spite of the facts that we used a low ionizing voltage in our experiments, which largely suppresses dissociative ionization processes, and that all measurements were carried out at a very high temperature, the BO_2^+ ion can have a double origin: $BO_2^+(BO_2)$ and $BO_2^+(B_2O_3)$. If the ionic current of BO_2^+ is summarized the selection of the component of $BO_2^+(BO_2)$ will give a lower value of BO_2 partial pressure, which will lead to increasing equilibrium constants of reactions (9)–(12) and hence to increasing absolute values of enthalpies of these reactions and of enthalpies of formation of magnesium borates.

Expression (13), which was used to determine enthalpies of reactions (9)–(12), consists of two summands. We have found the first summand experimentally, and the second by calculating thermodynamic functions of gaseous magnesium borates. The error in measuring equilibrium constants of reactions (9)–(12) cannot give the deviation of 50–60 kJ from the value calculated by Eq. (14). The scatter of the values of enthalpies of the studied reactions is rather high, though it does not exceed 30 kJ. It is extremely difficult to create conditions for the coexistence of monoatomic magnesium with BO_2 and magnesium borates in vapor. Partial pressures of Mg and BO_2 fall in the range of 10^{-7}–10^{-8} at, which practically corresponds to the detection limit of the instrument. As a rule, we deal with values of about 10^{-5}–10^{-6} at. We could not raise temperature to increase partial pressures of molecular forms of vapor, as in this case BO_2 dissociated into BO and oxygen. Unfortunately, we did not study gas-phase reaction (18), as it was fulfilled in [14, 15] when determining enthalpies of reactions involving the molecules $CaBO_2$, $SrBO_2$, and $BaBO_2$.

$$MO + BO = MBO_2. \quad (18)$$

The content of MgO molecules in vapor is about 0.5% of Mg, therefore at those temperatures, at which we observed molecules of BO, BO_2, and magnesium borates, the amount of magnesium oxide in the vapor was insufficient for measuring.

The error in the determination of the $\Delta\Phi^0$ value cannot be high. The thermodynamic functions of $MgBO_2$ and MgB_2O_4 molecules, which we have found, agree well with the data of the work [21] devoted to the quantum-chemical calculations of molecular constants of $CaBO_2$ and CaB_2O_4.

To reveal the degree of reliability of the obtained results, we have calculated values of atomization and formation enthalpies for gaseous magnesium borates, using Eq. (14) and published data on the enthalpies of formation of gaseous magnesium phosphates, molybdates, and tungstates [23], having eliminated from the consideration our data and the data of [6] on the enthalpy of atomization of the magnesium borates. The calculated values are 1605.4 kJ mol^{-1} for $MgBO_2$ and 3799.8 kJ mol^{-1} for MgB_2O_4. The standard enthalpies of formation are –610 and –1526 kJ mol^{-1}, respectively. Our values of the enthalpies of $MgBO_2$ and MgB_2O_4 formation are much closer to the calculated data than the data of [6].

Data for more exact estimate of enthalpies of formation of magnesium borates are explicitly insufficient. For comparison, there are 8 and 27 points, respectively, in the dependences of atomization enthalpies of gaseous salts on the enthalpies of atomization of anion-forming oxides plotted for isocation series of magnesium and barium salts.

EXPERIMENTAL

The work was fulfilled by the method of high-temperature mass spectrometry on an MS-1301 mass spectrometer at the energy of ionizing electrons of 25 V. Molybdenum effusion cells were heated by electron bombing. Temperature was measured by an EOP-66 optical pyrometer accurate to ±5 K in the temperature range of 1600–2200 K. The apparatus was preliminarily graduated by the CaF_2 vapor pressure [20].

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REFERENCES

1. Shugurov, S.M. and Lopatin, S.I., *Zh. Obshch. Khim.,* 2008, vol. 78, no. 10, p. 1644.
2. Lopatin, S.I. and Stolyarova V.L., *Fiz. Khim. Stekla,* 2006, vol. 32, no. 3, p. 489.
3. Palmer, G.H., *J. Nucl. Energy*, 1958, vol. 7, p. 1.
4. Blackburn, P.E. and Bűchler A., *J. Phys. Chem*., 1965, vol. 69, no. 12, p. 4250.
5. *JANAF Thermochemical Tables*, 3d Ed., Nat. Bur. Stand. U.S., 1985.
6. Gusarov, A,V., *Teplofiz. Vys. Temp*., 1970, vol. 8, no. 6, p. 1186.
7. Il'in, M.K., Makarov, A.V., and Nikitin, O.T., *Vestn. Mosk. Gos. Univ., Ser. 2: Khim*., 1974, vol. 15, no. 4, p. 436.
8. Kou, T. and Asano, M., *High Temp. Sci*., 1987, vol. 24, no. 1, p. 1.
9. Asano, M. and Kou, T., *J. Chem. Thermodyn*., 1988, vol. 20, no. 11, p. 1149.
10. Asano, M. and Kou, T., *J. Chem. Thermodyn*., 1990, vol. 22, no. 12, p. 1223.
11. Asano, M. and Kou, T., *J. Chem. Thermodyn*., 1989, vol. 2, no. 8, p. 837.
12. Asano M. and Kou, T., *High Temp. Sci*., 1990, vol. 29, no. 2, p. 171.
13. Stolyarova, V.L. and Seetharaman, S., *Vacuum*, 1998, vol. 49, no. 3, p. 161.
14. Lopatin, S.I., Semenov, G.A., and Shugurov S.M., *Zh. Obshch. Khim.,* 2001, vol. 71, no. 1, p. 68.
15. Lopatin, S.I., Semenov, G.A., Baranovskii, V.I., Shugurov, S.M., and Sizov, V.V., *Zh. Obshch. Khim.,* 2001, vol. 71, no. 9, p. 1422.
16. *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu: Spravochnik* (Energies of Breaking Chemical Bonds: Ionization Potentials and Electron Affinities: Handbook), Kondrat'ev, V.N., Ed., Moscow: Nauka, 1974.
17. Paule, R.C. and Mandel, J., *Pure Appl. Chem*., 1972, vol. 31, no. 3, p. 371.
18. Mann, J.B., *J. Chem. Phys*., 1967, vol. 46, no. 5, p. 1646.
19. Guido, M. and Gigli, G., *High Temp. Sci*., 1975, vol. 7, no. 2, p. 122.
20. *Termodinamicheskie svoistva individual'nykh veshchestv: spravochnic* (Thermodynamic Properties of Pure Substances: Handbook), Glushko, V.P., Ed., Moscow: Akad. Nauk SSSR, 1978–1984, vols. 1–4.

21. Baranovskii, V.V., Lopatin, S.I., and Sizov, V.V., *Zh. Obshch. Khim.,* 2000, vol. 70, no. 11, p. 1766.

22. Semenikhin, V.I., Minaeva, I.I., Sorokin, I.D., Nikitin, M.I., Rudnyi, E.B., and Sidorov, L.N., *Teplofiz. Vys. Temp.,* 1987, vol. 25, no. 4, p. 666.

23. Lopatin, S.I., *Zh. Obshch. Khim.,* 1999, vol. 69, no. 9, p. 1417.

24. Lopatin, S.I., *Zh. Obshch. Khim.,* 2007, vol. 77, no. 11, p. 1761.

25. Rusin, A.D. and Tataevskii, V.M., *Zh. Fiz. Khim*., 1963, vol. 37, no. 3, p. 716.