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

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Abstract—Vaporization of iodates of alkali metals was studied. Vapor above the iodates contains dimeric molecules alongside monomers. Standard enthalpies of formation of the gaseous molecules MIO_3 and $M(IO_3)_2$ were determined.

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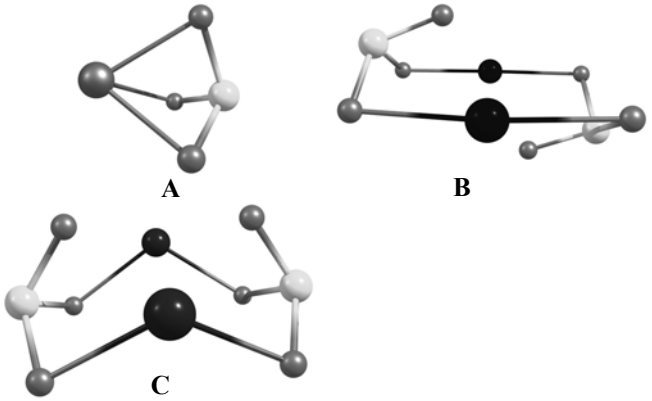
There is only one published work [2] devoted to the vaporization of alkali metal iodates and their structure in gaseous state studied by the matrix isolation method with the mass-spectral analysis of the vapor phase. It was proved that the molecules KIO_3, $RbIO_3$, and $CsIO_3$ are present in vapor above potassium, rubidium, and cesium iodates, respectively. Gaseous polymeric compounds were not detected.

It has been found by the mass-spectrometric analysis of vapor above cesium iodate [2] that at ~800 K the peaks of Cs^+ and I^+ ions were the most intensive in the mass spectrum, whereas the ionic currents of $CsIO_3^+$, $CsIO_2^+$, and $CsIO^+$ were much less. Measured appearance energies of the Cs^+, $CsIO_2^+$, and $CsIO_3^+$ ions were equal to 9.1, 10.3, and 9.2 eV, respectively, leading to a conclusion that the $CsIO_3^+$ ion was of the molecular origin, whereas the Cs^+ and $CsIO_2^+$ ions were of the fragment origin. Heating of lithium and sodium iodates under the same conditions was accompanied by violent oxygen evolution, and the analysis of the sublimates showed that they completely consisted of the corresponding iodides, therefore these iodates completely dissociated into iodides and oxygen.

The structure of iodates of alkali metals determined in [2] is of the C_{3v} symmetry and constitutes a trigonal bipyramid **A** with iodine and alkali metal atoms in apexes (see the figure). The tridentate binding of the alkali metal atom with oxygen atoms is the same as in the case of chlorates of alkali metals [3–9] studied by both experimental and quantum-chemical methods. Thermodynamic characteristics of gaseous iodates of alkali metals were not determined.

In the mass spectrum of vapor above sodium, potassium, rubidium, and cesium iodates peaks of M^+, I^+, I_2^+, MI^+, M_2I^+, MIO_3^+, $M_2IO_3^+$, and I_2^+ ions (hereinafter M = Na, K, Rb, Cs) were recorded, the ratio of their intensities depending on temperature and the alkali metal nature. The ratio of ionic currents MI^+/MIO_3^+ remained constant during the experiment and increased only at the very end of the experiment. After decreasing the ionic currents of MIO_3^+ and $M_2IO_3^+$ up to a noise level only M^+, I^+, I_2^+, MI^+, and M_2I^+ ions were detected in the mass spectrum.

To determine the origin of ions in the mass spectrum, their appearance energies were measured by the



Molecular structure of iodates of alkali metals. (**A**) MIO_3, (**B**) *trans*-$(MIO_3)_2$, and (**C**) *cis*-$(MIO_3)_2$.

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

disappearing ionic current method; the results obtained are presented in Table 1. The appearance energies of the I_2^+ and MI^+ ions coincide with ionization energies of the corresponding molecules within the limits of measuring errors [10]. The appearance energies of the M^+ and I^+ ions are much greater than the ionization energies of the corresponding alkali metals and monatomic iodine that is indicative of the formation of these ions as a result of dissociative ionization of more complex molecules. The appearance energy of $CsIO_3^+$ ion coincides within the limits of measuring errors with the value found in [2]. By analogy with metaborates [11], nitrates [12], phosphates [13], and halides of alkali metals [14], $M_2IO_3^+$ and M_2I^+ ions are formed by the dissociative ionization of dimeric molecules $(MIO_3)_2$ and $(MI)_2$, respectively. The appearance energies of the ions KIO_3^+ and $RbIO_3^+$ were determined for the first time. The measured values are slightly greater than the appearance energy of $CsIO_3^+$ [2] that confirms their molecular origin. The obtained data point to the fact that the vapor above the studied iodates consists of a mixture of iodates and iodides with a dominance of these latter. The I^+ ion seems to be formed during the dissociative ionization of the I_2 molecule as its appearance energy is much higher than the ionization energy of monatomic iodine. The M^+ ion can have a dual nature, being formed upon the dissociative ionization of both MI and MIO_3 molecules. To separate the values of the $M^+(MIO_3)$ and $M^+(MI)$ ionic currents, we used a one-temperature twin effusion chamber, placing an iodide in one cell and an iodate in the other, and compared ratios of $M^+(MI)$ ionic currents. As these ratios in the mass spectra of a vapor above MIO_3 and MI were approximately equal, we concluded that the ion M^+ is formed mainly as a result of the dissociative ionization of the MI molecules.

When sodium iodate was heated slowly the ions Na^+, I^+, and NaI^+ characteristic of the mass spectrum of vapor above NaI were recorded in the vapor mass spectrum. When temperature increased at a rate of 50 deg min^{-1} up to ~800 K, peaks of the ions $NaIO_3^+$ and $Na_2IO_3^+$ were observed in the mass spectrum within 2–5 min, their intensity decreasing fast up to a noise level. At the further temperature increase up to 1000 K only ions corresponding to the mass spectrum of vapor above NaI were observed in the vapor mass spectrum.

Table 1. Appearance energies of ions (±0.3 eV) in mass spectra of vapor above potassium, rubidium, and cesium iodates

Ion	K	Rb	Cs
M^+	–	8.6	7.9
I^+	11.0	11.0	11.0
I_2^+	9.2	9.2	9.2
MI^+	8.1	7.9	7.3
M_2I^+	8.5	8.6	7.7
MIO_3^+	10.2	9.5	9.7
$M_2IO_3^+$	10.7	9.5	7.8

The examination of the vapor mass spectra above the studied iodates of alkali metals and the appearance energies of the ions allow us to conclude that reactions (1)–(7) occur on heating iodates of alkali metals.

$$MIO_3(cr.) = MIO_3(gas), \quad (1)$$

$$2MIO_3(cr.) = M_2I_2O_6(gas), \quad (2)$$

$$2MIO_3(gas) = M_2I_2O_6(gas), \quad (3)$$

$$MIO_3(cr.) = MI(cr.) + 1.5O_2(gas), \quad (4)$$

$$MI(cr.) = MI(gas), \quad (5)$$

$$MIO_3(gas) = MI(cr.) + 1.5O_2(gas), \quad (6)$$

$$MI(gas) = M(gas) + I_2(gas). \quad (7)$$

To determine the enthalpies of formation of gaseous monomers and dimers of potassium, rubidium, and cesium iodates, we measured intensities of MIO_3^+ and $M_2IO_3^+$ ionic currents as functions of temperature and calculated the enthalpies of reactions (1)–(3) by Eq. (8). The enthalpies of reaction (3) were also determined by Eq. (9) using the corresponding iodides as standards of pressure [15].

$$\Delta_r H^0(T) = -R\frac{\partial \ln K_e(T)}{\partial(1/T)}, \quad (8)$$

$$\Delta_r H^0(0) = T[\Delta_r \Phi^0(T) - R\ln K_e(T)]. \quad (9)$$

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

For the correct determination of the enthalpies of potassium, rubidium, and cesium iodates sublimation by reactions (1) and (2) it is necessary that the activities of the iodates in a condensed phase were constant and equal to unity, i.e. the iodates should not react with formed iodides to give intermediate compounds or solid solutions. The absence of such reactions is proved by the fact that the intensities of MI^+, MIO_3^+, and $M_2IO_3^+$ ionic currents remained

unchanged on a long-term isothermal holding, and their values were reproduced on repeated temperature decrease and increase. Furthermore the sublimation enthalpies of the iodides determined as a result of measuring temperature dependences of MI^+ ionic currents agreed well with the values obtained from the reference data [15]. The values of enthalpies of reactions (1)–(3) reduced to the standard temperature 298 K are presented in Table 2. The temperature ranges of measuring temperature dependences of the intensities of MIO_3^+ and $M_2IO_3^+$ ionic currents were 633–785 K for KIO_3 (11 measuring series), 650–766 K for $RbIO_3$ (4 measuring series), and 644–757 K for $CsIO_3$ (6 measuring series). Results of each measuring series were reduced to the standard temperature 298 K, and then an average value was determined.

To reduce enthalpies of reactions (1)–(3) to the standard temperature, temperature dependences of heat capacities of condensed iodates are required. We have calculated them by the Landiya method [16], taking the heats and temperatures of melting and phase transitions of these compounds from [17]. Thermodynamic functions of MIO_3 and $(MIO_3)_2$ gaseous molecules were calculated by the statistical thermodynamics method in the approximation "rigid rotator–harmonic oscillator" using geometrical parameters and vibration frequencies calculated by a quantum-chemical method.

To select a computational method and a basis set, we have carried out a quantum-chemical investigation of the structure and molecular parameters of the $CsIO_3$ molecule. The results are given in Table 3 (HF, MP2, B3LYP are computation methods, further the chosen basis for iodine and cesium is shown). As a result we have chosen the density functional method with the hybrid functional B3LYP and the following basis set: the 3-21G(3d) basis for cesium atoms, the 6-31G(3d,f) for oxygen, and the LANL2DZ for iodine. The results obtained with this method and basis set agree well with the experimental data [2]. The applied computational method is analogous to that which we have applied in [18, 19] for the determination of molecular parameters of phosphates and perrhenates of alkali metals.

The quantum-chemical calculations have shown that in the case of gaseous iodates of alkali metals structure **B** of the C_{2v} symmetry (see the figure), which

Table 2. Enthalpies of reactions (1)–(3) and standard enthalpies of formation of monomers and dimers of gaseous potassium, rubidium, and cesium iodates

Iodate	$\Delta_r H^0(298)$, kJ				$-\Delta_f H^0(MIO_3, gas, 298)$, kJ mol^{-1}	$-\Delta_f H^0(M_2I_2O_6, gas, 298)$, kJ mol^{-1}
	1	2	3 calculation by Eq. (8)	3 calculation by Eq. (9)		
KIO_3	208±10	236±11	–204±18	–236±5	306±11	825±13
$RbIO_3$	208±10	197±12	–214±20	–222±5	313±13	846±12
$CsIO_3$	196±7	231±8	–196±16	–204±8	351±8	887±20

Table 3. Molecular parameters of the $CsIO_3$ molecule calculated in the present work by various methods and determined experimentally in [2]

Method + basis	r(I–O), Å	$r(O_{cycl}–O_{cycl})$, Å	r(Cs–I), Å	$r(Cs–O_{cycl})$, Å	ν_E (stretch.), cm^{-1}	ν_A (stretch.), cm^{-1}	ν_A (bend.), cm^{-1}	ν_E (bend.), cm^{-1}
Experiment	–	–	–	–	803.0	786.4	355.8	302.2
HF + LANL2DZ +3-21G(3d)	1.813	2.801	3.447	3.086	803.6	740.3	379.6	319.9
MP2 + LANL2DZ + 3-21G(3d)	1.834	2.849	3.403	3.071	818.4	824.1	360.7	294.7
B3LYP + LANL2DZ + LANL2DZ	1.848	2.879	3.570	3.223	728.5	755.4	327.4	279.2
HF + LANL2DZ + LANL2DZ	1.811	2.814	3.562	3.206	810.6	744.6	375.0	320.4
MP2 + LANL2DZ + LANL2DZ	1.830	2.864	3.596	3.262	829.4	828.9	349.4	295.6
HF + SBK + 3-21G(3d)	1.923	2.944	3.575	3.169	642.4	517.2	292.7	247.6
MP2 + SBK + 3-21G(3d)	1.866	2.899	3.603	3.246	795.2	769.0	333.2	266.5
B3LYP + SBK + 3-21G(3d)	1.915	2.950	3.584	3.199	678.0	640.0	290.7	237.0

Table 4. Molecular parameters, effective charges on atoms, bond orders, and dipole moments of molecules of gaseous iodates of alkali metals calculated by the density functional method

Parameter	$LiIO_3$	$NaIO_3$	KIO_3	$RbIO_3$	$CsIO_3$
r(M–O), Å	2.165	2.462	2.805	2.852	3.111
r(M–O'), Å	2.156	2.456	2.716	2.772	2.926
r(I–O), Å	1.803	1.801	1.800	1.800	1.799
r(I–O'), Å	1.804	1.802	1.802	1.801	1.803
r(I–M), Å	2.432	2.747	3.089	3.147	3.396
∠OIO, deg	96.1	99.0	100.9	100.4	101.6
Effective charge on atom (unit of e^- charge)					
M	0.55	0.56	0.68	0.72	0.77
O	–0.72	–0.72	–0.75	–0.76	–0.78
I	1.61	1.62	1.57	1.56	1.54
Bond order					
M–O	0.32	0.29	0.19	0.18	0.13
O–I	1.21	1.22	1.26	1.26	1.28
Dipole moment, D	0.65	3.00	5.00	5.18	6.05

represents a slightly distorted structure **A** described in [2] with one of I–O and M–O bonds slightly shorter than the remaining two bonds, has the minimal energy. The molecular parameters of gaseous iodates of alkali metals are presented in Table 4. Taken together low orders of alkaline metal-oxygen bonds, effective charges on alkali metal atoms close to unity, and practically constant lengths of oxygen-iodine bonds in the molecules of iodates of alkali metals allow us to describe the structure of the studied iodates within the limits of the "ion pair" model.

For gaseous dimers of the iodates we have studied structures **B** and **C** presented in the figure. The results are given in Table 5. Structure **B** has a minimal energy. The energy of the molecule with structure **C** corrected for a zero vibrational level on the average is higher than the energy of the molecule with structure **B** by 158 kJ.

The found values of enthalpies of reactions (1)–(3) have allowed us to calculate standard enthalpies of formation of monomers and dimers of gaseous potassium, rubidium, and cesium iodates presented in Table 2. The impossibility of the experimental determination of the enthalpies of formation of gaseous lithium and sodium iodates is connected first of all with a lower thermal stability of gaseous lithium and sodium salts [20]. Volatilities of potassium, rubidium, and cesium iodates are comparable, whereas the partial pressures of lithium and sodium iodates are considerably greater than those of the iodides. Therefore the equilibrium of reaction (6) for M = K, Rb, Cs is shifted to the left that makes it possible to suppress the dissociation of iodates to some degree, whereas for M = Na and Li it is shifted to the right.

The total energies of molecules found by the quantum-chemical calculations allow us to calculate the enthalpies of reactions (3). According to the quantum-chemical data, the enthalpies of dimerization of lithium, sodium, potassium, rubidium, and cesium iodates are –250, –225, –179, –184, and –282 kJ, respectively. The values found for potassium, rubidium, and cesium iodates considerably differ from the experimental values, which does not allow us to use the enthalpies of reactions (3) obtained on the basis of the quantum-chemical calculations carried out within the limits of the applied method and basis set.

As a result of our work we have found that the thermal stability of iodates of alkali metals decreases on passing from cesium iodate to sodium iodate. Correspondingly, the degree of dissociation of iodates by reaction (4) increases in the same order. The relative content of dimeric molecules in the vapor of the monomer–dimer systems decreases on passing from potassium iodate to cesium iodate, being ~35% for potassium iodate, ~30% for rubidium iodate, and ~18% for cesium iodate. Analogous trend in the

Table 5. Molecular parameters, effective charges on atoms, bond orders, and dipole moments of dimeric molecules of iodates of alkali metals calculated by the density functional method

Parameter	$(LiIO_3)_2$	$(NaIO_3)_2$	$(KIO_3)_2$	$(RbIO_3)_2$	$(CsIO_3)_2$
r(M–O), Å	2.057	2.369	2.714	2.745	2.975
r(M–O'), Å	2.154	2.436	2.744	2.755	3.091
r(I–O), Å	1.800	1.798	1.826	1.795	1.795
r(I–O'), Å	1.815	1.815	1.847	1.818	1.818
r(I–I), Å	4.792	5.262	5.844	5.922	6.290
r(M–M), Å	2.931	3.392	3.848	3.726	4.125
∠OIO, deg	109.9	108.7	107.6	106.8	106.1
∠OIO', deg	95.7	98.6	100.5	101.3	102.2
Effective charge on atom (unit of e^- charge)					
M	0.63	0.60	0.69	0.68	0.73
O	–0.77	–0.76	–0.73	–0.76	0.76
O'	–0.81	–0.80	–0.77	–0.81	–0.80
I	1.72	1.71	1.53	1.64	1.60
Bond order					
M–O	0.26	0.27	0.16	0.16	0.13
M–O'	0.18	0.18	0.14	0.15	0.12
O–I	1.25	1.27	1.34	1.29	1.27
O'–I	1.09	1.10	1.17	1.20	1.18
Dipole moment, D	0.0009	0.0005	0.0005	0.0003	0.0003

variation of the relative content of dimers in vapor was observed earlier for phosphates and perrhenates of alkali metals [18, 19].

It was found in [20] that the atomization enthalpies of gaseous salts in isocation series of gaseous salts linearly depend on the atomization enthalpies of the corresponding anion-forming gaseous oxides. The absence of reference data on the enthalpies of the gaseous I_2O_5 formation does not allow us to estimate the degree of reliability of our results. Nevertheless, the values of enthalpies of formation and atomization of gaseous potassium, rubidium, and cesium iodates determined in the present work allow us to estimate the enthalpies of atomization and formation of the gaseous iodine oxide I_2O_5 at 1574±18 and –114±18 kJ mol^{-1}, respectively. These values in combination with the data of [20], in turn, allow us to estimate formation enthalpies of gaseous iodates $LiIO_3$ and $NaIO_3$ at –309 and –256 kJ mol^{-1}, respectively. The above values in combination with the enthalpies of formation of potassium, rubidium, and cesium iodates agree with the trend in the variation of the enthalpies of formation of gaseous salts of alkali metals in the first group of the periodic system.

EXPERIMENTAL

The work was performed by the method of high-temperature mass spectrometry on an MS-1301 mass spectrometer at the ionizing voltage of 25 V. In the experiments we used analytical-grade potassium iodate. Rubidium and cesium iodates were prepared by adding excess of rubidium and cesium nitrates to a saturated solution of potassium iodate. As a result rubidium and cesium iodates, which are considerably less water-soluble than potassium iodate, were precipitated. The salts were purified by recrystallization from water. The samples were evaporated from platinum cells heated by a resistance furnace. Temperature was measured by a platinum–platinum-rhodium thermocouple accurate to ±1 K.

Quantum-chemical calculations were carried out using the GAMESS program complex [21] by the density functional DFT method in the B3LYP

approximation [22]. The 3-21G(3d) basis was selected for rubidium and cesium atoms, calculations for iodine atom were carried out using the LANL2DZ effective core potential [23], and the 6-31G(3d) potential for atoms of the other elements.

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