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THE KINETIC STUDY OF THERMAL DEHYDRATION OF OXALIC ACID DIHYDRATE

I. Crystalline powder material

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The thermal dehydration kinetics of crystalline powders of $(COOH)_2 \cdot 2\,H_2O$ was examined by thermogravimetry both at constant and linearly increasing temperatures. An Avrami–Erofeyev law is found to hold with a possibility that a phase-boundary controlled reaction proceeds simultaneously. This is supported by the particle size effect on the rate constant. The activation energy E for the dehydration is estimated as around 80 kJ mol^{-1}. It is likely that the effects of particle size and temperature on E are compensated by those on the frequency factor A.

The decomposition process of a solid which yields solid and gaseous products generally involves the following steps: the decomposition of the solid to give an amorphous intermediate, which then crystallizes, the diffusion of liberated gaseous molecules through the solid product, and the evaporation of gas from the surface of the solid product [1]. It is well known too that the kinetics of such a decomposition process is very sensitive to the experimental conditions. In this connection a systematic examination under various measuring and sample conditions is required in order to clarify the kinetics of solid state reactions, particularly for finely-powdered materials.

The dehydration of the crystalline powder of oxalic acid dihydrate has been chosen for the present study, since the kinetics of dehydration process had hardly been examined. The crystal structures of the dihydrate and the anhydrous acid are well characterized [2]. The dihydrate is dehydrated thermally in a single step at relatively low temperatures:

$$(COOH)_2 \cdot 2\,H_2O\ (s) \rightarrow (COOH)_2\ (s) + 2\,H_2O\ (g)$$

Experimental

Reagent grade oxalic acid dihydrate was recrystallized from an aqueous solution. The crystalline powder of dihydrate was ground manually using a mortar and pestle, and sieved to the fractions of 48–100, 100–170 and 170–200 meshes. The stoichiometry of water of crystallization was checked by thermogravimetry (100.14%). The minute plus error was due to a very slight sublimation of oxalic acid during the thermal dehydration.

TG–DTA traces were recorded at constant as well as at linearly increasing temperatures (ca. 0.53 K min^{-1}) using a Rigaku Thermoflex TG–DTA 8085E1 type instrument. DSC traces were obtained with a low temperature unit attached to the above instrument. About 0.1 mmol of the sample was weighed into a platinum crucible of 5 mm diameter and 2.5 mm height. All the measurements were made in a flowing N_2 at a rate of 30 ml min^{-1}. The dynamic runs were repeated five to six times and the mean with its standard deviation was assessed. Other experimental conditions were identical with those described earlier [3].

Results and discussion

Isothermal analysis

The appropriate model function $F(\alpha)$ for the isothermal dehydration of $(COOH)_2 \cdot 2\,H_2O$ was selected by plotting various $F(\alpha)$ against the time t assuming the kinetic equation:

$$F(\alpha) = kt \tag{1}$$

where k is the rate constant [4]. The $F(\alpha)$ examined in the present study is shown in Table 1. Table 2 lists the correlation coefficient r and standard deviation σ for the linear regression analysis of $F(\alpha)$ vs. t plot. In view of the linearity either one of A_m or R_n laws seems to be appropriate for the dehydration of $(COOH)_2 \cdot 2\,H_2O$. Furthermore, the most mathematically-appropriate $F(\alpha)$ was searched by "scanning" the exponents m and n using a computer. Either an A_m with $m = 3.31$ or R_n with $n = 1.09$ was "best" over the temperature range of 37.8–52.2°. We assume from such an analysis that the present dehydration proceeds theoretically (or ideally) via either an A_3 or R_1 law, and that the actual mechanism might be of complex combination of several laws [5]. In other words, there is a possibility that a complex mechanism operates which competes between the A_m and R_n laws in the present dehydration. In this respect it is interesting that a simultaneous operation of the A_m and R_n models has been proved by a direct observation for the dehydration of the single crystal material of the dihydrate [6].

Rate constants k derived at various temperatures using Eq. (1) in terms of $A_{3.31}$ and $R_{1.09}$ are shown in Table 3. Table 4 shows the Arrhenius parameters, together

Table 1 The kinetic model function $F(\alpha)$ for solid decompositions

$F(\alpha)$	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)
$\ln\left(\frac{\alpha}{1-\alpha}\right)$	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; $m = 2, 3$ and 4 (Avrami–Erofeyev functions)

Table 2 The typical correlation coefficient r and standard deviation σ of the least square fitting of $F(\alpha)$ vs. t plot of the isothermal dehydration at 40.6 °C in the α range of 0.1–0.9 *

Coefficient	$F(\alpha)$			
	D_1	D_2	D_3	D_4
r	0.9802	0.9569	0.9128	0.9435
$\sigma \cdot 10^2$	5.1206	6.0133	3.4411	1.8564
Coefficient	A_u	R_1	R_2	R_3
r	0.9963	0.9998	0.9932	0.9863
$\sigma \cdot 10^2$	10.657	0.53542	2.2553	2.4880
Coefficient	A_1	A_2	A_3	A_4
r	0.9647	0.9962	0.9985	0.9977
$\sigma \cdot 10^2$	12.926	3.0361	1.3389	1.2987

* For a particle size range of 48–100 meshes.

with the correlation coefficient r for the linear regression analysis. The particle size effect was not practically discernible on the Arrhenius parameters in the present study.

As for the particle size range of 48–100 meshes, the effect of grinding was examined on the Arrhenius parameters. As is shown in Table 5, no discernible effect was found between the ground and nonground materials.

Dynamic analysis

Figure 1 shows typical TG–DTA traces for the dehydration of $(COOH)_2 \cdot 2\,H_2O$. Table 6 shows the temperature as a function of α derived from TGA for various particle size ranges. Table 7 shows the dehydration temperature T and enthalpy change ΔH assessed from DTA and DSC, respectively.

Table 3 Rate constants k in terms of $A_{3.31}$ and $R_{1.09}$ at various temperatures for a particle size range of 170–200 meshes

Temperature, °C	$k \cdot 10^4$, s^{-1} $A_{3.31}$	$R_{1.09}$
37.8	0.8385	0.9143
40.9	1.1221	1.2242
42.3	1.4878	1.6568
43.6	1.5216	1.6604
45.5	1.7931	1.9970
46.4	2.1046	2.3710

Table 4 The activation energy E and frequency factor A from the isothermal analysis for various particle size ranges

Particle size range, mesh	$F(\alpha)$	E, kJ/mol	log A, s^{-1}	$-r$
48–100	$A_{3.31}$	77.8±12.7	9.02±2.11	0.9745
	$R_{1.09}$	79.5±12.5	9.35±2.08	0.9763
100–170	$A_{3.31}$	74.6± 9.4	8.44±1.52	0.9922
	$R_{1.09}$	78.3±10.9	9.09±1.67	0.9915
170–200	$A_{3.31}$	85.7± 6.9	10.3±1.2	0.9874
	$R_{1.09}$	88.5± 7.7	10.8±1.3	0.9851

Table 5 Grinding effect on the Arrhenius parameters in terms of A_3 for a particle size range of 48–100 meshes

Material	E, kJ/mol	log A, s^{-1}	$-r$
Ground	77.3±12.7	8.98±2.11	0.9742
Nonground	80.9± 5.3	9.55±0.88	0.9896

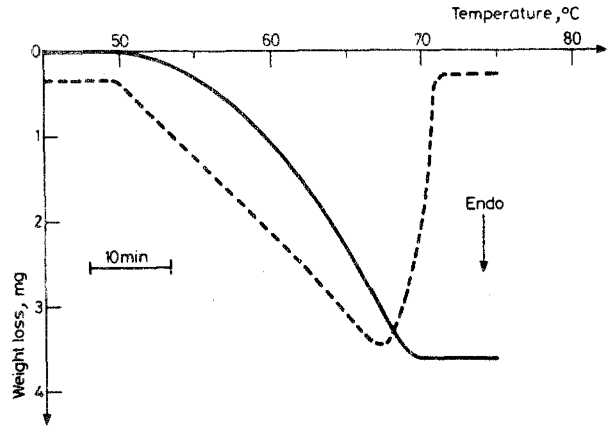


Fig. 1 Typical traces of TG (solid line) and DTA (broken line) recorded simultaneously for the dehydration of $(COOH)_2 \cdot 2H_2O$. Sample size: 12.60 mg; Particle size range: 100–170 meshes

Table 6 The temperature, °C as a function of the fraction dehydrated α from TG for various particle size ranges

α	Particle size range, mesh		
	48–100	100–170	170–200
0.1	55.9±0.2	55.3±0.2	54.7±0.3
0.2	58.5±0.2	57.9±0.2	57.3±0.3
0.3	60.6±0.2	59.9±0.2	59.4±0.3
0.4	62.3±0.2	61.6±0.2	61.1±0.3
0.5	63.7±0.2	63.1±0.2	62.6±0.2
0.6	65.0±0.2	64.4±0.2	63.9±0.2
0.7	66.1±0.1	65.5±0.2	65.1±0.2
0.8	67.3±0.2	66.7±0.2	66.2±0.2
0.9	68.6±0.2	68.0±0.2	67.5±0.2

Table 7 The dehydration temperature T from DTA and enthalpy change ΔH from DSC

Particle size range, mesh	Temperature, °C*			ΔH, kJ/mol H_2O
	T_i	T_{eo}	T_p	
48–100	49.5±0.2	51.6±0.4	67.6±0.2	59.0±1.6
100–170	49.1±0.3	50.2±0.2	67.4±0.2	
170–200	48.6±0.3	49.4±0.3	67.4±0.3	

* T_i, T_{eo}, and T_p refer to the temperatures of inception, extrapolated onset, and peak according to DTA, respectively.

It is reasonable to use the kinetic equation of Coats and Redfern in deriving kinetic parameters dynamically [7]:

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

Table 8 lists the kinetic parameters derived using Eq. (2) in terms of all the $F(\alpha)$ except A_u. In view of a relative correspondence between the parameters determined isothermally and those done dynamically, we adopt tentatively $A_{2.5}$ as the appropriate $F(\alpha)$ for the dynamic dehydration of $(COOH)_2 \cdot 2\ H_2O$ [8], since the linearity of Coats abd Redfern plot can not necessarily be a good criterion of selecting the appropriate kinetic model. The decrease in m from the isothermal value 3.31 to the dynamic one 2.5 may be due to the difference in the dehydration temperature between them and/or to the thermal stress during the heating in the dynamic dehydration [9].

Table 9 lists the kinetic parameters assessed using Eq. (2) in terms of $A_{2.5}$ for various particle size ranges. We see that k is hardly affected by the particle size, though

Table 8 Typical kinetic parameters in terms of various $F(\alpha)$ from the modified Coats and Redfern plots*

$F(\alpha)$	E, kJ/mol	$\log A$, s^{-1}	$-r$
D_1	313	45.4	0.9922
D_2	346	50.3	0.9963
D_3	388	56.4	0.9987
D_4	360	51.9	0.9975
R_1	154	20.7	0.9919
R_2	181	24.8	0.9979
R_3	191	26.2	0.9987
A_1	214	30.3	0.9982
A_2	104	13.1	0.9981
A_3	67.6	7.27	0.9980
A_4	49.3	4.32	0.9979

* For TG recorded at a heating rate of 0.528 deg/min for a particle size fraction of 48–100 meshes

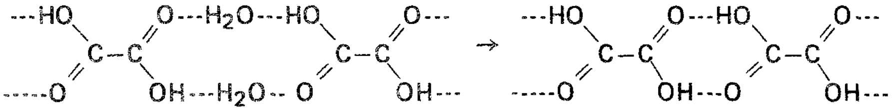
Table 9 Effect of particle size on the kinetic parameters from TG in terms of $A_{2.5}$

Particle size range, mesh	E, kJ/mol	$\log A$, s^{-1}	$k \cdot 10^4$, s^{-1} at 63.2 °C
48–100	82.01±0.84	9.59±0.14	7.00±0.06
100–170	81.92±0.75	9.59±0.12	7.41±0.06
170–200	80.54±0.88	9.39±0.14	7.62±0.09

there is a trend of increasing k with decreasing particle size. This fact supports the operation of one of A_m laws with a possibility of slight contribution of an R_n law as stated above. This might be another reason why the $A_{2.5}$ instead of $A_{3.31}$ is "apparently" appropriate for the dynamic dehydration of $(COOH)_2 \cdot 2\,H_2O$. Alternatively the $A_{2.5}$ law might originate from a complex mechanism of the random nucleation and its subsequent growth, although an A_m law with a nonintegral value of m particularly for a dynamic decomposition is not necessarily physically-meaningful but "apparent" one.

It is interesting to compare the activation energy E with the corresponding enthalpy change ΔH. The observed ΔH, 118.0±1.6 kJ per mole of the dihydrate is so much larger than E ($\sim$ 80 kJ mol^{-1}) that we can assume that a single water molecule would participate in the activated complex for breaking the bonds at phase boundaries [10].

In the course of dehydration of $(COOH)_2 \cdot 2\,H_2O$, the water molecules linked to the oxygen atoms of carboxyl group by hydrogen bonds [11] are dehydrated to yield the β-form of oxalic acid [12] as follows:



A considerable shrinkage occurs in the direction parallel to the infinite chain in the course of rearrangement of oxalic acid from the amorphous state. The activation energy E for this process would be much larger than that for merely breaking the hydrogen bonds of the dihydrate and than that for diffusion of the liberated water molecules.

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Zusammenfassung — Die Kinetik der thermischen Dehydratisierung von kristallinen Pulvern von $(COOH)_2 \cdot 2 H_2O$ wurde thermogravimetrisch bei konstanter und linear ansteigender Temperatur untersucht. Es wurde festgestellt, daß das Avrami—Erofeyev-Gesetz gefolgt wird und die Möglichkeit besteht, daß gleichzeitig eine phasen grenzflächen-kontrollierte Reaktion verläuft. Dies wird durch die Beeinflussung der Geschwindigkeitskonstante durch die Partikelgröße unterstützt. Die Aktivierungsenergie *E* für die Dehydratisierung wurde zu etwa 80 kJ mol^{-1} gefunden. Es ist wahrscheinlich, daß die Effekte von Partikelgröße und Temperatur auf *E* durch den des Häufigkeitsfaktors *A* kompensiert werden.

Резюме — Кинетика термической дегидратации кристаллических порошков дигидрата щавелевой кислоты была исследована методом термогравиметрии как при постоянной, так и линейно увеличивающейся температурах. Найдено, что закон Аврами–Ерофеева согласуется с возможностью, что контролированная реакция фаза-граница протекает одновременно. Это подтверждается влиянием размера частиц на константу скорости. Энергия активации *E* реакции дегидратации была установлена равной приблизительно 80 кдж • $моль^{-1}$. Вероятно, сто влияние размеров частиц и температуры на энергию активации *E* компенсируется влиянием их на частотный множитель *A*.