NON-ISOTHERMAL KINETIC STUDY ON THE THERMAL DEHYDRATION OF SODIUM TUNGSTATE DIHYDRATE[①]

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ABSTRACT　The thermal dehydration of sodium tungstate dihydrate has been studied by using differential scanning calorimetry (DSC). It was found that the dehydration takes place in a single thermal step at heating rates β= 2~ 15 K/ min, and the enthalpy change is (100. 4 $\pm$1. 9) kJ/ mol. In the main decomposition range of α= 0. 05~ 0. 95 when β= 2~ 5 K/ min, α= 0. 05~ 0. 80 when β= 10 K/ min and α= 0. 05~ 0. 75 when β= 15 K/ min, the fittest kinetic equation was deduced, and from this equation the calculated activation enegy E was 184. 3 kJ/ mol. According to this equation, the mechanism of dehydration should be the formation and the plate-like growth of randomly distributed nuclei. When $\beta \geqslant$10 K/ min, the dehydration obeys at least two kinetic equations.

Key words　non-isothermal kinetics　dehydration　sodium tungstate dihydrate

1　INTRODUCTION

Sodium tungstate dihydrate is used in the preparation of coated electrodes for electrocatalysis[1] and as fire retardant for fabrics[2]. Moreover, it has very important use in the study on the chemistry of polytungstates[3]. Its thermal dehydration had been studied by earlier workers. Using thermogravimetric(TG) analysis, Gadalla et al[2] reported that the dehydration takes place in a single step at low scan speeds, but in two steps at $\beta \geqslant$10 K/ min; and reported that activation energy is E = 25. 6 kJ/ mol. Using DSC, Guarini et al[4] reported that the contracting circle equation with E= 87. 8 kJ/ mol is the fittest one for the main decomposition of single crystal, and that the first order kinetic equation with E = 144. 6 kJ/ mol fits over the whole decomposition range for the crystal powder. So there is considerable difference in the kinetic equation and parameters about the dehydration of sodium tungstate dihydrate. The present study on the thermal dehydration of $Na_2WO_4 \cdot 2H_2O$ crystal powder was undertaken with the aim of obtaining the kinetic parameters and equation.

2　EXPERIMENTAL

Commerical $Na_2WO_4 \cdot 2H_2O$ of A. R. grade was refined by recrystallization, the product was dried in air at room temperature and screened without grinding. The sample size for experiment was in the range of 120~ 130 μm. The pattern of X-ray diffraction was matched with JCPDS card No. 13- 431, and the mass loss up to 473 K was (10. 94 $\pm$0. 19)% (calculated 10. 92%).

The DSC curves were recorded using a thermal analyzer DT-40 (Shimadzu, Japan). (4. 5 $\pm$0. 5) mg of sample were weighted in the standard aluminum pans. Reference pan was empty, and lids were added loosely to sample and reference pans. The measurement were car-

ried out in air atmosphere up to 473 K at different heating rates, namely, 2, 3, 4, 5, 10 and 15 K/ min respectively.

3   RESULTS AND DISCUSSION

3. 1   DSC curves
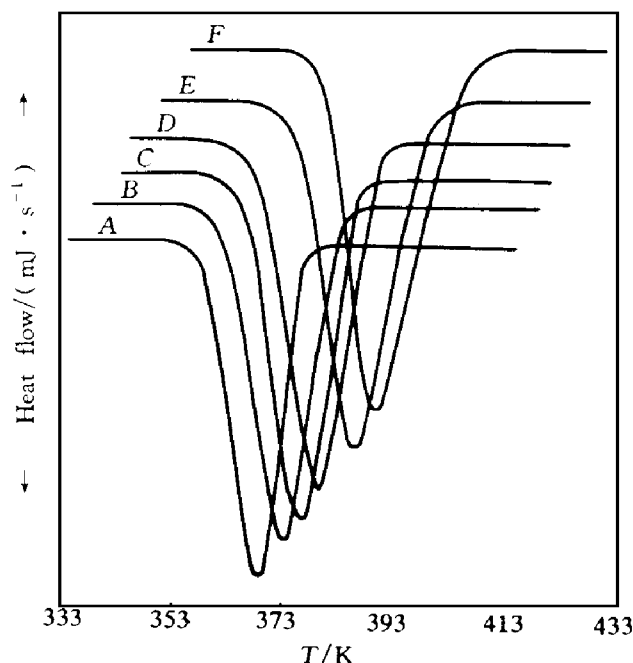
The DSC curves of six runs are collected in Fig. 1.

Fig. 1   DSC curve
A —2 K/ min; B —3 K/ min; C —4 K/ min;
D —5 K/ min; E —10 K/ min; F —15 K/ min

The overall shape of curves remains the same up to β= 15 K/ min, and no splitting is evidenced at higher β in disagreement with Ref. [5]. This result showed that the dehydration is a single thermal step at β= 2~ 15 K/ min. The mean value of the enthalpy change is (100. 4 ± 1. 9) kJ/ mol.

The fraction of decomposition α, the rate of decomposition ($d\alpha/ dt$) and temperature T were determinated directly from DSC curves using normal method[6]. In the main decomposition range(about α= 0. 05~ 0. 95), the relation of α and temperature T are collected in Fig. 2.

3. 2   Determination of the activation energy E

When the kinetic equation is unknown,

there are three methods to obtain the activation energy E of the reaction from the multi-heating-rates DSC curves.

The first method is Kissinger' s method[7] and takes the form

$$\ln(\beta/ T^{2}) = \text{constant} - E/(RT) \qquad (1)$$

where R is the gas constant and T is the temperature(K) at the maximum of $d\alpha/ dt$, namely, the peak temperature of the DSC curve. The values of α and T at maximam $d\alpha/ dt$ are listed in Table 1.
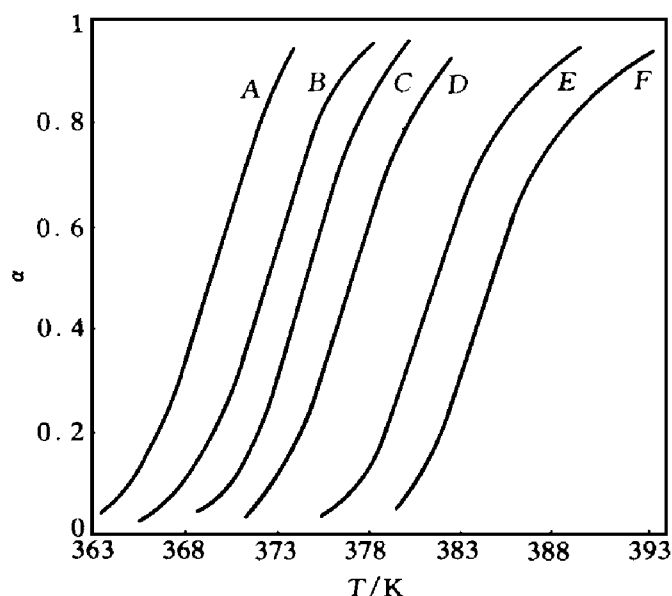

Fig. 2   Relation of the fraction of decomposition α and temperature T
A —2 K/ min; B —3 K/ min; C —4 K/ min;
D —5 K/ min; E —10 K/ min; F —15 K/ min

Table 1   The values of α and T at the maximum of $d\alpha/ dt$

$\beta/$ ($K\cdot min^{-1}$)	2	3	4	5	10	15
T/ K	370. 4	373. 6	375. 6	377. 9	382. 9	385. 6
α	0. 612	0. 624	0. 626	0. 602	0. 616	0. 600

By feeding data listed in Table 1, the regression line with correlation coefficient r = 0. 998 was obtained from the plot of $\ln(\beta/ T^{2})$ vs $1/ T$, then the activation energy E calculated from the slope of the line is 156. 7 kJ/ mol.

The second method is that proposed by Ozawa[8] and takes the form

$$\ln \beta = \text{constant} - 1. 05 E/(RT) \qquad (2)$$

where T is the temperature(K) at a given α value for a certain heating rate β. Therefore, at a given α value, a regression line should be obtained from the plot of $\ln\beta$ vs $1/T$ when the reaction mechanism doesn't change with the heating rate β, and E can be calculated from the slope of the line. In the present work, α takes values from 0. 10 to 0. 90 in steps 0. 10, the results are listed in Table 2.

The third method is that proposed by Friedman[9] and takes the form

$$\ln(d\alpha/dt) = \ln[Af(\alpha)] - E/(RT) \quad (3)$$

where A is the frequency factor, and $f(\alpha)$ is the function of α which represents the reaction mechanism. At a given α value, $(d\alpha/dt)$ and T can be taken directly from different DSC curves. If $f(\alpha)$ fits the different heating rate β at a given α value, the plot of $\ln(d\alpha/dt)$ vs $1/T$ should give a line, and E can be obtained from the slope of the regression line. The results of this method are also listed in Table 2.

Table 2 E and correlation coefficient r at different α value from the Ozawa and Friedman methods

α	Ozawa method		Friedman method	
	E/ (kJ·mol⁻¹)	Correlation coefficient	E/ (kJ·mol⁻¹)	Correlation coefficient
0. 10	140. 7	0. 999	179. 7	0. 985
0. 20	144. 8	0. 999	181. 2	0. 986
0. 30	147. 7	0. 999	188. 0	0. 989
0. 40	150. 2	0. 999	193. 0	0. 989
0. 50	149. 6	0. 999	191. 3	0. 992
0. 60	148. 0	0. 999	188. 4	0. 995
0. 70	145. 6	1. 000	184. 2	0. 991
0. 80	138. 0	0. 999	171. 6	0. 989
0. 90	124. 2	1. 000	141. 7	0. 986
Avg.	143. 2		179. 9	

Kissinger's method and Ozawa's method are the integral method which is based on the fundamental assumption that the heating rate of $\beta = dT/dt$ is a constant. However, in the present work, it was found that the heating rate is obviously not a constant in the proceeding of the reaction because of the effect of the reaction heat. Therefore, the results from these two methods are not advisable.

Although Friedman's method did not give better correlation coefficient r, it has an advantage over the integral method[10] to the determination of activation energy E, especially when a reaction is endothermic or exothermic[11]. Hence, the value of E from this method was considered to be the best proper for the present work. From Table 2, it can be seen that the values of E at $\alpha = 0. 10 \sim 0. 80$ are approximately no change and the average value is $E = 184. 7$ kJ/mol, but when $\alpha = 0. 90$, E value is obviously lower.

3. 3 Kinetic equation

The non-isothermal kinetic equations for dehydration can be written in general as

$$d\alpha/dt = A\exp(- E/(RT))f(\alpha) \quad (4)$$

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/(RT) \quad (5)$$

For a single DSC curve, the plot of $\ln[(d\alpha/dt)/f(\alpha)]$ vs $(1/T)$ should lead a line when the form of $f(\alpha)$ is correct. The value of E and A can be calculated from the slope and intercept respectively.

The most commonly used functions[10] were used to treat the experimental data. When a function not only could give the line with good correlation coefficient in the plot of $\ln[(d\alpha/dt)/f(\alpha)]$ vs $(1/T)$, but also could deduce the value of E in agreement with that obtained using Friedman's method, then this function is considered as the fittest one.

The calculation showed that in the range of $\alpha = 0. 05 \sim 0. 95$ for $\beta = 2 \sim 5$ K/min, $\alpha = 0. 05 \sim 0. 80$ for $\beta = 10$ K/min and $\alpha = 0. 05 \sim 0. 75$ for $\beta = 15$ K/min, there were five functions, $2(1 - \alpha)[- \ln(1- \alpha)]^{1/2}$, $3(1- \alpha)[- \ln(1- \alpha)]^{2/3}$, $(1- \alpha)$, $(1- \alpha)^{3/2}$ and $(1- \alpha)^2$, which all could give the line with good correlation coefficient in the plot of $\ln[(d\alpha/dt)/f(\alpha)]$ vs $(1/T)$, and five deduced average values of E were 184. 3, 104. 7, 409. 6, 533. 0 and 657. 6 kJ/mol respectively. It was obvious that only the deduced average value of E from the first function was in agreement with that obtained using Friedman's method (184. 7 kJ/mol for $\alpha =$

0. 10~ 0. 80), and no one was in agreement with that of Kissinger's method or Ozawa's method. Therefore the fittest function is $f(\alpha) = 2(1- \alpha)[- \ln(1- \alpha)]^{1/2}$, and the detailed results are listed in Table 3.

Table 3 Results using $f(\alpha)= 2(1- \alpha) \cdot [- \ln(1- \alpha)]^{1/2}$ for $\alpha= 0.05~ 0.95$

$\beta/$ $(K \cdot min^{-1})$	$E/(kJ \cdot mol^{-1})$	$\ln(A/s^{-1})$	r
2	184. 5	54. 0	0. 996
3	185. 3	54. 0	0. 996
4	194. 0	55. 0	1. 000
5	181. 4	52. 3	0. 999
10[*]	175. 1	51. 0	0. 996
15[* *]	185. 3	54. 1	0. 997
Avg.	184. 3	53. 4	

* $\alpha= 0.05~ 0.80$, * * $\alpha= 0.05~ 0.75$

The function $f(\alpha) = 2(1- \alpha)[- \ln(1- \alpha)]^{1/2}$ is the differential form of Avram-Erofeev's equation[10] for $n = 2$ which corresponds to the plate-like growth of randomly distributed nuclei on the surface of the phase. In fact, for the proceeding of non-isothermal decomposition of single crystal, Guarini et al[4] had observed using optical microscopy that the circular nuclei appear on the observed surface and subsequently expand laterally to occupy the whole surface. It is reasonable to consider that the most probable mechanism of thermal dehydration for the crystal powder of $Na_2WO_4 \cdot 2H_2O$ is the formation and the plate-like growth of randomly distributed nuclei.

The function $f(\alpha) = 2(1- \alpha)[- \ln(1- \alpha)]^{1/2}$ can fit for the whole main decomposition range(about $\alpha= 0.05~ 0.95$) when $\beta= 2~ 5$ K/ min, but it can not fit the whole main decomposition range when $\beta \geqslant 10K/min$, which can be seen clearly from Fig. 3. The fitting range is about $\alpha= 0.05~ 0.80$ at $\beta= 10$ K/ min, and about $\alpha= 0.05~ 0.75$ at $\beta= 15$ K/ min. This result showed that the dehydration obeys at least two kinetic mechanisms in the range of $\alpha= 0.05$
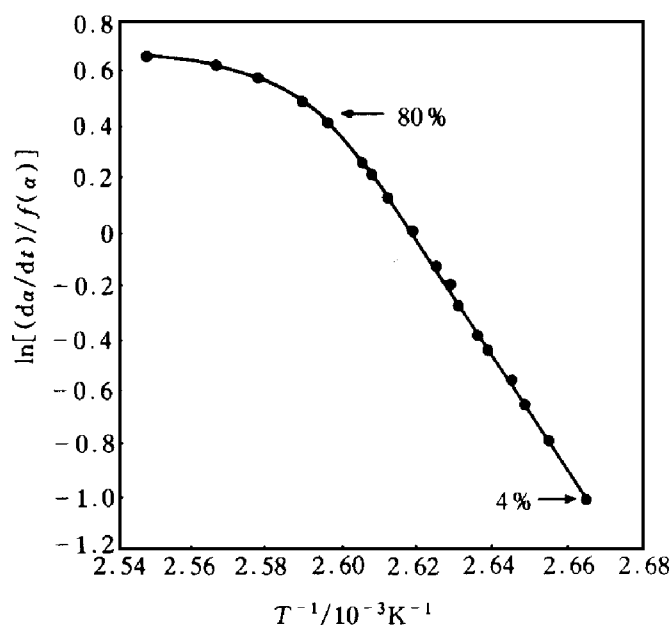

Fig. 3 The plot of $\ln[(d\alpha/dt)/f(\alpha)]$ vs $(1/T)$ using $f(\alpha)= 2(1- \alpha)[- \ln(1- \alpha)]^{1/2}$ when $\beta= 10$ K/ min

~ 0. 95 when $\beta \geqslant 10$ K/ min, which confirms that reported by Gadalla et al[2]. From this result, it can be explained that the value of E at $\alpha = 0.90$ is obviously lower than that at $\alpha= 0.10$ ~ 0. 80 in Friedman's method.

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