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KINETICS AND MECHANISM OF THE THERMAL DEHYDRATION STAGES OF $BaCl_2 \cdot 2\ H_2O$ BY MEANS OF SIMULTANEOUS TG—DSC

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ABSTRACT

The kinetics of the thermal dehydration stages of $BaCl_2 \cdot 2\ H_2O$

$$BaCl_2 \cdot 2\ H_2O(s) \rightarrow BaCl_2 \cdot H_2O(s) + H_2O(g) \quad (I)$$

$$BaCl_2 \cdot H_2O(s) \rightarrow BaCl_2(s) + H_2O(g) \quad (II)$$

were studied by means of TG—DSC recorded simultaneously at linearly increasing temperatures. Both dehydration stages were regulated by the random nucleation and subsequent growth mechanism. The mechanistic equation was expressed approximately as

$$[-\ln(1-\alpha)]^{1/m} = kt$$

(with $m \sim 3$ for both stages) where α is the fraction dehydrated at time t and k is the rate constant. The kinetic parameters from TG were in good agreement with those from the corresponding DSC.

INTRODUCTION

In a later paper [1], we will report that it is difficult to determine the mechanism of dehydration stages of $BaCl_2 \cdot 2\ H_2O$ uniquely by means of a conventional isothermal analysis, especially if an order parameter in a mechanistic equation is to be variable continuously. The activation energy, E, and frequency factor, A, are determined to be 26.7 kcal mole^{-1} and 1.9×10^{14} s^{-1} for the first stage and 19.0 kcal mole^{-1} and 1.7×10^{8} s^{-1} for the second stage using TG. It was also suggested that both dehydration stages should be regulated either by a phase boundary reaction or Avrami—Erofeyev mechanism [1].

On the other hand, Guarini and Spinicci [2] reported that the isothermal dehydration stages of $BaCl_2 \cdot 2\ H_2O$ are controlled by an Avrami—Erofeyev law

$$[-\ln(1-\alpha)]^{1/m} = kt$$

with $m = 2$, whereas the non-isothermal ones are controlled by the phase

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boundary reaction mechanism

$1-(1-\alpha)^{1/n}=kt$

with $n = 2$.

In this connection, it seems of interest to study the kinetics of dehydration stages of the dihydrate systematically by means of dynamic thermal analyses. The present paper deals with the kinetics of the thermal dehydration stages of $BaCl_2 \cdot 2\,H_2O$ using TG—DSC recorded simultaneously under various measuring conditions.

EXPERIMENTAL

Reagent grade $BaCl_2 \cdot 2H_2O$ was recrystallized twice from deionized water. The dihydrate was ground in a pestle and mortar and sieved to the fractions 100—170, 170—200, and 280—350 mesh. About 28.0 mg of sample was weighed into a platinum crucible of 5 mm diameter and 2.5 mm depth, without pressing, which was then tapped a few times on a desk. Dynamic TG—DSC traces were recorded simultaneously at heating rates of ca. 0.54, 1.06, and 2.06 K min^{-1} in a stream of dry N_2 with a flow rate of 25 ml min^{-1} using a Rigaku Thermoflex TG-DSC(8085E1). α-Alumina was used as reference material.

The transition of KNO_3 at 401 K was used as standard for the calibrations of enthalpy change and temperature. The area of the DSC peak was measured using a precision polar planimeter. Computations were carried out using an Apple II micro-computer. Graphical drawings were obtained using the micro-computer with a plotter.

RESULTS AND DISCUSSION

Typical TG—DSC traces obtained simultaneously for the thermal dehydration stages of $BaCl_2 \cdot 2\,H_2O$ are shown in Fig. 1.

The kinetic parameters E and A can be obtained in terms of an extended Coats and Redfern's equation which is one of the most reliable methods [3,4]

$$\ln\{F(\alpha)/T^2\} = \ln\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)-\frac{E}{R}\frac{1}{T} \qquad (1)$$

where $F(\alpha)$ is a function depending on the reaction mechanism, α is the fraction dehydrated at time t, T is the absolute temperature, R is the gas constant, and a is the linear heating rate. All the $F(\alpha)$ functions except a Prout—Tompkins law examined in a study to be published [1] can be applied to eqn. (1).

Table 1 shows the kinetic parameters E and A obtained in terms of eqn. (1) for the 11 mechanistic functions. It is deduced, in view of the reasonable order of magnitude of A, that an Avrami—Erofeyev mechanism (A_m) should regulate the dehydration stages of $BaCl_2 \cdot 2\,H_2O$. This argument is supported by the fact that the parameters for the A_m mechanism are comparable with

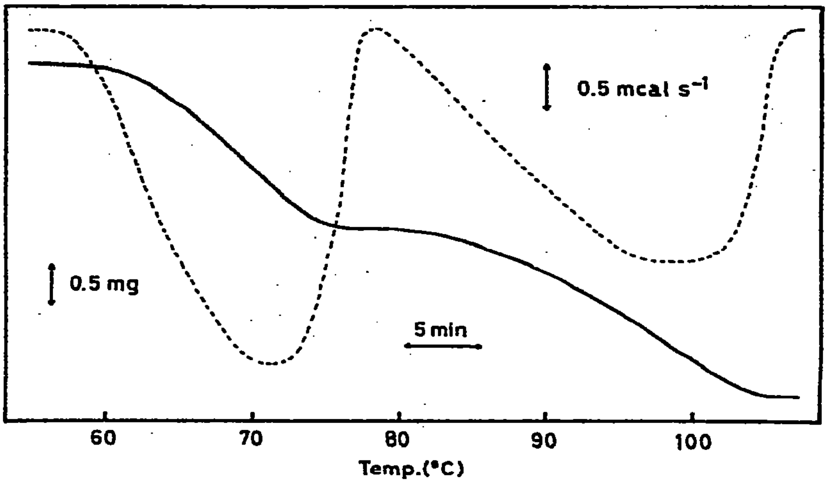

Fig. 1. Typical TG—DSC traces obtained simultaneously for the dehydration of $BaCl_2 \cdot 2$ H_2O. Particle size fraction, 170—200 mesh; ———, TG; — — — —, DSC.

those of the isothermal method [1], whereas the parameters for the alternative mechanism of a phase boundary reaction (R_n) are not.

The validity of the A_m mechanism may be confirmed by examining the effect of particle size on the rate constant. Table 2 shows the effect for the dehydration stages (I) and (II). The fact that k is practically unaffected by the particle size implies that the dehydration stages of $BaCl_2 \cdot 2\ H_2O$ are not controlled by the R_n mechanism, since k should increase with the decrease of radius of the particles in the case of the R_n mechanism [5]. The A_m mechanism suggested is probable in that the samples were very fine crystalline

TABLE 1

Kinetic parameters and the correlation coefficient r in the plot of $\ln\{F(\alpha)/T^2\}$ vs. $1/T$ using TG in the α range 0.2—0.9 *.

F(α)	Stage					
	(I)			(II)		
	E (kcal mole^{-1})	log$A$ (s^{-1})	—r	E (kcal mole^{-1})	log$A$ (s^{-1})	—r
D_1	85.5	51.8	0.9744	64.8	35.8	0.9837
D_2	95.0	57.8	0.9832	71.8	39.4	0.9905
D_3	107	65.0	0.9912	80.8	44.3	0.9959
D_4	99.0	59.7	0.9863	74.8	40.6	0.9927
R_1	42.1	24.1	0.9736	31.7	15.8	0.9829
R_2	49.9	29.0	0.9875	37.5	19.1	0.9935
R_3	52.9	30.7	0.9910	39.7	20.3	0.9958
A_1	59.4	35.5	0.9958	44.5	23.8	0.9981
A_2	29.0	15.9	0.9956	21.5	9.89	0.9980
A_3	18.9	9.22	0.9954	13.9	5.19	0.9978
A_4	13.8	5.87	0.9951	10.0	2.81	0.9977

* Particle size fraction: 170—200 mesh; heating rate, 1.06°C min^{-1}.

TABLE 2

The effect of particle size on the rate constant k (s^{-1}) at a heating rate of 1.06°C min^{-1} in terms of an $R_{1.5}$ mechanism *

Stage	Particle size fraction (mesh)					
	100–170		170–200		280–350	
	TG	DSC	TG	DSC	TG	DSC
(I)	8.77×10^{-4}	8.71×10^{-4}	1.17×10^{-3}	1.14×10^{-3}	1.07×10^{-3}	1.05×10^{-3}
(II)	7.27×10^{-4}	7.22×10^{-4}	7.88×10^{-4}	7.98×10^{-4}	7.51×10^{-4}	7.78×10^{-4}

* $R_{1.5} = 1 - (1 - \alpha)^{1/1.5}$. This function is used, since it is one of the possible mechanisms for the isothermal dehydration stages of $BaCl_2 \cdot 2 H_2O$ [1]. The similar effect of particle size on k is found in terms of any R_n or A_m mechanism.

TABLE 3

The effect of heating rate on the kinetic parameters E and A in terms of a given A_m mechanism *

Stage	m **	Heating rate (°C min^{-1})											
		0.54				1.06				2.06			
		E (kcal $mole^{-1}$)		log$A$ (s^{-1})		E (kcal $mole^{-1}$)		log$A$ (s^{-1})		E (kcal $mole^{-1}$)		log$A$ (s^{-1})	
		TG	DSC	TG	DSC	TG	DSC	TG	DSC	TG	DSC	TG	DSC
(I)	2.1	33.3	32.6	18.6	18.1	28.0	28.4	15.2	15.4	23.1	23.8	12.1	12.5
	2.8	24.7	24.1	12.9	12.6	20.7	21.0	10.4	10.6	17.0	17.5	8.11	8.44
(II)	2.9	18.2	17.6	7.76	7.37	14.9	14.8	5.84	5.77	13.7	14.3	5.18	5.57

* The range of α examined was 0.1–0.9.

** The values of 2.1, 2.8, and 2.9 for the A_m functions were adopted according to a previous study of the isothermal dehydration stages of $BaCl_2 \cdot 2 H_2O$ [1].

powders which were ground in a mortar with pestle [2].

It is also interesting to compare the kinetic parameters at different heating rates. Table 3 shows the effect of heating rate on the parameters for the particle size fraction 170—200 mesh. It is seen, as is expected in view of the thermal lag [6], that the parameters decrease with the increase of heating rate. This trend may be substantiated by the variation of dehydration temperatures, as shown in Table 4 [7]. The variation of parameters can also be explained by the compensation effect [8].

In this connection, it should be stressed that the dynamic thermal analysis must be made at as a low heating rate as possible, otherwise the agreement between the dynamic and isothermal methods could not be expected [9]. Moreover, it may be required, in some cases, to extrapolate the kinetic parameters at different heating rates to a zero heating rate in order to obtain the reliable parameters which might correspond with the isothermal data.

It is worth noting that TG and DSC methods give almost equal kinetic parameters for the dehydration stages of $BaCl_2 \cdot 2\,H_2O$. This may be due to the facts that (1) a rather smaller amount of the powdered sample was very slowly dehydrated in an atmosphere of flowing nitrogen, and (2) $BaCl_2 \cdot 2\,H_2O$ crystal has a layer structure in which the coordination group around the Ba^{2+} ion is composed of 4 Cl^- and 4 H_2O molecules [10].

It is also worth comparing the activation energies for the dehydration stages of $BaCl_2 \cdot 2\,H_2O$ with the corresponding enthalpy changes. The enthalpy changes for stages (I) and (II), ΔH_I and ΔH_{II}, respectively, were determined from the area of the DSC peak recorded simultaneously with TG. Table 5 shows the values of ΔH_I and ΔH_{II}, together with literature values. Our values appear to be somewhat different from others but to be reliable owing to the repeated runs under identical measuring conditions. It can be inferred from these values that the crystallization of the dehydrating product in each stage is completed, although this can be confirmed directly by observing the dehydration process using a high temperature X-ray camera [13].

It is seen that the activation energy for stage (I) is much larger than ΔH_I, whereas that for stage (II) is comparable with ΔH_{II}. This is also found for the isothermal dehydration stages of $BaCl_2 \cdot 2\,H_2O$ [1,2]. The slightly larger activation energy than ΔH_{II} for stage (II) cannot be explained in terms

TABLE 4

The extrapolated onset temperature, T_{eo} (°C), peak temperature, T_p (°C), and temperature of completion, T_c (°C), obtained from the DSC trace for the thermal dehydration stages of $BaCl_2 \cdot 2\,H_2O$ at various heating rates.

Stage	Heating rate (°C min^{-1})								
	0.54			1.06			2.06		
	T_{eo}	T_p	T_c	T_{eo}	T_p	T_c	T_{eo}	T_p	T_c
(I)	55.3	67.0	71.2	57.2	70.0	77.0	60.2	77.5	83.9
(II)	75.0	89.9	97.0	78.5	98.3	106.0	84.0	108.2	116.5

TABLE 5

Enthalpy changes, ΔH_I and ΔH_{II}, for the thermal dehydration stages (I) and (II) of $BaCl_2 \cdot 2\,H_2O$, respectively.

Ref.	Enthalpy change (kcal mole^{-1})		
	ΔH_I	ΔH_{II}	$\Delta H_I + \Delta H_{II}$
Present work *	13.91 ± 0.09	14.01 ± 0.09	27.92 ± 0.43
11	14.8	13.5	28.3
2	12.8 ± 0.8	13.2 ± 0.8	26.0
12	—	—	28.28 **

* Mean of seven measurements.

** Calculated from ΔH_f^0 values at 25°C.

of the similar assumption made by Osterheld and Bloom [14] for dehydration stage (1). The difference between ΔH_{II} and the corresponding activation energy may be due to a possible contribution from nucleation of the $BaCl_2$ crystal [15].

In conclusion, the non-isothermal dehydration stages of $BaCl_2 \cdot 2\,H_2O$ were found to be controlled by the Avrami—Erofeyev law. It is thus likely that the isothermal dehydration stages [1] may also follow the Avrami—Erofeyev mechanism, since the same mechanism for both isothermal and non-isothermal runs can be generally accepted, especially in the case of the non-isothermal run at a very low heating rate [9]. From the fact that the kinetic parameters at the lowest heating rate, 0.54°C min^{-1}, are comparable with those derived from the isothermal method [1], it appears that dehydration stages (I) and (II) of $BaCl_2 \cdot 2\,H_2O$ are regulated by $A_{2.8}$ and $A_{2.9}$ mechanisms, respectively. The m values of 2.8 and 2.9 for the A_m functions seem to be reasonable in connection with the crystal structure of solid products of $BaCl_2 \cdot H_2O$ and $BaCl_2$ [13].

Both isothermal and non-isothermal methods may be required in order to clarify the kinetics and mechanism of the thermal dehydration of hydrates, as was pointed out by other workers [4,16]. In addition to such thermal analyses, the direct observation [17] and structural knowledge [18] of the dehydrating sample could be useful in a systematic kinetic study of the decomposition of solids.

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