Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 877-884

DEHYDRATION REACTION OF MANGANESE(II) OXALATE DIHYDRATE IN THE SOLID STATE

New method in the study of non-isothermal kinetics

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(Received February 20, 1998; in revised form May 12, 1998)

Abstract

A new method was proposed for determining the most probable mechanism function of a solid phase reaction. According to Coats-Redfern's integral equation $E_{\beta\to0}$ was calculated by extrapolating β to zero using a series of TG curves with different heating rates. Similarly, $E_{\alpha\to0}$ was calculated according to Ozawa's equation. The most probable mechanism function of the solid phase dehydration of manganese(II) oxalate dihydrate was confirmed to be $G(\alpha)=(1-\alpha)^{1/2}$ by comparing $E_{\alpha\to0}$ with $E_{\beta\to0}$.

Keywords: dehydration, kinetics, manganese(II) oxalate dihydrate, mechanism, non-isothermal, TG-DTA

Introduction

Theoretically, according to Coats-Redfern's integral equation [1] for a sample heated at a definite heating rate (β), if a certain $G(\alpha)$ function gets the best correlation coefficient of $\ln[G(\alpha)/T^2]$ *vs.* $1/T$ in comparison with those of other $G(\alpha)$ functions, it will be confirmed as the $G(\alpha)$ function of the most probable mechanism function. Actually, in applying this method to a certain solid phase reaction, several $G(\alpha)$ functions often have very similar correlation coefficients, which makes it impossible to select the best one. Therefore, to select the most probable $G(\alpha)$ function some authors put forward a new method by combining integral and differential methods [2] or by combining non-isothermal and isothermal methods [3]. All these methods were conducted at a definite heating rate (β), thus thermal hysteresis would make the system to deviate from the state of equilibrium and the result obtained must be different from the true one. Therefore, it has been proposed to calculate first a series of E corresponding to different heating rates by integration method, then to evaluate $E_{\beta\to0}$ by extrapolating β to zero. Theoretically, $E_{\beta\to0}$ is the activation energy at thermal equilibrium and the most probable mechanism function $G(\alpha)$ can be confirmed by the criterion

1418-2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

$E_{\beta\to 0}$. Actually, in applying this method to a certain thermal reaction generally more than one $G(\alpha)$ functions were offered for selection, consequently, the same difficulty was encountered. For overcoming such difficulties the authors believe that the method used in studying homogeneous complex reactions may be applied to study solid phase reactions. For a certain solid phase reaction, $E_{\alpha\to 0}$ represents the activation energy of the main reaction at the beginning, where secondary reactions do not start yet. Therefore, it can best represent the nature of the reaction. On the basis of $E_{\alpha\to 0}$, the $E_{\beta\to 0}$ which fits best to $E_{\alpha\to 0}$ would be a match for the most probable mechanism function $G(\alpha)$.

Experimental

Manganese oxalate dihydrate was prepared by the usual method. All of the reagents used were of A.R. grade. Powder X-ray diffraction analysis confirmed that the sample was $MnC_2O_4\cdot 2H_2O$.

The sample was ground and sieved. A definite amount of the sample smaller than 60 mesh was put into the static atmosphere of a Rigaku (Japan) thermal analysis instrument using α-Al_2O_3 as reference substance. TG-DTA curves were obtained at heating rates of 3, 5, 10 and 15°C min^{-1}.

Results and discussion

Typical TG-DTA curves for the title compound at a heating rate of 10°C min^{-1} are shown in Fig. 1. The TG-DTA curves in Fig. 1 indicate that dehydration occurs in one step. The temperature range of dehydration is 113–150°C.

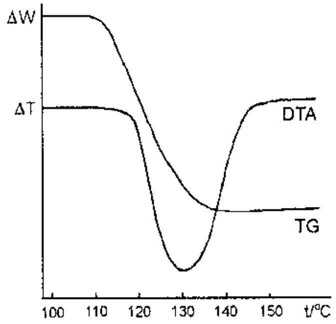

Fig. 1 Typical TG-DTA curves at heating rate: β=10°C min^{-1}

The mass loss of 19.94% is in agreement with the theoretical mass loss of 20.11%. Therefore, the dehydration of the sample can be described as

$$MnC_2O_4\cdot 2H_2O_{(s)} \xrightarrow{113-150^{\circ}C} MnC_2O_{4(s)} + 2H_2O_{(g)}$$

Table 1 Integral forms, $G(\alpha)$ used for the present analysis

No.	Name of function	Mechanism	Symbol	Integral form, $G(\alpha)$
1	Parabolic law	Diffusion, 1D	D_1	α^2
2	Valensi (Barrer) equation	Diffusion, 2D	D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$
3	Ginstling-Brounstein equation	Diffusion, 3D (cylindrical symmetry)	D_3	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
4	Jander equation	Diffusion, 3D (sphere symmetry)	D_4	$[1-(1-\alpha)^{1/3}]^2$
5	Anti-Jander equation	Diffusion, 3D	D_5	$[(1+\alpha)^{1/3}-1]^2$
6	Zhuralev, Lesokin and Tempelmen eq.	Diffusion, 3D	D_6	$\{[1/(1-\alpha)]^{1/3}-1\}^2$
7		Autocatalysis	Au	$\ln[\alpha/(1-\alpha)]$
8	Avrami-Erofeev equation	N and G (n=1)	A_1	$[-\ln(1-\alpha)]$
9	Avrami-Erofeev equation	N and G (n=1.5)	$A_{1.5}$	$[-\ln(1-\alpha)]^{1/1.5}$
10	Avrami-Erofeev equation	N and G (n=2)	A_2	$[-\ln(1-\alpha)]^{1/2}$
11	Avrami-Erofeev equation	N and G (n=3)	A_3	$[-\ln(1-\alpha)]^{1/3}$
12	Avrami-Erofeev equation	N and G (n=4)	A_4	$[-\ln(1-\alpha)]^{1/4}$
13		Contracted geometry shape (cylindrical symmetry)	R_1	$1-(1-\alpha)^{1/2}$
14		Contracted geometry shape (sphere symmetry)	R_2	$1-(1-\alpha)^{1/3}$
15	Mample power law		P_1	α
16	Mample power law		P_2	$\alpha^{1/2}$
17	Mample power law		P_3	$\alpha^{1/3}$
18	Mample power law		P_4	$\alpha^{1/4}$
19	Second order	Chemical reaction (n=2)	C_2	$(1-\alpha)^{-1}-1$
20	One and one-half order	Chemical reaction (n=1 or 1.5)	$C_{1/1.5}$	$(1-\alpha)^{-1/2}$
21				$1/(1-\alpha)$
22				$1/(1-\alpha)^2$

In order to obtain the kinetic parameters and the most probable mechanism of the dehydration reaction, Coats-Redfern's integral Eq. (1) was employed,

$$\ln\frac{G(\alpha)}{T^2}=\ln\frac{AR}{E\beta}-\frac{E}{RT} \qquad (1)$$

where $G(\alpha)$ represents the integral mechanism function (Table 1), α: proportion of mass loss of a sample, i.e.

$$\alpha=\frac{w_0-w_t}{w_0-w_\infty}$$

where w_0, w_t, and w_∞ represent the sample mass at beginning, at t°C and at the end of dehydration, respectively; β – heating rate (°C min^{-1}), A – pre-exponential factor, R – gas constant, E – apparent activation energy. By substituting the original data listed in Table 2, and all the forms of $G(\alpha)$ in Table 1, into Eq. (1), the corresponding values of E, A in Table 3 are obtained.

Table 2 Fundamental data obtained from TG curves

β=3°C min^{-1}		β=5°C min^{-1}		β=10°C min^{-1}		β=15°C min^{-1}	
$\alpha(t)$	t/°C	$\alpha(t)$	t/°C	$\alpha(t)$	t/°C	$\alpha(t)$	t/°C
0.1459	117.5	0.1	120.6	0.1268	127.4	0.0845	129.6
0.2958	118.4	0.2429	121.9	0.2676	128.4	0.2252	130.9
0.4366	119.3	0.3143	122.5	0.4085	130.2	0.3662	132.8
0.507	120.0	0.3857	123.1	0.4789	131.0	0.4366	133.4
0.5775	120.7	0.4571	123.6	0.5493	132.1	0.507	134.6
0.6479	121.4	0.5286	124.8	0.6197	133.3	0.5775	135.6
0.7183	122.3	0.6174	126.3	0.6901	134.2	0.6479	136.9
0.7887	123.3	0.7429	127.2	0.7606	135.3	0.7887	140.3
0.8732	124.3	0.8857	130.3	0.831	137.2	0.8732	142.7

Table 3 clearly shows that when samples of the same mass are heated at different heating rates (β), in the course of dehydration reaction function only No. (21) and (20) have the best fit of data and a regularity of thermal decomposition reaction, namely, to have good linear correlation coefficient and kinetic parameters which do not contradict the general rules of thermal decomposition ((E=80–250 kJ mol^{-1}, $\ln A$=16.91–69.01 s^{-1}) [4]. The above argument has provided an essential basis for determining the probable mechanism of the dehydration reaction. Table 3 also shows that E and $\ln A$ calculated in accordance with a definite $G(\alpha)$ equation vary regularly with the variation of heating rate. The higher the heating rate, the farther the sample will deviate from equilibrium and the farther the calculated E and ln$A$ will deviate from their true values. E and ln$A$ were evaluated by linear regression (for $\beta \neq 0$) or by extrapolation (to $\beta=0$) and are listed in Table 4.

Table 4 shows that the values of E and ln$A$ for No. (21) overstepped the general rule of thermal decomposition. Therefore, No. (20), i.e. $G(\alpha)=(1-\alpha)^{1/2}$ was selected as the kinetic equation of the most probable mechanism with E=168.45 kJ mol^{-1} and ln$A$=45.40 s^{-1}.

Table 3 Non-isothermal kinetic parameters of the dehydration reaction at different heating rates

No.	β					
	3°C min^{-1}			5°C min^{-1}		
	E/kJ mol^{-1}	ln$A$/s^{-1}	r*	E/kJ mol^{-1}	ln$A$/s^{-1}	r*
1	572.081	167.86	0.9199	516.89	149.03	0.8896
2	648.78	190.96	0.9359	579.53	167.62	0.9093
3	681.25	199.52	0.9422	606.11	174.28	0.9172
4	747.54	220.05	0.9528	660.49	190.98	0.9309
5	849.50	250.99	0.9787	723.84	210.01	0.9553
6	974.52	290.25	0.9757	847.44	248.33	0.9627
7	1065.36	318.76	0.8719	625.68	182.21	0.8875
8	423.92	123.45	0.9651	370.87	105.79	0.9474
9	284.25	80.49	0.9671	250.13	69.05	0.9520
10	208.69	57.15	0.9641	182.12	48.24	0.9456
11	136.94	34.87	0.9630	119.21	28.88	0.9437
12	101.07	23.64	0.9618	87.75	19.10	0.9418
13	346.23	98.60	0.9445	307.03	85.40	0.9198
14	370.49	105.75	0.9520	326.93	91.14	0.9297
15	282.76	79.51	0.9183	255.13	70.04	0.8871
16	138.11	34.98	0.9148	124.25	30.18	0.8820
17	89.89	19.94	0.9112	80.63	16.69	0.8766
18	65.78	12.33	0.9073	58.81	9.86	0.8708
19	623.23	185.21	0.9882	535.57	156.42	0.9822
20	163.68	43.78	0.9872	133.59	33.92	0.9900
21	333.92	96.95	0.9877	273.81	77.46	0.9905
22	674.39	202.56	0.9880	554.24	163.80	0.9907

Table 3 Continued

No.	β					
	10°C min^{-1}			15°C min^{-1}		
	E/kJ mol^{-1}	ln$A$/s^{-1}	r*	E/kJ mol^{-1}	ln$A$/s^{-1}	r*
1	459.47	129.14	0.9162	407.18	112.38	0.8645
2	512.78	144.61	0.9307	453.87	125.77	0.8856
3	534.67	149.74	0.9363	473.54	130.19	0.8941
4	579.13	163.19	0.9460	513.70	142.28	0.9091
5	644.99	182.56	0.9735	558.47	155.30	0.9409
6	728.59	208.36	0.9684	651.00	183.52	0.9453
7	543.19	154.38	0.9480	587.27	165.46	0.8508
8	321.66	89.04	0.9574	285.79	77.51	0.9270
9	216.21	57.48	0.9613	192.85	49.91	0.9326
10	157.46	39.78	0.9557	139.49	33.94	0.9238
11	102.73	23.17	0.9538	90.73	19.23	0.9203
12	75.36	14.77	0.9519	66.34	11.78	0.9167
13	269.88	72.60	0.9378	238.74	62.58	0.8960
14	286.20	77.16	0.9448	253.45	66.63	0.9070
15	226.37	60.01	0.9140	200.19	51.56	0.8607
16	109.81	25.08	0.9093	96.69	20.78	0.8528
17	70.96	13.24	0.9043	62.19	10.32	0.8442
18	51.54	7.22	0.8988	44.94	4.99	0.8350
19	450.55	128.11	0.9826	406.14	113.78	0.9695
20	105.35	24.53	0.9920	96.17	21.48	0.9936
21	217.45	58.96	0.9925	199.15	52.96	0.9940
22	441.63	127.07	0.9927	405.10	115.19	0.9942

*r – linear correlation coefficient

According to Ozawa's integral equation

$$\log\beta = \log\frac{AE}{Rf(\alpha)} - 2.315 - 0.4567\frac{E}{RT} \qquad (2)$$

where $f(\alpha)$ is the differential expression for a definite reaction mechanism and the others have the same meaning as before.

Equation (2) shows that for a given α, $f(\alpha)$ is constant, $\log\beta$ depends linearly on $1/T$ and the apparent activation energy E for a definite α can be calculated from the slope of the line. For this reason a group of α *vs.* t curves of different heating rates were drawn using the data in Table 2. The apparent activation ener-

Table 4 Kinetic parameters used for extrapolation of $E_{\beta\rightarrow0}$

β/°C min^{-1}	No. (20)		No. (21)	
	E/kJ mol^{-1}	ln$A$/s^{-1}	E/kJ mol^{-1}	ln$A$/s^{-1}
15	96.17	21.48	199.15	52.96
10	105.35	24.53	217.45	58.96
5	133.59	33.92	273.81	77.46
3	163.68	43.78	333.92	96.95
0	168.45	45.4	343.40	100.12

gies E for different α were calculated according to Eq. (2) by employing the α *vs.* t curves and are listed in Table 5.

The data show that E varies with α, which is due to the complexity of solid phase reactions. $E_{\alpha\rightarrow0}$ was obtained by extrapolating α to zero (Table 5). The data show that $E_{\alpha\rightarrow0}$=162.48 kJ mol^{-1} which is very close to $E_{\beta\rightarrow0}$ (=168.45 kJ mol^{-1}). Therefore, equation No. (20), namely, $G(\alpha=(1-\alpha)^{-1/2}$ is the kinetic equation of the most probable mechanism function of the dehydration reaction.

Table 5 The variation of E for α at series heating rate

α	β/°C min^{-1}				E/ kJ mol^{-1}
	3	5	10	15	
0.8	123.2	128.5	136.2	140.2	121.63
0.7	121.8	126.7	134.0	137.7	128.42
0.6	120.8	125.2	132.5	136.0	132.36
0.5	120.2	124.1	131.3	134.4	139.54
0.4	119.3	123.7	130.2	133.0	145.09
0.3	118.5	122.5	129.1	132.0	146.02
0.2	118.0	121.5	128.1	130.8	151.68
0					162.48

Table 6 Expressions for the kinetic compensation effect

β/°C min^{-1}	ln$A = aE + b$
15	ln$A = 0.2934E - 7.1325$
10	ln$A = 0.2960E - 6.9620$
5	ln$A = 0.3016E - 6.8511$
3	ln$A = 0.3053E - 6.7679$
0	ln$A = 0.3071E - 6.6877$

According to the expression of the kinetic compensation effect [5] a series of expression of the kinetic compensation effect were calculated for different heating rates (β). Those for β→0 were also evaluated by extrapolation. The results are listed in Table 6.

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This work was supported by the key discipline fund of Tianjin Bureau of Higher Education.

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