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# Kinetics and mechanism of the dehydration of ammonium oxalate monohydrate

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## Abstract

The dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$ has been studied by isothermal and non-isothermal TG. From the non-isothermal experiments, the best-fitting rate law appears to be A1.5, A3, or D3. Data from isothermal experiments gave the best fit with an R2 rate law. A value of 73 kJ mol$^{-1}$ was found for the activation energy, and the nature of the variation between runs was explored.

## INTRODUCTION

Kinetics studies on solid state reactions are conveniently carried out using both isothermal and non-isothermal techniques. While an enormous range of materials has been studied, definitive, comparative studies on many systems are lacking. The analysis of data, in view of sample-to-sample variations, is a non-trivial problem. Analysis of data from non-isothermal studies is best carried out using the procedure of Reich and Stivala [1]. Model reactions, such as the dehydration of $CaC_2O_4 \cdot H_2O$, have been extensively studied [2]. Recently, we have studied the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ using both isothermal and non-isothermal methods [3]. It was found that the reaction is best considered as following an Avrami A1.5 rate law and that older methods based on the rate law

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

give completely erroneous results [3, 4]. This occurs because of the fact that many of the rate laws applicable to solid state reactions, e.g. Avrami, diffusion control, etc., cannot be represented by the integrated from of eqn. (1). Consequently, many of the older studies reported results which must be considered as suspect owing to the data analysis procedures. In an

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early study, the dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$ was studied isothermally and non-isothermally and found to give a reasonable fit to the $(\alpha, t)$ data using a zero-order rate law [5]. An activation energy of 87.7 kJ $mol^{-1}$ was indicated. Using the method of Coats and Redfern [6] with non-isothermal TG data, an index of reaction of 2/3 and an activation energy of 138 kJ $mol^{-1}$ were found [6]. In view of the advances in instrumentation and data analysis procedures, we have studied the dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$ using both isothermal and non-isothermal TG.

## EXPERIMENTAL

Reagent grade $(NH_4)_2C_2O_4 \cdot H_2O$ was used without further treatment.

TG studies were carried out using a Perkin–Elmer TGA-7 with a TAC-7 thermal analysis controller. Samples were heated from 30 to 300°C at rates of 2.5, 5.0, and 10.0°C $min^{-1}$ in a dry nitrogen atmosphere with a flow rate of 30 $cm^3$ $min^{-1}$. At least four runs were made at each heating rate. Isothermal experiments were carried out at 55, 60, 65, 70, and 75°C. From the percent change in mass, the value of $\alpha$ was detemined as a function of time or temperature.

Kinetic analysis of data from the non-isothermal experiments was carried out using the procedure of Reich and Stivala [1]. Analysis of the data from isothermal runs was carried out by fitting the $(\alpha, t)$ data to 17 rate laws [3] using a computer program written in BASIC.

## RESULTS AND DISCUSSION

The dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$ takes place smoothly in a single step between 90 and 130°C. A typical TG curve is shown in Fig. 1.

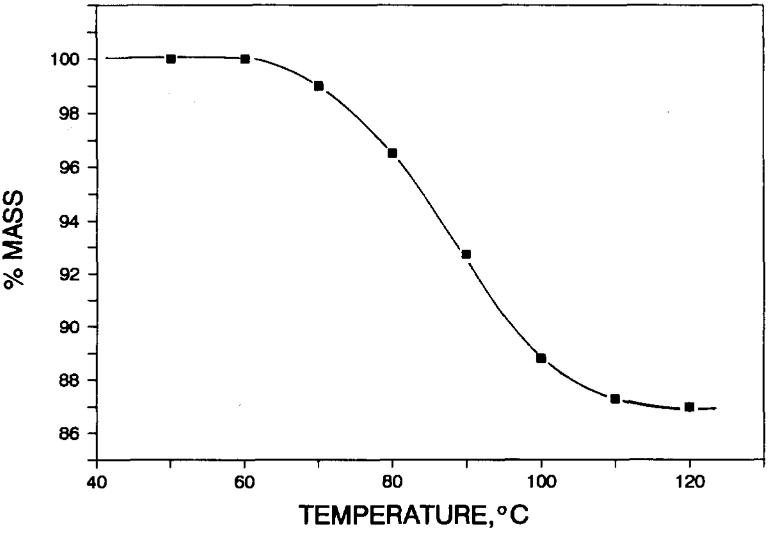

Fig. 1. TG curve for the dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$.

TABLE 1

Results of fitting the data from non-isothermal experiments to rate laws using the Reich and Stivala method in 29 combinations

| Best fit | | Second-best fit | |
|---|---|---|---|
| Rate law | Frequency | Rate law | Frequency |
| A1.5 | 6 | P3 | 6 |
| A3 | 6 | D4 | 5 |
| D3 | 6 | A2 | 4 |
| A2 | 4 | R2 | 4 |
| F1 | 3 | R3 | 3 |
| A4 | 2 | A4 | 3 |
| P3 | 1 | A1.5 | 2 |
| R2 | 1 | F1 | 1 |

It is generally a problem that when a solid state reaction is studied under non-isothermal conditions at different heating rates, only a limited number of $\alpha$ values can be determined at specific temperatures. This problem prevented the application of the Reich and Stivala analysis to the same sets of $\alpha$ values obtained at heating rates of 10 and 5°C $\min^{-1}$ as were used at 5 and 2.5°C $\min^{-1}$. For example, the runs at 10 and 5°C $\min^{-1}$ were analyzed in the temperature range of 91–103°C, while those at 5 and 2.5°C $\min^{-1}$ were analyzed in the range 83–95°C.

When the Reich and Stivala procedure was used to analyze the data

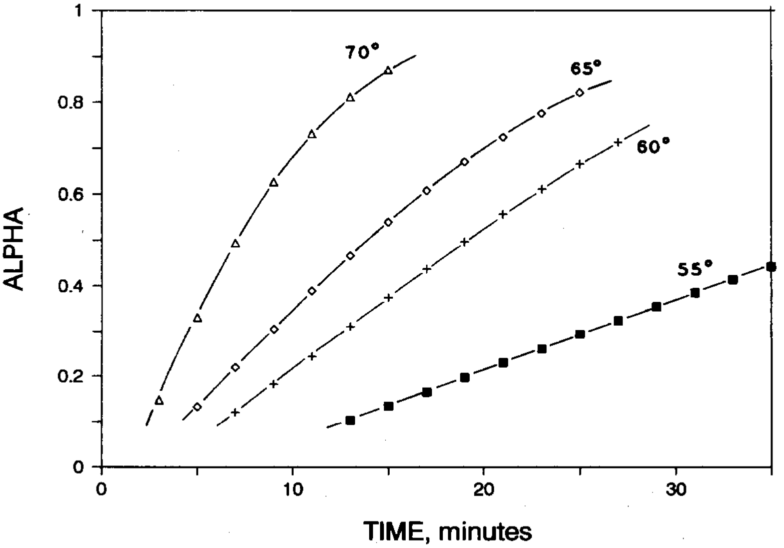

Fig. 2. Typical plots of $\alpha$ versus time for the dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$.

TABLE 2

Results of fitting ($\alpha$, $t$) data from isothermal studies to 17 rate laws

| Temp. (°C) | Run | Best fit | | Second-best fit | |
|---|---|---|---|---|---|
| | | Rate law | $r$ | Rate law | $r$ |
| 55 | 1 | R2 | 0.9997 | A2 | 0.9996 |
| | 2 | R2 | 0.9997 | A1.5 | 0.9996 |
| | 3 | R2 | 0.9998 | A2 | 0.9996 |
| | 4 | R3 | 0.9999 | A1.5 | 0.9998 |
| | 5 | A1.5 | 0.9999 | R1 | 0.9997 |
| 60 | 1 | R2 | 0.9998 | A2 | 0.9995 |
| | 2 | R1 | 0.9999 | A2 | 0.9996 |
| | 3 | A1.5 | 0.9999 | R1 | 0.9999 |
| | 4 | R1 | 0.9998 | A2 | 0.9998 |
| | 5 | A1.5 | 0.9999 | R3 | 0.9997 |
| 65 | 1 | R3 | 0.9999 | A1.5 | 0.9998 |
| | 2 | R3 | 0.9999 | A1.5 | 0.9994 |
| | 3 | R2 | 0.9999 | A1.5 | 0.9995 |
| | 4 | R3 | 0.9995 | A1.5 | 0.9988 |
| 70 | 1 | R3 | 0.9999 | A1.5 | 0.9998 |
| | 2 | R2 | 0.9999 | A2 | 0.9996 |
| | 3 | R2 | 0.9999 | A2 | 0.9994 |
| | 4 | F1 | 0.9996 | D1 | 0.9986 |
| | 5 | R3 | 0.9996 | A1.5 | 0.9994 |
| 75 | 1 | R2 | 0.9999 | A2 | 0.9997 |
| | 2 | R2 | 0.9998 | A2 | 0.9997 |
| | 3 | R2 | 0.9998 | R1 | 0.9997 |
| | 4 | R3 | 0.9995 | A1.5 | 0.9990 |
| | 5 | R2 | 0.9999 | A1.5 | 0.9994 |
| | 6 | R2 | 0.9999 | A2 | 0.9994 |
| | 7 | R3 | 0.9999 | A1.5 | 0.9999 |
| | 8 | R3 | 0.9999 | A1.5 | 0.9997 |

from non-isothermal runs, there was a considerable variation as to the best-fitting rate law. Table 1 shows the results obtained from the analysis of the data. Both the best-fitting and the second-best-fitting rate law are shown because in some cases there is very little difference in the standard error of estimate (SEE).

While several rate laws were indicated as the best-fitting ones in several of the 29 combinations of runs analyzed, the most likely possibilities are A1.5, A3, and D3. Each of these rate laws was indicated as giving the best fit in six cases. The A2 rate law gave the best fit in four cases. These results are not surprising in view of the similar mathematical form of some of these rate laws [3]. A distinction between these possible rate laws is not possible given the sample-to-sample variation and the sensitivity of the data analysis technique.

TABLE 3

Rate laws indicated for isothermal dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$ during 28 runs

| Best fit | | Second-best fit | |
|---|---|---|---|
| Rate law | Frequency | Rate law | Frequency |
| R2 | 12 | A1.5 | 13 |
| R3 | 10 | A2 | 10 |
| A1.5 | 3 | R1 | 3 |
| R1 | 2 | D2 | 1 |
| F1 | 1 | R3 | 1 |

TABLE 4

Rate constants for the isothermal dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$ using an R2 rate law

| Temperature (°C) | $k$ ($min^{-1}$) |
|---|---|
| 55 | 0.011 ± 0.002 |
| 60 | 0.018 ± 0.003 |
| 65 | 0.024 ± 0.004 |
| 70 | 0.035 ± 0.006 |
| 75 | 0.054 ± 0.010 |

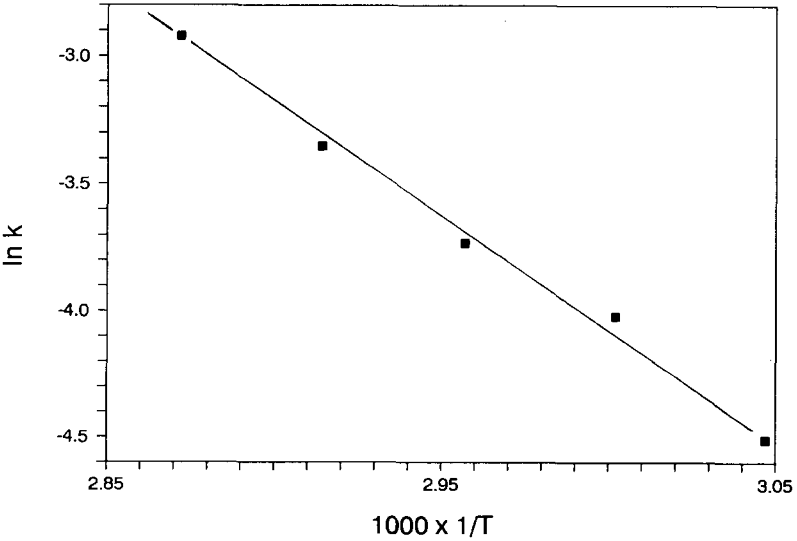

Fig. 3. Arrhenius plot for the dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$.

Figure 2 shows typical rate plots for the isothermal dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$. Table 2 shows the results of fitting the $(\alpha, t)$ data to the 17 rate laws tested [3] with both the best-fitting and second-best-fitting cases shown. It can be seen that in almost every case, two rate laws give correlation coefficients which are about identical. In some cases, removal of one data point from the calculation can reverse the roles of the two rate laws [7, 8]. Table 3 summarizes the frequency of the best-fitting and second-best-fitting rate laws for the data from isothermal experiments. It is seen that the R2 and R3 rate laws gave the best fit in 22 of the 28 runs, with A1.5 and A2 giving the second-best fit in 23 of the 28 runs. However, in every case where R2 or R3 rate laws gave the best fit to the data, A1.5 or A2 was the second-best case and the largest difference in correlation coefficient was 0.0005. If the total (best fitting and second-best fitting) number of cases is considered, the Avrami rate laws are indicated in 26 instances and the receding area or volume rate laws in 23 instances. It is impossible to say in any definite way what the actual mechanism is on the basis of fitting data to rate laws.

For purposes of calculation of activation energy, the R2 rate law was presumed to be most appropriate and the rate constants obtained are shown in Table 4. Treatment of these data by means of the Arrhenius equation yields an activation energy of 73 kJ mol$^{-1}$ (Fig. 3). This value is not very close to the value of 87.7 kJ mol$^{-1}$ reported earlier. It is drastically different from the value of 138 kJ mol$^{-1}$ obtained using the Coats and Redfern method [5].

It is readily apparent that kinetic studies on solid state reactions can be expected to yield useful data only if certain precautions are kept in mind. First, a reasonable number of runs must be made so that sample-to-sample variations can be minimized. Second, data of highest quality must be analyzed using comprehensive procedures that test a wide range of rate laws [2, 3]. Only then can a rate law be determined with any degree of certainty. The dehydration of $(NH_4)_2C_2O_4 \cdot H_2O$ provides a useful model reaction for testing kinetic methods.

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