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Calculation of the Kinetic Parameters of Dehydration of Lithium Peroxide Monohydrate in Nonisothermic Regime by Derivatographic Method

Yu. A. Ferapontov, L. L. Ferapontova, and S. B. Pugin

OAO Roskhimzashchita Corporation, Morshanskoe sh. 19, Tambov, 392680 Russia
e-mail: nihi@tambovnihi.ru

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Abstract—The dehydration of lithium peroxide monohydrate was studied by derivatography under nonisothermic conditions for the calculation of main kinetic parameters in the temperature range 90–146°C. Experimental conditions (sample size and the linear heating rate) caused by thermoconductivity of the object under investigation were determined. It is shown that the process under study proceeds according to the kinetic law close to the first order one (n = 0.85±0.03). Values of the activation energy and the pre-exponential factor [E_a = 86.0±0.8 kJ mol^{-1}, k_0 = (2.19±0.16)×10^{11} min^{-1}] were obtained. A suggestion was formulated that the dehydration mechanism of lithium peroxide monohydrate was analogous to that of the hydrates of the alkaline earth metal (calcium, barium, and strontium) peroxides.

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In the course of selection of optimal technological parameters for the process of synthesis of lithium peroxide from hydrogen peroxide and lithium hydroxide with the subsequent dehydration of the intermediate lithium peroxide monohydrate ($Li_2O_2 \cdot H_2O$) [1, 2] in the superhigh frequency field a necessity appeared of the quantitative evaluation of main kinetic parameters of the dehydration process which were not reported previously. The knowledge of the kinetics of this process, first of all of the activation energy, is necessary for evaluation of the synthesis conditions permitting to minimize the probability of thermal decomposition of lithium peroxide. The latter reaction not only decreases the content of target substance in the reaction product, but also provokes the formation of the fire hazard situation due to the liberation of atomic oxygen, one of the strongest oxidants [3].

Kinetics of topochemical reactions as a rule is studied under isothermic conditions, and evaluation of main kinetic parameters is sufficiently laborious. But the progress in the laboratory technique makes the use of non-isothermal methods of investigation of kinetics of the topochemical processes more and more convenient. In particular, thermogravimetric (TGA) and differential thermal (DTA) analyses are especially effective under the condition of linear temperature growth [4, 5].

Dehydration of lithium peroxide monohydrate may be schematically described by Eq. (1).

$$Li_2O_2(solid) \rightarrow Li_2O_2(solid) + H_2O(gas)\uparrow. \quad (1)$$

Rate of the irreversible heterogenous process accompanied by formation of one gaseous product leaving the reaction zone is described by the following kinetic Eq. (2) [6].

$$(dW/d\tau)(1/W_k) = k_0 e^{-E/RT}(W/W_k)^n, \quad (2)$$

where W_k is the mass loss of the sample under investigation, W is the mass loss of the sample up to the time τ, k_0 is the pre-exponential factor, E is the activation energy of the process, n is the reaction order, T is the absolute temperature, R is the universal gas constant.

Under the conditions of linear programmed heating when $dT/d\tau = q$ Eq. (2) may be represented as Eq. (3):

$$(dW/dT)(1/W_k) = (k_0/q)e^{-E/RT}(W/W_k)^n, \quad (3)$$

where q is the heating rate for the sample under study.

Modern derivatographs permit to fix simultaneously with high accuracy the variation of the mass of the studied sample in the course of heating (TG curve) as well as the rate of this process (DTG curve). In this case $dW/d\tau$ value will be proportional to the deflection of DTG curve from the zero line h [7].

$$dW/dT = \alpha h, \quad (4)$$

$$W_k = a\int_0^{T_k}(dW/dT)dT = aF, \quad (5)$$

$$W = a\int_0^{T}(dW/dT)dT = a(F - f), \quad (6)$$

where α and a are the scaling coefficients, F is the area under the DTG curve, limited by the zero line, f is the area under the DTG curve at the current time.

Under the given experimental conditions α, a, and F are constants, and the Eq. (3) considering the Eqs. (4)–(6) may be written as Eq. (7).

$$\alpha h = (k_0/q)e^{-E/RT}[(F - f)/F]^n F. \quad (7)$$

Transformation of the Eq. (7) gives Eq. (8) or Eq. (9).

$$\log \alpha h = \log (k_0/q) - E/(2.3RT) + \log [(F - f)^n/F^{n-1}], \quad (8)$$

$$\log [h/(F - f)^n] = \log [k_0/q\alpha F^{n-1}] - E/(2.3RT). \quad (9)$$

When the reaction order is evaluated correctly, dependence of log $[h/(F - f)]$ on $1/T$ is a straight line with the slope proportional to the activation energy.

Procedures for evaluation of the reaction order are sufficiently thoroughly described [4, 5, 8–13]. In this work the reaction order was evaluated by the simple and reliable method developed by Kissinger [9] based on the evaluation of temperature of the maximum of the effect under study and the asymmetry of the DTG curve. Asymmetry of DTG curve is determined by Eq. (10). It is calculated planimetrically as the ratio of segments a and b formed by the projection of the ascending and descending branches of TG curve on the zero line.

$$S = \frac{d^2W/dT^2 \text{ of the descending branch of DTG}}{d^2W/dT^2 \text{ of the ascending branch of DTG}} = \frac{b}{a}. \quad (10)$$

This ratio is connected with the reaction order as follows:

$$S = 0.63n^2. \quad (11)$$

Padmanadkhan et al. [14] showed that the pre-exponential factor k_0 for topochemical reactions proceeding in the narrow temperature interval may be evaluated from the formula

$$(k_0/q)(RT_s^2/E)e^{-E/RT_s} = 1, \quad (12)$$

where T_s is the temperature of the extremum of the effect under study on the DTG curve.

Data on the experimental conditions and main kinetic parameters of the process under investigation obtained by the mathematical treatment of the experimental data are listed in the table.

Main characteristic values necessary for further mathematical treatment are shown in Fig. 1. It illustrates the results of thermal analysis of $Li_2O_2 \cdot H_2O$ by an example of the sample no. 2 from the table.

It follows from the presented data that the dehydration of lithium peroxide monohydrate begins at 91.2±1.4°C, passes through the maximum point at 112.2±1.3°C and ends at 145.7±1.6°C (first endothermic effect on DTA and DTG curves). Under these conditions the mass loss of the sample of 27.4±0.2% takes place while theoretical water content in the sample under study is 28%. This fact demonstrates the complete dehydration of $Li_2O_2 \cdot H_2O$ under the experimental conditions. The presence of a single endothermic effect on DTA curves in the temperature range 80–160°C shows that no side reactions such as hydrolysis of lithium peroxide with water vapor capable to influence the reliability of the calculated results take place.

The reaction order equal to 0.85±0.03 was evaluated from the asymmetry of DTG curves by

Conditions of thermal analysis and main kinetic parameters of dehydration of lithium peroxide monohydrate

Exp. no.	Mass of the sample, m, mg	Heating rate, q, deg min^{-1}	Mass loss, %	Asymmetry parameters of DTG curve, mm		Extremum temperature on DTG curve, °C	Reaction order, n	Pre-exponential factor, $k_0 \times 10^{11}$, min^{-1}	Activation energy E_a, kJ mol^{-1}
				a	b				
1	78.33	5	27.5	0.56	1.14	110.9	0.88	2.03	86.4
2	79.76	5	27.6	0.55	1.15	111.1	0.87	2.26	86.8
3	75.61	7	27.4	0.50	1.09	111.7	0.85	2.08	85.8
4	76.48	7	27.3	0.49	1.11	111.8	0.84	2.12	85.7
5	74.14	10	27.1	0.44	1.04	113.5	0.82	2.35	85.2

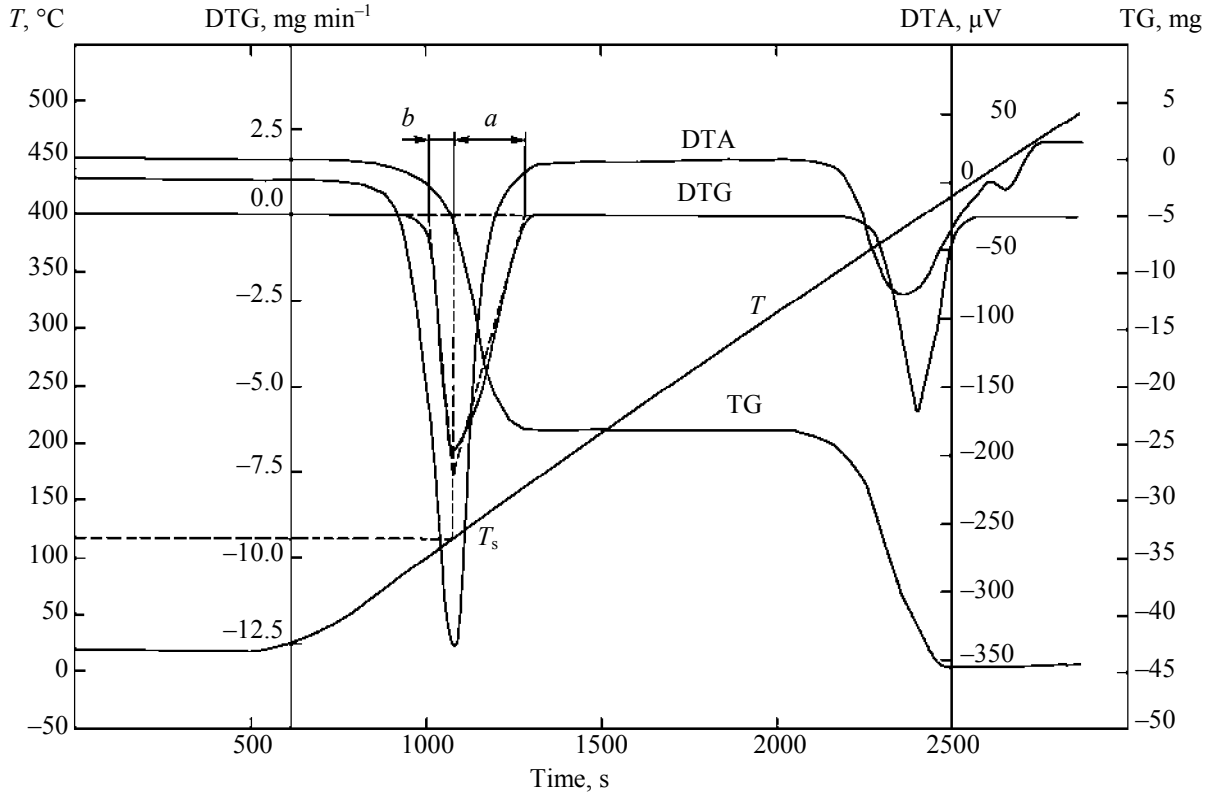

Fig. 1. Complex thermal analysis of $Li_2O_2 \cdot H_2O$ with the designation of characteristic values necessary for calculation of the dehydration kinetic parameters.

formula (11). On the basis of evaluation of the temperature values from TG curves and calculation of h, F, and f values from DTG curves dependences of log $[h/(F - f)^n]$ values from $1/T$ were plotted. All of them have practically identical character. Figure 2 illustrates such dependence for the sample no. 2 from the table.

Dependence of log $[h/(F - f)^n]$ on $1/T$ is close to linear in all temperature range under consideration showing that calculation of the reaction order of $Li_2O_2 \cdot H_2O$ dehydration was correct. The activation energy of the process under study was evaluated from the graphic data presented by formula (13) [15].

$$E_a = 19.11 \tan \alpha \xi. \quad (13)$$

Here tan α is the tangent of the angle of the straight line to the abscissa axis, ξ is the ratio of scale by the abscissa axis to the scale by the axis of ordinates.

The pre-exponential factor for the description of kinetics of dehydration of $Li_2O_2 \cdot H_2O$ according to Eq. (3) was found from Eq. (12) considering the activation energy value and the rate of heating of the sample.

As seen from the data presented the activation energy of the dehydration of lithium peroxide monohydrate is 86.0±0.8 kJ mol^{-1}, the pre-exponential factor is k_0 (2.19±0.16)×10^{11} min^{-1}, and the reaction order is 0.85±0.03 indicating that the dehydration of lithium peroxide monohydrate occurs according to the kinetic rule close to the first order.

It seems interesting to note that close values of activation energies of dehydration of lithium peroxide

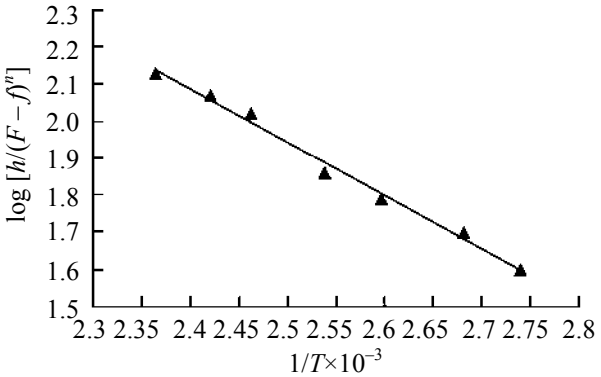

Fig. 2. Dependence of log $[h/(F - f)^n]$ on $1/T$ for dehydration of $Li_2O_2 \cdot H_2O$.

monohydrate and hydrates of alkaline earth metal peroxides such as calcium, barium, and strontium [16, 17] permit the suggestion that the mechanism of these processes is analogous. Liberation of water molecules proceeds in one stage, and it is not complicated with side reactions.

EXPERIMENTAL

Thermogravimetric and differential thermal analysis of the samples was carried out under non-isothermal conditions on a Setaram TAG-24 research complex (France). For the evaluation of main kinetic parameters of dehydration of lithium peroxide monohydrate five consecutive experiments were carried out. Sample size was 70–80 mg. Temperature was registered with the accuracy 0.01°C, mass variation of samples was measured with the accuracy up to 0.01 mg. The samples under investigation were placed in the corundum crucible. Temperature was measured with platinum–platinorhodium thermocouple placed inside the investigated sample and calibrated against the routine reference points. Experiments were carried out in air at atmospheric pressure, heating rate 5–10 deg per min. Such heating rate provides the equivalence of temperatures in the total sample in the course of the experiment. At the heating rates below 5 deg min^{-1} and above 12 deg min^{-1} significant deflection of the temperature curve T from the straight line is observed. It leads to significant error while calculation of kinetic parameters of the process under investigation. This fact arises from nonequivalence in temperature of the outer and the inner layers of the sample under study resulting from the insufficient thermoconductivity of lithium peroxide monohydrate.

Samples $Li_2O_2 \cdot H_2O$ for thermal analysis were prepared by the reaction of solid lithium hydroxide and 50% water solution of hydrogen peroxide of the "specially pure" grade at 30°C and 1.85 $LiOH/H_2O_2$ molar ratio. The reaction mixture was maintained for 2 h at 30°C for the establishing equilibrium between the phases. Solid $Li_2O_2 \cdot H_2O$ was filtered off, washed with distilled water, and dried at room temperature over the layer of sorbent to remove chemically non-bound water [18, 19]. In the course of the experiments the temperature was maintained by a water bath with the accuracy ±0.2°C. For the evaluation of chemical composition the active oxygen, lithium hydroxide, and lithium carbonate content was evaluated. While the evaluation of active oxygen the samples were preliminary stabilized with boric acid, and then permanganatometric titration was carried out [20]. For evaluation of LiOH content the samples were boiled in water for 15–20 min to decompose peroxides, and the solution obtained was titrated with 0.1 N sulfuric acid in the presence of phenolphthaleine. Lithium carbonate content was evaluated according to Fresenius [21]. The preparation under study had the following composition (wt %): $Li_2O_2 \cdot H_2O$ 98.4, LiOH 0.4, Li_2CO_3 1.2. The substance obtained contained no non-hydrated lithium peroxide (Li_2O_2) and chemically non-bound water.

Besides, the individuality of $Li_2O_2 \cdot H_2O$ was confirmed by qualitative X-ray phase analysis on a DRON-6 diffractometer with the filtered CuK_α-radiation (λ = 0.154051 nm). Scanning step 0.05°C, scanning range $20^o < 2\theta < 120^o$, exposition time in each point 3 s [19].

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