Thermochimica Acta, 24 (1978) 1–7

THE KINETIC ISOTOPE EFFECT IN DEHYDRATION OF IONIC SOLIDS
I. THE KINETICS OF DEHYDRATION OF CALCIUM OXALATE MONOHYDRATE

EMANUEL P. MANCHE
York College of the City University of New York, Department of Natural Sciences, Jamaica, NY 11451 (U.S.A.)
BENJAMIN CARROLL
Rutgers-the State University- Department of Chemistry, Newark, NJ 07102 (U.S.A.)
(Received 20 June 1977)

ABSTRACT

The hydrogen isotope effect in the activation energy for the dehydration of calcium oxalate monohydrate has been investigated as a function of the progress of the reaction using thermogravimetry. Although the activation energy appears to decrease during the course of the reaction, contrary to the data in the literature no significant isotope effect is apparent when the activation energy for the protonated and deuterated hydrates are compared at the same degree of conversion. Theoretical considerations rule out an isotope effect greater than one kilocalorie, a value which is well within the experimental error for non-isothermal kinetics.

INTRODUCTION

With the appearance of the publication of Heinzinger and Rao[1] on the hydrogen isotope effect among the different dehydration stages of copper sulfate pentahydrate, interest in this isotope for studying dehydration processes in crystals has increased considerably. Investigations have proceeded in several directions. One direction may be termed equilibrium studies using natural water for the formation of the hydrates. Here the mass spectrometer has been used to analyze the D/H ratio at various stages of dehydration[2, 3]. Another direction has been the studies of fully deuterated and fully protonated hydrates. In this case, the relative thermal stability and phase transition temperatures have been investigated[4, 5]. The kinetics of the dehydration process of deuterated and of protonated hydrates constitutes another type of study. The latter work has centered on the activation energy of the process using non-isothermal procedures.

The kinetic isotope effect found in some cases have been enormous. For example[6], it has been reported that the activation energy for the initial stage of dehydration of the copper sulfate pentahydrate is 19 kcal mol^{-1} for the protonated sample compared to 33 kcal mol^{-1} for the deuterated one; for the monohydrate the activation energies are reported as 30 and 53 kcal mol^{-1}, respectively. Yet, the reported enthalpies of these reactions did not distinguish between the protonated and deuterated hydrates.

In the case of calcium oxalate monohydrate, values of 12 and 31 kcal mol^{-1} for the H_2O and D_2O varieties, respectively, have been reported[7]. Chaudhuri and Pathak[8] and others[9] have investigated the activation energy of the dehydration of a number of double salts and have discerned no clear trend in the relative values for the fully deuterated and fully protonated compounds, the isotope effect going either way. We have reinvestigated the isotope effect of the activation energy for calcium oxalate monohydrate in view of the fact that this compound is a primary standard in thermal procedures. We have used a thermogravimetric procedure.

Investigators working with solid state chemical reactions are in the habit of characterizing a reaction with a single set of kinetic parameters. Here the assumption is made that the thermal decomposition of a solid involves a single mechanism. This view has resulted in numerous curve fitting procedures for obtaining the set of kinetic parameters[11].

Solid state chemical reactions may involve nucleation, nuclei growth, diffusion of reactants and products, and movement of phase boundaries. Hydrates of salts contain water molecules, anions, and cations packed together yielding a characteristic structure which usually collapses upon dehydration. The resulting anhydrous structure may bear no resemblance to the original hydrate. In addition to structural changes which will involve increasing imperfections in the crystal during the progress of the reaction, there are imposed experimental conditions that appear to influence the kinetics, such as particle size and shape, size of sample, and heating rates[12].

To yield more meaningful kinetic results, differential thermal methods may be considered[11]. The methods are based upon slopes, but the more differential the method becomes the greater the experimental scatter. These methods also involve as a rule an analytical function for the progress of the reaction, $f(\alpha)$, which is taken to be independent of the temperature. We have used such method in the past[13, 17], but the reliability of the activation energy is not better than ± 5 to ± 10% and represents an average value over an appreciable part of the reaction. In looking over the number of non-isothermal methods for determining the activation energy, since such procedures were used in the previously reported isotope effects, we chose the method of heating rates for the present purpose. The method involves relatively a large amount of experimental work and yields only a single kinetic parameter. However, it appears to allow the following of the activation energy during the entire course of the reaction with as great an accuracy as can be obtained with non-isothermai procedures.

Most important, the method of heating rates is an experimental procedure that makes possible the calculation of the activation energy as a function of the progress of the reaction without any assumption as to the form of the function describing the progress of the reaction. The particular method of heating rates as described by Flynn and Wall[14] and Ozawa[15] was used.

CALCULATION OF THE ACTIVATION ENERGIES

Defining the progress of the reaction in terms of α, the degree of conversion, the rate of the reaction may be written as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where T is the temperature. Assuming an Arrhenius relationship for the temperature part of the function and using a linear heating rate, Φ, eqn (1) becomes

$$\frac{d\alpha}{dT} = \frac{A}{\Phi} e^{-E/RT} f(\alpha) \tag{2}$$

where A is the Arrhenius factor, E_a the activation energy, R the gas constant, and $f(\alpha)$ is the function that describes the progress of the reaction. It is usual to assume some particular form for $f(\alpha)$ to determine E_a for the thermal curve[17, 18]. However, if a series of linear heating rates are used, then this assumption may be avoided.

Rearranging eqn (2) it may be shown that

$$F(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{AE_a}{R\Phi}\left[\frac{e^{-x}}{x} + \int_{-\infty}^{-x} \frac{e^{x}}{x} dx\right] \tag{3}$$

where $x = E_a/RT$.

The assumption implicit in eqn (3) are that both A and E_a are independent of the temperature and that $F(\alpha)$ is a unique function of the degree of conversion. Defining the function in brackets in eqn (3) as $p(x)$ we write

$$\log F(x) = \log \frac{AE_a}{R} - \log \Phi + \log p(x) \tag{4}$$

Doyle[19] has shown that log $p(x)$ may be approximated by

$$\log p(x) \cong -2.315 - 0.457\, E_a/RT \tag{5}$$

for $E_a/RT \geqq 20$. In our present work $20 < E_a/RT < 30$. In this range, the error in eqn (5) is as high as 1.1 % at $x = 20$ to less than 0.2 % at $x = 30$. In comparing the activation energies for the light and heavy hydrates at the same values of α, the error involved in eqn (5) is vanishingly small.

Substituting eqn (5) in (4) and taking the derivative with respect to $(1/T)$,

$$\left[\frac{\log \Phi}{(1/T)}\right]_{\alpha} = \left(\frac{0.457}{R}\right) \cdot E_a \tag{6}$$

or

$$E_a = -4.35 \left[\frac{d \log \Phi}{d\,(1/T)}\right]_{\alpha} \tag{7}$$

Thus, plots of log Φ versus $(1/T)$ at a fixed degree of conversion yield E_α. The various values of E_α were obtained for the range of $\alpha = 0.3$ to 0.9.

EXPERIMENTAL

The $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$ were prepared from Fisher Scientific Company reagent grade calcium oxalate monohydrate powder, lot number 751593. A small quantity of this salt was sieved with an Allen-Bradley Sonic Sifter. The fraction passing through the 53 μ sieve was collected and used for all the experiments described in this paper. The powder was divided into two parts and placed in an oven set at 200°C for 24 h. The two samples were transferred to two previously prepared chambers, one saturated with H_2O and the other with D_2O. After a few days, the samples were transferred to desiccating chambers containing P_2O_5.

The identity of each of these salts was made from absorption spectra taken on a Beckman 4240 infrared spectrophotometer as well as from stoichiometric considerations from thermogravimetry.

Thermogravimetric curves were obtained using a Perkin-Elmer TGS-1 thermobalance and a Perkin-Elmer UU-1 temperature programmer. Small gauge chromel–alumel thermocouples, referenced to 0°C ice bath, were used to adjust the programmer to give optimum furnace temperature linearity in the range of temperatures investigated in this study.

For each analysis, 5.00 mg of sample was weighted in a platinum crucible. For this purpose, a Cahn G-2 microbalance was used. The sample was then transferred to the stirrup of the thermobalance. Dry nitrogen gas was allowed to flow at a rate of 20 ml min^{-1} during the course of the reaction. To test whether this gas flow was adequate to prevent a reversing reaction, duplicate runs were made using a flow-rate of 40 ml min^{-1}. Comparison of the resulting thermograms indicated no discernible differences.

Eight samples of $CaC_2O_4 \cdot H_2O$ were analyzed at heating rates of 0.3125, 0.625, 1.25, 2.5, 5, 10, 20, and 40°C min^{-1}. Similarly, eight samples of $CaC_2O_4 \cdot D_2O$ were analyzed at these same heating rates.

RESULTS

From each of the thermograms, the actual weight losses were normalized in terms of fractional weight losses, α. The temperature at constant conversion for α = 0.3, 0.5, 0.7 and 0.9 were recorded for all sixteen. A least square linear plot of log of heating rate (Φ) versus the reciprocal absolute temperature $(1/T)$, was made for the dehydration of each of the salts. From the slopes, the activation energy were calculated according to eqn (7), i.e.,

$$E_\alpha = -4.35\,[\mathrm{d}\log \Phi/\mathrm{d}(1/T)]$$

A least square solution was obtained for the slopes of log Φ vs. $1/T$ as well as the

TABLE 1

RESULTS OF THE KINETIC ANALYSIS OF THE THERMOGRAVIMETRIC DATA

Fractional conversion, α	*E_a (kcal mol^{-1})*	
	$CaC_2O_4 \cdot H_2O$	*$CaC_2O_4 \cdot D_2O$*
0.3	22.5 ± 1.5	24.3 ± 1.8
0.5	20.5 ± 1.2	22.2 ± 1.5
0.7	19.3 ± 1.1	20.7 ± 1.4
0.9	18.3 ± 1.0	19.5 ± 1.2

standard deviation of the slopes. The data are summarized in Table 1. A definite trend is seen from these results, namely, that the activation energy decreases during the progress of the reaction. However, comparison of the protonated and deuterated salts show that, at the same point of the dehydration, there is no significant isotope effect.

This result may be seen more clearly in Fig. 1 where plots at $\alpha = 0.3$ and 0.7 for the protonated and deuterated hydrates are given for the log of the heating rate versus the reciprocal of the temperature.

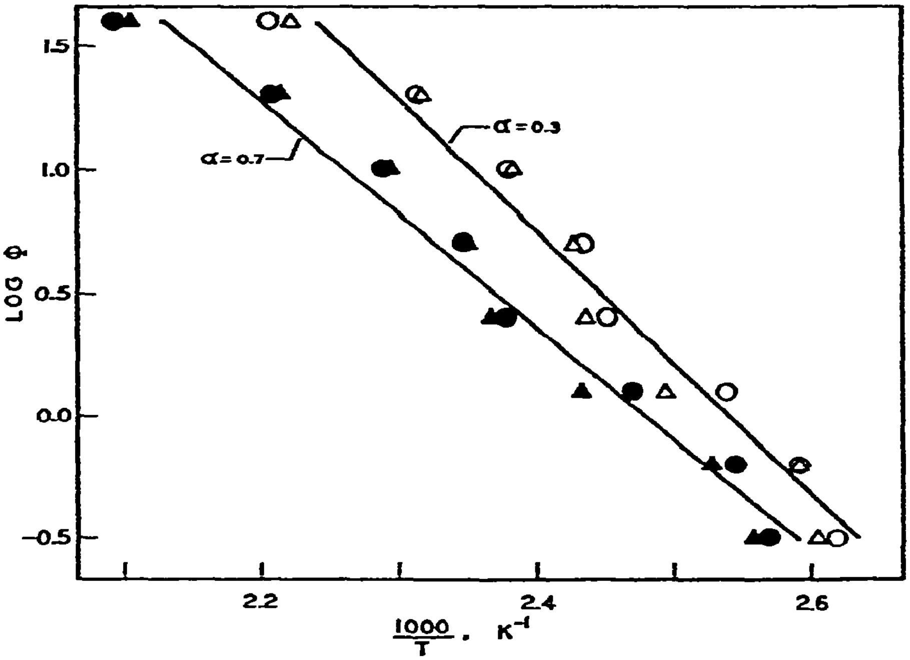

Fig. 1. Least square plot of the logarithm of the heating rate, Φ, versus the reciprocal of the absolute temperature for the dehydration of $CaC_2O_4 \cdot H_2O$ (circles) and $CaC_2O_4 \cdot D_2O$ (triangles), at $\alpha = 0.3$ (open symbols) and $\alpha = 0.7$ (darkened symbols). A single curve has been drawn through all points for a single value of α. The activation energies calculated at $\alpha = 0.3$ and 0.7 are 23.3 ± 1.1 and 19.9 ± 0.8 kcal mol^{-1}, respectively.

DISCUSSION

The average value of about 20 kcal mol^{-1} for the activation energy for the protonated calcium oxalate monohydrate is about the same as that previously reported using other non-isothermal procedures[17, 20]. The decreasing value of some 20% during the progress of the reaction is not entirely unexpected in view of enormous structural changes that the reacting solid continuously undergoes. The difference in activation energies between the deuterated and protonated hydrates as listed in Table I cannot be considered significant in view of the uncertainty in the precision of each of the values at the same point of conversion.

It is interesting to estimate the theoretical range of the isotope effect for the activation energy. The dehydration may be considered as consisting of bond cleavage, diffusion of the water molecule to the surface of the crystal followed by desorption. The maximum isotope effect in each of these processes may be estimated as follows:

The desorption may be considered as having an activation energy approximating the latent heat of vaporization, this being about 10 kcal mol^{-1}. This contribution to the activation energy may be taken as a constant during the progress of the dehydration. The difference in the activation energy for the desorption of H_2O and D_2O, at a mean temperature value of 150°C, may be calculated on the basis of the Van Hook equation[16].

$$\ln\left[\frac{P_{H_2O}}{P_{D_2O}}\right] = \frac{A}{T^2} + \frac{B}{T} + C \tag{8}$$

The Van Hook values for the constants A and B yield a final value of about 150 calories as the difference between the latent heat of D_2O and H_2O*.

The possible isotope effect for the remaining 10 kcal mol^{-1} in the activation energy may be ascribed in part to bond cleavage. Here, one may use absolute rate theory. The Bigeleisen[10] treatment indicates, that depending upon the activated complex postulated, the isotope difference in activation energy can cover a range from zero to the differences in the zero point energies of the reacting molecules and their respective activated complexes. Consider the primary isotope effect where the bond linking the hydrogens of the water molecule to some other atom in the hydrated crystal is cleaved in the early stage of dehydration. The corresponding stretching mode in the transition state would become the aperiodic motion along the reaction coordinate and the corresponding stretching frequency would be excluded from the sum of the zero point energies in the transition state. This would yield a factor of 1.05, the square root of the ratio of the mass of D_2O to H_2O, for the activation energy change since the difference in the zero point energy of the initial states of the reactants would determine the change in activation energies for this process. This

---

* The Van Hook equation has been used beyond the 130°C limit. The value of 150 calories represents an average obtained with constants I and with II (ref. 16).

factor would lead to an increase of about 0.5 kcal mol^{-1} for the deuterated salt since there is only some 10 kcal remaining for non-desorption stage.

If a diffusion mechanism is considered, the upper limit appears to be a factor 1.11 this being the ratio of the masses of D_2O to H_2O. The activation energy for diffusion mechanism may be considered as consisting of two parts, one for the creation of a vacancy and the other for the jump frequency, the energy to move the water molecule into the unoccupied site. Both parts are roughly of the same values.

Thus, the kinetic isotope effect may be as high as one kcal mol^{-1}. For a total activation of 20 kcal, the isotope effect, if it exists, would be swamped by the experimental error.

ACKNOWLEDGMENTS

The authors wish to thank Howard Schwartz and Barton A. Chase for their assistance in the experimental part of this work.

REFERENCES

1 K. Heinzinger and T. S. Rao, *Z. Naturforsch., Teil A*, 22 (1967) 2111.
2 K. Heinzinger and B. Maiwald, *Bull. Chem. Soc. Jpn.*, 45 (1972) 2237.
3 B. Maiwald and K. Heinzinger, *Z. Naturforsch., Teil A*, 27 (1972) 819.
4 P. D. Garn, in R. F. Schwenker, Jr. and P. D. Garn (Eds.), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 921.
5 A. C. Glatz, I. Litant and B. Rubin, in R. S. Porter and J. F. Johnson (Eds.), *Analytical Calorimetry*, Vol. 2, Plenum, 1970, p. 255.
6 H. Oki, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, 43 (1970) 3263.
7 H. G. Wiedemann and A. van Tets, *Naturwissenschaften*, 54 (1967) 442.
8 N. R. Chaudhuri and G. K. Pathak, *Thermochim. Acta*, 12 (1975) 71.
9 N. R. Chaudhuri, G. K. Pathak and S. Mitra, in I. Buzás, (Ed.), *Thermal Analysis*, Heyden and Sons, New York, 1974, p. 615.
10 J. Bigeleisen, *J. Chem. Phys.*, 17 (1949) 675.
11 J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stand.*, A70 (1966) 487.
12 M. R. Alvarez, J. J. Icaza, E. H. Bocanegra and M. J. Tello, *Thermochim. Acta*, 12 (1975) 117.
13 B. Carroll and E. P. Manche, *J. Appl. Polym. Sci.*, 9 (1965) 1895.
14 J. H. Flynn and L. A. Wall, *Polym. Lett.*, 4 (1966) 323.
15 T. Ozawa, *Bull. Chem. Soc. Jpn.*, 38 (1965) 1881.
16 W. A. Van Hook, *J. Phys. Chem.*, 72 (1968) 1234.
17 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
18 B. Carroll and E. P. Manche, *Thermochim. Acta*, 3 (1972) 449.
19 C. D. Doyle, *J. Appl. Polym. Sci.*, 6 (1962) 639.
20 W. J. Fisco, *Doctoral Dissertation*, Rutgers University, 1969.