# Kinetics of the Thermal Dehydration of Magnesium Oxalate Dihydrate in a Flowing Atmosphere of Dry Nitrogen

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The kinetics of isothermal dehydration of MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in a dry nitrogen flow have been studied in detail by use of many accurate thermogravimetric data acquired on a microcomputer. This dehydration proceeded as a two-dimensional phase boundary reaction, R2. In general, the nucleation in the phase boundary reaction occurs so rapidly that the reaction rate is only determined by following the chemical process occurring at the reactant-product interface. However, the present dehydration was affected by the nucleation process, and its dehydration fraction curve showed a sigmoidal character especially at lower temperatures than ca. 160 °C. We succeeded in separately evaluating the rate constants  $k_{\rm N}$  for the nucleation and  $k_2$  for the R<sub>2</sub> process by detailed analysis of the dehydration fraction curve. The value of  $k_N$  became comparable to that of  $k_2$  at lower temperatures, whereas at higher temperature the former became much larger than the latter and the overall dehydration had a characteristic of natural R<sub>2</sub> reaction. The values of activation energies and preexponential factors for both processes were determined from the temperature dependency of  $k_N$  and  $k_2$ . Those were 430 kJ mol<sup>-1</sup> and  $3.73 \times 10^{49}$  s<sup>-1</sup> for the nucleation process, and 111 kJ mol<sup>-1</sup> and  $3.40 \times 10^9$  s<sup>-1</sup> for two-dimensional phase boundary process, respectively.

### Introduction

Several studies<sup>1-7</sup> have been carried out on the kinetics of the thermal dehydration of magnesium oxalate dihydrate. Dollimore and his co-workers<sup>1</sup> found that the rate of dehydration depended upon the water vapor pressure. Phadnis and Karkhanavala<sup>2</sup> showed that the values of activation energy of the dehydration varied considerably depending upon the weight of the specimen. Shkarin et al.<sup>3</sup> showed that the dehydration was described by nearly first-order kinetic law, and its activation energy and preexponential factor had values of 96 kJ mol<sup>-1</sup> and  $1.3 \times 10^7$ s<sup>-1</sup>, respectively. On the other hand, Mu and Perlmutter<sup>4</sup> reported them as 155.6 kJ mol<sup>-1</sup> and  $2.8 \times 10^{16}$  s<sup>-1</sup>, respectively, and found that the dehydration took place as a second-order reaction. Mourad and Nashed<sup>5</sup> showed that the dehydration was characterized by Mampel's equation,<sup>6</sup> but the Arrhenius plots consisted of two linear sections which intersected at 215 °C, and the values of activation energy were 51.5 and 76.6 kJ mol<sup>-1</sup> for the lower and higher temperature sections, respectively. Tanaka and Tokumitsu<sup>7</sup> studied the dehydration by means of the dynamic TG-DSC and the isothermal thermogravimetric (TG) methods. They concluded that the dehydration was regulated by the Avrami-Erofe'ev<sup>8,9</sup> mechanisms. Thus, for the thermal dehydration of  $MgC_2O_4 \cdot 2H_2O$ , the kinetic parameters and the mechanisms reported have been often different from each others. These differences seem to be attributable to the difference in the measuring condition and in the method of preparing samples. However, in these reports, a clear explanation has scarcely been made for the initial nucleation step of the thermal dehydration of MgC<sub>2</sub>O<sub>4</sub>. 2H<sub>2</sub>O.

Recently, we<sup>10,11</sup> studied the kinetics of the thermal dehydration

of calcium oxalate monohydrate on the basis of a new method which applied a microcomputer to the acquisition of a great number of accurate TG data and processing of them. We succeeded in separating the apparently simple dehydration into two processes corresponding to the elimination of water molecules and the external diffusion of water molecules eliminated.

This paper is concerned with the determination of the kinetic parameters and the mechanisms of the dehydration of magnesium oxalate dihydrate in a dry nitrogen flow, on the basis of many accurate thermogravimetric data acquired on a microcomputer, as described in previous articles.<sup>10,11</sup> The experiment was performed isothermally in the flowing atmosphere of dry nitrogen at various temperatures in order to examine the dehydration mechanism in detail, and we succeeded in evaluating separately the rate constants for the nucleation and for the main dehydration process.

#### **Experimental Section**

Reagent. Magnesium oxalate dihydrate was synthesized as follows: 300 mL of a 0.13 M solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 M = 1 mol dm<sup>-3</sup>) and 4.0 g of KOH were added to 300 mL of a 0.13 M solution of  $(COOCH_3)_2$ , the mixture was permitted to stand for a week, and the crystals precipitated were filtered and washed with distilled water. The crystals were air-dried at room temperature and stored in a desiccator. The specimen was identified by means of TG, IR spectrophotometry, and X-ray diffraction analysis, and sieved to three fractions: 100-150, 200-250, and less than 300 mesh.

Apparatus. Figure 1 shows a block diagram of the experimental system. The isothermal dehydration in a flowing nitrogen (99.999%) atmosphere (flow rate: 50 mL min<sup>-1</sup>) was followed with a Shinku Riko TGD-5000RH differential microbalance. In the present weight loss examination, the temperature of the specimen was coordinated so as to arrive at a given value within 20 s for the intact acquisition of the data for the initial stage of the dehydration.

After the specimen of about 12 mg was weighted into a platinum crucible and set in the balance, the furnace was maintained at a constant temperature within  $\pm 0.5$  °C until the dehydration

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Figure 1. Block diagram of the experimental system.



Figure 2. Isothermal dehydration of MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (100–150 mesh). Plots of  $\alpha$  against time: (1) 191.0 °C, (2) 170.5 °C, (3) 161.5 °C, and (4) 154.5 °C.

TABLE I: Commonly Used  $F(\alpha)$  for Solid-Phase Reaction

$F(\alpha)$	symbol	rate-controlling process
$\overline{\alpha^2}$	D1	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 equation
$1-2\alpha/3-(1-\alpha)^{2/3}$	D₄	three-dimensional diffusion; Ginstring-Brounshtein equation
$1 - (1 - \alpha)^{1/2}$	R <sub>2</sub>	two-dimensional phase boundary reaction
$1 - (1 - \alpha)^{1/3}$	R3	three-dimensional phase boundary reaction
$-\ln(1-\alpha)$	$\mathbf{F}_1$	first-order reaction
$(-\ln (1-\alpha))^{1/n}$	A <sub>n</sub>	random nucleation; Avrami-Erofe'ev equation, $n = 1$ , 2, 3, 4,

was completed. The output voltages for weight loss from the microbalance were amplified and acquired on a microcomputer (MZ-80C) via an AD converter (ICL7109 modified in 13 bit). The AD converter was connected to the microcomputer by an interface card (MZ-80 I/O-1). A printer (MP-80) and an X-Y plotter (WX-4675) were connected to the microcomputer.

For each dehydration process, about 700 data concerning the weight loss were collected at given time intervals, and the fraction of dehydration ( $\alpha$ ) was calculated from these data.

Also the process of isothermal dehydration was visually traced by use of a Nikon Model S-Po polarizing microscope. The specimen was introduced in an oven controlled at constant temperatures, and dehydrated isothermally in the flowing atmosphere of dry nitrogen for a given length of time.

The X-ray powder diffraction patterns were obtained with a Rigaku Geigerflex RAD-rA diffractometer by the use of Cu K $\alpha$  radiation and a nickel filter.

Infrared absorption spectra were measured from 250 to 4000  $cm^{-1}$  in a KBr disk with a Hitachi 295 spectrophotometer.

#### **Results and Discussion**

Figure 2 shows a plot of the fraction of dehydration ( $\alpha$ ) against the time (t) of the reaction at various temperatures. There is no evidence of an intermediate monohydrate because of the smoothness of each curve. The curves obtained at 161.5 and 154.5 °C suggest that the main process of dehydration follows the initial reaction of slow rate at lower temperatures.

The kinetics of solid-state reactions can be represented by the general equation

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



Figure 3. Typical  $F(\alpha)$  vs t plots for the isothermal dehydration of MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (100-150 mesh).

TABLE II:	<b>Rate Constants</b>	(k) Obtained	at Various	Temperatures
for R <sub>2</sub> React	tion <sup>a</sup>			

				_
temp/°C	$\alpha$ range <sup>b</sup>	۴	$k \times 10^3/s$	
148.0	0.04-0.90	0.9994	0.0386	
153.0	0.03-0.96	0.9998	0.0602	
154.5	0.02-0.96	0.9997	0.0740	
157.0	0.02-0.96	0.9997	0.0936	
160.0	0.020.98	0.9999	0.1122	
161.5	0.02-0.99	1.0000	0.1460	
165.0	0.06-0.98	0.9998	0.1979	
170.5	0.01-0.98	0.9997	0.2763	
180.5	0.03-0.94	0.9995	0.5687	
191.0	0.05-0.95	0.9996	1.077	
196.0	0.060.96	0.9997	1.468	
200.5	0.12-0.99	0.9998	2.016	
206.5	0.11-0.99	0.9999	2.546	
211.0	0.14-0.99	0.9999	3.524	
217.0	0.18-0.98	0.9999	4.606	
222.0	0.22-0.98	0.9999	5.895	

<sup>a</sup>100-150 mesh specimen. <sup>b</sup> $\alpha$  range means the linear range of the R<sub>2</sub> vs t plots. <sup>c</sup>Correlation coefficient.

TABLE III: Activation Energy and Preexponential Factor for Dehydration of MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O

specimen	$E/kJ \text{ mol}^{-1}$	$A/s^{-1}$
100–150 mesh	105.6	$8.30 \times 10^{8}$
200-250 mesh	109.8	$2.91 \times 10^{9}$
less than 300 mesh	105.8	$1.33 \times 10^{9}$

where k is the rate constant and  $F(\alpha)$  is a function depending on the reaction mechanism. Table I shows the theoretical model functions used commonly.<sup>12</sup> The kinetic mechanism of the present dehydration was judged by the linearity of the plots of  $F(\alpha)$ functions calculated from  $\alpha(t)$  obtained against time for the thermal dehydration, in accordance with eq 1.

Figure 3 shows the examination of the linearity on the basis of the experimental data at 154.5 and 191 °C for some typical  $F(\alpha)$  functions. At 191 °C, the plot of  $1 - (1 - \alpha)^{1/2}$  vs t, i.e., the plot of the  $R_2(\alpha)$  function vs t, gives a straight line over the nearly whole range of the process of dehydration. Thus the

<sup>(12)</sup> Sharp, J. H.; Brindley, G. W.; Achar, B. N. N. J. Am. Ceram. Soc. 1966, 49, 379.



Figure 4. Arrhenius plots for the isothermal dehydration of  $MgC_2O_4$  ·  $2H_2O$ .



Figure 5. Optical microscopic observation for the dehydration of Mg-C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. (1) Typical crystal of a hydrated specimen. (2) Surface of the crystal after heating for 8 min at 170 °C in a flowing atmosphere of dry nitrogen. (3) Same as (2) after heating for 15 min at 170 °C in a flowing atmosphere of dry nitrogen. (4) Same as (2) after heating for 25 min at 170 °C in a flowing atmosphere of dry nitrogen.

dehydration seems to have the characteristic of the two-dimensional phase boundary reaction (R<sub>2</sub>). At 154.5 °C, after a slow dehydration, the main dehydration is found to be suitable to R<sub>2</sub> reaction. Table II shows the rate constants for the R<sub>2</sub> reactions determined from the slopes of the R<sub>2</sub>( $\alpha$ ) vs t plots at various temperature. The activation energies and preexponential factors were determined from the Arrhenius plots (Figure 4) of these rate constants and are shown in Table III.

It has been known that the  $R_2$  reaction is characterized by the rapid initial production of a complete reactant-product interface at the edge of preferred crystallographic surfaces, and its rate is determined by the advance of the reaction interface.<sup>13</sup> To confirm the  $R_2$  mechanism for the present dehydration, the various stages of dehydration were observed by use of optical microscopy. Figure 5 shows the advance of the dehydration of MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. The





Figure 6. Bonding structure of MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O.<sup>14</sup>

TABLE IV:	Effect of	Particle Size	(r <sub>0</sub> )	on the	Rate	Constant	(k)	)
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$r_0/\mu m$	temp/°C	k/s <sup>-1</sup>
$146.5 \pm 1.6$	170.0	$2.98 \times 10^{-4}$
	191.0	$1.09 \times 10^{-3}$
	201.0	$1.95 \times 10^{-3}$
	211.0	$3.38 \times 10^{-3}$
$84.2 \pm 1.3$	170.0	$3.32 \times 10^{-4}$
	191.0	$1.28 \times 10^{-3}$
	201.0	$2.33 \times 10^{-3}$
	211.0	$4.14 \times 10^{-3}$
$45.8 \pm 9.1$	170.0	$4.55 \times 10^{-3}$
	191.0	$1.67 \times 10^{-3}$
	201.0	$2.97 \times 10^{-3}$
	211.0	$5.18 \times 10^{-3}$

series of photographs show that the nuclei appear on the edges or cracks of the surface. These nuclei grow until a interface is built up, and then the interface advances into the center of the surface. These findings support the conclusion that the present dehydration proceeds as two-dimensional phase boundary reaction  $(R_2)$ .

The  $R_2$  mechanism for this dehydration is also supportable by considering the crystal structure of MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O reported by Lagier et al.<sup>14</sup> They have showed that the crystal structure is monoclinic, with space group C2/c. In this structure, the oxalate ions act as a quadridentate ligand, and the water molecules lie on the plane to be parallel to (100) planes. Their coordinations are shown in Figure 6. It is reasonable to consider that the dehydration takes place on the planes as a contracting area reaction.

On the other hand, the rate constant (k) for a phase boundary controlled reaction is known to be represented by the equation<sup>13</sup>

$$= k_{\rm G}/r_0 \tag{2}$$

where  $k_{\rm G}$  is the velocity of the interface advancing and  $r_0$  is the initial radius of the particles. For the present dehydration, the relations between the particle size and the k at various temperatures were examined and are shown in Table IV. Here, the values of  $r_0$  were measured as an average radius of 50-500 particles, and were 146.5 ± 1.6, 84.2 ± 1.3, and 45.8 ± 9.1  $\mu$ m for the specimens of 100-150, 200-250, and below 300 mesh, respectively. The values of k decreased with increasing values of  $r_0$ .

On the basis of the above finding, the main process of the present dehydration seems to be represented by the  $R_2$  mechanism. At temperatures higher than ca. 160 °C, as shown in Figure 7a, the experimental values of  $\alpha$  is in fair agreement with the theoretical  $\alpha(t)$  curve calculated on the assumption that the dehydration takes place only by the  $R_2$  mechanism. This fact shows that in the present dehydration the nucleation step occurs rapidly at temperatures higher than ca. 160 °C, and the reaction rate is only determined by the chemical process occurring at the reactant-product interface. However, at temperatures lower than 160

<sup>(13)</sup> Hulbert, S. F. J. Br. Ceram. Soc. 1969, 6, 11.

<sup>(14)</sup> Lagier, J. P.; Pezernat, H.; Dubernat, J. Rev. Chim. Miner. 1969, 6, 1081.



**Figure 7.** The fitness of the theoretical curve for the experimental  $\alpha(t)$  plots.

°C, the theoretical  $\alpha(t)$  curve does not fit to the experimental values in the initial acceleratory period, as shown in Figure 7b. This finding indicates that another dehydration mechanism including the initial process of the dehydration should be considered. Yoshioka et al.<sup>15</sup> proposed a modified phase boundary model combining the nucleation. This kinetic equation was sufficient to account for the kinetics of the thermal decomposition of Mg-(OH)<sub>2</sub> that had a sigmoidal character in the  $\alpha(t)$  curve, as shown in Figure 2.

The microscopic observation of nuclei formation of the present dehydration, as shown in Figure 5, suggests that the nuclei form relatively slowly during the course of the reaction. In such a case, the overall rate of the dehydration will depend not only on the rate process at which the actual reaction occurs at the interface, but also on the rate of the nuclei formation. If the formation of nuclei is much slower than the interfacial reaction itself, then it will become the rate-controlling step and will affect the overall kinetics. From this point of view, we attempt the explanation of the sigmoidal  $\alpha(t)$  curve by a modification of Yoshioka's proposal.<sup>15</sup>

If the nuclei of dehydration are formed at the edge of particular plane according to the exponential law,<sup>16</sup> the rate of nucleation is

$$dN/dt = k_N N_0 \exp(-k_N t)$$
(3)

where N is the number of nuclei formed on the plane at time t,  $N_0$  is the total number of the potential nucleus forming sites at the edge of the plane, and  $k_N$  is the rate constant for the nuclei formation. When a great number of nuclei cover the edge of the plane, an interface between the hydrated and dehydrated salt is

TABLE V: Rate Constant  $(k_N)$  for the Nucleation and Rate Constant  $(k_2)$  for the  $R_2$  Reaction Separated from the Overall Dehydration<sup>a</sup>

temp/°C	$k_{\rm N}/{\rm s}^{-1}$	$k_2/s^{-1}$	$k_{\rm N}/k_2$
148.0	$1.41 \times 10^{-4}$	7.83 × 10 <sup>-5</sup>	1.80
153.0	$6.85 \times 10^{-4}$	$6.50 \times 10^{-5}$	10.5
154.5	9.54 × 10 <sup>-4</sup>	7.91 × 10⁻⁵	12.1
157.0	$1.84 \times 10^{-3}$	9.74 × 10⁻⁵	18.9
160.0	$3.30 \times 10^{-3}$	$1.10 \times 10^{-4}$	30.0

<sup>a</sup> For specimen 100-150 mesh.

formed around the plane. If the interface advances from the edge to inward of the plane at a constant rate, then the overall fraction of dehydration at time t is governed by equations

$$\alpha(t) = \sum_{t_j} \frac{1}{N_0} \left( \frac{\Delta N}{\Delta t} \right)_{t_j} \alpha(t, t_j)$$
(4)

$$N_0 = \sum_{t_i} \Delta N_{t_i} \tag{5}$$

where  $\Delta N_{t_i}$  is the number of the nuclei formed in the time interval  $t_j \rightarrow t_j + \Delta t$ , and  $\alpha(t,t_j)$  is a discrete dehydration fraction at time t which is due to the nuclei formed at time  $t_j$ . For the present dehydration,  $\alpha(t,t_j)$  is given by

$$\alpha(t,t_j) = 2k_2(t-t_j) - (k_2(t-t_j))^2$$
(6)

which is derived from the  $R_2$  equation

$$-((1 - \alpha(t,t_j))^{1/2} = k_2(t - t_j)$$
(7)

Here  $k_2$  is the rate constant of  $R_2$  reaction separated from the overall dehydration. Further, the  $\alpha(t,t_j)$  has to satisfy the following requirements

 $t < t_i$ 

 $t_i \le t < t_i + 1/k_2$ 

 $t \ge t_i + 1/k_2$ 

when

$$\alpha(t,t_j) = 0 \tag{8}$$

when

$$\alpha(t,t_i) = 2k_2(t-t_i) - (k_2(t-t_i))^2$$
(9)

when

$$\alpha(t,t_j) = 1 \tag{10}$$

Since the formation of the nuclei is a continuum, the summation in eq 4 can be replaced with an integration

$$\alpha(t) = \int_0^t \frac{1}{N_0} \left(\frac{\mathrm{d}N}{\mathrm{d}t}\right)_{t_j} \alpha(t,t_j) \,\mathrm{d}t_j \tag{11}$$

Considering above requirements (8), (9), and (10), this integration can be done as follows:

when  $t < 1/k_2$ 

$$\alpha(t) = \int_0^t k_N \exp(-k_N t_j) [2k_2(t-t_j) - k_2^2(t-t_j)^2] dt_j$$
  
=  $-k_2^2 t^2 + 2k_2 \left(1 + \frac{k_2}{k_N}\right) t - \frac{2k_2}{k_N} \left(1 + \frac{k_2}{k_N}\right) [1 - \exp(-k_N t)]$   
(12)

 $t \geq 1/k_2$ 

when

5

$$\alpha(t) = \int_{0}^{t^{-1/k_{2}}} k_{N} \exp(-k_{N}t_{j}) dt_{j} + \int_{t^{-1/k_{2}}}^{t} k_{N} \exp(-k_{N}t_{j}) [2k_{2}(t-t_{j}) - k_{2}^{2}(t-t_{j})^{2}] dt_{j}$$
  
= 1 + exp $\left[ -k_{N} \left( t - \frac{1}{k_{2}} \right) \right] \left( \frac{2k_{2}}{k_{N}} \right) \left[ 1 - \left( 1 + \frac{k_{2}}{k_{N}} \right) \times (1 - \exp(-k_{N}/k_{2})) \right]$  (13)

<sup>(15)</sup> Yoshioka, H.; Amita, K.; Hashizume, G. Netsu Sokutei 1984, 11, 115.

<sup>(16)</sup> Brown, W. E.; Dollimore, D.; Gallway, A. K. In *Comprehensive Chemical Kinetics*; Banford, C. H., Tipper, C.F. H., Eds.; Elsevier: Amsterdam, 1980, Vol. 22, p 45.



Figure 8. Arrhenius plots of  $k_N$ ,  $k_2$ , and k:  $k_N$ , rate constant for nucleation in Table V;  $k_2$ , rate constant for  $R_2$  reaction in Table V; k, rate constant for overall dehydration in Table II.

TABLE VI: Activation Energies and Preexponential Factors for Nucleation and R<sub>2</sub> Reaction Separated from Overall Dehydration

 reaction	E/kJ mol <sup>-1</sup>	$A/s^{-1}$	
nucleation	430.6	$3.73 \times 10^{49}$	
$R_2$	111.2	$3.40 \times 10^{9}$	

The rate constants  $k_N$  and  $k_2$  were determined as parameters for the best fit of eq 12 and 13 for the experimental  $\alpha(t)$  values by use of a nonlinear least-squares method. The values of  $k_{\rm N}$ ,  $k_2$ , and their ratios at various temperatures are shown in Table V.

The solid curve in Figure 7c displays the fraction of dehydration calculated on the basis of eq 12 and 13 by use of  $k_{\rm N}$  and  $k_2$  in Table V. The curve fits very well with the experimental  $\alpha(t)$  plots over a wide range of dehydration.

Figure 8 shows the Arrhenius plots of  $k_N$  and  $k_2$ . From this figure and Table V, it appears that the dehydration proceeds as a simple R<sub>2</sub> reaction at temperatures higher than 160 °C, whereas at 160 °C the dehydration is affected by the nucleation, and at 148 °C the rate of the nucleation becomes comparable to that of the  $R_2$  reaction. From this finding, it is illustrated that at temperatures below 160 °C  $\alpha(t)$  curves have a sigmoidal character and at higher temperatures they do not have a sigmoidal character. When the dehydration occurred at higher temperatures expected at the condition of  $k_N \gg k_2$ , eq 12 can be approximated by the equations

$$\alpha(t) = 2k_2t - k_2^2 t^2 \tag{14}$$

$$1 - (1 - \alpha(t))^{1/2} = k_2 t \tag{15}$$

Therefore, the dehydration apparently takes place as a natural two-dimensional phase boundary reaction, R<sub>2</sub>, at higher temperatures.

The activation energies and preexponential factors for the R<sub>2</sub> process and nucleation process of the present dehydration were obtained from the Arrhenius plots of Figure 8. Table VI shows their values. The values of activation energy and preexponential factors reported by the other investigators<sup>3,4</sup> are rather comparable to those of the  $R_2$  process. These reported values seem to be a mixture of those for the nucleation process and for the main process. On the other hand, the values obtained in this study are determined separately for the nucleation and for the main  $R_2$ process of the dehydration.

On the basis of the above finding, we conclude that the dehydration in a flowing atmosphere of dry nitrogen proceeds as a two-dimensional phase boundary reaction which is affected by the nucleation process especially at temperatures lower than ca. 160 °C, whereas the dehydration has a characteristic of the natural  $R_2$  reaction at temperatures higher than 160 °C.

Registry No. MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, 6150-88-5.

# Effect of Water Concentration on Photoreduction of Anthraquinone-2-sulfonate by 2-Propanol in Aqueous Acetonitrile Solution

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Irradiation of anthraquinone-2-sulfonate (AQS) in the presence of 2-propanol (0.08 M) in aqueous acetonitrile solution with nitrogen laser (337 nm) gave AQS radical anion (AQS<sup>--</sup>) in a yield depending very much on water content, the highest yield being obtained in the solution of 40-60 vol % water content. This is attributable to exponential increase with water concentration of the decay rate of triplet AQS and of the deprotonation rate of AQSH\* resulting from hydrogen abstraction of triplet AQS from 2-propanol. The dependence of these rates on water concentration was treated satisfactorily with Perrin's equation to give an average value of 3.3 Å for the radius of the solvation sphere surrounding triplet AQS and AQSH<sup>•</sup> in which a water molecule must exist to quench triplet AQS and to accept a proton from AQSH, respectively. Laser excitation and continuous irradiation gave apparently different  $pK_a$  values of AQSH<sup>•</sup>. The meaning of this observation was also discussed.

### Introduction

The photophysics and photochemistry of anthraquinones have been extensively studied over the past three decades<sup>1-19</sup> not only

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