

KINETIC STUDIES ON THE DEHYDRATION OF AMMONIUM OXALATE MONOHYDRATE

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ABSTRACT

The dehydration of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ has been studied using both isothermal techniques and thermogravimetric analysis (TGA). For the isothermal process, the activation energy was found to be 87.7 kJ/mole and the data provide the best fit to a zero order rate law. For the TGA curves, the best fit is found for a 2/3 order and the activation energy of 138 kJ/mole was found. These results are discussed in comparison with those for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ which is a commonly used standard for solid state kinetics.

INTRODUCTION

The kinetic study of solid state reactions by nonisothermal techniques is currently a topic receiving a great deal of attention (Brown and Phillpotts, 1978). The use of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to study kinetics by non-isothermal techniques has resulted in a great body of literature in this area. A sizeable number of kinetic equations are employed for different systems.

The applicability of the numerous kinetic equations has been tested most often by studying the dehydration of calcium oxalate monohydrate (Freeman and Carroll, 1958; Horowitz and Metzger, 1963; Coats and Redfern, 1964; Nair and Ninan, 1978). This process has an activation energy of about 90 kJ/mole and obeys a reaction order of about 2/3. Because the dehydration of calcium oxalate monohydrate is often used as a model for solid state reactions, we have studied the kinetics of dehydration of ammonium oxalate monohydrate as an alternative. This report describes the results of isothermal and TGA studies on that compound.

EXPERIMENTAL

The ammonium oxalate monohydrate used in this work was reagent grade material from Matheson, Coleman, and Bell, and it was used without further treatment. Isothermal kinetic studies were carried out as previously described (House and Strode, 1968; Strode and House, 1972). The extent of the dehydration process was determined from the mass loss from several samples heated in an oil bath maintained at constant temperature. The observed mass losses were used to calculate α , the fraction of the reaction complete. TGA results were obtained using a Perkin-Elmer Thermogravimetric Analysis System, TGS-2. Both mass loss and first derivative curves were obtained. Samples were heated at 10 °C/min (B) in a dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

Figure 1 shows the TGA and first derivative curves for $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

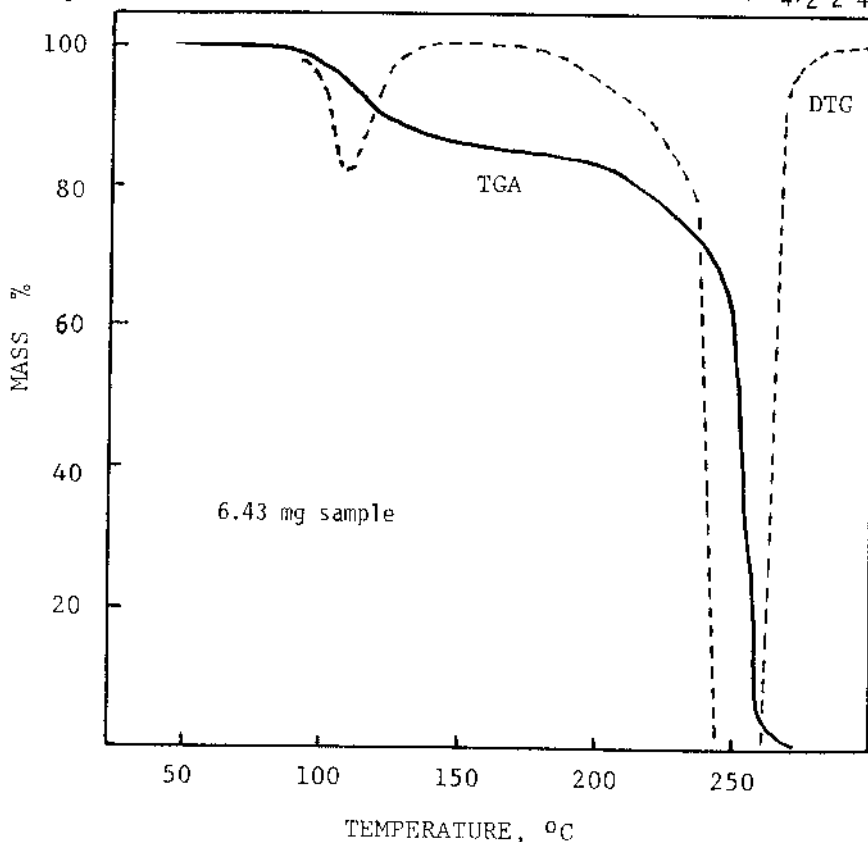


Figure 1. TGA and first derivative curves for ammonium oxalate monohydrate.

Dehydration occurs in the region of 100-125 °C. This segment of the curve has been analyzed by us using the equation derived by Coats and Redfern (1964),

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (1)$$

where n is the reaction order, α is the fraction of the reaction complete, E is the activation energy, T is the absolute temperature, A is the frequency factor, and R is the molar gas constant. A recent comparison showed that other kinetic equations appear to have no advantage over this equation (Nair and Ninan, 1978). For solid state reactions, there is theoretical justification for reaction orders of 0, 1/2, 2/3, and 1. However, the optimum order for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was previously reported as 0.71 (Coats and Redfern, 1964), although the most recently used value is 0.65 (Nair and Ninan, 1978). Accordingly, Equation (1) was used to test these assumed kinetic orders using a linear regression analysis. These results are shown in Table 1.

Table 1. Kinetic parameters for the dehydration of ammonium oxalate monohydrate calculated using the Coats and Redfern equation (α ranges from 0.14 to 0.75 in each case).

<u>Assumed Order</u>	<u>Ea, kJ/mole</u>	<u>Intercept</u>	<u>A, sec⁻¹</u>	<u>Correlation Coefficient</u>
0	116	27.81	2.93×10^{15}	0.982
1/2	134	29.49	1.80×10^{16}	0.990
2/3	141	31.56	1.48×10^{17}	0.992
0.71	166	39.53	5.07×10^{20}	0.979
3/4	145	32.74	5.00×10^{16}	0.980
1	98.8	19.72	7.74×10^{11}	0.983

The data shown in Table 1 indicate that the best fit of the data is provided by a reaction order of 2/3, although the relationship is still not perfectly linear. Since an order of 0.71 had provided the optimum fit to the data for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, that value was tried here (Coats and Redfern, 1964). The fit which was obtained was not, however, as good as that provided by a 2/3 order equation. From the data shown in Table 1, it is readily apparent that any order from 1/2 to 3/4 provides about the same activation energy and correlation coefficient when the appropriate function, $f(\alpha)$ is plotted against $1/T$.

For a reaction taking place in the solid state, the general kinetic equation,

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

can readily be integrated to provide rate laws for any desired order of reaction. Probably the most frequently encountered expression is the first order one,

$$-\ln(1 - \alpha) = kt \quad (3)$$

This rate law was used to test the kinetic data obtained from the isothermal reactions carried out in this work. However, it was found that this rate law did not fit the data, but rather a good fit was provided by the zero order rate law, $\alpha = kt$. Typical plots of α vs. time are shown in Figure 2.

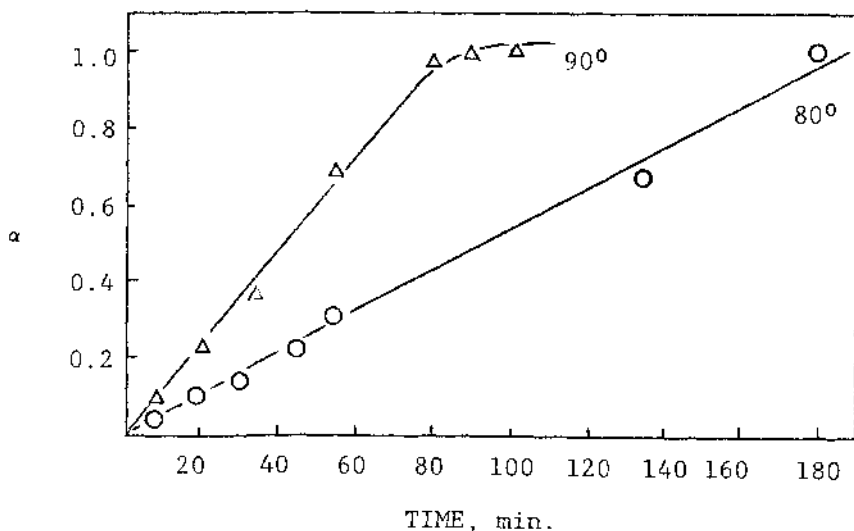


Figure 2. Typical plots of α vs. time for dehydration of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

The plots were found to be linear over almost the entire reaction. A linear regression analysis of the data in the linear portions of the curves provides the rate constants shown in Table 2.

Table 2. Rate constants for the dehydration of ammonium oxalate monohydrate.

Temperature, °C	k, sec ⁻¹
80	9.02 x 10 ⁻⁵
85	1.34 x 10 ⁻⁴
90	2.13 x 10 ⁻⁴
95	2.99 x 10 ⁻⁴

The rate constants shown in Table 2 provide a linear Arrhenius plot. A linear regression analysis of the $\ln k$ and $1/T$ values yields an activation energy of 87.7 kJ/mole with a correlation coefficient of 0.9987. This activation energy is almost identical to that reported for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (Coats and Redfern, 1964), but is quite different from that obtained from the analysis of the TGA curves. Using a heating rate of 10°C/min under non-isothermal conditions, it is possible that the reaction becomes a diffusion controlled one in which the rate of escape of H_2O is the limiting factor. However, this might not be the rate controlling process when samples are heated isothermally for long periods of time and a different order and activation energy could result. Whether this difference in activation energy for dehydration of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ under isothermal and non-isothermal conditions is due to hydrogen bonding of ammonium ions to the oxalate ions is not known. This could not, of course, be a factor in the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and in that case similar results have been obtained for isothermal and non-isothermal studies. It may be that under non-isothermal conditions where the water must be lost rapidly, the diffusion of H_2O is retarded by hydrogen bonding or some other means. Although the majority of reactions when studied isothermally or non-isothermally yield similar results, we have recently observed different kinetic behavior for systems studied both ways (House and Smith, 1977).

The TGA curve shown in Figure 1 indicates that at temperatures above 190 °C the anhydrous $(\text{NH}_4)_2\text{C}_2\text{O}_4$ begins to decompose. The decomposition is gradual at first and the fraction decomposed follows the first order equation,

$$\ln \ln \frac{1}{(1-\alpha)} - 2 \ln T = \ln \frac{AR}{BE} - \frac{E}{RT} \quad (4)$$

very well. The final product of this reaction can not be established because an abrupt change in the reaction occurs beginning at 245 °C and leads to complete decomposition. In the interval from 200 to 240 °C, the values for α and T have been analyzed using Equation (3) and an activation energy of 90.9 kJ/mole results with a correlation coefficient for the fit being 0.9986.

Decomposition of simple oxalates such as CaC_2O_4 leads to the carbonate by loss of CO . However, this process has an activation energy of about 250 kJ/mole (Nair and Ninan, 1978). Because of the low activa-

tion energy for the initial decomposition of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, it is likely that the reaction involves the loss of ammonia by a proton transfer. The activation energy found here is very close to that which we have found for other such processes. The latter stage of decomposition does not follow any simple kinetic pattern. It most certainly does not lead to the carbonate as does the decomposition of calcium oxalate.

The results of this study show that the dehydration and decomposition of ammonium oxalate monohydrate is somewhat more complicated than that of calcium oxalate monohydrate.

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