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Kinetic Study of Boron Oxide Prepared by Dehydration of Boric Acid

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The kinetic parameters of dehydration of boric acid had been investigated by using TG-DTG data and the Doyle method. The reaction took place in two stages and the demarcation point of the two stages was near at $\alpha = 0.63$. The dehydration was completed with a final solid weight of 56.29 % with two reaction stages in series in the temperature range of 100-800 °C. The activation energy E and frequency factor K for the two stages are143.919 kJ/mol, 3.1874×10^{14} and 69.902 kJ/mol, 2.52367 × 105, respectively. The reaction rate expressions were:

$$\frac{d\alpha}{dT} = 4.78070 \times 10^{14} e^{-1.7310} \times \frac{10^4}{T}\left[(1-\alpha)^{-1/3} - 1\right]^{-1} \quad \text{(step-1)}$$

$$\frac{d\alpha}{dT} = 3.78551 \times 10^{14} e^{-8.047} \times \frac{10^3}{T}\left\{(1-\alpha)^{2/3}\,[1-(1-\alpha)^{1/3}]\right\}^{-1} \quad \text{(step-2)}$$

Keywords: Kinetic parameters, Boric acid, Dehydration, Doyle method.

INTRODUCTION

Being one of the most important boron compounds, boron oxide has been widely used in many industrial applications. It usually used as fluxing agent in silicate decomposition, dopant agent of semiconductor material, as well as high-energy fuels and additive of fire-resistant paint and special glassware. With special physical and chemical properties, boron oxide plays a significant role in the production of organic and inorganic boron compounds having superior properties. As a starting material, attention has been drawn to the utilization of boron oxide, especially in the production such as elemental boron, boron carbide, composite oxide structure catalyst, boron nitride, metal borates and boric acid esters[1-5].

Boron oxide having the highest boron content was produced by the decomposition of boric acid. Currently the methods commonly used for preparation of boron oxide are atmospheric method and vacuum method in muffle furnace[6,7]. When boric acid is heated constantly, boron oxide is obtained as a final product. The reaction takes place in two steps: boric acid to metaboric acid (step-1) and metaboric acid to boron oxide (step-2).

$$H_3BO_3 \rightarrow HBO_2 + H_2O \quad \text{(step-1)}$$

$$HBO_2 \rightarrow 1/2B_2O_3 + 1/2H_2O \quad \text{(step-2)}$$

when the heating temperature is above 100 °C, the reaction will happen in accordance with step-1, boric acid converts to metaboric acid, by losing one water molecule. As the heating temperature rises in the range of 105-160 °C, metaboric acid has three crystalline forms *i.e.*, orthorhombic metabolic acid (HBO_2-III, melting point: 176 °C at the temperature ≤ 130 °C; monoclinic metaboric acid (HBO_2-II, melting point: 200.9 °C) at the temperature of 130-150 °C and cubic metaboric acid (HBO_2-I, melting point: 236 °C) at the temperature of 150-160 °C. Boron oxide is gained when temperature is above 170 °C[8-12].

In recent years, methods allowing the kinetic analysis of TG and DTG data have been developed. The thermal dehydration of boron minerals has been investigated by using different methods[13,14]. However kinetic analysis of boric acid dehydration with a rate expression is rare in literature. So, to propose a rate expression for the reaction is very meaningful. In this work, by analysis of TG and DTG data, the kinetic parameters of the dehydration of boric acid were obtained. The rate expression was developed by combining method of Doyle and mechanistic models of solid reaction.

EXPERIMENTAL

Boric acid used in the experiment was prepared in our laboratory with the purity of 99.9 % (wt %). Thermo gravimetric/derivative thermo gravimetric analysis (TG-DTG) is conducted on a STA 449F3 (Netzsch) thermo gravimetric analyzer. The dehydration experiments of boric acid with a sample of 20 mg placed in a platinum crucible were performed

in the temperature range 0-800 °C. Thermo gravimetric/derivative thermo gravimetric analysis curves were taken at different heating rates (3, 5, 10, 20 °C min^{-1}) under flowing nitrogen atmosphere with a flow rate of 30 mL/min and a purge time of 0.5 h. The thermo balance measures mass to 0.0001 mg, with accuracy of ± 0.1 %.

Kinetic analysis: The dehydration of boric acid takes into two stages, through the intermediate material of metaboric acid as follows:

$$H_3BO_3 \rightarrow HBO_2 + H_2O \rightarrow B_2O_3 + 2H_2O$$

That is in accordance with the report in literature. So the kinetic data of these two different stages are investigated. Generally solid-phase kinetic equation can be written as:

$$\frac{d\alpha}{dT} = Ke^{-E/RT}f(\alpha) \quad (1)$$

If heating rate is constant, eqn. 1 can be expressed as:

$$\frac{d\alpha}{dT} = \frac{K}{\beta}e^{-E/RT}f(\alpha) \quad (2)$$

where β is heating rate, α is the conversion fraction, K is the frequency factor, T is the absolute temperature, E is the activation energy, R is the universal gas constant and f(α) is a function of α, which reflects the reaction mechanism.

Commonly, there are two methods used to calculate kinetic parameters as follows:

(A) When f(α) is known or presupposed, integrating of eqn. 2 gives the following expression:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{K}{\beta}e^{-E/RT}\,dT \quad (3)$$

Defining $g(\alpha)$, $\int_0^\alpha \frac{d\alpha}{f(\alpha)}$, x = E/RT, eqn. 3 converts to:

$$g(\alpha) = -\frac{KE}{\beta R}\int_\infty^x \frac{e^{-x}}{x^2}\,dx \quad (4)$$

Defining $P(X) = \int_\infty^x \frac{e^{-x}}{x^2}\,dx$, using the method of Doyle to deal with P(x):

$$\log P(X) = -2.315 - 0.4567X \quad (5)$$

with the expression of P(X), eqn. 4 can be converted as following:

$$\log g(\alpha) = \left[\log \frac{KE}{\beta R} - 2.315\right] - 0.4567\frac{E}{RT} \quad (6)$$

A plot of log g(α) *vs.* 1/T gives a straight line of slope -E/R.

The frequency factor K can be calculated from the intercept of this straight line.

(B) When f(α) is unknown, activation energy E is calculated by the method of Ozawa. The eqn. 6 can be rewritten as:

$$\log \beta = \left[\log \frac{KE}{R} - \log g(\alpha) - 2.315\right] - 0.4567\frac{E}{RT} \quad (7)$$

For different heating rates β, if α keeps constant, log g(α) is a certain value. So, keeping α same, a plot of log β *vs.* 1/T gives a straight line of slope -E/R.

As to solid-phase reaction, main mechanism model there are sixteen kinds, which can be divided into six types according to the method of Doyle shown in Table-1. Thus, when doing linear fit, mechanism models in the same mechanism type have the same r-square value, Variance S, intercept A, slope B and the activation energy E just have a little difference. So, when determining the reaction mechanism of a solid phase reaction (expression f(α) of in the equation $\frac{d\alpha}{dT} = Ke^{-E/RT}f(\alpha)$), steps can be taken as following:

TABLE-1
KINDS OF MECHANISM MODELS

No.	$\int_0^\alpha \frac{d\alpha}{f(\alpha)}$	f(α)	Symbol	Type classified by Doyle method
1#	α	1	P_4	
2#	$\alpha^{1/2}$	$2\alpha^{1/2}$	P_3	
3#	$\alpha^{1/4}$	$4\alpha^{3/4}$	P_2	I type
4#	$\alpha^{1/3}$	$3\alpha^{2/3}$	P_1	
5#	α^2	$1/2\alpha^{-1}$	D_1	
6#	$\alpha^3/^2$	$2/3\alpha^{-1}/^2$	P_5	
7#	(1-α) ln (1 - α) + α	$[-\ln (1-\alpha)]^{-1}$	D_2	II type
8#	[–ln (1 - α)]	(1-α)	N_1	
9#	$[-\ln (1 - \alpha)]^{1/3}$	$3(1\alpha) [-\ln (1-\alpha)]^{2/3}$	N_4	
10#	$[-\ln (1 - \alpha)]^{2/3}$	$3/2(1-\alpha) [-\ln (1-\alpha)]^{1/3}$	N_2	III type
11#	$[-\ln (1 - \alpha)]^{1/2}$	$2(1-\alpha) [-\ln (1-\alpha)]^{1/2}$	N_3	
12#	$[-\ln (1 - \alpha)]^{1/4}$	$4(1-\alpha) [-\ln (1-\alpha)]^{1/4}$	N_5	
13#	$(1-2/3\alpha) - (1-\alpha)^{2/3}$	$3/2[(1-\alpha)^{-1/3} - 1]^{-1}$	D_4	IV type
14#	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	B_1	V type
15#	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	B_2	
16#	$[1 - (1 - \alpha)^{1/3}]^{-1}$	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-}_{1}$	D_3	VI type

(1) Obtaining activation energy E by the method of Ozawa through thermal analysis curves of multiple different heating rates and defining it as sample standard E_0.

(2) Choosing a thermal analysis curve with a constant heating rate and doing linear fit of log g(α) *vs.* 1/T for mechanism models of six categories, respectively. Setting the models with the calculated E that do not differ more than 10 % compared with E_0 as selected mechanism models of first step.

(3) Selecting models that accord with the distinguishing standard of frequency factor ($10^4 \leq K = 10^{24}$) for solid-phase reaction from selected mechanism models of first step and defining them as selected mechanism models of second step. Choosing a model with the minimum Variance from them as final desired model. So, the activation energy E and frequency factor K of the final desired model are we need.

RESULTS AND DISCUSSION

In order to obtain the kinetic parameters and the rate expression for the dehydration of boric acid, Thermo gravimetric/derivative thermo gravimetric analysis curves were taken at different heating rates (3, 5, 10, 20 °C min^{-1}). For heating rate 10 °C min^{-1}, the thermal behaviour of boric acid sample was given in Fig. 1. The reaction started at above 100 °C and performed in the range of 0-800 °C in good agreement with literature[16]. A significant weight loss was observed within the temperature range of 130-300 °C. The dehydration ended at the temperature around of 750 °C with a final solid weight of

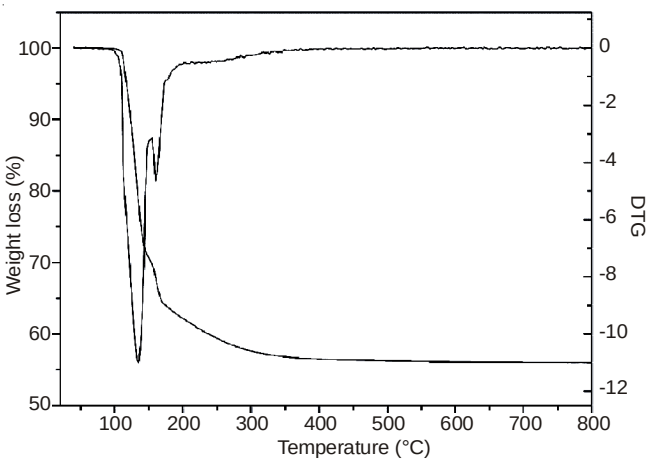

Fig. 1. Thermogravimetric and derivative thermogravimetric analysis curves of boric acid

56.29 %, which was consistent with the theoretical weight 56.33 %. For DTG, there were two temperature peaks at around 139 and 180 °C, which meant at the temperature the weight loss rate was maximum corresponding to the first and the second step dehydration of boric acid. The conversion fraction α for boric acid converting to boron oxide was calculated for the purpose to obtain the reaction rate expression and its variation with temperature was shown in Fig. 2.

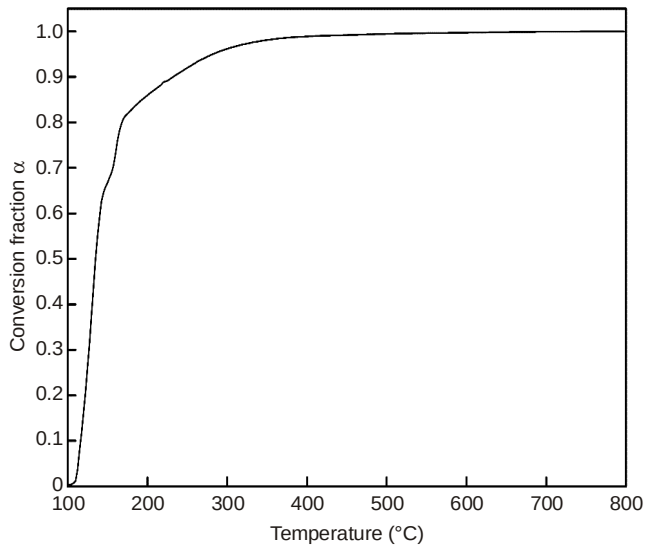

Fig. 2. Conversion fraction α of dehyhdration of boric acid with respect to temperature

Activation energy E plays a significant role in gaining the rate expression. The dehydration of boric acid takes into two stages and it can be seen from TG-DTG curves that the demarcation point of the two stages was near at α = 0.63. So, it is essential to obtain first the standard E_{01} and E_{02} for the two stages by using the method of Ozawa. Keeping α constant at 0.3 and 0.8 corresponding to the two stages, for different heating rates, value of 1/T was given in Table-2. Using eqn. 7 and doing a plot of log β *vs*. 1/T shown in Fig. 3 gave a straight line of slope –E/R. The results of r-square value, variance S and the activation energy E_0 were played in Table-3. Obviously, activation energy E_0 for the two stages was 145.560 and 71.528 kJ/mol, respectively.

TABLE-2
VALUE OF 1/T WITH RESPECT TO β AT CONSTANT α

α	β (°C min^{-1})	1/T ($k^{-1}\times 10^{-3}$)
0.3	20	2.386
	10	2.425
	5	2.467
	3	2.498
0.8	20	2.180
	10	2.259
	5	2.343
	3	2.406

TABLE-3
RESULTS OF r-SQUARE VALUE, VARIANCE S AND THE ACTIVATION ENERGY E_0 CALCULATED BY THE METHOD OF OZAWA AT DIFFERENT α

α	$S \times 10^{-2}$	r	E_0(kJ/mol)
0.3	0.505237	0.999532	145.560
0.8	0.155473	0.999496	71.528

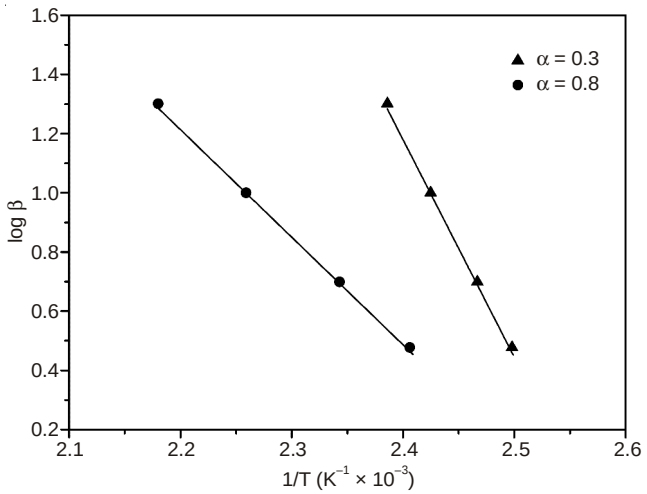

Fig. 3. Ozawa treatment for dehydration of boric acid

The key to obtain the reaction rate expression is to gain the activation energy E and frequency factor K. As standard E_0 for the two stages was known, things should be done according to the three steps for gaining the rate expression. Data selected of thermal analysis curve at the heating rate β = 20 °C min^{-1} was shown in Table-4. Using the method of Satava and doing linear fit of log g(α) *vs*. 1/T with the selected data that α < 0.6 was for the first stage and α > 0.6 was for the second stage for mechanism models of six categories, respectively. Results of kinetic parameters for the two stages were shown in Tables 5 and 6. For the first stage, 5#(132.58 kJ/mol), 7#(140.893 kJ/mol), 13#(143.919 kJ/mol) and 16#(150.108 kJ/mol) were suitable due to that they do not differ more than 10 % compared with E_{01}. However the variance S of 13# was the minimum, so, 13# was the most suitable for the first stage. Table-6 for second stage shown 16# was the most suitable. Therefore, the activation energy E and frequency factor K for the two stages were 143.919 kJ/mol, 3.1874×10^{14} and 69.902 kJ/mol, 2.52367×10^5. The rate expressions of the reaction were:

$$\frac{d\alpha}{dT} = 3.1874\times10^{14} e^{-1.43919} \times \frac{10^5}{RT}\left\{\frac{3}{2}\left[(1-\alpha)^{-1/3}-1\right]^{-1}\right\}$$

TABLE-4
VALUE OF 1/T WITH RESPECT TO α
AT THE HEATING RATE β = 20 °C min^{-1}

α	1/T ($k^{-1}\times 10^{-3}$)	α	1/T ($k^{-1}\times 10^{-3}$)	α	1/T ($k^{-1}\times 10^{-3}$)
0.10	2.502	0.36	2.360	0.60	2.277
0.12	2.487	0.38	2.352	0.64	2.267
0.14	2.471	0.40	2.347	0.66	2.256
0.16	2.456	0.42	2.341	0.68	2.246
0.18	2.444	0.44	2.336	0.70	2.234
0.20	2.433	0.46	2.330	0.72	2.224
0.22	2.421	0.48	2.325.	0.74	2.213
0.24	2.412	0.50	2.319	0.76	2.203
0.26	2.403	0.52	2.314	0.78	2.192
0.28	2.394	0.54	2.309	0.80	2.180
0.30	2.386	0.56	2.303	0.82	2.168
0.32	2.377	0.58	2.298	0.84	2.157
0.34	2.369	0.60	2.288	0.86	2.145

TABLE-5
KINETIC PARAMETERS CALCULATED BY DOYLE METHOD FOR THE FIRST STAGE OF THE DEHYDRATION OF BORIC ACID

No.	Type	r	log K	E(kJ/mol)	$S\times 10^{-2}$
1#	I	0.998362	13.38469	128.154	1.00643
2#			13.34558	125.318	1.09002
3#			12.75980	118.659	0.904853
4#			13.31861	124.132	0.987392
5#			13.64832	132.58	1.07409
6#			13.44093	129.446	0.954791
7#	II	0.999096	14.75309	140.893	1.03642
8#	III	0.999668	7.85459	79.745	0.698831
9#			8.44915	85.662	0.635926
10#			8.90594	90.724	0.708001
11#			8.13548	75.426	0.674921
12#			8.30146	82.487	0.642976
13#	IV	0.999289	14.5034	143.919	0.184368
14#	V	0.999367	6.93113	72.740	0.879269
15#	VI	0.999544	15.25921	155.431	0.74018
16#			15.04915	150.108	0.770016

TABLE-6
KINETIC PARAMETERS CALCULATED BY DOYLE METHOD FOR THE SECOND STAGE OF THE DEHYDRATION OF BORIC ACID

No.	Type	r	log K	E(kJ/mol)	$S\times 10^{-2}$
1#	I	0.996734	2.92873	27.663	0.465088
2#			3.04291	29.188	0.438964
3#			2.78547	22.907	0.499037
4#			3.03170	28.472	0.45696
5#			3.49763	34.593	0.401973
6#			3.19027	30.139	0.472907
7#	II	0.998942	4.70652	49.858	0.686876
8#	III	0.998274	4.59038	44.539	0.748239
9#			4.37095	40.504	0.704370
10#			4.55674	43.943	0.773341
11#			4.60183	47.865	0.718642
12#			4.69529	48.726	0.690947
13#	IV	0.999540	4.90283	56.353	0.502474
14#	V	0.999683	3.17083	29.247	0.220335
15#	VI	0.999842	5.26725	64.339	0.191486
16#			5.40203	69.902	0.177767

$$= 4.78070\times 10^{14} e^{-1.7310} \times \frac{10^4}{T}\left[(1-\alpha)^{-1/3} - 1\right]^{-1} \quad \text{(step-1)}$$

$$\frac{d\alpha}{dT} = 2.52367\times 10^{5} e^{-6.9902} \times \frac{10^4}{RT}\left\{\frac{3}{2}(1-\alpha)^{2/3}\,[1-(1-\alpha)^{1/3}]^{-1}\right\}$$

$$= 3.78551\times 10^{4} e^{-8.047} \times \frac{10^3}{T}\left\{(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}\right\} \text{(step-2)}$$

Conclusion

The kinetic analysis of dehydration of boric acid was taken by the method of Doyle and the kinetic parameters have been investigated by using TG-DTG data. The reaction took place in two stages and the demarcation point of the two stages was near at α = 0.63 observed from the TG-DTG curves. The reaction started at above 100 °C and had a significant weight loss within the temperature range of 130-300 °C. The dehydration was completed with a final solid weight of 56.29 % with two reaction stages in series in the temperature range of 100-800 °C. The activation energy E and frequency factor K for the two stages are 143.919 kJ/mol, 3.1874×10^{14} and 69.902 kJ/mol, 2.52367×10^{5}, respectively. The reaction rate expressions were:

$$\frac{d\alpha}{dT} = 4.78070\times 10^{14} e^{-1.7310} \times \frac{10^4}{T}\left[(1-\alpha)^{-1/3} - 1\right]^{-1} \text{(step-1)}$$

$$\frac{d\alpha}{dT} = 3.78551\times 10^{14} e^{-8.447} \times \frac{10^3}{T}\left\{(1-\alpha)^{2/3}\,[1-(1-\alpha)^{1/3}]^{-1}\right\} \text{(step-2)}$$

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