

The kinetics of the isothermal dehydration of lithium sulfate monohydrate under a self-generated temperature condition

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Abstract

The rate behavior of the isothermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was studied under a self-generated temperature condition by recording the mass loss and temperature deviation from the pre-set isothermal temperature. The sample temperature during the reaction was influenced by the effect of self-cooling. The rate process under such a temperature condition could be divided into three distinct stages: acceleratory, nearly constant rate, and deceleratory periods. The constant rate period was processed kinetically using the Friedman method. The apparent values of Arrhenius parameters during the constant rate process remained constant irrespective of the sample mass examined.

INTRODUCTION

In our previous studies on the kinetics of the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [1–8], it was revealed that the reaction of each particle in the sample matrix proceeds by the advancement of the reaction interface produced by the surface nucleation and growth at the very early stage of reaction [3, 6]. Although the kinetics was interpreted on the basis of the contracting geometry Rn model, the overall behavior of the sample matrix estimated by the conventional linear fitting of the thermo-analytical (TA) data to a particular kinetic model function, $f(\alpha)$, did not necessarily indicate obedience to the Rn functions [1, 2]. Formally, the processes under both isothermal and linearly increasing temperature conditions have been characterized by a combination of an Avrami–Erofeyev model Am , which dominates during the earlier stage, with an Rn

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model, which predominates as the reaction proceeds [2]. A similar kinetic obedience was observed for the isothermal dehydration under vacuum [9].

A more detailed investigation of the isothermal dehydration revealed that the overall rate process is divided into three distinct stages: the acceleratory period observed in the range of fractional reaction α below 0.15; the approximately constant rate period within the restricted range of $0.2 < \alpha < 0.5$; and the deceleratory period in the range of $\alpha > 0.5$ [8]. The acceleratory period is understood as corresponding to the surface nucleation and growth of crystallites of the product [4]. Usually, the completion of the surface reaction, i.e. the formation of product layer, is followed by the deceleratory process. The nearly constant rate stage observed here seems to arise from the effects of self-cooling [3] and the change in the partial pressure of water vapor [5], which is accompanied by the change in the kinetic behavior. This has been demonstrated by a series of kinetic studies on the thermal dehydration of the present compound [9–14]. This is related to the fact that the process is greatly affected by the sample size [7, 8]. During the quasi-constant rate stage, however, the gradients in the temperature and partial pressure of the evolved gas may decrease compared with those under the condition where the reaction rate changes. This is an advantage of the kinetic use of controlled transformation rate thermal analysis (CRTA) [15] and/or quasi-isothermal and quasi-isobaric thermal analysis (QOTA) [16], which may be an alternative experimental solution of the kinetics of solid-state reactions [17].

In the present study, the quasi-constant rate stage in the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was analyzed kinetically in order to estimate the value of the kinetic approach to constant rate transformations.

EXPERIMENTAL

Reagent grade lithium sulfate monohydrate (Katayama Chem. Ind.) was dissolved in water, and prolate single crystals were obtained by slow evaporation at ambient temperature. The crystals were crushed with a mortar and pestle and screened to a particle size fraction of $-100 + 170$ mesh. The sample was characterized by IR spectroscopy, as well as by TG, and was stored for more than three weeks before TA measurements to avoid the ageing effect.

The nominal sample sizes were 2.5, 7.5 and 20.0 mg, packed by light tapping into a cylindrical platinum crucible 5 mm in diameter and 2.5 mm in height. The mass-change traces were obtained using a Shimadzu TGA-50 system in nitrogen flowing at a rate of 30 ml min^{-1} . In this system, a temperature sensor is positioned just over the upper surface of the sample, and the temperature program is set up in an isothermal mode, then a linear temperature increase to a pre-determined temperature, and then holding

at this temperature. The pre-set isothermal temperature was changed from 79 to 100°C. It was determined that the PID parameters for the temperature regulation did not compensate the enthalpy change of the reaction, so that a nearly constant-rate dehydration stage was produced, in which the temperature change during the reaction reflected the effect of self-cooling.

RESULTS AND DISCUSSION

Figure 1 shows a typical plot of the rate of conversion $d\alpha/dt$ against α , together with the temperature profile during the course of reaction. In this measurement, the temperature program was automatically changed to isothermal mode after the temperature rose linearly up to 94°C. The temperature reached the pre-determined temperature at $\alpha < 0.05$ and the reaction rate was acceleratory during the linear heating. On reaching the pre-set temperature, the sample temperature decreases rapidly due to the self-cooling effect. The reaction rate fluctuates in the range of $0.05 < \alpha < 0.15$, accompanied by a change in the sample temperature. A quasi-constant overall rate is observed over the range $0.2 < \alpha < 0.5$, followed by a deceleratory period at $\alpha > 0.5$. At this stage, the sample temperature recovers from the transient temperature decrease and becomes equilibrated with the surroundings, as the reaction proceeds. A similar rate behavior and variation of sample temperature were observed irrespective of the sample size examined and of the preset temperature in the range of 79–100°C.

For the kinetic analysis, the following formula is applied

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where A , E , R and T are the apparent pre-exponential factor, the apparent

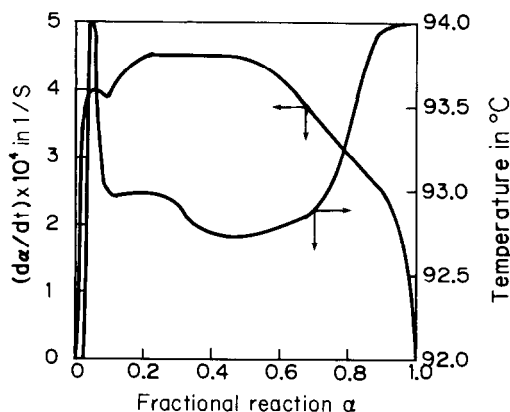


Fig. 1. Typical plot of $d\alpha/dt$ versus α and the temperature profile for the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (20.0 mg).

activation energy, the gas constant and the temperature, respectively. The kinetic model function $f(\alpha)$ is usually derived on the basis of physico-geometric features of the reaction proceeding in a particle of the sample matrix [18]. The applicability of eqn. (1) to the present reaction can be estimated by introducing the generalized time θ [19–22]

$$\theta = \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (2)$$

First differentiation gives

$$\frac{d\theta}{dt} = \exp\left(-\frac{E}{RT}\right) \quad (3)$$

Combining eqn. (1) with eqn. (3)

$$\frac{d\alpha}{d\theta} = Af(\alpha) \quad (4)$$

Equation (1) is thus expressed by

$$\frac{d\alpha}{dt} = \frac{d\alpha}{d\theta} \frac{d\theta}{dt} \quad (5)$$

Equations (3) and (5) show that $d\alpha/dt$ is proportional to $\exp(-E/RT)$ at a given α , having a constant value of $d\alpha/d\theta$. Because eqns. (3), (4) and (5) hold for any temperature change, eqn. (1) can be applied to any TA data obtained under any condition of temperature change [22]. Taking logarithms of eqn. (1), we obtain

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln[Af(\alpha)] \quad (6)$$

Thus the plot of $\ln(d\alpha/dt)$ against the reciprocal temperature at a given α represents a straight line with a slope of $-E/R$, known as the Friedman plot derived originally for chemical processes under a linearly increasing temperature [23].

Figure 2 represents typical plots of $\ln(d\alpha/dt)$ against $1/T$ at $\alpha = 0.35$, in which fairly linear relationships are observed for the sample masses examined. The E values thus calculated at different sample masses indicated good agreement within statistical error, in contrast to the mass-dependent change in the E values observed under isothermal and linearly increasing temperature conditions [7, 8].

The apparent values of E obtained at the various α values are illustrated in Fig. 3. Irrespective of the sample mass examined, nearly constant E

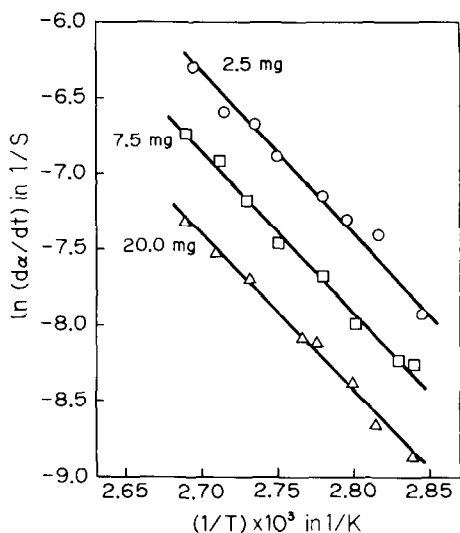


Fig. 2. Typical plots of $\ln(d\alpha/dt)$ versus $1/T$ for the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

values are obtained in the range $0.3 < \alpha < 0.6$, which is slightly later than the constant rate period of mass loss. Such a constant E value is a prerequisite for the applicability of eqn. (1) for the rate process under investigation, assuming that the reaction within the range of constant E values is regulated by a certain rate-determining step included in the process. Table 1 lists the mean values of E within the range of $0.3 < \alpha < 0.6$ obtained for the respective sample masses.

According to eqn. (5), the kinetics can be characterized by dividing the rate process into the enthalpy- and entropy-dependent terms, expressed by

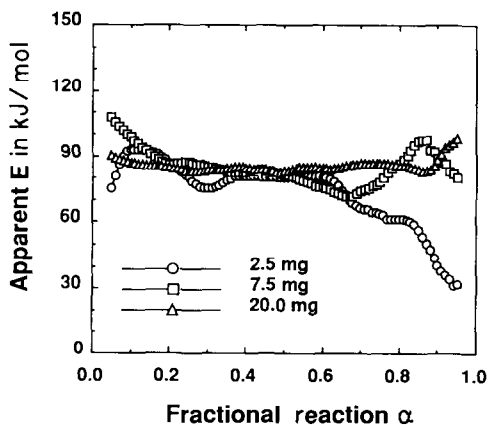


Fig. 3. The α dependence of the apparent value of E for the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

TABLE 1

The mean values of E for the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ obtained in the range of $0.3 < \alpha < 0.6$

Sample mass/mg	$E/(\text{kJ mol}^{-1})$	σ^a
2.5	79.7	1.6
7.5	81.6	2.5
20.0	84.1	0.6

^a Standard deviation.

$d\theta/dt$ and $d\alpha/d\theta$, respectively. Using the values of E listed in Table 1, the entropy-dependent term was determined at various α values. Figure 4 shows the α dependence of the $d\alpha/d\theta$ values. The values of $d\alpha/d\theta$ are different at various α values, in contrast to the constant value of $d\alpha/dt$ in the range of $0.2 < \alpha < 0.5$ (Fig. 1). It is likely that the $f(\alpha)$ -dependent term, $d\alpha/d\theta$, is greatly affected by a systematic change in the temperature, even in the present case of a temperature variation of less than 0.5°C . The differences in the values of $d\alpha/d\theta$ and its α dependency among the sample masses seem to result from the slight differences in the E values listed in Table 1, a simple mathematical consequence known as the interdependence of the Arrhenius parameters, i.e. the kinetic compensation effect [24–26].

On determining the pre-exponential factor, together with the mathematical form of $f(\alpha)$, it should be considered that the constant value of A at different values of α within the range of the kinetic analysis is also a prerequisite for the applicability of eqn. (1), as is the case of the E value. In addition, the mis-estimation of $f(\alpha)$ leads to a distortion of the Arrhenius

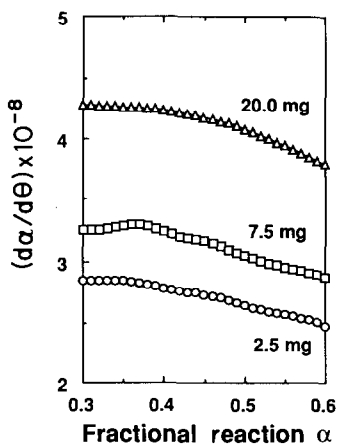


Fig. 4. The plots of $d\alpha/d\theta$ versus α for the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

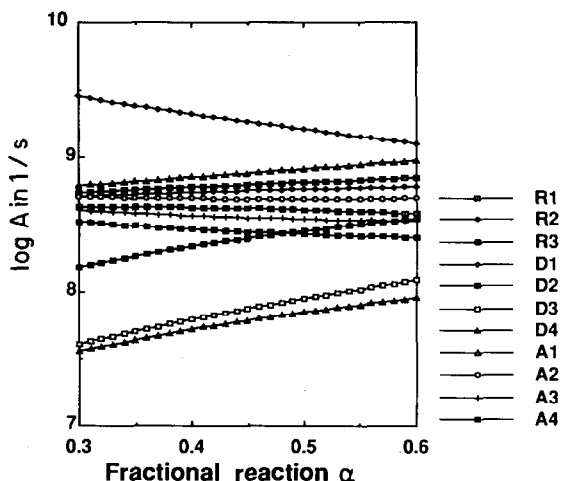


Fig. 5. The α dependence of $\log A$ for the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

parameters [27], expressed by a simple mathematical consequence. Figure 5 shows the logarithms of the A values obtained at different α values for the sample mass of 20.0 mg, by assuming the possible forms of $f(\alpha)$ listed elsewhere [18]. The constant value of A can be estimated assuming the two- and three-dimensional phase-boundary-controlled models: $R2 = (1 - \alpha)^{1/2}$ and $R3 = (1 - \alpha)^{2/3}$, respectively. Table 2 lists the logarithmic values of A averaged over the range $0.3 < \alpha < 0.6$. The obedience to the R2 or R3 law was also observed for sample masses of 2.5 and 7.5 mg. This is in good agreement with the reaction geometry of the particles in the sample matrix observed microscopically [6], and differs from the kinetic obedience determined from the conventional isothermal and dynamic TA curves in the same range of α [1, 2].

Usually, in conventional kinetic analyses of TA curves under isothermal and linearly increasing temperature conditions, the gradients of temperature and gaseous pressure in the sample matrix diminish the reliability of

TABLE 2

The mean values of $\log A$ for the thermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ obtained in the range of $0.3 < \alpha < 0.6$

Sample mass/mg	$R2 = (1 - \alpha)^{1/2}$		$R3 = (1 - \alpha)^{2/3}$	
	$\log A/(/s)$	σ^a	$\log A/(1/s)$	σ^a
2.5	8.57	0.02	8.61	0.03
7.5	8.63	0.02	8.67	0.03
20.0	8.75	0.02	8.79	0.03

^a Standard deviation.

the kinetics obtained based on the physico-geometry of the reaction of a particle, due to the distribution of the fractional reaction of a particle within the sample matrix [28]. In some particular cases, the reaction as a whole proceeds according to the one-dimensional phase-boundary-controlled law [8], as in the case of evaporation of a liquid from a surface. It has been strongly recommended as an experimental solution of the gradients that the sample mass should be reduced in the TA measurements [17]. This, in turn, sometimes introduces an interdependent change in the Arrhenius parameters among the series of reactions, because of the consequent reduction in the temperature interval analyzed [24–26]. The above experimental results support the applicability of the $f(\alpha)$ based on a single particle to the constant transformation stages of solid-state reactions. It seems, however, that the sample mass is again an important experimental factor in determining whether the kinetics is described on the basis of the reaction behavior of a particle or of the overall behavior of the sample matrix. A constant value of E can be obtained for both kinetic treatments [29]. However, constant Arrhenius parameters, E and A , can only be obtained when the process is correctly described by the physico-geometric $f(\alpha)$ applied. Reduction of the sample mass may reduce the range of reaction rate controlled and, thus, the temperature interval of kinetic analysis. Then the mutual dependence of the Arrhenius parameters could also be caused by such an experimental factor, as was noticed mathematically [30].

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