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KINETICS OF $BaBr_2 \cdot 2H_2O$ DEHYDRATION: COMPARISON BETWEEN POWDERED CRYSTALLINE AND SINGLE CRYSTAL MATERIALS

H. TANAKA

Chemistry Laboratory, Faculty of School Education, Hiroshima University, Shinonome, Minami-ku, Hiroshima, 734 (Japan)

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ABSTRACT

The kinetic mechanisms of thermal dehydration stages of $BaBr_2 \cdot 2H_2O$ of powdered crystalline and single crystal materials were studied by means of TG–DSC and hot stage optical microscopy. Kinetic evaluation of the TG traces of the dehydration stages from $BaBr_2 \cdot 2H_2O$ to $BaBr_2 \cdot H_2O$ and $BaBr_2$ yields different kinetic mechanisms for powdered crystalline and single crystal materials. The isothermal and dynamic analyses lead to different kinetic laws for the dehydration stages.

INTRODUCTION

Lately, it has been recognized that it is more difficult to determine unequivocally kinetic mechanisms of solid decompositions from thermal analyses than we thought. It is important to study these reaction kinetics systematically from various aspects. Isothermal and dynamic thermal analyses are required in general to elucidate kinetic mechanisms and kinetic parameters. It is important to examine the material effect on the kinetics too, e.g., a comparison of the decomposition kinetics between powdered and single crystalline materials.

Isothermal dehydration kinetics of powdered crystalline $BaCl_2 \cdot 2H_2O$ have been found to differ from those of the single crystal material [1]. At varying temperatures, however, the same kinetic laws have been estimated for these dehydration stages.

It is interesting to study such kinetics of other salt hydrates along these lines. The thermal dehydration processes of $BaBr_2 \cdot 2H_2O$ have been chosen for the present study. The dehydration proceeds stepwise as follows [2]

$$BaBr_2 \cdot 2H_2O(s) \rightarrow BaBr_2 \cdot H_2O(s) + H_2O(g) \qquad (I)$$

$$BaBr_2 \cdot H_2O(s) \rightarrow BaBr_2(s) + H_2O(g) \qquad (II)$$

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EXPERIMENTAL

Reagent grade $BaBr_2 \cdot 2H_2O$ from Mitsuwa Chemical Co., Japan (99.8%) was purified by recrystallization. The single crystals of the dihydrate, which were colorless, transparent, and plate-like, were grown by slow evaporation of the solution over anhydrous $BaBr_2$ in a small desiccator. Crystalline powders of the dihydrate were obtained by rapid cooling, which were manually ground using a mortar and pestle, and sieved to a fraction of 100–170 mesh size.

TG and DSC traces were recorded simultaneously under an N_2 stream (25 ml min^{-1}) at constant temperatures as well as at a fixed heating rate (ca. 0.54 K min^{-1}), using a Rigaku Thermoflex TG-DSC 8085 E1 type instrument. The sample (25 mg for the crystalline powders; 25–42 mg for the single crystals) was weighed into a platinum crucible of 5 mm diameter and 2.5 mm height.

The dehydrating crystal was observed using an optical microscope with Linkam TH-600 programmable heating stage under nearly identical conditions as the TG–DSC run.

Computation of kinetic parameters was made with a microcomputer.

RESULTS AND DISCUSSION

Appropriate kinetic model functions, $F(\alpha)$, for the isothermal dehydration stages of $BaBr_2 \cdot 2H_2O$ were estimated conventionally by plotting various $F(\alpha)$ functions against time, t, assuming the following kinetic equation [3]

$$F(\alpha) = kt$$

where k is the rate constant. The functions $F(\alpha)$ examined in the present study are given in Table 1. The appropriate $F(\alpha)$ estimated is summarized in Table 2 for the two dehydration stages of powdered and single crystalline materials. In Fig. 1, the typical isothermal gravimetric traces are shown.

Table 3 gives typical correlation coefficients, r, of the above regression analysis of $F(\alpha)$ vs. t plots for the dehydration stages of powdered and single crystalline $BaBr_2 \cdot 2H_2O$. It seems difficult to specify which function is "most" appropriate for a given solid decomposition from the isothermal analysis alone [4]: R_1 may not necessarily be ruled out, for example, in the first stage of the powdered material. According to direct observation of the first stage by hot stage microscopy, there seems to be a combination of R_n and A_m for the powdered materials.

It is worthwhile examining the above kinetics from dynamic thermal analysis, e.g., TG. In Fig. 2, typical TG traces of $BaBr_2 \cdot 2H_2O$ dehydration are shown. Table 4 shows the temperature, T, as a function of fraction dehydrated, α, for the dehydration stages I and II. We see from Table 4 that

TABLE 1

Kinetic model functions, $F(\alpha)$, used in the kinetic analysis of $BaBr_2 \cdot 2H_2O$ dehydration stages

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

TABLE 2

The kinetic model functions, $F(\alpha)$, estimated from the isothermal analysis of the dehydration stages of $BaBr_2 \cdot 2H_2O$

Material	Stage	
	I	II
Powder	A_4	A_2
Single crystal	D_2	R_3

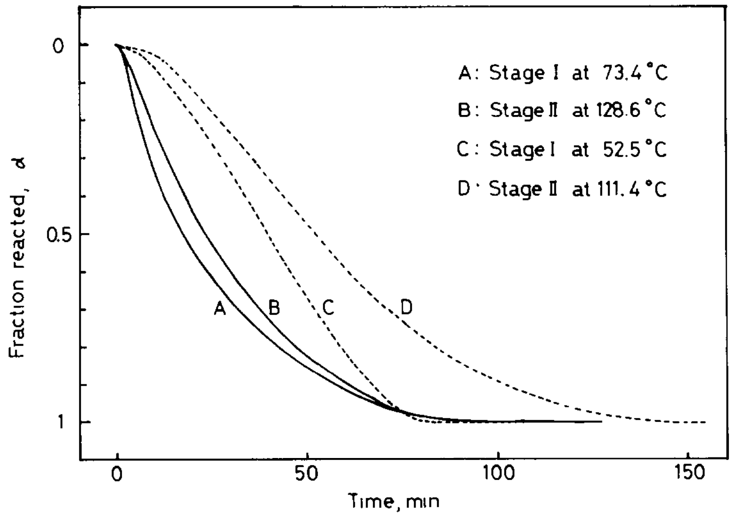

Fig. 1. Typical isothermal gravimetric traces of the dehydration stages of powdered crystalline (- - - - -) and single crystal (———) $BaBr_2 \cdot 2H_2O$.

TABLE 3

The correlation coefficients, r, for the least-squares fitting of F(α) vs. t plots for the isothermal dehydration stages of $BaBr_2 \cdot 2H_2O$

F(α)	Crystalline powder		Single crystal	
	Stage I [a]	Stage II [b]	Stage I [c]	Stage II [d]
D_1	0.98863	0.99678	0.99627	0.99895
D_2	0.97048	0.98984	0.99954	0.99549
D_3	0.93276	0.96635	0.98774	0.97548
D_4	0.95930	0.98366	0.99758	0.99062
A_u	0.99791	0.99798	0.98425	0.99376
R_1	0.99934	0.98993	0.96976	0.98417
R_2	0.99471	0.99945	0.99320	0.99884
R_3	0.98901	0.99888	0.99743	0.99995
A_1	0.97039	0.99086	0.99891	0.99509
A_2	0.99573	0.99978	0.99133	0.99791
A_3	0.99905	0.99740	0.98292	0.99318
A_4	0.99959	0.99509	0.97753	0.98965

[a,b,c,d] Recorded at temperatures of 52.5, 111.4, 73.4, and 128.6°C, respectively.

the single crystal material is much more thermally stable than the powdered crystalline material. It is interesting here to determine the kinetic parameters using the above α–T relationship and to compare the results between the two materials. Tables 5 and 6 list typical kinetic parameters derived in terms of all the F(α) functions in Table 1, except A_u, using the modified equation of Coats and Redfern [5] for dehydration stages I and II, respectively.

We may single out the most appropriate functions for the dynamic dehydration stages of $BaBr_2 \cdot 2H_2O$, assuming reasonable orders of magnitude for the activation energy, E, and frequency factor, A, as well as the

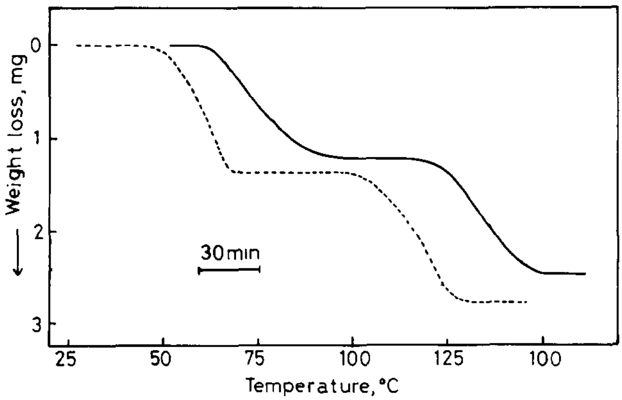

Fig. 2. Typical TG traces of the dehydration stages of powdered crystalline (- - - - - -) and single crystal (———) $BaBr_2 \cdot 2H_2O$.

TABLE 4

Temperature (°C) as a function of the fraction dehydrated, α, from TGA of the dynamic dehydration stages of $BaBr_2 \cdot 2H_2O$ [a]

α	Stage I		Stage II	
	Powder	Single crystal	Powder	Single crystal
0.1	52.4 ± 0.6	62.6 ± 0.6	108.3 ± 0.6	120.6 ± 1.2
0.2	55.4 ± 0.5	65.6 ± 0.6	112.0 ± 0.5	124.3 ± 1.0
0.3	57.7 ± 0.4	68.3 ± 0.5	114.8 ± 0.5	127.2 ± 1.0
0.4	59.5 ± 0.4	70.9 ± 0.5	116.9 ± 0.4	129.9 ± 0.9
0.5	61.1 ± 0.4	73.5 ± 0.5	118.9 ± 0.4	132.4 ± 0.9
0.6	62.5 ± 0.3	76.4 ± 0.5	120.6 ± 0.4	134.8 ± 0.9
0.7	63.7 ± 0.3	79.0 ± 0.6	123.3 ± 0.3	137.3 ± 0.9
0.8	64.8 ± 0.3	82.1 ± 0.6	124.1 ± 0.4	140.1 ± 1.0
0.9	66.0 ± 0.3	85.6 ± 0.8	126.2 ± 0.3	143.2 ± 1.0

[a] Mean of five measurements and its standard deviation.

linearity of the Coats and Redfern plot. The activation energies are reported to be 19.4 and 25.3 kcal mol^{-1} for the isothermal dehydration stages I and II of powdered crystalline $BaBr_2 \cdot 2H_2O$, respectively [2]. For dehydration stage I of powdered crystalline $BaBr_2 \cdot 2H_2O$, the A_2 law seems to be reasonable. The shift of exponent m from 4 in the case of an isothermal run to 2 may be caused by a possible increase in the frequency of nucleation in the bulk due to thermal agitation in the dynamic dehydration [6]. An R_n law proved to operate by optical microscopy, which implies that there is a combination of

TABLE 5

Typical activation energies, E, and frequency factors A derived from the Coats and Redfern plot for dehydration stage I of $BaBr_2 \cdot 2H_2O$

$F(\alpha)$	Powder			Single crystal		
	E (kcal mol^{-1})	log A (s^{-1})	$-r$ [a]	E (kcal mol^{-1})	log A (s^{-1})	$-r$ [a]
D_1	59.3	35.7	0.99501	40.1	21.9	0.95006
D_2	66.8	40.4	0.99805	44.8	24.7	0.96305
D_3	76.3	46.2	0.99906	50.9	28.1	0.97620
D_4	69.9	41.9	0.99874	46.8	25.4	0.96800
R_1	29.0	15.8	0.99474	19.4	8.81	0.94666
R_2	35.2	19.7	0.99891	23.3	16.1	0.96878
R_3	37.5	21.1	0.99903	24.8	12.0	0.97486
A_1	42.6	25.1	0.99742	28.0	14.6	0.98474
A_2	20.7	10.5	0.99727	13.3	5.11	0.98309
A_3	13.3	5.51	0.99709	8.43	1.86	0.98116
A_4	9.67	2.99	0.99690	5.98	0.21	0.97893

[a] Correlation coefficient of the linear regression analysis.

TABLE 6

Typical activation energies, E, and frequency factors, A, derived from the Coats and Redfern plot for dehydration stage II of $BaBr_2 \cdot 2H_2O$

F(α)	Powder			Single crystal		
	E (kcal mol^{-1})	log A (s^{-1})	$-r$ [a]	E (kcal mol^{-1})	log A (s^{-1})	$-r$ [a]
D_1	61.8	31.2	0.99173	60.8	29.4	0.96098
D_2	69.7	35.5	0.99626	67.8	33.0	0.97224
D_3	79.9	40.7	0.99920	76.8	37.4	0.98333
D_4	73.1	36.8	0.99762	70.7	34.0	0.97645
R_1	30.1	13.5	0.99129	29.6	12.6	0.95891
R_2	36.7	17.0	0.99813	35.4	15.6	0.97761
R_3	39.2	18.3	0.99916	37.6	16.6	0.98261
A_1	44.6	22.0	0.99937	42.4	19.8	0.99043
A_2	21.5	8.81	0.99932	20.4	7.72	0.98964
A_3	13.8	4.35	0.99927	13.1	3.61	0.98875
A_4	10.0	2.09	0.99922	9.40	1.52	0.98774

[a] Correlation coefficient of the linear regression analysis.

the A_m and R_n laws [7]. With regard to stage II of the powdered material, A_2 also seems to be appropriate. In the case of the single crystal material, D_2 appears not to be probable contrary to the isothermal analysis but either A_1 or R_3 seems to be appropriate in stage I. From a direct observation of the dehydrating single crystalline dihydrate on a hot stage, the R_3 law was found to operate. As for stage II of the single crystal material, approximately $A_{1.5}$ may tentatively be adopted, although the physical meaning of the exponent is not so clear in this case [8].

In the present case it is difficult to specify a single kinetic model for a given solid-state reaction, because the kinetic mechanism may change with α [2] and two or more mechanisms may operate simultaneously [7,9], even in a single crystal material. Competing mechanisms are much more probable in the case of the powdered material which should contain different defects and morphological distribution of the particles.

Table 7 shows approximate kinetic parameters estimated dynamically in terms of the "most" probable F(α) function, although these parameters cannot be determined unequivocally since these are dependent of the kinetic model function adopted. The kinetic parameters derived in the present study and those reported earlier are comparable with the observed enthalpy changes, ΔH, of stages I and II: 14.7 ± 0.3 and 15.4 ± 0.1 kcal mol^{-1}, respectively. The difference between E and ΔH may be ascribed to an activation energy for random nucleations of the solid product [10].

The present behavior of powdered and single crystalline materials is comparable to that of the phase transition of a solid complex [11]. The subsequent dehydration of the single crystalline material in stage II is probably explained by a "powdering process" during the preceding dehydration of stage I.

TABLE 7

Approximate kinetic parameters estimated dynamically using the averaged $\alpha - T$ relationships [a] in terms of the probable $F(\alpha)$ function for the dehydration stages of $BaBr_2 \cdot 2H_2O$

Stage	Powder				Single crystal			
	$F(\alpha)$	E (kcal mol^{-1})	log A (s^{-1})	k (s^{-1}) [b]	$F(\alpha)$	E (kcal mol^{-1})	log A (s^{-1})	k (s^{-1}) [b]
I	A_2	22.5	11.7	1.69×10^{-3}	R_3	25.5	12.3	9.29×10^{-5}
II	A_2	24.0	10.2	1.03×10^{-3}	$A_{1\,5}$ [c]	27.0	11.3	3.30×10^{-4}

[a] See Table 4.

[b] Values at temperatures of 67.3 and 125.7°C for stages I and II, respectively.

[c] $F(\alpha) = [-\ln(1-\alpha)]^{2/3}$.

In conclusion, the kinetic mechanisms of thermal dehydration stages of $BaBr_2 \cdot 2H_2O$ of powdered and single crystalline materials are different. Moreover, the isothermal and dynamic analyses lead to different kinetic laws for the dehydration stages. These differences are due to various factors, such as distributions of the shape of particles as well as defects and the thermal agitation in the case of dynamic runs. The results imply that many kinetic data evaluated earlier from TG, etc., are rather superficial, particularly in the case of powdered crystalline materials [12].

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