Thermochimica Acta, 102 (1986) 263–269
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE DEUTERIUM ISOTOPE EFFECT ON THE KINETICS OF THE THERMAL DEHYDRATION OF CALCIUM OXALATE MONOHYDRATE

YOSHIO MASUDA

Chemistry Division, General Education Department, Niigata University, Niigata 950-21 (Japan)

YOSHIO ITO, RYOKOU ITO and KEIICHI IWATA

Department of Chemistry, Faculty of Science, Niigata University, Niigata 950-21 (Japan)

(Received 25 November 1985)

ABSTRACT

The deuterium isotope effect in the thermal dehydration of calcium oxalate monohydrate was investigated by means of non-isothermal thermogravimetry.

The dehydration consisted of a first order reaction (F_1) and a two-dimensional phase boundary reaction (R_2). The F_1 was the rate determining step at lower temperatures and the R_2 which was the main process of dehydration dominated the dehydration at higher temperatures.

The activation energies and pre-exponential factors for these processes were larger for the deuterated specimen than those for the protonated one. The ratio of the rate constants for the R_2 process, $k(HR_2)/k(DR_2)$, was 1.01, and the kinetic deuterium isotope effect in the R_2 process was not recognized significantly. The ratio for the F_1 process, $k(HF_1)/k(DF_1)$ decreased with increasing temperature and the mean value was 1.37.

INTRODUCTION

Many studies have been carried out on the hydrogen isotope effect in the thermal dehydration of inorganic hydrated crystals. For example, Wiedemann and Tets [1] found an enormous deuterium isotope effect in the thermal dehydration of calcium oxalate monohydrate. They reported that the activation energies for the dehydration were 12 and 31 kcal mol^{-1} in their values for the protonated specimen and for the deuterated one, respectively. Whereas, Manche and Carroll [2,3] investigated the dehydration of the same hydrated salts on the basis of thermogravimetric data and concluded that the isotope effect was not found significantly when the activation energies of dehydration of both the hydrates were compared at dehydration fractions of the same degree.

Tanaka and Negita [4] reported enthalpy changes in the thermal dehydration of 15.21 ± 0.04 and 15.37 ± 0.05 kcal mol^{-1} for $CaC_2O_4 \cdot H_2O$ and

0040-6031/86/$03.50

$CaC_2O_4 \cdot D_2O$, respectively. They suggested that the origin of the deuterium isotope effect in the enthalpy change was attributable to the difference between the heat of vaporization of H_2O and D_2O.

Recently, authors [5] have reported on the kinetics of thermal dehydration of $CaC_2O_4 \cdot H_2O$ on the basis of a new method which applied a microcomputer to acquisition and processing of the thermogravimetric data. We suggested that the dehydration consisted of two mechanisms which corresponded to the elimination of water molecules and to the external diffusion of the eliminated water. In the present study, the thermal dehydration of $CaC_2O_4 \cdot D_2O$ was analyzed by the same method as described in the previous paper and the deuterium isotope effect on these two mechanisms was evaluated by a comparison of the results obtained with those from $CaC_2O_4 \cdot H_2O$.

EXPERIMENTAL

Reagents

Deuterated calcium oxalate monohydrate was prepared as follows: $CaC_2O_4 \cdot H_2O$ of guaranteed grade (99.7%) was sieved to a narrow fraction (250–300 mesh) and was dehydrated in an oven at 500 K for two days. The dehydrated calcium oxalate was placed in a chamber saturated with D_2O for a few days.

The deuterated specimen was identified by means of spectroscopy and thermogravimetry, stored in a desiccator and used without further purification.

Apparatus

The experimental apparatus and the procedures employed for the analysis of TG data were described in detail previously [5].

RESULTS AND DISCUSSION

Figure 1 shows the plots of $\ln[(d\alpha/dT)\beta]$ vs. $1/T$ for the dehydration of $CaC_2O_4 \cdot D_2O$ in nitrogen flow atmosphere, where α is the dehydrating fraction, T is the absolute temperature and β is the heating rate. Two kinds of parallel lines were recognized in the ranges $0.06 \leq \alpha \leq 0.10$ and $0.75 \leq \alpha \leq 0.95$. This fact indicates that the dehydration consists of two independent reactions as well as that of $CaC_2O_4 \cdot H_2O$. The values of activation energies, 133 and 79.7 kJ mol^{-1}, were calculated from the slopes of these two kinds of parallel lines.

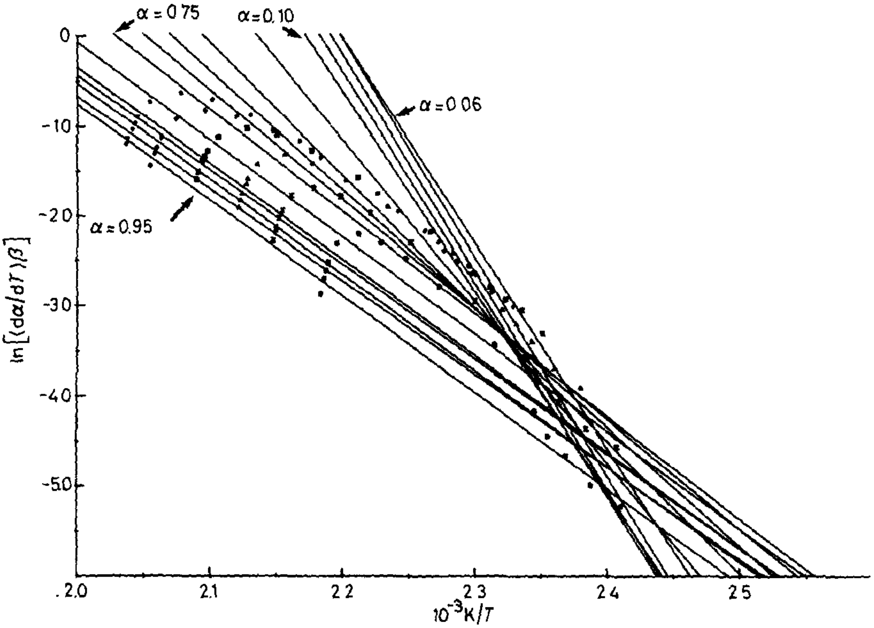

Fig. 1. The plots of $\ln[(d\alpha/dT)/\beta]$ vs. $1/T$ for the different dehydrating fractions (α) of thermal dehydration of $CaC_2O_4 \cdot D_2O$, in N_2 flowing atmosphere.

Figure 2 shows the relations between activation energy (E) and dehydrating fraction (α) in the dehydration of $CaC_2O_4 \cdot D_2O$, together with those of $CaC_2O_4 \cdot H_2O$. The results analyzed according to the previous method are shown in Table 1, and compared with those of $CaC_2O_4 \cdot H_2O$.

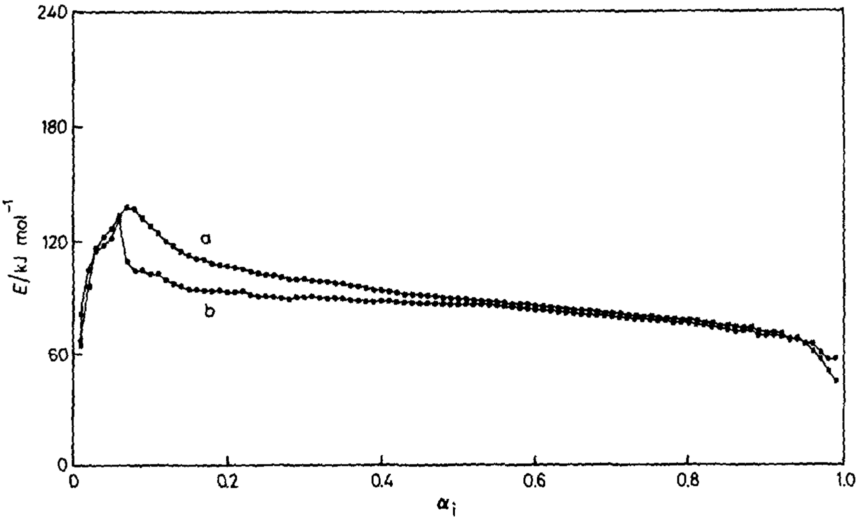

Fig. 2. Relation between activation energy E and dehydrating fraction α. Symbols a and b are the indications for the dehydration of the deuterated and protonated monohydrate of calcium oxalate, respectively.

TABLE 1

Results of analysis of the thermal dehydrations of deuterated and protonated monohydrate of calcium oxalate in N_2 flow atmosphere

	$CaC_2O_4 \cdot D_2O$		$CaC_2O_4 \cdot H_2O$	
Reaction	F_1	R_2	F_1	R_2
α-range [a]	0.06–0.57	0.09–0.95	0.03–0.58	0.07–0.95
E/kJ mol^{-1}	133	79.7	119	77.5
A/min^{-1}	6.72×10^{15}	5.63×10^{8}	1.12×10^{14}	3.15×10^{8}
Proportion/% [b]	24.5	75.5	23.7	76.3

[a] α-range shows the range in which each reaction takes place.

[b] Proportion shows the ratio of each reaction to a whole dehydration.

The values of activation energies (E) for the deuterated specimen are slightly larger than those for the protonated one in both the two-dimensional phase boundary reaction (R_2) and the first order reaction (F_1).

In the previous paper, it was assumed that the R_2 reaction corresponded to the elimination process of water molecules and the F_1 reaction to the external diffusion process of the eliminated water.

In the elimination process (R_2), the activation energy corresponds to the difference between the zero point energy of the reactant hydrate and that of the activated complex. Since the latter seems not to be so different in both the hydrates, the deuterium isotope effect on the activation energy can be attributed to the difference in the former. The zero point energy of the reactants is also related to the reciprocal of the square root of reduced mass of the reactant molecule. Therefore, it is reasonable that the value of the ratio of the activation energy (1.03) for the R_2 process of the deuterated specimen to that of the protonated one is nearly equal to that of the square root of ratio (1.05) of the reduced mass of these hydrates.

On the other hand, as pointed out by Manche and Carroll [2], it is reasonable that the value of the ratio (1.13) of the activation energy for the diffusion process of deuterated specimen to the protonated one is nearly equal to that of the ratio (1.11) of the mass of D_2O and H_2O.

These findings supported the previous proposal on the mechanism of the dehydration, i.e., the R_2 process was related to the elimination of the water molecules in the hydrate and the F_1 process to the external diffusion of the eliminated water molecules from the surface of particles.

The values of the pre-exponential factors increased with the increase in the activation energies. This finding seems to indicate the presence of some kinetic compensation effect in these reactions.

The rate constants for the deuterated specimen, $k(DF_1)$ and $k(DR_2)$ were calculated on the basis of the above kinetic parameters of the F_1 and the R_2 reactions, respectively (Table 2). Although the value of $k(DR_2)$ is larger than that of $k(DF_1)$ in the region of low temperatures, the latter

TABLE 2

The calculated rate constants $k(DF_1)$ and $k(DR_2)$ at various temperatures [a]

Temperature (K)	$k(DF_1)$ (min)	$k(DR_2)$ (min)
370	1.12×10^{-3}	3.15×10^{-3}
375	2.00×10^{-3}	4.45×10^{-3}
380	3.50×10^{-3}	6.23×10^{-3}
385	6.05×10^{-3}	8.65×10^{-3}
390	1.03×10^{-2}	1.19×10^{-2}
395	1.73×10^{-2}	1.62×10^{-2}
400	2.86×10^{-2}	2.20×10^{-2}
410	7.63×10^{-2}	3.95×10^{-2}
420	1.93×10^{-1}	6.89×10^{-2}
430	4.68×10^{-1}	1.17×10^{-1}
440	1.09	1.94×10^{-1}
450	2.45	3.15×10^{-1}
460	5.30	5.01×10^{-1}
470	1.11×10	7.81×10^{-1}
480	2.26×10	1.19
490	4.46×10	1.80
500	8.56×10	2.65

[a] $k(DF_1)$ and $k(DR_2)$ are the rate constants for the F_1 and the R_2 reactions of deuterated specimen, respectively.

becomes larger than the former above 394 K. This reversing temperature agreed approximately with the temperature at which the rate of dehydration was accelerated, as shown in Fig. 3. The reversing temperature was slightly

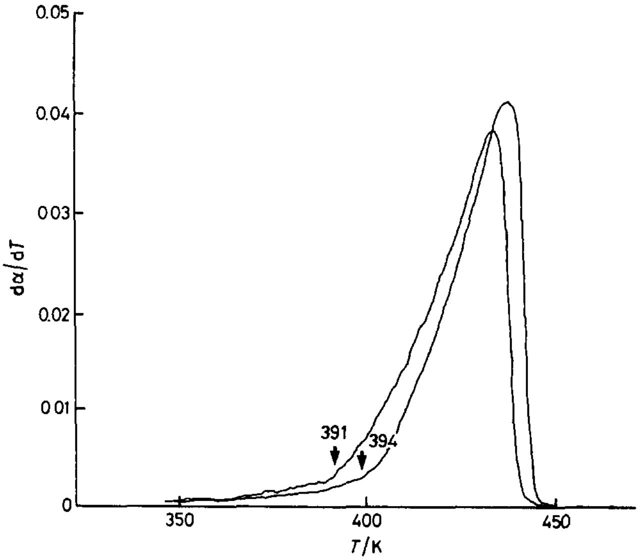

Fig. 3. Typical DTG curves obtained at heating rate at 2.5 K min^{-1} for the dehydration (1) $CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$ and (2) $CaC_2O_4 \cdot D_2O \rightarrow CaC_2O_4 + D_2O$.

higher than that (391 K) of the protonated specimen, which was consistent with the fact that the differential thermogravimetric (DTG) curve of the deuterated specimen shifted to a higher temperature side than that of the protonated one (Fig. 3).

These facts show that the dehydration of $CaC_2O_4 \cdot D_2O$ proceeds by the same process as that of $CaC_2O_4 \cdot H_2O$ though the rate is slightly lower than that of $CaC_2O_4 \cdot H_2O$.

The rate constants for both processes of dehydration of deuterated hydrate, $k(DF_1)$ and $k(DR_2)$, were compared with those of the protonated hydrate, $k(HF_1)$ and $k(HR_2)$, respectively. The value of $k(HR_2)/k(DR_2)$ scarcely changed in the temperature range where the dehydration was dominated by the R_2 reaction, and the mean value was 1.01 which was

TABLE 3

The comparison with the rate of dehydration of deuterated and that of protonated species at various temperatures [a]

Temperature (K)	$k(HF_1)/k(DF_1)$	$k(HR_2)/k(DR_2)$
370	1.58	
375	1.49	
380	1.40	
385	1.32	
390	1.25	
395	1.18	1.09
400		1.08
405		1.08
410		1.07
415		1.06
420		1.05
425		1.04
430		1.04
435		1.03
440		1.02
445		1.01
450		1.01
455		1.00
460		0.99
465		0.99
470		0.98
475		0.98
480		0.97
485		0.97
490		0.96
495		0.95
500		0.95

[a] $k(HF_1)$ and $k(HR_2)$ are the rate constants for the F_1 and the R_2 reactions of protonated specimen, respectively, and $k(DF_1)$ and $k(DR_2)$ are those of deuterated specimen, respectively.

comparable with the value (1.025) reported by Manche and Carroll [3] (Table 3). This finding shows that the rate of the elimination process (R_2) is little influenced by the deuteration of the water molecules. Whereas, the $k(\mathrm{HF_1})/k(\mathrm{DF_1})$ showed a large value at low temperatures and it decreased with increasing temperature, as shown in Table 3. The mean value was 1.37. Therefore, the slow rate of the dehydration of $CaC_2O_4 \cdot D_2O$ seems to be due to the sluggish F_1 process. The eliminated water is condensed at low temperature, so the apparent large value of $k(\mathrm{HF_1})/k(\mathrm{DF_1})$ may be related to the evaporation and diffusion of H_2O and D_2O. The difference in the heat of vaporization for D_2O and H_2O ($\Delta(\Delta H_{\mathrm{vap}})$) has been reported as ca. 200 cal mol^{-1} at 373 K [6]. On the other hand, the ratio of diffusion rate of H_2O to that of D_2O can be estimated as 1.05 from the masses of H_2O and D_2O. Multiplying this value, 1.05 by the factor $\exp(\Delta(\Delta H_{\mathrm{vap}})/RT)$, where R is the universal gas constant and T is the absolute temperature, we can obtain values which are comparable with the mean value, 1.37, in the low temperature range.

REFERENCES

1 H.G. Wiedemann and A. van Tets, Naturwissenschaften, 54 (1967) 442.
2 E.P. Manche and B. Carroll, Thermochim. Acta, 24 (1978) 1.
3 E.P. Manche and B. Carroll, J. Phys. Chem., 81 (1977) 2637.
4 H. Tanaka and H. Negita, Thermochim. Acta, 41 (1980) 305.
5 Y. Masuda, Y. Ito, R. Ito and K. Iwata, Thermochim. Acta, 99 (1986) 205.
6 The Chemical Society of Japan (Ed.), Kagaku Binran (Handbook of Chemistry), Maruzen, Tokyo, 1968, p. 69.