Thermochimica Acta, 52 (1982) 195–199
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

KINETICS AND MECHANISM OF THERMAL DEHYDRATION OF LITHIUM SULFATE MONOHYDRATE BY MEANS OF TG AND DSC

HARUHIKO TANAKA

Chemistry Laboratory, Faculty of School Education, Hiroshima University, Shinonome, Hiroshima 734 (Japan)

(Received 23 June 1981)

ABSTRACT

The thermal dehydration of finely powdered $Li_2SO_4 \cdot H_2O$ was examined by means of dynamic TG–DSC recorded simultaneously as well as TG at constant temperatures. The dehydration was controlled by a random nucleation and subsequent growth mechanism. The kinetic equation was expressed as $[-\ln(1-\alpha)]^{1/1.5} = kt$, where α is the fraction dehydrated at time t and k is the rate constant. The activation energy of ca. 30 kcal $mole^{-1}$ was derived, which was much larger than the corresponding enthalpy change of 12.55±0.07 kcal $mole^{-1}$.

INTRODUCTION

Recently, we have reported that various runs are required in determining kinetic parameters for the solid decompositions from thermal analyses [1]. It seems worthwhile to examine the kinetics of thermal dehydration of salt hydrates extensively, although a number of papers have appeared on the kinetics of these dehydrations.

An earlier kinetic study on the thermal dehydration of lithium sulfate monohydrate by means of TG at constant temperatures showed that the dehydration was controlled by a nucleation and growth mechanism [2]. The process had activation energies of 14.3 and 28.6 kcal $mole^{-1}$ in air at a pressure of 2 mm Hg above and below 98°C, respectively.

It seems of interest to study the dehydration of $Li_2SO_4 \cdot H_2O$ by means of dynamic TG and DSC, since both isothermal and non-isothermal studies seem to be necessary for the determination of reliable kinetic parameters [1,3]. The present paper deals with the thermal dehydration of $Li_2SO_4 \cdot H_2O$ in a flow of nitrogen by means of dynamic TG–DSC as well as TG at constant temperatures.

0040-6031/82/0000-0000/$02.75

EXPERIMENTAL

Reagent grade lithium sulfate monohydrate was ground and sieved to the fraction 170–200 mesh. TG–DSC traces were recorded simultaneously at various heating rates in a flow of nitrogen at a rate of 50 ml min^{-1}, using an apparatus of TG–DSC (8085 E1) of Rigaku Denki Co. About 20.0 mg of sample were used. TG traces at constant temperatures were also recorded under the same condition as that in the dynamic run. Other experimental procedures and computational work were the same as those described previously [1].

RESULTS AND DISCUSSION

Isothermal study

From the analysis of TG traces at constant temperatures according to a previous method [1], the dehydration of $Li_2SO_4 \cdot H_2O$ was found to follow either a random nucleation and subsequent growth (A_m) or a phase boundary reaction (R_n) mechanism. The exponents m and n in the kinetic equations of $[-\ln(1-\alpha)]^{1/m} = kt$ and $1-(1-\alpha)^{1/n} = kt$ were derived to be 1.5 ± 0.1 and 3.1 ± 0.2, respectively, over the temperature range 95.2–103.7°C. In the equations, α is the fraction dehydrated, k is the rate constant, and t is the time. Table 1 shows the rate constants derived in terms of the two equations at various temperatures.

From the Arrhenius plots, activation energies, E, and frequency factors, A, were calculated as is shown in Table 2. It is seen that nearly equal values result regardless of the assumed mechanisms, $A_{1.5}$ and $R_{3.1}$. It is interesting that these values are comparable with that reported earlier [2] for the dehydration below 98°C in air at a reduced pressure but not for that above 98°C. It seems that an additional study is needed in order to clarify the dehydration mechanism of $Li_2SO_4 \cdot H_2O$.

Non-isothermal study

Typical TG–DSC traces obtained simultaneously for the thermal dehydration of $Li_2SO_4 \cdot H_2O$ are shown in Fig. 1. The dehydration temperature was determined at various heating rates from the DSC traces. Table 3 shows the temperature of inception, T_i, the extrapolated onset temperature, T_{eo}, and the peak temperature, T_p. By extrapolating the T_i values to the zero heating rate, the thermodynamic (equilibrium) dehydration temperature may be estimated as ca. 80.0°C.

From the repeated DSC traces, the enthalpy change, ΔH, for the dehydration was also determined to be 12.55 ± 0.07 kcal $mole^{-1}$. The observed value of ΔH is a little less than that of 13.69 determined at the temperature range 17–47°C [4] and that of 13.57 from the standard enthalpy of formation at 25°C [5]. The reason for this difference is not clear at this stage, being too large to be explained by the change in heat capacity with the temperature.

TABLE 1

Rate constants, k, obtained from TG at constant temperatures in terms of $A_{1\,5}$ and $R_{3\,1}$ mechanisms [a]

Temp (°C)	$k \times 10^4$ (s^{-1})	
	$A_{1\,5}$	$R_{3\,1}$
95 2	3.5455	1 2443
98 5	5 8420	2 0633
99.7	5 6786	2 0256
102 5	8 3413	2 9745
103 7	8 8166	3 1230

[a] For the α range 0 3–0 9

TABLE 2

Kinetic parameters and correlation coefficients derived from the Arrhenius plot

F(α)	E (kcal mole^{-1})	log A (s^{-1})	$-r$
$A_{1\,5}$	29 5±0 9	14 1±0 6	0 9836
$R_{3\,1}$	29 9±0 9	13 9±0 6	0 9840

TABLE 3

Dehydration temperatures from DSC at different heating rates

Heating rate (°C min^{-1})	Dehydration temp (°C)		
	T_i	T_{eo}	T_p
0 55	82 0	83 4	98 8
1 03 [a]	83 0±1 1	86 5±0 9	107 0±0 5
2 02	87.6	90 2	115 2

[a] Mean of seven observed values

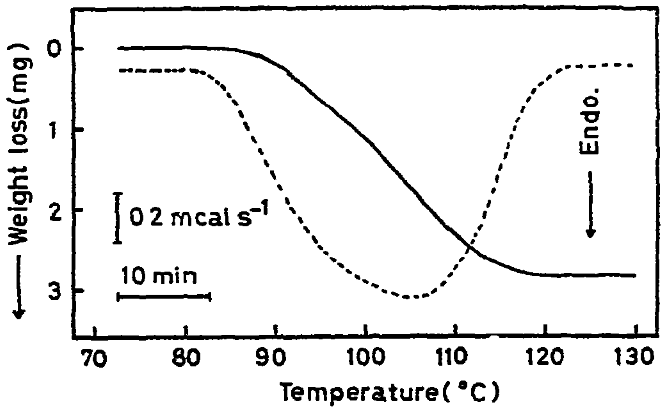

Fig. 1. Typical traces of TG (————) and DSC (- - - - - -) recorded simultaneously for the dehydration of $Li_2SO_4 \cdot H_2O$

Kinetic parameters by means of dynamic thermal analyses are to be derived in terms of the well-known equation [6]

$$\ln\{F(\alpha)/T^2\} = \ln\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)-\frac{E}{R}\frac{1}{T} \tag{1}$$

where $F(\alpha)$ is a function depending on the mechanism of non-isothermal dehydration. T is the absolute temperature, R is the gas constant, and a is the linear heating rate. If the $F(\alpha)$ estimated for the corresponding isothermal run is to be used for the non-isothermal one, the values of E and A are easily derived [1]. Table 4 shows kinetic parameters at various heating rates by means of dynamic TG. Table 5 shows the corresponding values by means of dynamic DSC recorded simultaneously with TG.

It is seen that the parameters from the $A_{1.5}$ mechanism at lower heating rates are compatible with those of isothermal runs and the size of parameters is reasonable, whereas the parameters from the $R_{3.1}$ mechanism are not. It may follow that both the isothermal and non-isothermal dehydrations of crystalline powders of $Li_2SO_4 \cdot H_2O$ in a flow of nitrogen are regulated by the $A_{1.5}$ mechanism. It is interesting that an A_m mechanism was also proposed for the isothermal dehydration of $Li_2SO_4 \cdot H_2O$ in air at various pressures, though the m value was slightly different [2].

It may be noted that the parameters from TG are slightly smaller than those from DSC. This may result from a slight time-lag of liberation of water through the solid product [7].

It seems worthwhile comparing the value of E, which is assumed to be ca. 30 kcal mole^{-1} both from the TG at constant temperatures and dynamic TG and DSC, with the enthalpy change, $\Delta H = 12.55 \pm 0.77$ kcal mole^{-1}. This may be one of the many exceptions to the well-known rule that E is nearly equal to ΔH in endothermic decompositions. The exceedingly higher value of E than ΔH may result from the contribution of nucleation of the solid product to the activation energy [8]. The contribution of nucleation may vary depending on the experiment, since the possibility of nucleation is sensitive to the sample and measuring conditions such as number of defects in crystal, packing, atmosphere, temperature etc. The above argument

TABLE 4

Kinetic parameters by means of dynamic TG at various heating rates [a]

Heating rate (°C min^{-1})	Temp range (°C)	E (kcal mole^{-1})		$\log A$ (s^{-1})		$-r$	
		$A_{1.5}$	$R_{3.1}$	$A_{1.5}$	$R_{3.1}$	$A_{1.5}$	$R_{3.1}$
0.55	88.8–106.3	28.4	39.5	13.7	19.7	0.9918	0.9853
1.17	95.5–114.1	27.8	38.7	13.3	19.1	0.9921	0.9857
2.41	98.5–122.5	21.8	30.5	9.8	14.3	0.9909	0.9841

[a] For the α range 0.1–0.9

TABLE 5

Kinetic parameters by means of dynamic DSC recorded simultaneously with TG at various heating rates [a]

Heating rate (°C min^{-1})	Temp range (°C)	E (kcal mole^{-1})		log A (s^{-1})		$-r$	
		$A_{1.5}$	$R_{3.1}$	$A_{1.5}$	$R_{3.1}$	$A_{1.5}$	$R_{3.1}$
0.55	88.2–106.0	29.3	40.8	14.2	20.5	0.9914	0.9848
1.17	94.5–113.2	29.7	42.1	14.4	21.0	0.9869	0.9799
2.41	97.5–121.1	23.0	32.6	10.5	15.5	0.9894	0.9831

[a] For the α range ca. 0.1–0.9

seems to be supported by the fact that the rate of dehydration of $Li_2SO_4 \cdot H_2O$ was dependent on the sample and measuring conditions [2].

If the rate limiting stage in the dehydration is a chemical reaction, the activation energy might often be comparable with the corresponding value of ΔH. It is interesting to note that the lower activation energy for the dehydration of $Li_2SO_4 \cdot H_2O$, which was reported to be 14.3 kcal mole^{-1} in air at a pressure of 2 mm Hg above 98°C, resulted from such a limiting stage of chemical reaction [2].

In conclusion, the analyses of dynamic TG and DSC as well as TG at constant temperatures are very useful for studying the kinetics and mechanism of solid decompositions.

ACKNOWLEDGEMENT

The author wishes to thank H. Fujimaru for his aid in the experimental part of this work.

REFERENCES

1 H. Tanaka, S Ohshima, S Ichiba and H Negita, Thermochim Acta, 48 (1981) 137

2 V.G Vasilèv and Z V Ershova, Russ J Phys Chem , 46 (1972) 1197

3 J M Criado and J Morales, Thermochim Acta, 16 (1976) 382; 19 (1977) 305

4 G H Price and W I Stuart, J Chem Soc , Faraday Trans I, 69 (1973) 1498

5 J A Dean (Ed), Lange's Handbook of Chemistry, McGraw-Hill, New York, 1979, Sect 9

6 J Zsakó, J. Therm Anal., 5 (1973) 239

7 J Zsakó, E. Kekedy and Cs Varhelyi, J. Therm. Anal., 1 (1969) 339

8 W E. Garner, in W E Garner (Ed), Chemistry of the Solid State, Butterworths, London, 1955, p 219