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THE DEUTERIUM ISOTOPE EFFECT IN ENTHALPY CHANGE ON THE THERMAL DEHYDRATION OF CALCIUM OXALATE MONOHYDRATE

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ABSTRACT

The enthalpy changes in the thermal dehydrations of calcium oxalate monohydrate and its deuterium analogue were determined as 15.21 ± 0.04 and 15.37 ± 0.05 kcal $mole^{-1}$, respectively by means of differential scanning calorimetry. The isotope effect calculated from measured vibrational frequency shifts on deuteration of the hydrate was found to be in good agreement with that observed. The origin of the deuterium isotope effect in the enthalpy change is briefly discussed.

INTRODUCTION

A number of studies have been carried out on the thermal dehydration of hydrated crystals from various aspects. Some have dealt with the kinetics of dehydration and/or its hydrogen isotope effects. For example, kinetic deuterium isotope effects were studied during the thermal dehydrations of copper sulphate pentahydrate [1] and calcium oxalate monohydrate [2].

Recently, Manche and Carroll [3] studied extensively the kinetic isotope effect of deuterium in the thermal dehydration of calcium oxalate monohydrate. They concluded that such an isotope effect should be quite small; the magnitude may be a few percent at most and the enormous isotope effects reported so far by other workers may be ruled out.

On the other hand, a number of workers have determined thermodynamic parameters during the dehydration of salt hydrates. The studies along these lines have been done mainly by measuring vapour pressures [4,5].

Some question of deuterium isotope effects in the enthalpy change during the dehydration, however, seems to remain unsolved. It may be reasonable to use such experimental methods as conventional calorimetry and tensimetry in order to determine the isotope effect. Alternatively, it seems inter-

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esting to examine the problem by means of differential scanning calorimetry (DSC) in that DSC has been increasingly developed and widely used.

Calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$, has been chosen for the salt hydrate in present study, since the hydrate is often used as a primary standard in the thermal dehydration of salt hydrates.

EXPERIMENTAL

Calcium oxalate monohydrate was prepared by the double decomposition of reagent grade ammonium oxalate and calcium chloride as follows. The precipitate was obtained by adding 10 ml of 0.2 M solution of ammonium oxalate to 200 ml of 0.01 M solution of calcium chloride. The mixture was made slightly alkaline with an aqueous solution of ammonia and warmed. The precipitate was then washed with hot water by decantation, filtered through a glass filter, carefully washed with hot water, and dried.

The monohydrate thus obtained was identified by IR spectrophotometry, thermogravimetry (TG), and titrimetry with a standard solution of potassium permanganate after dissolving the hydrate in dilute nitric acid.

The monohydrate was ground and sieved to 280 mesh or smaller. About 15 mg of the monohydrate were thermally dehydrated in a stream of dry nitrogen gas. The anhydrous product was rehydrated with water vapour in a small sealed bottle at room temperature. About 15 mg of its deuterium analogue, $CaC_2O_4 \cdot D_2O$, were prepared using 99.8% deuterium oxide under identical conditions. Each moist sample was dried in a sealed chamber containing anhydrous calcium oxalate as a desiccant at room temperature [6]. The identification of each sample was made by means of IR spectra as well as by thermogravimetry.

TG and DSC measurements were carried out using a Rigaku Thermoflex TG—DSC 8085E1 type instrument at a heating rate of 5 K min^{-1} in a stream of dry nitrogen gas at a flow rate of 40 ml min^{-1}. About 15 mg of sample placed in a platinum crucible of 2.5 × 5 mm diameter were used, with α-alumina as reference material throughout the measurements.

Infrared spectra of $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$ were recorded on a Hitachi Model EP1-G_2 IR spectrophotometer in the range 4000—400 cm^{-1}. The spectra were obtained by both the nujol mull and KBr pellet techniques at room temperature.

The enthalpy change was determined from the area of the DSC peak using a precision planimeter of Koizumi Sokki Seisakusho (KP-46). The area was then converted to the enthalpy change through calibration data for the heat of transition of KNO_3 at 401 K.

RESULTS AND DISCUSSION

The thermal dehydrations of calcium oxalate monohydrate and its deuterium analogue are expressed as

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O \qquad (1)$$

$$CaC_2O_4 \cdot D_2O \rightarrow CaC_2O_4 + D_2O \qquad (2)$$

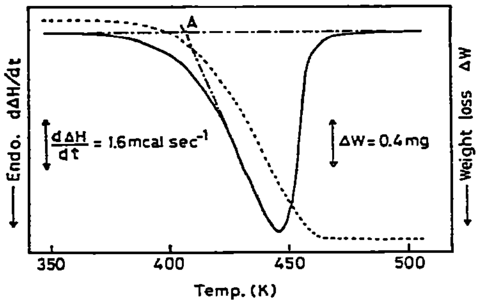

Fig. 1. Typical curves of TG (broken line) and DSC (solid line) for the thermal dehydration of calcium oxalate monohydrate.

Typical TG—DSC curves obtained simultaneously are shown in Fig. 1. The TG trace was quite useful in checking the stoichiometry of the water of hydration in each sample. The purity of the salt hydrate prepared was found to be quite satisfactory by thermogravimetry and titrimetry, although synthetic calcium oxalate monohydrate is liable to contain various impurities [7].

The observed enthalpy change ΔH in eqn. (1) is given in Table 1, along with literature values [4,5]. In the determination of ΔH, the effects of the flow rate of dry nitrogen gas and the heating rate on the peak areas of the DSC curves were examined in the ranges 20—80 ml min^{-1} and 0.625—10 K min^{-1}, respectively. Comparison of the resulting peak areas revealed no discernible differences in the present study.

The dehydration temperature of $CaC_2O_4 \cdot H_2O$ was determined as 408 K from point A in Fig. 1 where the base line intersects with the tangent of maximum slope of the DSC peak. It can be seen from Table 1 that the ΔH value from DSC measurements is in good agreement with those obtained by tensimetry.

The deuterium isotope effect in the enthalpy change for the dehydration of calcium oxalate monohydrate is given in Table 2. It is seen that the enthalpy change, $\Delta H'$, in eqn. (2) is larger than the ΔH value by ca. 1.1%. The difference in dehydration temperature was not recognized between $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$ from the analyses of TG and DSC curves.

It seems worthwhile to calculate the difference in enthalpy change

TABLE 1

The enthalpy change, ΔH, in the dehydration of calcium oxalate monohydrate

Temp. (K)	ΔH (kcal mole^{-1})	Method	Ref.
408	15.21 ± 0.04 *	DSC	Present work
402—434	16.6 ± 0.2	Tensimetry	4
298	15.7 ± 0.9	Tensimetry	5

* Mean of eight observed values and its probable error.

TABLE 2

The deuterium isotope effect in enthalpy change during the thermal dehydration of calcium oxalate monohydrate

	ΔH (kcal mole^{-1})	$\Delta H'$ (kcal mole^{-1})	$\delta\Delta H$ * (kcal mole^{-1})
Obs.	15.21 ± 0.04 **	15.37 ± 0.05 **	0.16 ± 0.06
Calc.	(15.21)	15.34	0.13

* $\delta\Delta H = \Delta H' - \Delta H$, where $\Delta H'$ denotes the enthalpy change in the dehydration of $CaC_2O_4 \cdot D_2O$.

** Mean of eight observed values and its probable error.

between $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$, $\delta\Delta H$, from the partition function ratio according to the method of Swain and Bader [8]. The partition function for n normal vibrations of the hydrate, Q_v, is given by

$$Q_v = \prod^{n} \frac{\exp(-u/2)}{1 - \exp(-u)} \quad \text{and } u = hc\omega/kT \tag{3}$$

where h is Planck's constant, c is the velocity of light, ω is the fundamental vibrational frequencies, k is Boltzmann's constant, and T is the absolute temperature. The enthalpy difference between a hydrate and its deuterium analogue, δH, is then given by

$$\begin{aligned} \delta H &= RT^2 \frac{\partial \ln(Q_v'/Q_v)}{\partial T} \\ &= RT \sum_n \left\{ \frac{u'}{\exp(u') - 1} + \frac{u'}{2} \right\} - RT \sum_n \left\{ \frac{u}{\exp(u) - 1} + \frac{u}{2} \right\} \end{aligned} \tag{4}$$

where the prime refers to the deuterium analogue.

TABLE 3

Observed frequencies (cm^{-1}) of IR absorption bands for hydration waters in calcium oxalate monohydrate and its deuterium analogue

$CaC_2O_4 \cdot H_2O$	Intensity *	$CaC_2O_4 \cdot D_2O$	Intensity *
3490	s	2590	s
3440	s	2558	s
3338	s	2472	s
3262	m	2410	m
3060	s	2302	s
1622	vs	1222	s
950	m	796	s
886	m	644	m
666	s	504	s
598	m	410	w
418	w	402	w

* vs = Very strong, s = strong, m = medium, and w = weak.

TABLE 4

Fundamental frequencies, ω, of IR absorption bands for hydration waters in calcium oxalate monohydrate and its deuterium analogue

Assignment *	ω (cm^{-1})	
	$CaC_2O_4 \cdot H_2O$	$CaC_2O_4 \cdot D_2O$
OH stretching	3465	2574
	3199	2387
OHO bending	1622	1222
H_2O libration **	775	590
	775	590
	775	590

* Assigned according to refs. 9—11.

** Mean value of measured frequencies due to the libration is adopted to the three possible librations about the axes of inertia, because the twisting mode of libration is inactive [12].

The calculation of δH for calcium oxalate monohydrate was made assuming the following: (a) the libration of the hydration water in the crystal is a three-dimensional harmonic oscillation; (b) only the internal and librational frequencies for the hydration water are shifted upon deuteration of the hydrate; the stretching vibration between calcium ion and hydration water, the restricted translation of hydration water, and the vibration of oxalate ion can be neglected; (c) the internal and librational frequencies are constant in the temperature range 298—408 K.

The measured vibrational frequencies of $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$ were used in the calculation since IR spectra reported by other workers [9—11] are inconsistent. The measured vibrational frequencies due to the hydration water are shown in Table 3. Of these frequencies, the fundamental frequencies assigned are listed in Table 4. The calculation of δH for water vapour was made using internal vibrational frequencies taken from the literature [13].

The values of δH for calcium oxalate monohydrate and water vapour at 408 K were thus calculated as 3.479 and 3.352 kcal $mole^{-1}$, respectively. It is evident that the difference between them, 0.127 kcal $mole^{-1}$, refers to the calculated $\delta \Delta H$ value. Therefore, the calculated $\Delta H'$ value is found to be 15.34 kcal $mole^{-1}$ if the value of 15.21 kcal $mole^{-1}$ is adopted for ΔH. The calculated $\Delta H'$ value is in good agreement with that observed, 15.37 ± 0.05 kcal $mole^{-1}$. The magnitude of the isotope effect thus determined seems to be reasonable in the light of isotope effects of only a few percent observed by other workers [3,14].

It seems interesting to discuss the origin of the isotope effect, $\delta \Delta H$, in calcium oxalate monohydrate. The enthalpy change for the dehydration of salt hydrates, ΔH, can be assumed to consist of the following quantities

$$\Delta H = \Delta H_{diss} + \Delta H_{vap} \quad (5)$$

where ΔH_{diss} is the heat of dissociation of salt hydrate to give the anhydrous salt and water, and ΔH_{vap} is the heat of vaporization of water. We thus obtain the following relation

$$\delta\Delta H = \delta\Delta H_{\mathrm{diss}} + \delta\Delta H_{\mathrm{vap}} \qquad (6)$$

Using ΔH_{vap} values for H_2O and D_2O given in the literature [15], the $\delta\Delta H_{\mathrm{vap}}$ value may be estimated as ca. 0.17 kcal mole^{-1} at the dehydration temperature 408 K. It can be seen that $\delta\Delta H_{\mathrm{vap}}$ should contribute to $\delta\Delta H$ much more than $\delta\Delta H_{\mathrm{diss}}$ and that ΔH_{diss} of $CaC_2O_4 \cdot H_2O$ may be larger than that of $CaC_2O_4 \cdot D_2O$.

It is probable that the major contribution of $\delta\Delta H_{\mathrm{vap}}$ to $\delta\Delta H$ is also valid during the thermal dehydration of other salt hydrates in which the magnitude of isotope effects seems to amount to only a few percent [3].

REFERENCES

1 H. Oki, E. Kyuno and R. Tsuchiya, Bull. Chem. Soc. Jpn., 43 (1970) 3263.
2 H.G. Weidemann and A. Van Tets, Naturwissenschaften, 54 (1967) 442.
3 E.P. Manche and B. Carroll, J. Phys. Chem., 81 (1977) 2637; Thermochim. Acta, 24 (1978) 1.
4 S. Shimizu and M. Taniguchi, Nippon Kagaku Kaishi (J. Chem. Soc. Jpn., Chem. Ind. Chem.), (1977) 953.
5 N. Gerard, G. Wattelle-Marion and A. Thrierr-Sarel, Bull. Soc. Chim. Fr., (1968) 4367.
6 H.F. Walton, Inorganic Preparations, Prentice-Hall, New Jersey, 1948, pp. 24—25.
7 H.J. Arnott, F.G.E. Pautard and H. Steinfink, Nature (London), 208 (1965) 1197.
8 C.G. Swain and R.F. Bader, Tetrahedron, 10 (1960) 182.
9 M.J. Schmelz, T. Miyazawa, S. Mizushima, T.J. Lane and J.V. Quagliano, Spectrochim. Acta, 9 (1957) 51.
10 I. Petrov and B. Soptrajanov, Spectrochim. Acta, Part A, 31 (1975) 309.
11 P. Carmona, Spectrosc. Lett., 8 (1977) 645.
12 J. Van der Elsken and D.W. Robinson, Spectrochim. Acta, 17 (1961) 1249.
13 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York, 2nd edn., 1970, p. 89.
14 N.R. Chaudhuri and G.K. Pathak, Thermochim. Acta, 12 (1975) 71.
15 Nippon Kagakukai (Ed.), Kagaku Binran (Handbook of Chemistry), Maruzen, Tokyo, 1958, p. 69.