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KINETICS OF THE THERMAL DEHYDRATION STAGES OF $BaCl_2 \cdot 2\,H_2O$ BY MEANS OF TG AT CONSTANT TEMPERATURES

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ABSTRACT

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

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

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

were studied by means of TG at constant temperatures. Two possible mechanisms of Avrami–Erofeyev and phase-boundary reaction were assigned for each stage by plotting various functions against time. Activation energies were determined from the Arrhenius plot as 26.2~26.9 and 18.6~19.4 kcal mole^{-1} for stages (I) and (II), respectively. The kinetics of dehydration stage (I) was also examined by means of DSC recorded simultaneously with TG at constant temperatures.

INTRODUCTION

It is generally accepted that it is hard to determine the reaction mechanism from the dynamic method alone, although this has some advantages over the isothermal method. Among others, a comparison of kinetic parameters under the same conditions of measurement is cited [1–3].

It has been also widely believed that the reaction mechanism can be elucidated from the conventional isothermal method in a rather simple way. However, we have reported that the correct kinetic model cannot necessarily be selected uniquely from the isothermal analyses if order parameters in such mechanistic equations as phase boundary reaction and Avrami–Erofeyev mechanisms can be not only integers but also non-integers [4].

The present paper deals with the problem of isothermal analyses in determining the reaction mechanism and kinetic parameters for the solid state reaction. For this purpose, the dehydration stages of $BaCl_2 \cdot 2\,H_2O$, which were studied earlier [5–8], have been examined by means of TG at constant temperatures.

EXPERIMENTAL

Crystalline $BaCl_2 \cdot 2\,H_2O$ powders were classified by sieving and the 170–200 mesh fraction used. Simultaneous TG–DSC measurements at various constant temperatures were done in a stream of dry N_2 using a Rigaku Thermoflex TG-DSC(8085E1). Other experimental conditions were the same as those described in a previous study [8].

RESULTS AND DISCUSSION

It is well-known that $BaCl_2 \cdot 2\,H_2O$ is subjected to the stepwise dehydration via $BaCl_2 \cdot H_2O$ to $BaCl_2$ [6,8].

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

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

For the isothermal dehydration stages of $BaCl_2 \cdot 2\,H_2O$, the equation

$$F(\alpha) = kt \qquad (1)$$

can be assumed where $F(\alpha)$ is a function depending on the isothermal dehydration mechanism, α is the fraction dehydrated, k is the rate constant, and t is time. The $F(\alpha)$ examined in the present study are listed in Table 1. The correct $F(\alpha)$ for the dehydration stages of $BaCl_2 \cdot 2\,H_2O$ may be estimated, at least to some extent, by plotting it against t [4].

From the correlation coefficient r and error δ as a measure of linearity in the least square fitting for plots of $F(\alpha)$ vs. t, it is deduced that either the R_n or A_m mechanism controls the dehydration stages of $BaCl_2 \cdot 2\,H_2O$. Table 2 lists the values of r and δ for both stages. The best values of n and m were found by "scanning" using the computer [4]. The mean values of n and m over the temperature ranges 53.8–64.6°C for stage (I) and 81.3–96.9°C for stage (II) are listed in Table 3. The

TABLE 1

Various mechanistic functions

$F(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha - (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion (Jander function)
$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion (Ginstling–Broushtein function)
$\ln[\alpha/(1-\alpha)]$	A_u	Autocatalytic reaction (Prout–Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase boundary reaction: $n = 1, 2$, and 3 (one-, two-, and three-dimensional, respectively)
$[-\ln(1-\alpha)]^{1/m}$	A_m	Random nucleation, $m = 1$
		Random nucleation and subsequent growth, $m = 1.5, 2, 3$, and 4 (Avrami–Erofeyev functions)

TABLE 2

The correlation coefficients, r, and error, δ, in the plots of $F(\alpha)$ vs t for the isothermal dehydration stages (I) and (II) of $BaCl_2$ 2 H_2O in the α range 0 2–0 9

Stage[a]	Coefficient[b]	$F(\alpha)$											
		D_1	D_2	D_3	D_4	A_u	R_1	R_2	R_3	A_1	A_2	A_3	A_4
(I)	r	0 9929	0 9803	0 9547	0 9728	0 9964	0 9969	0 9993	0 9972	0 9880	0 9997	0 9977	0 9955
	$\delta\times10^2$	2 708	3 473	1 981	1 080	8 778	1 757	0 6392	0 9724	8 158	0 7761	1 412	1 542
(II)	r	0 9937	0 9784	0 9434	0 9682	0 9986	0 9972	0 9980	0 9937	0 9772	0 9982	0 9995	0 9988
	$\delta\times10^2$	3 073	4 697	3 224	1 565	6 256	1 843	1 265	1 782	14 92	2 083	0 7793	0 8915

[a] The temperatures were 53.8 and 81 3°C for stages (I) and (II), respectively

[b] δ refers to the error defined by the equation, $\delta=[\Sigma\epsilon_i^2/(N-1)]^{1/2}$, where ϵ_i is the deviation from the straight line and N is the number of experimental data

TABLE 3

The best values of n and m for R_n and A_m mechanisms obtained from TG analysis in the α range 0.2–0.9

Stage	n	m
(I)	1.54±0.06	2.08±0.07
(II)	1.50±0.03	2.92±0.09

plots of the appropriate F(α) vs. t at a given temperature are given for each stage in Fig. 1.

Values of k at various temperatures deduced from the plot of F(α) vs. t using the mean order parameters are listed in Tables 4 and 5. Table 6 shows the activation energy, E, and frequency factor, A, for the dehydration stages of $BaCl_2 \cdot 2H_2O$ obtained from the Arrhenius plot.

It is seen that meaningful kinetic parameters can be deduced irrespective of the

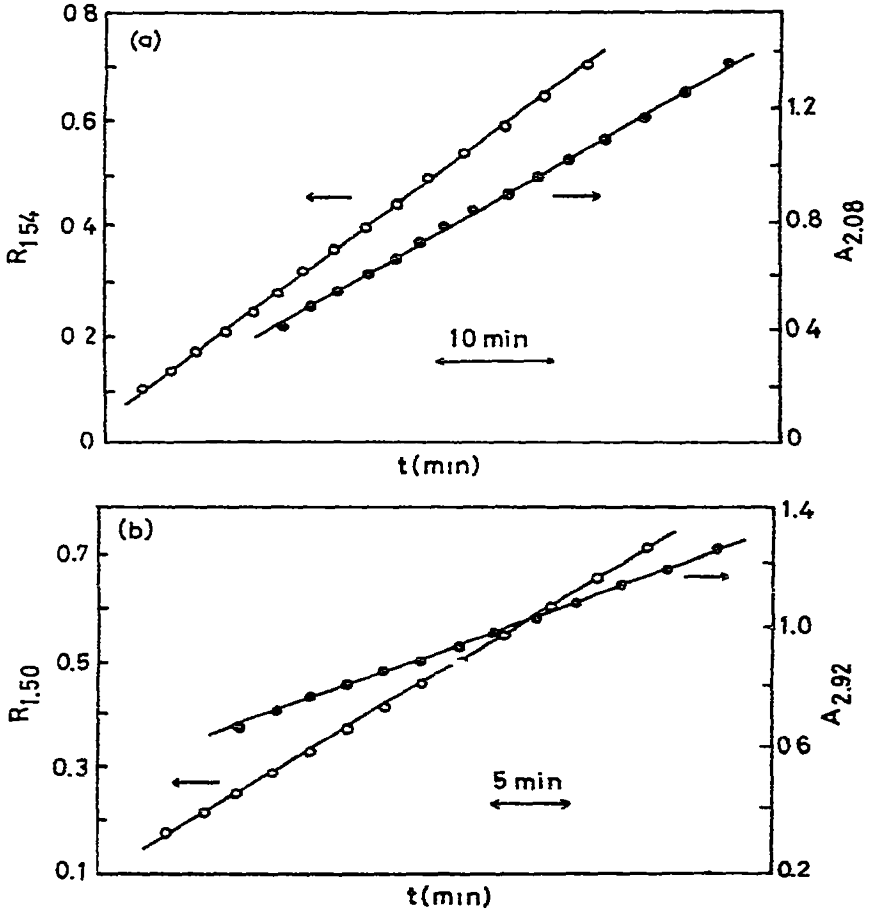

Fig 1 Typical plots of the appropriate F(α) vs. t from the analyses of TG. (a) Stage (I) at 53.8°C in the α range 0.15–0.85. (b) Stage (II) at 81.3°C in the α range 0.25–0.85

TABLE 4

The rate constants, k, for $R_{1.54}$ and $A_{2.08}$ mechanisms at various temperatures for stage (I)

Temp (°C)	k (s^{-1})×10^4	
	$R_{1.54}$	$A_{2.08}$
53.8	2.715	4.05
56.2	3.607	5.354
58.6	4.813	7.119
60.9	6.163	9.213
64.6	10.23	15.01

actual dehydration mechanism if any F(α), which gives a straight line plot of F(α) vs. t, is used. This trend was also recognized for the other thermal decompositions [4,9]. In such a case, however, it is very difficult to determine the reaction mechanism uniquely from the isothermal analysis alone.

It seems worthwhile looking at the dehydration of $BaCl_2 \cdot 2\,H_2O$ in the light of DSC recorded simultaneously with TG at constant temperatures. From the DSC peak area, the enthalpy change for the dehydration stage (1), ΔH_I, was found to be 14.59 ± 0.20 kcal mole^{-1}. The enthalpy change for stage (II) could not be evaluated due to the poorly defined base line. The value of ΔH_I is much smaller than the corresponding activation energy. As pointed out by Osterheld and Bloom [5], this dehydration is one of the exceptions to the ordinary pattern for endothermic dehydrations where the value of E is nearly equal to that of ΔH [10]. They explained the higher value of E in terms of a transition state where the dihydrate structure was retained but with the lattice interaction removed for half of the water molecules [5].

The higher activation energy in the present study may be explained alternatively by assuming that the activation energy should include some contribution from the nucleation [10].

It is interesting to evaluate the kinetic parameters also by means of DSC for the dehydration stage (I) of $BaCl_2 \cdot 2\,H_2O$. In a similar manner to the above treatment, R_n and A_m mechanisms were selected from various F(α) for the dehydration stage (I) of $BaCl_2 \cdot 2\,H_2O$. The correlation coefficient r and error δ in the F(α) vs. t plot are

TABLE 5

The rate constants, k, for $R_{1.50}$ and $A_{2.92}$ mechanisms at various temperatures for stage (II)

Temp (°C)	k (s^{-1})×10^4	
	$R_{1.50}$	$A_{2.92}$
81.3	3.063	3.255
91.0	6.755	7.024
94.8	8.494	8.700
96.9	9.463	10.08

TABLE 6

Kinetic parameters for the thermal dehydration stages of $BaCl_2 \cdot 2H_2O$ derived from Arrhenius plots for R_n and A_m mechanisms

Stage	R_n			A_m		
	E (kcal mole^{-1})	log A (s^{-1})	$-r$	E (kcal mole^{-1})	log A (s^{-1})	$-r$
(I)	26.69 ± 0.23	14.28 ± 0.15	0.99878	26.41 ± 0.19	14.27 ± 0.13	0.99915
(II)	19.11 ± 0.33	8.29 ± 0.20	0.99742	18.88 ± 0.25	8.17 ± 0.15	0.99850

TABLE 7

The correlation coefficients, r, and error, δ, in the plots of various F(α) vs t for the isothermal DSC trace for the dehydration stage (I) of $BaCl_2$ $2H_2O$ at 53.8°C in the α range 0.2–0.9

Coefficient	F(α)											
	D_1	D_2	D_3	D_4	A_u	R_1	R_2	R_3	A_1	A_2	A_3	A_4
r	0.9981	0.9888	0.9614	0.9812	0.9992	0.9948	0.9994	0.9997	0.9845	0.9991	0.9997	0.9991
$\delta \times 10^2$	1.655	3.409	2.749	1.223	4.334	2.280	0.6369	1.229	12.31	1.446	0.5462	0.6998

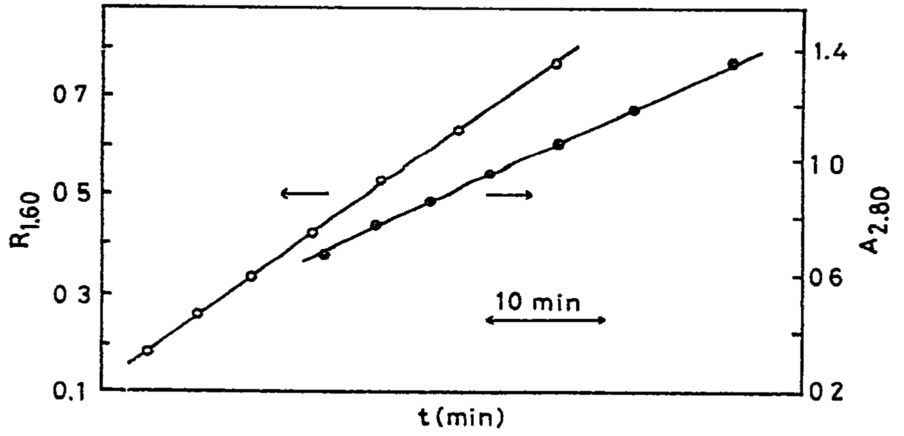

Fig. 2. Typical plots of the appropriate F(α) vs. t from the analyses of DSC for the dehydration stage (I) at 53.8°C in the α range 0.28–0.90.

TABLE 8

The rate constants, k, for the thermal dehydration stage (I) of $BaCl_2 \cdot 2H_2O$ evaluated for $R_{1.60}$ and $A_{2.80}$ mechanisms by means of DSC

Temp (°C)	k (s^{-1})×10^4	
	$R_{1.60}$	$A_{2.80}$
53.8	2.754	3.155
56.2	3.652	4.174
58.6	4.840	5.524
60.9	6.187	7.081
64.6	10.42	11.92

TABLE 9

Kinetic parameters for the thermal dehydration stage (I) of $BaCl_2 \cdot 2H_2O$ evaluated from the Arrhenius plots for $R_{1.60}$ and $A_{2.80}$ mechanisms by means of DSC

F(α)	E (kcal mole^{-1})	log A (s^{-1})	$-r$
$R_{1.60}$	26.72±0.29	14.30±0.19	0.99817
$A_{2.80}$	26.71±0.29	14.35±0.19	0.99814

listed in Table 7. The best order parameters of n and m for stage (I) were then determined to be 1.60 ± 0.06 and 2.80 ± 0.07, respectively, over the temperature range 53.8–64.6°C. Plots of F(α) vs. t for the $R_{1.60}$ and $A_{2.80}$ functions are shown in Fig. 2. The rate constants k at various temperatures at the fixed values of n and m are listed in Table 8. Table 9 shows the kinetic parameters derived from the Arrhenius plots. It is seen that the result from DSC is in good agreement with that from TG, although the order parameters are slightly different.

In summary, both R_n and A_m mechanisms seem to be appropriate for each stage of the isothermal dehydration of $BaCl_2 \cdot 2\,H_2O$ in view of plots of $F(\alpha)$ vs. t. It may be noted here that the A_m mechanism was suggested for the dehydration stages by means of DSC at constant temperatures [6]. It seems, however, that the direct observation of dehydrating crystals or dynamic thermal analyses would be required in order to confirm the dehydration mechanism [8].

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