Thermochimica Acta, 92 (1985) 219-222
Elsevier Science Publishers B.V., Amsterdam

THERMAL DEHYDRATION MECHANISM OF OXALIC ACID DIHYDRATE II. SINGLE CRYSTAL MATERIAL

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ABSTRACT

The thermal dehydration mechanism of single crystalline oxalic acid dihydrate was examined by thermogravimetry both at constant and linearly increasing temperatures, and polarized microscopy. Phase boundary controlled mechanisms, R_n, proved to operate with a combination of one of Avrami-Erofeyev laws A_m. A nonintegral value of exponent n, 1.3, in the kinetic function R_n was obtained from the isothermal analysis. The activation energy was found to be around 85 kJ/mol. The significance of the nonintegral exponent is discussed.

INTRODUCTION

In general it is difficult to determine kinetic mechanisms of solid decompositions from thermal analyses such as TG, DTA, and DSC[1]. It is important to combine these results with other physico-chemical investigations[2].

Lately it has been reported that the thermal dehydration of crystalline powders of oxalic acid dihydrate is regulated by one of random nucleations and their subsequent growth mechanisms A_m with a possible competition of a phase boundary controlled reaction mechanism R_n[3]. It is interesting to examine the dehydration kinetics of the single crstalline material of the dihydrate too, because it may differ from those of the crystalline powder material[4]. Accordingly, the dehydration mechanism of single crystalline oxalic acid dihydrate was studied by thermogravimetry and polarizing microscopy.

EXPERIMENTAL

Small single crystals(15~30 mg) of oxalic acid dihydrate were grown slowly from the aqueous solution at room temperature. TG traces were recorded at constant as well as at increasing temperatures at a linear heating rate of ca. 0.57 °C/min, using a Rigaku Thermoflex TG-DTA 8085 E1 type instrument. The sample was weighed into a platinum crucible of 5 mm diameter and 2.5 mm height. Ignited alumina was used as reference material. All the measurements were made under N_2 stream at a rate of 30 ml/min. Kinetic analysis was made using a microcomputer.

Thin sections of the partially dehydrated single crystal were prepared carefully by abrasing 'with an abrasive cloth and paper, and with abrasives, after fixing the crystal onto a slide glass with a synthetic encloser. These thin sections were observed using an Olympus polarizing microscope.

The dehydrating crystal was also observed with a hot stage microscope.

Proceedings of ICTA 85, Bratislava

TABLE 1. Kinetic model functions for solid decompositions

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	$1-2\alpha/3-(1-\alpha)^{2/3}$	Three-dimensional diffusion(Ginstling-Broushtein function)
A_u	$\ln[\alpha/(1-\alpha)]$	Autocatlytic 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 its subsequent growth; m= 2, 3, and 4(Avrami-Erofeyev functions)

RESULTS AND DISCUSSION

Figure 1 shows the isothermal gravimetric traces of the $(COOH)_2 \cdot 2H_2O$ dehydration. Appropriate kinetic model functions $F(\alpha)$ were estimated conventionally from the various $F(\alpha)$ as listed in Table 1. Either an A_m or R_n was selected as the appropriate over the temperature range 55.8-64.5 °C, where the exponent m and n are 2.4 and 1.3, respectively. In Table 2 are shown typical correlation coefficients r of the regression analysis of $F(\alpha)$ vs. t plots for the dehydration of $(COOH)_2 \cdot 2H_2O$ single crystal. Table 3 shows the rate constants k derived isothermally in terms of the $A_{2.4}$ and $R_{1.3}$ functions. The activation energy E and frequency factor A calculated from the Arrhenius plot are shown in Table 4.

Figure 2 shows typical TG-DTA traces recorded simultaneously for the dehydration of $(COOH)_2 \cdot 2H_2O$. In Table 5 are shown the Arrhenius parameters derived for

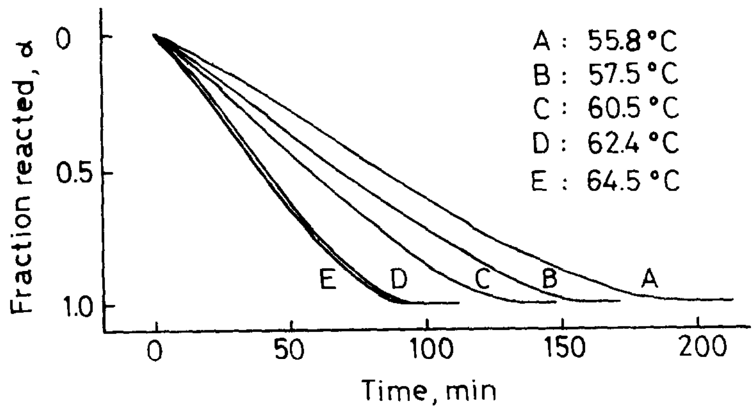

Fig. 1. Isothermal gravimetric traces at different temperatures.

TABLE 2. Typical correlation coefficients r of the regression analysis of F(α) vs. t plots

F(α)	-r	F(α)	-r
D_1	0.98273	R_2	0.99697
D_2	0.96768	R_3	0.99199
D_3	0.92776	A_1	0.97394
D_4	0.95585	A_2	0.99822
A_u	0.99500	A_3	0.99788
R_1	0.99830	A_4	0.99556

TABLE 3. The rate constants $k(10^3/s)$ at various temperatures from the isothermal gravimetric analysis in terms of $A_{2.4}$ and $R_{1.3}$ functions

Temp.(°C)	$A_{2.4}$	$R_{1.3}$
55.8	1.210	0.954
57.5	1.399	1.105
60.5	1.669	1.317
62.4	2.450	1.973
64.5	2.569	2.027

TABLE 4. The Arrhenius parameters with the standard deviation and the correlation coefficient r

F(α)	E(kJ/mol)	logA(1/s)	-r
$A_{2.4}$	85.0±12.0	9.57±1.82	0.9733
$R_{1.3}$	86.0±13.0	9.61±1.99	0.9689

TABLE 5. The kinetic parameters from dynamic thermal analysis

F(α)	E(kJ/mol)	logA(1/s)	-r
D_1	168	22.4	0.9893
D_2	186	25.0	0.9945
D_3	209	28.1	0.9980
D_4	193	25.6	0.9961
R_1	81.2	9.08	0.9886
R_2	95.8	11.2	0.9966
R_3	102	12.0	0.9979
A_1	114	14.5	0.9982
A_2	54.4	5.06	0.9981
A_3	34.3	1.84	0.9979
A_4	24.3	0.205	0.9976

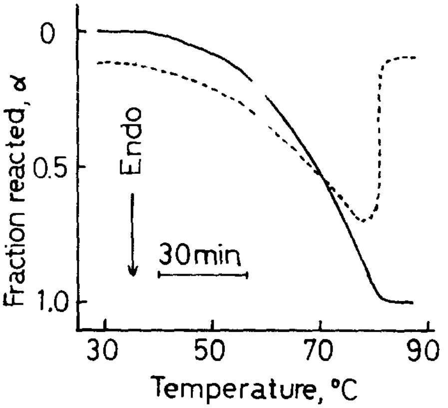

Fig. 2. Typical TG(——) and DTA(----) traces recorded simultaneously.

the dynamic dehydration of $(COOH)_2 \cdot 2H_2O$, using the modified Coats and Redfern's equation[2,5] and the α-T relation averaged over four runs.

We see from Table 5 that R_1 and R_2 laws yield comparable kinetic parameters with those determined isothermally(see Table 4). It is noted here that E and logA are calculated as 87.5 kJ/mol and 10.0 1/s, respectively with the r value of -0.9930 in terms of $R_{1.3}$ using the above method. On the other hand, the $A_{2.4}$ law does not lead to such a correspondence, as is obvious from Table 5. We then adopt the $R_{1.3}$ as the appropriate F(α) for the thermal dehydration of single crystalline

$(COOH)_2 \cdot 2H_2O$, assuming that the kinetic parameters from isothermal analysis are nearly equal to those from dynamic analysis of a run at very law heating rates[6].

The nonintegral exponent n, 1.3, is likely to arise from a combination of R_1 and R_2 laws[7]. We may be able to neglect a deviation, if at all, from the integral due to a mechanism change during the dehydration[8] in the α range of 0.1 – 0.9. According to visual observation of the dehydration crystal on heating stage, the white product covered the whole surface in the early stage of dehydration. The mechanism of further dehydration proved to be mainly of a combination of R_1 and R_2 by observing the thin sections with a polarizing microscope. It seems in general that the procedure of fitting kinetic model functions $F(\alpha)$ to thermal data using only integral exponents of the $F(\alpha)$ is imperfect. The actual decomposition is far from the ideal model, on which the theoretical kinetic functions are based.

Figure 3 is a microscopic view of the thin section of partially dehydrated single crystal in polarized light. We see that the dehydration proceeds mainly by a phase boundary controlled reaction mechanism R_n. At the same time, it is likely that a random nucleation and its subsequent growth mechanism A_m operates to some extent. It is interesting to note that such nucleations seem to occur mainly at a spiral growth front which arised from a screw dislocation during the crystal growth from solution. In this respect, it seems reasonable that the dehydration of powdered crystalline oxalic acid dihydrate is regulated mainly by an A_m with a possible combination of R_n law[3].

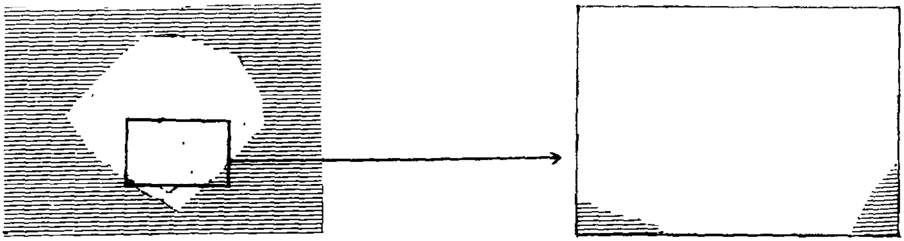

Fig. 3. A typical microscopic view of the thin section of partially dehydrated single crystalline $(COOH)_2 \cdot 2H_2O$. ▨ : Product □ : Reactant

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