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Thermochimica Acta 333 (1999) 21–26

thermochimica acta

Kinetics and mechanism of thermal decomposition of mercuric oxide

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Accepted 13 April 1999

Abstract

The dissociative evaporation scheme has been used for interpretation of the kinetics and mechanism of thermal decomposition of HgO. A comprehensive analysis of literature data provided explanation for the main features of the process, in particular, the comparatively low decomposition rate above 400°C, which is at odds with the high equilibrium pressure of the gaseous products, and the existence of an additional low-temperature decomposition region within the 160–220°C interval. It has been shown that decomposition in the high-temperature region follows the $HgO(s) \rightarrow Hg(g) + O$ scheme, and in the low-temperature domain it proceeds by the $Hg_2O(s) \rightarrow 2Hg(g) + O$ reaction. The formation of $Hg_2O(s)$ on the HgO surface at low temperatures is in accord with the previously developed theoretical concepts of the mechanism of autocatalysis in the presence of a film of a solid product. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Decomposition mechanism; Dissociative evaporation; Kinetics; Mercuric oxide

1. Introduction

The mercuric oxide (HgO) belongs to a group of substances which played an important role in the development of chemistry. In their investigation of thermal decomposition of HgO, Scheele (1771), Priestly (1774) and Lavoisier (1775) discovered and studied oxygen [1]. The first thermodynamic studies of HgO decomposition were performed by Myers (1873), Echols (1881), Carnelley and Walker (1888) and Pelabon (1889) [2]. In 1913, Taylor and Hulett [2] measured the equilibrium vapor pressure for HgO within the 360–480°C interval. These data remain to our times the only reliable thermodynamic characteristics [3] of the equilibrium

$$HgO(s) = Hg(g) + 1/2\ O_2. \qquad (1)$$

The kinetics of HgO decomposition in vacuo was first studied by Roginsky et al. [4], who showed that the thermal decomposition proceeds on the crystal surface rather than in the gaseous phase, so that the decomposition kinetics followed a contracting-sphere law. No induction and initial self-acceleration periods were observed. This is in accord with the suggestion put forward later by Roginsky [5] that these periods can appear only during the nucleation and growth of new-phase nuclei, where one of the products is obtained in solid form. By contrast, Erofeev and Trusova [6] found that the decomposition was autocatalyzed by the mercury liberated. They found the activation energy, E_a, to be 238 kJ mol^{-1}. In the sixties, the kinetics of HgO decomposition was studied by Taylor [7] who found E_a=201.3±6 kJ mo1^{-1} for crystals 0.1 mm in size and, most comprehensively, by Derbinsky et al. [8–14]. We are going to consider the results obtained by them later.

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PII: S0040-6031(99)00086-6

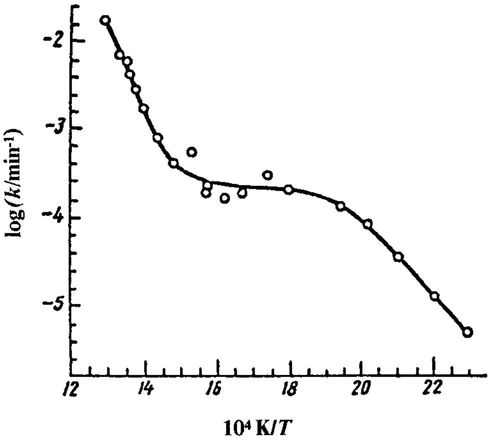

Fig. 1. Temperature dependence of the rate constant for HgO decomposition in vacuum. (Reproduced from [14], by permission of the Journal Editor.)

Despite the apparent simplicity of process (1), which reduces to decomposition of a solid reactant into two gaseous products, its mechanism still remains unclear. Although the total equilibrium pressure of the products at 400°C is about 230 Torr [2], the rate constant for HgO decomposition at this temperature is fairly small, about $n \times 10^{-5}\ \mathrm{s}^{-1}$ in vacuum [7,12]. Still more puzzling is the unusual shape of the Arrhenius plot (Fig. 1) [14], where, besides the conventional region of high-temperature decomposition of HgO (400–500°C), one observes also a region of low-temperature decomposition (160–220°C) with a smaller E_a, and an intermediate region (220–400°C), within which the decomposition rate remains practically constant.

The objective of this work was to find an interpretation of the mechanism and of the above-mentioned features in HgO decomposition using the dissociative evaporation scheme. This approach was employed earlier to explain the mechanism and kinetics of thermal decomposition of oxides [15], nitrates [16–18], azides [19], carbonates [20], $Li_2SO_4 \cdot H_2O$ [21], $Mg(OH)_2$ [22], Ag_2O [23], and of a number of other inorganic compounds [24].

2. Theoretical

The method to be employed here consists in comparing experimental data on the kinetic parameters with their theoretical values. The calculations are based on the classical evaporation model of Hertz–Langmuir, extended to the cases of dissociative evaporation of compounds. The scheme of theoretical calculation of the main kinetic parameters (the flux of the gaseous product J, the rate constant k, the product partial pressure P and the parameters of the Arrhenius equation, E_a and A) has been described in a number of previous publications [15–24]. Therefore, we will present only some final relations necessary for the calculations in this work.

In the case of a binary compound S decomposed in vacuo into gaseous products A and B

$$\mathrm{S(s)} \rightarrow a\mathrm{A(g)} + b\mathrm{B(g)}, \tag{2}$$

the flux of product A can be expressed through the equivalent partial pressure P_A (in atm) of this product corresponding to the hypothetical equilibrium of reaction (2) in the form

$$J_A = \frac{\gamma M P_A}{(2\pi M_A R T)^{1/2}}, \tag{3}$$

where M and M_A are the molar masses of the reactant and product A, γ the coefficient of conversion from atmospheres to pascals, and R the gas constant.

The flux of gaseous products J is connected with the rate constant k. For spherical particles, the fraction decomposed is described by the contracting volume model

$$\frac{d\alpha}{dt} = 3(1-\alpha)^{2/3} k. \tag{4}$$

Taking into account some obvious relationships, $\alpha \equiv 1 - m/m_0$, $m = (4/3)\pi r^3 \rho$ and $J = -(dm/dt)(4\pi r^2)^{-1}$, where m, r and ρ are the mass, radius and density of reactant spherical particle(s), we obtain on rearrangement of Eq. (4) a simple expression

$$J = \rho r_0 k. \tag{5}$$

From Eqs. (3) and (5), we have

$$P_A = \frac{(2\pi M_A R T)^{1/2}}{\gamma M} \rho r_0 k. \tag{6}$$

This equation will be used for the calculation of the equivalent partial pressure of product A from the experimental k value.

A theoretical value of the partial pressure of product A can be calculated from the equilibrium constant

K_p for reaction (2). In the absence of an excess of reaction products in the reactor atmosphere, the situation corresponding to the *equimolar* evaporation mode, the partial pressure P_A can be expressed [15] as

$$P_{\mathrm{A}}^{\mathrm{e}} = a\left(\frac{K}{F}\right)^{1/\nu}\left(\frac{M_{\mathrm{A}}}{M_{\mathrm{B}}}\right)^{b/2\nu} = \frac{a}{F^{1/\nu}}\left(\frac{M_{\mathrm{A}}}{M_{\mathrm{B}}}\right)^{b/2\nu} \times \exp\left(\frac{\Delta_{\mathrm{r}}S_T^0}{\nu R}\right)\exp\left(-\frac{\Delta_{\mathrm{r}}H_T^0}{\nu RT}\right), \qquad (7)$$

where

$$F \equiv a^a \times b^b, \qquad (8)$$

$$\nu = a + b, \qquad (9)$$

and

$$K_P = P_{\mathrm{A}}^a \cdot P_{\mathrm{B}}^b. \qquad (10)$$

Here $\Delta_{\mathrm{r}}H_T^0$ and $\Delta_{\mathrm{r}}S_T^0$ are, respectively, the changes of the enthalpy and entropy in process (2).

If the partial pressure P'_{B} of one of the gaseous components greatly exceeds the equivalent pressure P_{B} of the same component released in the decomposition and if, in addition to that, the magnitude of P'_{B} remains constant in the process of decomposition, we call such evaporation mode *isobaric*. In this case,

$$P_{\mathrm{A}}^{\mathrm{i}} = \frac{K_P^{1/a}}{P_{\mathrm{B}}^{\prime b/a}} = \frac{1}{P_{\mathrm{B}}^{\prime b/a}}\exp\left(\frac{\Delta_{\mathrm{r}}S_T^0}{aR}\right)\exp\left(\frac{\Delta_{\mathrm{r}}H_T^0}{aRT}\right). \qquad (11)$$

As can be seen from Eq. (7) and Eq. (11), the calculated activation energies for reaction (2) should be different for the equimolar and isobaric modes of decomposition, i.e.

$$E_{\mathrm{a}}^{\mathrm{e}} = \Delta_{\mathrm{r}}H_T^0/\nu, \qquad (12)$$

for the equimolar mode and

$$E_{\mathrm{a}}^{\mathrm{i}} = \Delta_{\mathrm{r}}H_T^0/a, \qquad (13)$$

for the isobaric one.

In order to take into account the partial transfer of the energy released in the condensation of low-volatile A product to the reactant, we introduced, as before [21–23], into calculations of the enthalpy of decomposition reaction (2) an additional term $\tau a \Delta_{\mathrm{c}}H_T^0$ (A), where the coefficient τ corresponds to the fraction of the condensation energy transferred to the reactant.

Table 1
Thermodynamic functions [25,26] used in the calculations

Species	State of aggregation	$\Delta_{\mathrm{f}}H_{298}^0$ (kJ mol^{-1})	S_{298}^0 (J mol^{-1} K^{-1})
Hg_2O	s	−91.3	125.6
HgO	s	−90.9	70.3
Hg	g	61.4	175.0
O_2	g	0	205.0
O	g	249.2	160.9

Table 2
Parameters used in the calculations of decomposition rates

Parameter	Symbol	Value
Molar mass of HgO	M	0.217 kg mol^{-1}
Molar mass of Hg	M_{Hg}	0.201 kg mol^{-1}
Molar mass of O	M_{O}	0.016 kg mol^{-1}
Density of HgO	ρ	11 080 kg m^{-3}
Enthalpy of reaction (15)	$\Delta_{\mathrm{r}}H_{298}^0$	401.5 kJ mol^{-1}
Enthalpy of reaction (16)	$\Delta_{\mathrm{r}}H_{298}^0$	463.3 kJ mol^{-1}
Entropy of reaction (15)	$\Delta_{\mathrm{r}}S_{298}^0$	265.6 J mol^{-1} K^{-1}
Entropy of reaction (16)	$\Delta_{\mathrm{r}}S_{298}^0$	385.3 J mol^{-1} K^{-1}
Condensation heat of reaction $2Hg(g) + O \rightarrow Hg_2O(s)$	$\Delta_{\mathrm{c}}H_{298}^0$	−463.3 kJ mol^{-1}
Gas constant	R	8.3145 J mol^{-1} K^{-1}
Pressure conversion factor	γ	101 325 Pa atm^{-1}

Thus, we can write

$$\Delta_{\mathrm{r}}H_T^0 = a\Delta_{\mathrm{f}}H_T^0(\mathrm{A}) + b\Delta_{\mathrm{f}}H_T^0(\mathrm{B}) - \Delta_{\mathrm{f}}H_T^0(\mathrm{S}) + \tau a \Delta_{\mathrm{c}}H_T^0(\mathrm{A}). \qquad (14)$$

Table 1 lists the initial values of the thermodynamic functions [25,26] for all components of the assumed reactions and Table 2, all the other parameters necessary for subsequent calculations.

3. Results and discussion

3.1. Mechanism of high-temperature decomposition

Consider first the results of HgO decomposition studies made at high temperatures (>650 K). We believe the investigations of Derbinsky et al. on HgO decomposition in oxygen [12] and mercury vapor [13] to be extremely important in this respect. An analysis of the data obtained permits one to establish the true composition of the primary decomposition products. By the theory, the temperature dependence of the decomposition rate or, in other words, the activation energy measured under dissociative evaporation of the reactant in an environment containing an excess of one of the gaseous products should differ substantially from that obtained in an environment free of decomposition products. In the case of reaction (1), when the decomposition mode is changed from equimolar (in vacuo) to isobaric (in O_2 atmosphere), the activation energy should change, as seen from a comparison of Eq. (12) and Eq. (13), by a factor 1.5. At the same time, the average activation energy measured [12] for five mercury oxide samples was found to be 193 ± 8 kJ mol^{-1} ($n=8$) in vacuo, and 201.7 ± 3 kJ mol^{-1} ($n=3$) in O_2 atmosphere, which is the same within experimental error. This suggests that the primary product of HgO decomposition is not molecular oxygen O_2 but rather its atomic species or, in other words, that the decomposition proceeds by the reaction

$$\mathrm{HgO(s)} \rightarrow \mathrm{Hg(g)} + \mathrm{O}. \tag{15}$$

This suggestion is supported also by a comparison of experimental values of E_a with theoretical calculations made for reactions (1) and (15). Considering that the enthalpies of these reactions are 152.3 and 401.5 kJ mol^{-1}, and the numbers of moles of the gaseous products are, accordingly, 1.5 and 2, the theoretical values of E_a should be 101.5 kJ mol^{-1} for reaction (1) and 200.8 kJ mol^{-1} for reaction (15).

One more argument for the validity of reaction (15) is provided by a study of HgO decomposition in Hg vapor [13]. We used the experimental data characterizing the dependence of the degree of decomposition α on time for 829 and 839 K [13] to estimate the activation energy. It was found to be 334 ± 30 kJ mol^{-1}, i.e. 1.7 times higher than that in vacuo. This agrees quite well with the twofold increase of the activation energy expected by reaction (15) when going from the equimolar to isobaric mode.

3.2. Mechanism of low-temperature decomposition

An analysis of the specific features of HgO decomposition in the low-temperature region pointed out in [15] fixes attention on the following points:

1. The slope of the Arrhenius plot, i.e. activation energy, is found to be substantially lower than it is in the high-temperature region (84 kJ mol^{-1} against 201 kJ mol^{-1}, respectively).
2. In contrast to the high-temperature region, the initial period of decomposition proceeds here with acceleration.
3. During low-temperature decomposition, the samples of red mercury oxide become dark brown or almost black.
4. A microscopic study of the crystals [8] revealed that low-temperature decomposition proceeds not by the contracting-sphere model but rather with the reaction interface localized (in the form of dark bands) at the points of the most intense reaction (the centers or corners of the hexagonal crystals).

An analysis of these features permits a conclusion that the low-temperature process is actually decomposition of the black mercury oxide

$$\mathrm{Hg_2O(s)} \rightarrow 2\mathrm{Hg(g)} + \mathrm{O}. \tag{16}$$

The lower oxide Hg_2O forms, in its turn, in the interaction of Hg vapor with the oxygen atoms produced in decomposition of HgO at the interface between the two solid phases (HgO/Hg_2O). Due to the formation of a film of the solid product (Hg_2O) on the surface of HgO and partial transfer of the energy released in Hg_2O formation to the reactant, HgO decomposition proceeds at a considerably higher rate than that from an open surface. In accordance with the concepts developed in our earlier publications [22,23,27], transfer of one half of this energy ($\tau=0.5$) to the reactant reduces the enthalpy of HgO decomposition from 401.5 to 285.7 kJ mol^{-1}. As a result, the activation energy of process (15) decreases to $285.7/2\cong143$ kJ mol^{-1}.

Because the activation energy corresponding to reaction (16) is 154 kJ mol^{-1}, decomposition of Hg_2O should proceed faster with increasing temperature than its formation in process (15). Therefore the area of the reactant covered by the Hg_2O film should decrease. This conclusion is in agreement with the decrease of the degree of blackening of HgO crystals with temperature pointed out in [14]. For the same reason, i.e. because of the Hg_2O area decreasing with increasing temperature, the value of E_a (84 kJ mol^{-1}) found for the low-temperature portion of the Arrhenius plot, turns out to be noticeably smaller than its theoretical value (154 kJ mol^{-1}), and above 280°C the decomposition rate constant does not increase at all. The scatter in the decomposition rate measurements observed within the 280–380°C interval is most probably due to the fact that the mass losses occurring under steady-state decomposition of HgO which proceeds at a slow rate are superimposed upon by the fairly uncertain losses associated with the formation and subsequent decomposition of Hg_2O during the sample heating to the desired temperature.

3.3. Experimental and theoretical rate constants

To estimate the validity of the above mechanism of HgO decomposition, compare the experimentally observed (Fig. 1) and theoretically calculated decomposition rates for both temperature intervals. The rate constant can be derived from the relationship

$$k = \frac{\gamma M P_{\mathrm{A}}}{\rho r_0 (2\pi M_{\mathrm{A}} R T)^{1/2}}, \qquad (17)$$

where P_{A}, depending on the actual mode of decomposition, is given by Eq. (7) or Eq. (11). HgO decomposition in vacuum [14] corresponds to the equimolar mode, and therefore P_{A} should be calculated using Eq. (7).

Based on the microscopic measurements of HgO particles [12], we set $r_0=5\ \mu\mathrm{m}=5\times10^{-6}$ m. We disregarded the self-cooling effect in the calculations, because the powder sample 10 mg in mass was placed in a plane-bottom crucible in a thin layer, which did not exceed in thickness 0.05 mm. Besides, the decomposition rate constant at low temperatures did not exceed $10^{-6}\ \mathrm{s}^{-1}$, and at high temperatures, $10^{-4}\ \mathrm{s}^{-1}$. However, in the latter case the influence of self-cooling on the results of calculation cannot be totally excluded.

The calculated and experimental values of the rate constants for the central temperatures of the two decomposition intervals are presented in Table 3. A comparison shows that the results agree within a factor 2–3, which, considering experimental errors and the approximations made in the calculations, should be regarded as quite satisfactory.

Table 3
Experimental and theoretical values of the rate constant

Reaction	T (K)	P_{Hg} (atm)	k (s^{-1})	
			Theory	Experiment
(16)	460	1.9×10^{-11}	1.1×10^{-7}	3.0×10^{-7}
(15)	723	2.7×10^{-8}	1.2×10^{-4}	5.3×10^{-5}

4. Conclusions

The application of the dissociative evaporation scheme permits one to explain all the above features observed in thermal decomposition of HgO. The low decomposition rate of the oxide is due to the oxygen evolving during the decomposition in the form of free atoms rather than molecules. This mechanism is substantiated by the agreement between the theoretical and calculated values of E_{a} and by the absence of the effect of oxygen environment on E_{a}. The appearance of the unusual region of low-temperature decomposition of HgO in the Arrhenius plot (Fig. 1) is caused by decomposition of the lower mercury oxide Hg_2O. Its formation is associated, in its turn, with the formation of a reaction interface separating the two solid phases (HgO/Hg_2O), and with a partial transfer of the Hg_2O formation energy to the reactant, which stimulates decomposition of HgO. The validity of the proposed decomposition mechanisms is supported by a good agreement between the experimental and theoretical values of the rate constants for both portions of the Arrhenius plot.

References

[1] B.I. Kazakov, in: Popular Library of Chemical Elements, Part 2, Nauka, Moscow, 1977, p. 245 (in Russian).
[2] G.B. Taylor, G.A. Hulett, J. Phys. Chem. 17 (1913) 565–591.
[3] E.K. Kazenas, D.M. Chizhikov, Pressure and Composition of Vapor under Oxides of Chemical Elements, Nauka, Moscow, 1976 (in Russian).
[4] S.Z. Roginsky, L.V. Sapozhnikova, N.A. Kucherenka, Ukr. Khim. Zh. (in Russian) 4 (1929) 99–119.
[5] S.Z. Roginsky, Trans. Faraday Soc. 34 (1938) 961–975.
[6] B.V. Erofeev, K.I. Trusova, Zh. Fiz. Khim. (in Russian) 12 (1938) 346–360.
[7] D. Taylor, J. Chem. Soc. (1962) 1047–1050.
[8] E.A. Prodan, M.M. Pavlyuchenko, I.A. Derbinsky, Dokl. Akad. Nauk BSSR (in Russian) 9 (1965) 585–587.
[9] E.A. Prodan, I.A. Derbinsky, M.M. Pavlyuchenko, Dokl. Akad. Nauk BSSR (in Russian) 10 (1966) 877–880.
[10] I.A. Derbinsky, E.A. Prodan, M.M. Pavlyuchenko, Izv. Akad. Nauk BSSR (in Russian) 3 (1966) 119–122.

[11] M.M. Pavlyuchenko, I.A. Derbinsky, E.A. Prodan, Dokl. Akad. Nauk SSSR (in Russian) 186 (1969) 136–138.

[12] I.A. Derbinsky, M.M. Pavlyuchenko, E.A. Prodan, A.A. Kozyro, L.A. Rusak, in: Heterogeneous Chemical Reactions, Nauka i Tekhnika, Minsk, 1970, pp. 190–204 (in Russian).

[13] I.A. Derbinsky, M.M. Pavlyuchenko, E.A. Prodan, Kinet. i Kataliz (in Russian) 12 (1971) 1055–1057.

[14] I.A. Derbinsky, E.A. Prodan, M.M. Pavlyuchenko, Izv. Vuzov, Khimiya i Khim. Tekhnol. (in Russian) 14 (1971) 1295–1298.

[15] B.V. L'vov, Spectrochim. Acta, Part B 52 (1997) 1–23.

[16] B.V. L'vov, Mikrochim. Acta (Wien) 2 (1991) 299–308.

[17] B.V. L'vov, A.V. Novichikhin, Spectrochim. Acta, Part B 50 (1995) 1427–1448.

[18] B.V. L'vov, A.V. Novichikhin, Spectrochim. Acta, Part B 50 (1995) 1459–1468.

[19] B.V. L'vov, Thermochim. Acta 291 (1997) 179–185.

[20] B.V. L'vov, Thermochim. Acta 303 (1997) 161–170.

[21] B.V. L'vov, Thermochim. Acta 315 (1998) 145–157.

[22] B.V. L'vov, A.V. Novichikhin, A.O. Dyakov, Thermochim. Acta 315 (1998) 135–143.

[23] B.V. L'vov, Thermochim. Acta 333 (1999) 13–19.

[24] B.V. L'vov, A.V. Novichikhin, Thermochim. Acta 290 (1997) 239–251.

[25] V.A. Ryabin, M.A. Ostroumov, T.F. Svit, Thermodynamic Characteristics of Substances. Handbook, Khimiya, Leningrad, 1977 (in Russian).

[26] G.V. Samsonov (Ed.), Physical and Chemical Characteristics of Oxides. Handbook, Metallurgiya, Moscow, 1978 (in Russian).

[27] B.V. L'vov, Spectrochim. Acta, Part B, 53 (1998) 809–820.