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Kinetic analysis of the dehydration processes in some iodate hydrates

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Abstract

A kinetic analysis (E^{*}_{deh}, A) has been made of the dehydration processes of $M(IO_3)_2 \cdot 6H_2O$ (M is Ca^{2+}, Sr^{2+}), $M(IO_3)_2 \cdot 4H_2O$ (M is Mg^{2+}, Co^{2+}, Ni^{2+}), $M(IO_3)_2 \cdot 2H_2O$ (M is Ni^{2+}, Zn^{2+}), $M(IO_3)_2 \cdot H_2O$ (M is Ca^{2+}, Sr^{2+}, Ba^{2+}) and their deuterates on the basis of thermogravimetric data. The general differential method of non-isothermal kinetics was used. The most probable kinetic equation has been determined ($F(\alpha)$), describing the mechanism of the individual stages of the dehydration for the different hydrates. A comparative analysis has been made of the kinetic data for each hydrate and deuterate pair.

Keywords: Dehydration; Deuterate; Hydrate; Iodate; Kinetics; Mechanism; TG

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1. Introduction

Using the methods of TG, DTA and DSC, we have studied [1-5] the thermal dehydration of $M(IO_3)_2 \cdot 6H_2O$ (M is Ca^{2+}, Sr^{2+}), $M(IO_3)_2 \cdot 4H_2O$ (M is Mg^{2+}, Co^{2+}, Ni^{2+}), $M(IO_3)_2 \cdot 2H_2O$ (M is Ni^{2+}, Zn^{2+}), and $M(IO_3)_2 \cdot H_2O$ (M is Ca^{2+}, Sr^{2+}, Ba^{2+}), and their respective deuterates. Information about the course of the dehydration process, $T_{\mathrm{max,deh}}$ and $\Delta H^{\ominus}_{\mathrm{deh}}$, was obtained on the basis of these studies. For a complete description, it was important to also undertake a kinetic analysis to

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determine the activation energy E^*_{deh} and the pre-exponential factor A for each hydrate-deuterate pair using the thermogravimetric data that we obtained under non-isothermal conditions and presented in refs. 1–5. This interest is also determined by the fact that existing publications contain sparse data concerning the kinetics of the dehydration process of this group of iodate hydrates. There is no information at all for the isotope effect.

Information concerning these processes has been published in ref. 6, but only the determination of E^*_{deh} from the DTA data for $M(IO_3)_2 \cdot 6H_2O$ (M is Ca^{2+}, Sr^{2+}) $Mg(IO_3)_2 \cdot 4H_2O$ and $M(IO_3)_2 \cdot H_2O$ (M is Ca^{2+}, Sr^{2+}, Ba^{2+}). The E^*_{deh} has also been determined from thermogravimetric data for $Ba(IO_3)_2 \cdot H_2O$ in refs. 7 and 8.

2. Experimental

The kinetic analysis used a computer program written in BASIC and based on a manual procedure for determining E^*_{deh} and A under non-isothermal conditions [9–12]. The general differential method was applied and the basic equation of non-isothermal kinetics was used in a logarithmic form [11]

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}T}{F(\alpha)}\right] = \ln\frac{A}{b} - \frac{E^*}{R}\frac{1}{T}$$

where $\alpha = (m_0 - m_T)/(m_0 - m_{\text{end}})$ is the conversion degree, m_0 and m_{end} are the initial and final mass of the hydrate in g, and m_T is the mass (in g) for a given T; b is the rate of heating in K s^{-1} ($b = \mathrm{d}T/\mathrm{d}\tau$), A is the pre-exponential factor in s^{-1}, $R = 8.314$ J K^{-1} mol^{-1}, and $F(\alpha)$ is the kinetics models (in a differential form).

The 25 kinetic equations taken from the relevant literature [9, 11] describe a process of the type

$$\mathrm{A(solid)} \rightarrow \mathrm{B(solid)} + \mathrm{C(gas)}$$

Numerical differentiation of the experimental $\alpha - T$ data is made after their approximation with a cubic parametric B-spline, as described in ref. 10, which reflects most accurately the nature of the non-isothermal data processed.

The kinetic analysis involves determining the kinetic equations $F(\alpha)$, from those introduced into the program (25 in all), for which the dependence of $\ln[(\mathrm{d}\alpha/\mathrm{d}T)/F(\alpha)]$ on $1/T$ is linear. The criteria for selecting $F(\alpha)$ are the values of the calculated correlation coefficients R and standard deviations σ. In cases where the dehydration process takes place in several stages, the kinetic analysis was carried out for each stage separately.

The processed TG curves from the derivatograms presented in refs. 1–5 were taken under identical conditions for all compounds: in a medium of air; heating rate, 5 K min^{-1}; sample weight, 150 mg; and particle size, <230 mesh. The $T_{\max}$ of the dehydration processes, as shown in Table 1, were taken from the same derivatograms. The crystallinity of the initial and final products was demonstrated by X-ray analysis.

Experiments were made to obtain analogous data from the DSC curves, using a standard computer program. However, the nature of the recorded peaks describing

Table 1
Kinetic parameters, E^*_{deh} and ln A, of the dehydration processes of $M(IO_3)_2 \cdot nH_2O(D_2O)$ obtained from TG data

Phase transition	Form	E^*_{deh} in kJ mol^{-1}	ln(A/s^{-1})	Kinetic model [a] $F(\alpha)$		Correl. coeff. R	Stand. deviation σ	T_{max} in °C (DTA)	Ref.
$Ca(IO_3)_2 \cdot 6H_2O \rightarrow Ca(IO_3)_2 \cdot H_2O + 5H_2O$	H	115	32.2	$(1-\alpha)[-\ln(-\alpha)]^{1/3}$	G	0.987	0.293	110	1
	D	93	24.9	$[-\ln(1-\alpha)]^{-1}$	D	0.998	0.104	90	
$Ca(IO_3)_2 \cdot H_2O \rightarrow Ca(IO_3)_2 \cdot H_2O$	H	127	31.1	$1-\alpha$	G	0.997	0.073	160	
	D	135	32.8	$1-\alpha$	G	0.999	0.028	160	
$Sr(IO_3)_2 \cdot 6H_2O \rightarrow Sr(IO_3)_2 \cdot H_2O + 5H_2O$	H	81	23.2	α	NL	0.966	0.172	95	1
	D	65	17.1	$1-\alpha$	G	0.997	0.061	75	
$Sr(IO_3)_2 \cdot H_2O \rightarrow Sr(IO_3)_2 + H_2O$	H	87	18.1	$\alpha^{2/3}$	R	0.995	0.056	175	
	D	111	25.0	$(1-\alpha)^{1/2}$	G	0.991	0.139	165	
$Mg(IO_3)_2 \cdot 4H_2O \rightarrow Mg(IO_3)_2 + 4H_2O$	H	79	16.2	$(1-\alpha)^{2/3}$	R	0.995	0.056	165	3
130–190°C	D	63	13.7	$(1-\alpha)^{2/3}$	R	0.997	0.044	160	
190–230°C	H	95	18.2	$1-\alpha$	G	0.998	0.015		
	D	90	18.3	$(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	D	0.997	0.027		
$Co(IO_3)_2 \cdot 4H_2O \rightarrow Co(IO_3)_2 + 4H_2O$	H								
95–125°C		67	18.1	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	G	0.901	0.186	120	4
125–160°C		86	17.4	$\alpha^{2/3}$		0.918	0.153	150	
160–210°C		83	18.1	$(1-\alpha)^{1/2}$	R	0.998	0.025	200	
$Ni(IO_3)_2 \cdot 4H_2O \rightarrow Ni(IO_3)_2 \cdot 2H_2O + 2H_2O$	H	76	18.3	$1-\alpha$	G	0.981	0.078	120	4
	D	68	16.7	$1-\alpha$	G	0.978	0.151	130	
$Ni(IO_3)_2 \cdot 2H_2O \rightarrow Ni(IO_3)_2 + 2H_2O$	H	118	21.5	$[(1-\alpha)^{-1/3}-1]^{-1}$	D	0.998	0.089	230	
	D	136	26.7	α^{-1}	D	0.998	0.599	210	
$Ni(IO_3)_2 \cdot 2H_2O \rightarrow Ni(IO_3)_2 + 2H_2O$	H	178	39.0	$1-\alpha$	G	0.987	0.149	220	5
	D	188	37.9	$1-\alpha$	G	0.948	0.236	235	
$Zn(IO_3)_2 \cdot 2H_2O \rightarrow Zn(IO_3)_2 + 2H_2O$	H	123	27.8	$\alpha^{2/3}$		0.997	0.349	140	5
	D	128	28.7	$\alpha^{2/3}$		0.993	0.173	145	
$Ca(IO_3)_2 \cdot H_2O \rightarrow Ca(IO_3)_2 \cdot 0.5H_2O + 0.5H_2O$	H	66	15.1	$(1-\alpha)[-\ln(1-\alpha)]^{4/5}$	G	0.948	0.108	200	2
	D	61	13.6	$(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	G	0.952	0.094	180	
$Ca(IO_3)_2 \cdot 0.5H_2O \rightarrow Ca(IO_3)_2 + 0.5H_2O$	H	127	24.5	$(1-\alpha)^{1/3}$		0.988	0.088	245	
	D	151	31.8	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	G	0.997	0.015	230	
$Sr(IO_3)_2 \cdot H_2O \rightarrow Sr(IO_3)_2 + H_2O$	H	120	30.5	$(1-\alpha)^{1/3}$		0.999	0.034	170	2
	D	94	19.1	$(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	D	0.994	0.143	150	
$Ba(IO_3)_2 \cdot H_2O \rightarrow Ba(IO_3)_2 + H_2O$	H	44	9.3	1	N1	0.983	0.119	110	2
	D	38	8.7	1	N1	0.999	0.034	110	

[a] The assignments, G, R, D, NL, N1, are according to ref. 11.

this process made their processing impossible. In most cases the program refused to compute E^*_{deh}.

3. Experimental results and discussion

The data for E^*_{deh} and $\ln A$ obtained from the kinetic analysis are collected and presented in Table 1, together with the corresponding kinetic equation $F(\alpha)$ and $T_{\max}$ of the dehydration process.

An analysis of the data from Table 1 shows that the mechanisms of the dehydration processes of the investigated hydrates cannot be described using the same kinetic equation. However, it follows from the form of the equations found that in most cases the process is controlled by a boundary reaction (R) or by the law of Avrami–Erofeev (G). In some of the investigated compounds, however, at certain stages of the dehydration process which are indicated as inflections in the TG curves, the diffusion process is rate-determining, i.e. $F(\alpha)$ are equations of a diffusion type (D). This is the case with $Ca(IO_3)_2 \cdot 6D_2O$ (first stage) and $Ni(IO_3)_2 \cdot 4H_2O(D_2O)$ (second stage). In the case of $Sr(IO_3)_2 \cdot D_2O$, the process is controlled by the diffusion within the entire area of the dehydration.

For $Mg(IO_3)_2 \cdot 4H_2O(D_2O)$, it was impossible to describe the process with only one equation, although no step-like dehydration is to be observed in the TG and DTA curves [3]. In this case, with the use of all the kinetic models contained in the program, the dependence of $\ln[(\mathrm{d}\alpha/\mathrm{d}T)/F(\alpha)]$ on $1/T$ showed an inflection, which demonstrates a change in mechanism.

It follows from an analysis of the kinetic data for the investigated pairs of ordinary and deuterated hydrates that in $M(IO_3)_2 \cdot 2H_2O(D_2O)$ (M^{2+} is Ni^{2+}, Zn^{2+}) and $Ba(IO_3)_2 \cdot H_2O(D_2O)$, the mechanism of the dehydration process within the entire temperature interval is the same for both compounds, while the E^*_{deh} values calculated on the basis of the respective kinetic equation correlate with the $T_{\max}$, or $\delta T_{\max}$ values, respectively, recorded from the DTA curves. Other cases have also been recorded in which, for a given pair of hydrates, the dehydration process is the same for only one of its stages, e.g. in $Ca(IO_3)_2 \cdot 6H_2O$, $M(IO_3)_2 \cdot 4H_2O$ (M^{2+} is Mg^{2+}, Ni^{2+}) and their corresponding deuterates. The kinetic data further indicate that with some of the investigating compounds the dehydration process in the ordinary hydrate follows a mechanism that is different from that of the corresponding deuterate, e.g. in the pairs $Sr(IO_3)_2 \cdot nH_2O$–$Sr(IO_3)_2 \cdot nD_2O$ ($n = 6$ and 1), see Table 1. The $\delta E^*_{\mathrm{deh}}$ values recorded for them are 16 kJ mol^{-1} ($n = 6$) and 26 kJ mol^{-1} ($n = 1$), respectively. It is noteworthy that these compounds also show a larger difference in the recorded $T_{\max}$ ($\delta T_{\max} = 20°\mathrm{C}$) for the dehydration process [1, 2]. It may be assumed in this case that the large isotope effect in relation to $T_{\max}$ is also related to the kinetic factor, without ruling out the role of the thermodynamic factor or of some other factors.

The computed formal kinetic parameters (E^*_{deh} and A) for the dehydration processes of the investigated iodate hydrates show that E^*_{deh} varies within the range 40–190 kJ mol^{-1}, while the pre-exponential factor A varies from 5×10^3 to 3×10^{16} s^{-1}.

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