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Kinetic Studies on the Dehydration of Calcium Oxalate Monohydrate

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The dehydration of $CaC_2O_4\cdot H_2O$ has been studied both isothermally and nonisothermally using thermogravimetric analysis. It was found that material which had aged for 1 year behaved differently from the original sample. Isothermal dehydration of the original material followed an R1 rate law and gave an activation energy of 60.1 ± 6.6 kJ mole^{-1}. The reaction appears to be independent of particle size. Analysis of the data from nonisothermal experiments gave about equally good results with R2 and R3 rate laws. The isothermal dehydration of aged $CaC_2O_4\cdot H_2O$ followed R1, A2, or A3 rate laws and appears to have an activation energy of 118 ± 15 kJ mole^{-1}. Sample to sample variation between runs is similar to that of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$. © 1993 Academic Press, Inc.

Introduction

There is an intense interest in kinetic studies on solid state processes (*1–3*). It is generally believed that isothermal methods are preferable to nonisothermal ones (*4*) although such a conclusion may be unwarranted at this time (*5, 6*). Since the work of Freeman and Carroll (*7*), the dehydration of $CaC_2O_4\cdot H_2O$ has been the subject of numerous kinetic studies and it is probably the model reaction for testing kinetic methods (*6*). Coats and Redfern used this reaction as a model for the application of a data analysis method based on the rate law

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n e^{-E/RT}, \qquad (1)$$

where the symbols have their usual meanings (*8*). It was reported that $n = \frac{2}{3}$ gave the best fit with a corresponding activation energy of 21.7 kcal mole^{-1}. An order of $\frac{1}{2}$ has also been suggested (*9*). Nair and Ninan utilized the dehydration of $CaC_2O_4\cdot H_2O$ in a study of the effects of heating rate and sample mass (*10*). Data analysis was carried out using the Coats and Redfern (*8*), MacCallum and Tanner (*11*), and Horowitz and Metzger (*12*) methods which are all based on the rate law shown in Eq. (1). A value of $n = 0.65$ was reported for the dehydration. The apparent activation energy and preexponential factor were found to vary substantially with heating rate and sample mass. There have been numerous other studies on the reaction (*6*).

Tanaka *et al.* have provided the most detailed study of this reaction (*6*). These workers used both isothermal and nonisothermal techniques for samples heated in air and analyzed the data using a range of rate laws. It was reported that kinetics of the dehydration process is independent of particle size and that the reaction follows an Avrami A2 rate law (actually 1.984 ± 0.056) or a receding area R2 rate law (actually 2.018 ± 0.053). However, the values of n for the Rn rate law ranged from 1.69 to 2.78 and the values of m for the Am rate law varied from 1.47 to 2.44 when numerous runs in the temperature range 140.6–165.1°C were considered. The nature of sample to sample variation in samples stud-

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ied under identical conditions was not reported.

In spite of the large number of previous studies, the dehydration of $CaC_2O_4 \cdot H_2O$ is still not completely understood. The nature of sample to sample variations is of considerable interest (*5*) and currently available thermoanalytical instruments are enormously better than those available a comparatively short time ago. Accordingly, we have studied the dehydration of $CaC_2O_4 \cdot H_2O$ using both isothermal and nonisothermal techniques in an effort to understand some of these effects.

Experimental

The $CaC_2O_4 \cdot H_2O$ was obtained by the slow addition with constant stirring of a hot solution of $CaCl_2$ to a heated solution of $(NH_4)_2C_2O_4$ in water. The solid product was separated by filtration and allowed to dry. Prior to use, the solid was ground using a mortar and pestle. Microscopic examination of the particles showed them to be spherical or oval in general shape.

Kinetic studies were carried out using a Perkin–Elmer TGA-7 thermogravimetric system under the control of a TAC-7 controller using IBM-PC software. Samples ranged from 8.0 to 14.0 mg and they were studied in a nitrogen atmosphere using a flow rate of 40 cm^3 min^{-1}. In the nonisothermal experiments, hearing rates of 2.5, 5.0, and 10.0°C min^{-1} were used. The (α, T) data were analyzed by the procedure of Reich and Stivala (*13*). Isothermal experiments in the range 110–130°C were carried out and the (α, t) data were analyzed according to 17 different rate laws.

Results and Discussion

The original sample of $CaC_2O_4 \cdot H_2O$ was studied within a few weeks of its preparation. After the kinetic studies had been completed, the sample was stored in a closed container. Approximately 1 year later, a portion of the sample was removed, placed in hexane, and subjected to ultrasound. This experiment was performed to fragment the sample so that it could be determined if this treatment affected the kinetics of dehydration subsequently. The TGA curve was quite different from that of the original sample and it was initially believed that fragmentation using ultrasound caused the reaction to be different from that of material not so treated. However, TG analysis of the unsonicated material which had been stored for approximately 1 year was performed. It was found that the TGA curve for the aged material was different from that of the original specimen and that it was virtually identical to that of the aged sample which had been sonicated. Several replications of this procedure showed that no effect on the kinetics of dehydration was produced by treating the material with ultrasound, but the observed effect was due to the aging of the $CaC_2O_4 \cdot H_2O$ for about 1 year. Microscopic examination of the sample before and after treatment with ultrasound showed that a drastic reduction in particle size occurred as a result of the treatment with ultrasound. However, the kinetic behavior was unaltered, in accordance with previous reports that the reaction is not affected by particle size (*6*). The appearance of the aged sample was not different from that of the original sample.

While it has previously been observed that the dehydration of $CaC_2O_4 \cdot H_2O$ is not affected by particle size, the observed effect of aging has not been reported. It has long been known that the history of a solid sample may affect the kinetics of its subsequent reactions (*1*, *12*). Figure 1 shows typical TGA curves for dehydration of the freshly prepared $CaC_2O_4 \cdot H_2O$ and a sample that has been stored for approximately 1 year. These curves show that the aged material loses water at a somewhat lower temperature and in a narrower temperature range than the original sample. Because of this effect, we discuss the kinetics of the dehydration of the two materials separately.

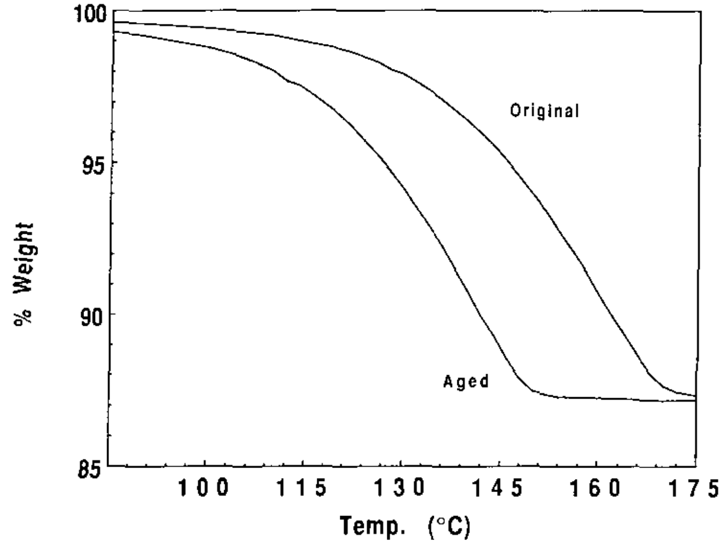

FIG. 1. Typical TGA curves for the dehydration of the original and aged $CaC_2O_4 \cdot H_2O$.

Original $CaC_2O_4 \cdot H_2O$

The dehydration of $CaC_2O_4 \cdot H_2O$ was studied both isothermally and nonisothermally. Typical curves showing α as a function of time for the isothermal experiments are shown in Fig. 2. The reaction could be conveniently studied in the range 110–130°C. The portion of the curves $0.1 < \alpha < 0.9$ was selected for analysis by means of the rate laws shown in Table I. Table II shows the results of this analysis. The best fitting and second best fitting rate laws are shown since there was a very small difference in goodness of fit in some cases.

It can be seen that the R1: $1 - (1 - \alpha)^{2/3}$ rate law gave the best fit in 10 of the 15 runs and the second best fit in three cases. The

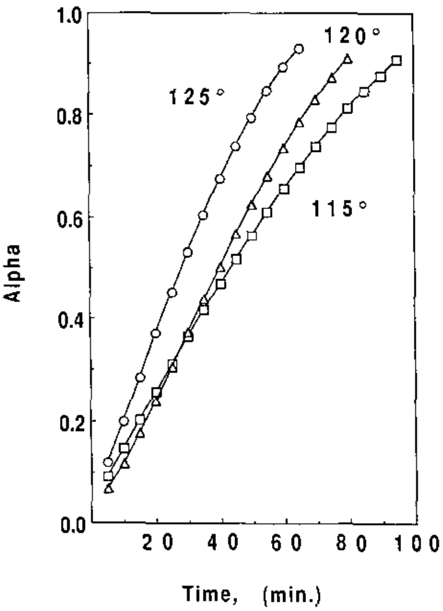

FIG. 2. Typical plots of α vs time for the dehydration of the original $CaC_2O_4 \cdot H_2O$.

TABLE I

RATE LAWS USED TO FIT THE ISOTHERMAL KINETIC DATA

	$g(\alpha)$		$g(\alpha)$
F1	$-\ln(1 - \alpha)$	F2	$1/(1 - \alpha)^{a}$
A1.5	$[-\ln(1 - \alpha)]^{2/3}$	F3	$[1/(1 - \alpha)]^{2a}$
A2	$[-\ln(1 - \alpha)]^{1/2}$	D2	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
A3	$[-\ln(1 - \alpha)]^{1/3}$	D3	$[1 - (1 - \alpha)^{1/3}]^2$
A4	$[-\ln(1 - \alpha)]^{1/4}$	D1	α^2
R1	$1 - (1 - \alpha)]^{2/3a}$	R2	$1 - (1 - \alpha)^{1/2}$
R3	$1 - (1 - \alpha)]^{1/3}$	P1	$\alpha^{1/2}$
B1	$\ln[\alpha/(1 - \alpha)]^{a}$	E1	$\ln \alpha^{a}$
D4	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$		

[a] Not tested in the Reich and Stivala method. See M. E. Brown and C. A. R. Phillpots, *J. Chem. Educ.* **55**, 556 (1978) for a description of these processes.

TABLE II

RATE LAWS FOR ISOTHERMAL DEHYDRATION OF THE ORIGINAL $CaC_2O_4 \cdot H_2O$

Temp. (°C)	Run	Best fit		Second best fit	
		Rate law	r	Rate law	r
110	1	$1 - (1 - \alpha)^{2/3}$	0.99856	$[-\ln(1 - \alpha)]^{1/2}$	0.99842
	2	$1 - (1 - \alpha)^{2/3}$	0.99997	$[-\ln(1 - \alpha)]^{1/2}$	0.99990
	3	$1 - (1 - \alpha)^{2/3}$	0.99999	$[-\ln(1 - \alpha)]^{1/2}$	0.99989
115	1	$1 - (1 - \alpha)^{2/3}$	0.99999	$1 - (1 - \alpha)^{1/2}$	0.99930
	2	$1 - (1 - \alpha)^{1/2}$	0.99999	$[-\ln(1 - \alpha)]^{2/3}$	0.99938
	3	$1 - (1 - \alpha)^{2/3}$	0.99995	$[-\ln(1 - \alpha)]^{1/2}$	0.99979
120	1	$1 - (1 - \alpha)^{2/3}$	0.99981	$[-\ln(1 - \alpha)]^{1/2}$	0.99970
	2	$1 - (1 - \alpha)^{2/3}$	0.99989	$[-\ln(1 - \alpha)]^{1/2}$	0.99987
	3	$1 - (1 - \alpha)^{1/2}$	0.99982	$1 - (1 - \alpha)^{2/3}$	0.99973
125	1	$1 - (1 - \alpha)^{2/3}$	0.99952	$[-\ln(1 - \alpha)]^{1/2}$	0.99911
	2	$[-\ln(1 - \alpha)]^{1/4}$	0.99918	$\ln[\alpha/(1 - \alpha)]$	0.99837
	3	$[-\ln(1 - \alpha)]^{1/3}$	0.99994	$1 - (1 - \alpha)^{2/3}$	0.99940
130	1	$[-\ln(1 - \alpha)]^{1/2}$	0.99975	$1 - (1 - \alpha)^{2/3}$	0.99971
	2	$1 - (1 - \alpha)^{2/3}$	0.99994	$[-\ln(1 - \alpha)]^{1/2}$	0.99981
	3	$1 - (1 - \alpha)^{2/3}$	0.99998	$[-\ln(1 - \alpha)]^{1/2}$	0.99993

A2: $[-\ln(1 - \alpha)]^{1/2}$ rate law was the best fitting in only one case but provided the second best fit in nine of the 15 cases. Consequently, with regard to the isothermal experiments, the R1 rate law was considered as the most appropriate one. Table III shows the rate constants obtained by fitting the α, t data to the R1 rate law. These rate constants were correlated by means of the Arrhenius equation (see Fig. 3) to yield an activation energy of 60.1 ± 6.6 kJ mole^{-1} and a value for ln A (min^{-1}) of 13.97. Coats and Redfern reported an activation energy of 90.8 kJ mole^{-1} (*8*). Tanaka *et al.* reported an activation energy of 118.4 ± 1.1 kJ mol^{-1} and a ln A (sec^{-1}) of 10.97 ± 0.13. However, a temperature range of 140.6–165.1°C was used in that study and when the data were fitted to an R*n* type rate law, *n* was treated as a variable parameter and the rate law was given as R2.018. Also, while reactions were carried out at temperatures in the specified range, no mention was given of sample to sample variation between runs at the same temperature and the indicated *n* ranged from 1.69 to 2.78. In accordance with the present work which shows A2 as the next most likely rate law, an A1.904 rate law gave virtually an identical fit to the data (*6*). Thus, it appears that the dehydration of $CaC_2O_4 \cdot H_2O$ can be adequately modeled by an R1 or an A2 rate law.

TABLE III

RATE CONSTANTS FOR THE ISOTHERMAL DEHYDRATION OF THE ORIGINAL $CaC_2O_4 \cdot H_2O$ (R1 RATE LAW)

Temperature (°C)	$10^2 \times k$ (min^{-1})^a
110	0.668 ± 0.060
115	1.030 ± 0.209
120	1.187 ± 0.237
125	1.546 ± 0.190
130	1.763 ± 0.098

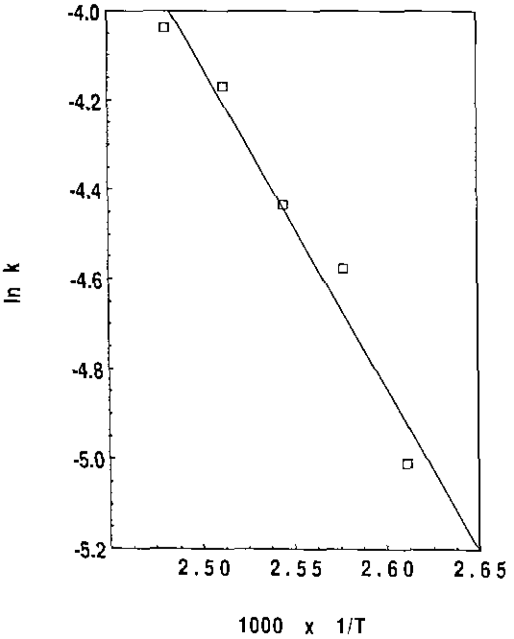

FIG. 3. Arrhenius plot for the dehydration of the original $CaC_2O_4 \cdot H_2O$.

Nonisothermal studies on the original $CaC_2O_4 \cdot H_2O$ were carried out using heating rates of 2.5, 5.0, and 10.0°C min^{-1} with 5, 4, and 5 runs being made, respectively. Since the Reich and Stivala procedure (*13*) makes use of data from two runs at heating rates differing by a factor of two, 20 combinations of the data from the 2.5 and 5.0°C min^{-1} runs were made and 20 combinations of the data from the 5.0 and 10°C min^{-1}

TABLE IV

RATE LAWS INDICATED FOR THE NONISOTHERMAL DEHYDRATION OF THE ORIGINAL $CaC_2O_4 \cdot H_2O$

Rate law	Best fit frequency	Second best fit frequency
10 and 5°C min^{-1} runs		
R2: $1 - (1 - \alpha)^{1/2}$	9	8
R3: $1 - (1 - \alpha)^{1/3}$	5	11
A1.5: $[-\ln(1 - \alpha)]^{2/3}$	4	—
F1: $-\ln(1 - \alpha)$	2	1
5 and 2.5°C min^{-1} runs		
R3: $1 - (1 - \alpha)^{1/3}$	9	6
R2: $1 - (1 - \alpha)^{1/2}$	4	12
A1.5: $[-\ln(1 - \alpha)]^{2/3}$	4	—
F1: $-\ln(1 - \alpha)$	2	—
D1: α^2	2	—

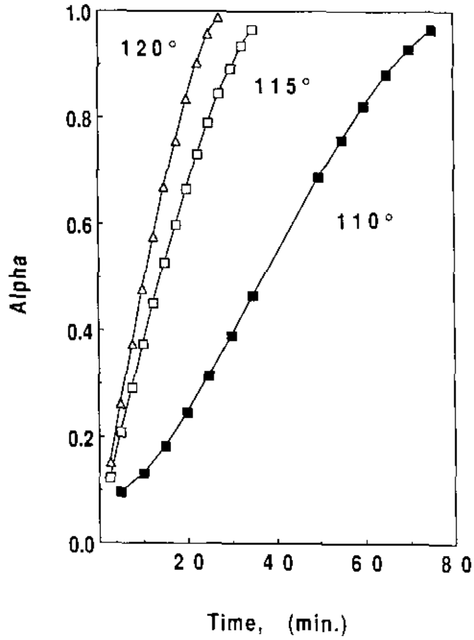

FIG. 4. Typical plots of α vs time for the dehydration of aged $CaC_2O_4 \cdot H_2O$.

were also prepared. Analysis of these data by the Reich and Stivala procedure gave the results shown in Table IV.

The data shown in Table IV indicate that R2 and R3 rate laws give the best or second best fit for dehydration of the original $CaC_2O_4 \cdot H_2O$ with almost identical frequencies. It should be pointed out that while the Reich and Stivala method tests 12 of the rate laws shown in Table I, it does not fit the data to the R1 rate law. Consequently, it is possible that the R1 rate law is the most appropriate for this reaction although a very good fit to the data is provided by the R2 or R3 rate laws. The A1.5 rate law also gave the best fit in certain cases. When all the data are considered, it is apparent that the dehydration of the original $CaC_2O_4 \cdot H_2O$ is adequately modeled by an R*n* (n = 1–2) or an A*m* rate law. However, the freshly prepared $CaC_2O_4 \cdot H_2O$ used in this work gave a greatly different activation energy from that previously reported by Tanaka *et al.* (*6*).

Aged $CaC_2O_4 \cdot H_2O$

Isothermal studies on aged $CaC_2O_4 \cdot H_2O$ showed significant differences from those on the original sample. Typical α, t curves are shown in Fig. 4. The dehydration reaction was studied at 110, 115, and 120°C with the results obtained shown in Table V when the α, t data were fitted to the 17 rate laws. The reaction was studied only to 120°C because it occurs much faster than that of the original sample. It can be seen from these data that there was greater variation in the indicated rate laws but R1, A2, and A3 accounted for seven best fits and five second best fits of the eight cases. These results are

TABLE V

RATE LAWS FOR ISOTHERMAL DEHYDRATION OF AGED $CaC_2O_4 \cdot H_2O$

Temp. (°C)	Run	*Best fit* Rate law	*Best fit* r	*Second best fit* Rate law	*Second best fit* r
110	1	$[-\ln(1 - \alpha)]^{1/4}$	0.99985	$[-\ln(1 - \alpha)]^{1/3}$	0.99974
	2	$[-\ln(1 - \alpha)]^{1/3}$	0.99976	$[-\ln(1 - \alpha)]^{1/4}$	0.99957
115	1	$[-\ln(1 - \alpha)]^{1/3}$	0.99949	$\ln[\alpha/(1 - \alpha)]$	0.99933
	2	$1 - (1 - \alpha)^{2/3}$	0.99998	$[-\ln(1 - \alpha)]^{1/2}$	0.99979
	3	$1 - (1 - \alpha)^{2/3}$	0.99980	$[-\ln(1 - \alpha)]^{1/3}$	0.99968
120	1	$[-\ln(1 - \alpha)]^{1/2}$	0.99990	$1 - (1 - \alpha)^{2/3}$	0.99989
	2	$1 - (1 - \alpha)^{2/3}$	0.99997	$[-\ln(1 - \alpha)]^{1/2}$	0.99985
	3	$[-\ln(1 - \alpha)]^{1/3}$	0.99980	$\ln[\alpha/(1 - \alpha)]$	0.99952

TABLE VI

RATE LAWS INDICATED FOR THE NONISOTHERMAL DEHYDRATION OF AGED $CaC_2O_4 \cdot H_2O$

Rate law	Best fit frequency	Second best fit frequency[a]
10 and 5°C min^{-1} runs		
A1.5: $[-\ln(1 - \alpha)]^{2/3}$	3	—
F1: $-\ln(1 - \alpha)$	3	—
R3: $1 - (1 - \alpha)^{1/3}$	1	3
*D*1: α^2	2	—
R2: $1 - (1 - \alpha)^{1/2}$	—	2
A2: $[-\ln(1 - \alpha)]^{1/2}$	—	2
5 and 2.5°C min^{-1} runs		
A1.5: $[-\ln(1 - \alpha)]^{2/3}$	4	—
A2: $[-\ln(1 - \alpha)]^{1/2}$	—	4
D1: α^2	3	—
F1: $-\ln(1 - \alpha)$	1	1
D3: $[1 - (1 - \alpha)^{1/3}]^2$	1	0

[a] Isolated runs gave second best fit with other rate laws.

within the normal distribution of results due to sample to sample variation (*5, 6*). For the determination of the rate constants, the correct rate law was assumed to be R1. Rate constants of $(1.378 \pm 0.078) \times 10^{-2}$), $(1.902 \pm 0.086) \times 10^{-2}$), and $(3.379 \pm 0.046) \times 10^{-2}$) min^{-1} were obtained for reactions at 110, 115, and 120°C, respectively. These rate constants yield an activation energy of 118 ± 15 kJ $mole^{-1}$ which is identical to that reported by Tanaka *et al.* (*6*).

While the rate law followed for the dehydration of aged $CaC_2O_4 \cdot H_2O$ appears to be slightly affected by the aging process, the activation energy is drastically different. Microscopic examination of the original material and that which had aged showed no obvious damage or changes in crystal structure.

Nonisothermal studies were conducted on the aged $CaC_2O_4 \cdot H_2O$ at heating rates of 2.5, 5.0, and 10.0°C min^{-1} with three runs being made at each heating rate. Thus, there are nine combinations of runs to be analyzed from the 2.5 and 5.0°C min^{-1} runs and a like number from the 5.0 and 10.0°C min^{-1} runs. Analysis of these data by the Reich and Stivala method gave the results shown in Table VI.

It can be seen that considerable variation occurred when the data from the nonisothermal experiments were considered. There was no apparent reason for this variation but it is more extreme than most sample to sample variations (*5*). When all the data are considered, the A1.5 rate law was most frequently selected as the best fitting one. This is in accordance with earlier studies (*6*) and the behavior of the original sample used in this work.

In this work, we have studied a reaction that has been studied by many workers over a long period of time (*6*). Most of the earlier studies used data analysis methods which could not identify the most likely rate laws. However, it appears that the aging of $CaC_2O_4 \cdot H_2O$ has a pronounced effect on its dehydration. This may explain some of the widely differing results obtained by many workers who were unaware of this phenomenon.

The reactivity of aged solids is frequently lower than that of freshly prepared materials owing to the removal of defects or nuclei by annealing. However, in some cases the behavior is the opposite, as is observed here. Nucleation can be caused by physical damage or infection of the surface by addition of partially dehydrated product (*14*). If the loss of a very small amount of water from the surface of the $CaC_2O_4 \cdot H_2O$ has occurred during aging, it is possible that local regions where CaC_2O_4 is present have become nucleated in this way. It is also possible that the nuclei in the freshly prepared and aged materials are of different types. Also, a large preexponential factor is consistent with a high energy product which is amorphous or microcrystalline (*14*). From the isothermal studies, the ln *A* is 30.9 (*A* in min^{-1}) for the aged material and 14.0 for the freshly prepared material. While the data for dehydration of the aged material is not extensive, this large difference suggests submicroscopic physical damage that not only enhances the dehydration but also results in a product having different crystallinity than the original material.

This work has shown that the dehydration of $CaC_2O_4 \cdot H_2O$ is best considered as an Rn (n = 1–3) or an Am (m = 1.5–2) process which agrees with earlier work (*6*). It has also been shown that the nature of sample to sample variations requires that a significant number of runs be made in order to identify the correct rate law (*5*), a fact not always considered by many workers.

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