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DEUTERATION EFFECTS ON THE THERMAL DECOMPOSITION PROCESSES OF INORGANIC SOLIDS

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INTRODUCTION

With the improvement of thermal analysis equipments, more quantitative studies using, e.g., TG have become possible on solid state reactions. The kinetic deuterium isotope effect in the thermal dehydration of $CaC_2O_4 \cdot H_2O$, for example, has been examined from TGA and the activation energies for the dehydration of the hydrate and its deuterium analog have been reported to be 12 and 31 kcal/mol, respectively[1]. This has been reinvestigated both isothermally[2] and nonisothermally[3] and concluded that such an isotope effect should be quite smaller than those reported earlier[1,4].

Recently deuteration effects on the thermal stabilities, enthalpy changes, and kinetics of thermal dehydration of various solids have been examined using TG and DSC[5-14]. From these studies the direction and size of such isotope effects have been found to vary from sample to sample. It is appropriate to review here these studies since the results are useful for a better understanding of the decomposition processes of solids. The present paper deals with the decompositions of crystalline powdered solids, particularly with hydrate dehydrations.

THERMAL STABILITY

Thermal stabilities of solids can be compared easily from dynamic thermal analyses[13]. The term thermal stability comprises both thermodynamic and kinetic stabilities for solid decompositions. The former depends on the reaction free energy(the enthalpy change ΔH and entropy change ΔS) and the thermodynamic equilibrium decomposition temperature T is regulated by $\Delta H/\Delta S$. On the other hand, the latter depends on the activation free energy(the activation energy E and activation entropy $\Delta S^{\ddagger}$).

In the decomposition of solids E is usually a liitle larger than ΔH, and both E and ΔH should be examined in explaining deuterium isotope effects in the thermal stabilities for solid decompositions, as the decomposition temperature T derived from dynamic thermal analyses depends not only on the thermodynamics but also on the kinetics[13]. Table 1 shows the temperatures where the fraction dehydrated is 0.5 according to TG, $T_{1/2}$, as a measure of the thermal stability of solids.

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ENTHALPY CHANGE

Several studies have appeared on the deuteration effect on ΔH of the dehydration of salt hydrates by means of DTA[4,15] but the accuracy is not high enough to draw any decisive conclusion. The deuteration effect on the standard enthalpy change $\Delta H°$ of $Li_2SO_4 \cdot H_2O$ dehydration was measured by tensimetry: the isotopic difference in $\Delta H°$, $\delta\Delta H°$, was found to be 1150 J/mol[16].

It is reasonable to determine such deuteration effect on ΔH by means of DSC in that it has been increasingly developed and widely used[5]. In the fourth column of Table 1 are summarized the isotopic differences of ΔH. We see that there is a trend of positive values of $\delta\Delta H$. It seems that DSC has the advantage of tensimetry in determining $\delta\Delta H$ of the thermal dehydration of salt hydrates.

We can assume here that $\delta\Delta H$ consists of the two terms:

$$\delta\Delta H = \delta\Delta H_{diss} + \delta\Delta H_{vap},$$

where $\delta\Delta H_{diss}$ and $\delta\Delta H_{vap}$ are the isotopic differences in ΔH of dissociation from a protonated solid compound to the solid product and liquid water, and in ΔH of vaporization of the water, respectively. It appears that in general the contribution of $\delta\Delta H_{vap}$ to $\delta\Delta H$ is relatively large in comparison with that of $\delta\Delta H_{diss}$[5].

KINETICS

Studies of kinetic deuterium isotope effects in the thermal decomposition of solids have proceeded in two directions: using isothermal and non-isothermal methods. The kinetic deuterium isotope effect in the thermal dehydration of $CaC_2O_4 \cdot H_2O$ was investigated by thermogravimetry at constant temperatures[2]. In this study the isothermally determined rates at small interval of time t, $\Delta\alpha/\Delta t$, were compared at the same degree of progress of the reaction α. The advantage of this procedure of determining the kinetic isotope effect is that there is no need for specifing the kinetic model functions. The rate of dehydrations for $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$, k_H/k_D, were found to be 1.025±0.012. The smaller isotope effect than the theoretical estimate was explained on the basis of the kinetic compensation effect[2].

The deuterium isotope effect in the thermal dehydration of $CaC_2O_4 \cdot H_2O$ was also studied by thermogravimetry at linearly increasing temperatures[3]; using a method of heating rates as described by Flynn and Wall[17] and Ozawa[18]. No significant isotope effect in activation energy E was recognized at the same α between the monohydrate and its deuterium analog. This result is reasonable in that a normal kinetic isotope effect in E greater than one kcal/mol is well within the experimental error for such dynamic thermal analyses[3]. In view of this, enormous kinetic isotope effects reported earlier are dubious. This is probably due to rate measurements under different sample conditions between the hydrate and their deuterium analogs.

TABLE 1. Deuteration effects on the kinetics and thermodynamics of the thermal dehydration of solids by means of TG and DSC

No.	Reaction	$T_{1/2}$	$\delta\Delta H$(kJ/mol)	E(kJ/mol)	logA(1/s)	k(10^3/s)^a	Ref.
I	$CaC_2O_4 \cdot H_2O-H_2O$	135^b	0.67±0.37	90.0±5.0	—	—	3,5
	$CaC_2O_4 \cdot D_2O-D_2O$	135^b		92.9±6.3	—	—	
II_a	$CuSO_4 \cdot 5H_2O-2H_2O$	57.9	2.34±0.93	70.5±1.7	8.53±0.28	2.87±0.10	13
	$CuSO_4 \cdot 5D_2O-2D_2O$	61.1		73.3±1.7	8.89±0.28	2.37±0.10	
II_b	$CuSO_4 \cdot 3H_2O-2H_2O$	80.7	1.17±0.75	86.7±1.7	10.2±0.3	2.59±0.18	13
	$CuSO_4 \cdot 3D_2O-2D_2O$	79.1		82.3±1.5	9.63±0.22	2.80±0.11	
III	$H_3BO_3-H_2O$	98.5	2.9±2.5	96.5±2.9	10.7±0.4	1.26±0.05	6
	$D_3BO_3-D_2O$	98.3		93.3±2.9	10.2±0.5	1.24±0.10	
IV_a	$BaCl_2 \cdot 2H_2O-H_2O$	68.3	1.71±0.68	78.9±0.7	9.22±0.10	1.43±0.04	12
	$BaCl_2 \cdot 2D_2O-D_2O$	68.8		92.3±1.1	11.3±0.2	1.56±0.10	
IV_b	$BaCl_2 \cdot H_2O-H_2O$	94.6	0.93±0.74	75.2±1.0	7.74±0.15	1.20±0.03	12
	$BaCl_2 \cdot D_2O-D_2O$	95.9		72.7±1.2	7.32±0.17	1.05±0.03	
V	$Li_2SO_4 \cdot H_2O-H_2O$	87.3	1.63±1.11	80.8±1.3	8.80±0.27	1.24±0.02	10
	$Li_2SO_4 \cdot D_2O-D_2O$	87.7		79.3±0.9	8.56±0.19	1.18±0.02	
VI_a	$K_2Mg(SO_4)_2 \cdot 6H_2O-2H_2O$	77.3	1.53±0.42	125±5	15.9±0.7	2.37±0.10	11
	$K_2Mg(SO_4)_2 \cdot 6D_2O-2D_2O$	79.5		114±4	14.2±0.6	1.71±0.06	
VI_b	$K_2Mg(SO_4)_2 \cdot 4H_2O-2H_2O$	134.4	0.5±1.9	116±8	12.9±1.0	10.2±0.5	11
	$K_2Mg(SO_4)_2 \cdot 4D_2O-2D_2O$	132.2		111±4	12.2±0.5	10.0±0.3	
VI_c	$K_2Mg(SO_4)_2 \cdot 2H_2O-2H_2O$	181.7	0.3±1.9	117±3	11.2±0.4	5.60±0.10	11
	$K_2Mg(SO_4)_2 \cdot 2D_2O-2D_2O$	182.0		127±3	12.3±0.4	5.58±0.15	
VII_a	$SrCl_2 \cdot 2H_2O-H_2O$	80.4	1.2±0.8	116±2	14.4±0.3	1.77±0.03	14
	$SrCl_2 \cdot 2D_2O-D_2O$	80.6		118±3	14.6±0.5	1.77±0.02	
VII_b	$SrCl_2 \cdot H_2O-H_2O$	119.6	0.8±0.8	113±2	12.1±0.2	1.34±0.02	14
	$SrCl_2 \cdot D_2O-D_2O$	119.9		112±2	12.0±0.3	1.30±0.02	

[a] Value at the mean temperature of $T_{1/2}$ of the hydrate and its deuterate.

[b] Extrapolated onset temperature according to DSC.

Deuteration effects on the kinetics of thermal decompositions of several solids were examined further by thermogravimetry using an integral method in terms of the kinetic function $F(\alpha)$ determined isothermally[8-12]. It followed that the kinetic isotope effects are detectable through the statistics which require a comparable amount of experimental work with the isothermal or heating rate method and are rather insensitive to the kinetic function adopted[9]. In Table 1 are summarized the kinetic deuterium isotope effects determined from TGA.

We see that there is a trend of the kinetic compensation effect between the protium and deuterium compounds. This fact suggests that the activation energy and activation entropy should be considered in explaining such kinetic deuterium isotope effects. The rate constant k is also appropriate for the comparison between the pair. The thermal stability discussed above is correlated with the kinetics as well as with the enthalpy change ΔH, since the temperatures measured by means of dynamic thermal analyses are in general far from the thermodynamic equilibrium temperatures, particularly for runs at higher heating rates. This is exemplified by the reaction II_b (see Table 1), i.e.,the dehydration temperature of hydrate tends to be higher than the deuterate in the case of smaller k of the hydrate.

No significant- and inverse kinetic isotope effects in k seem to imply that neither phase boundary controlled- nor diffusion mechanisms should regulate the reactions[14]. Normal kinetic isotope effects would be observed if the reaction could be regulated by the chemical reaction at phase boundaries, since the bond in the activated complex is assumed in general to be nearly broken or weakened in the course of endothermic reactions such as the dehydration. Diffusion mechanisms would also give rise to normal isotope effects. On the other hand, the Avrami-Erofeyev laws may yield from normal- to inverse isotope effects, depending on the state of activated complex for random nucleations and their growth processes.

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