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Kinetic analysis of thermal decomposition of boric acid from thermogravimetric data

Fatih Sevim†, Fatih Demir, Murat Bilen* and Hüseyin Okur

Department of Chemical Engineering, Engineering Faculty, Atatürk University, 25240, Erzurum, Turkey
*Eti Holding A.Ş., Research and Development Dept., İstanbul Yolu Üzeri, 9. km, Güvercinlik, Ankara, Turkey
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Abstract–The kinetic parameters of the thermal decomposition of boric acid have been investigated by using TGA data. Suzuki and Coats-Redfern methods have been applied for the kinetic investigation. It was determined that decomposition kinetics of boric acid occurred in two steps and both regions suitably fit a first-order kinetic model. According to Coats-Redfern method, the activation energy and frequency factor were found as 79.85 kJ·mol^{-1} and 3.82×10^{4} min^{-1} for region I and 4.79 kJ·mol^{-1} and 4.045×10^{-5} min^{-1} for region II, respectively. The activation energies and frequency factors were found as 4.45 kJ·mol^{-1} and 4.08×10^{8} min^{-1} for the Suzuki method.

Key words: Boric Acid, Thermal Decomposition, Suzuki Method, Coats-Redfern Method

INTRODUCTION

Boric acid (H_3BO_3) is produced industrially from borate minerals and brines. Alkali and alkaline earth metal borates (such as borax, colemanite, ulexite or kernite) react with strong acids to form boric acid. Turkey has the 65% of world borate reserves; boric acid is obtained from colemanite ($2CaO\cdot3B_2O_3\cdot5H_2O$) concentrations by a reaction with sulfuric acid. The purity of boric acid produced by Eti Bor A.Ş., which is an establishment of Eti Holding A.Ş., is 99.9%, and boric acid product is classified in two groups according to the sulfate content, which is normal sulfate (include max. 500 ppm SO_4) and low sulfate (include max. 130 ppm SO_4).

Boric acid is used by many industries, with the largest use in the glass and ceramic industry where it is mainly used in textile grade glass fibers, borosilicate glasses, enamels, frits and glazes. In these applications, boron accelerates melting and refining, enhances color, increases resistance to mechanical and thermal shock, decreases the thermal expansion coefficient, reduces glaze viscosity and surface tension and enhances the glaze strength and durability [Roskill Inf. Ltd., 1995]. Boric acid also has many other application areas, such as fire retardant material, in nuclear applications, in medical and pharmaceutical sector, in photography, and in the electronic sector. In addition, boric acid is a starting material for the manufacture of many borates, per borates, fluoborates, boron carbide, boron oxide, boron esters, borides and other boron alloys [Kraschwit, 1997].

In recent years, several methods have been developed to allow the kinetic analysis of TG and DSC data. The differential thermal analysis and kinetic parameters for carbonate minerals has been extensively reported in the literature [Olszak-Humienik and Mozejko, 1999; Yun and Lee, 1999].

The thermal dehydration of boron minerals and boron products has been investigated by using different methods. Şener et al. [2000] examined the dehydration kinetics of ulexite by using TG, DTA and DTG, and determined the structural changes in the ulexite by means of X-ray diffractometry, scanning electron microscopy and mercury porosimeter. Park et al. [2000] developed a kinetic analysis method by using a dynamic model that accounts for the thermal decomposition behavior of polymers with the variation of the conversion. Demir et al. [2003] also investigated the kinetic parameters of the thermal decomposition of magnesite by using TG data. They found that the process fits a first order kinetic model, and the Coats-Redfern method gives more reliable results than the Suzuki method. Okur and Eymir [2003] studied the calcinations kinetics of ulexite by using TGA data. In this study, reaction parameters were determined by using Coats-Redfern and Genetic Algorithm methods and the results were compared.

When boric acid is heated slowly, it loses water and converts to metaboric acid. Metaboric acid has three different crystal modifications [Zachariasen, 1963]:

Orthorhombic metaboric acid: (HBO_2-III, melting point: 176 °C)
Monoclinic metaboric acid: (HBO_2-II, melting point: 200.9 °C)
Cubic metaboric acid: (HBO_2-I, melting point: 236 °C)

When the dehydration temperature is below 150 °C, the boric acid is always in the form of metaboric acid (HBO_2). Above 150 °C, the boric acid loses all its water and transforms to boron oxide (B_2O_3). Crystalline boron oxide has a melting point of 450 °C, but amorphous boron oxide does not have a specific melting temperature [Kocakuşak et al., 1998]. Amorphous boron oxide starts to soften at 325 °C and becomes fluid at 500 °C.

After dehydration of boric acid (H_3BO_3), boron oxide (B_2O_3) forms. Boron oxide has many different application areas due to its superior physical and chemical properties. Boron oxide is a main constituent in the production of organic and inorganic boron compounds like elemental boron, metal borates, and boric acid esters. It is also used as a catalyst in the production of organic compounds and as a flukes in metallurgy. In addition, boron oxide is also used in glass, glass fibers, optical fibers, ceramics, metal coatings, boron alloys, electronic industry and fire retardants.

In the present work, the kinetic parameters of the thermal decomposition of boric acid were investigated by using TGA data and by means of Coats-Redfern and Suzuki methods [Coats and Redfern,

†To whom correspondence should be addressed.
E-mail: fsevim@atauni.edu.tr

Table 1. Chemical analysis of boric acid

Boric acid	
B_2O_3	56.27%
SO_4	190 ppm
Na	46 ppm
Ca	52 ppm
Fe	22 ppm
Al	18 ppm
SiO_2	38 ppm
Mg	250 ppm
K	19 ppm
Pb	8 ppm
Cu	3 ppm
Ni	5 ppm

1964; Suzuki et al., 1978]. The particle size effect of boric acid was not investigated since the particle size of boric acid produced by Eti Bor A.Ş. changes in a narrow region. To our knowledge, this is the first time that thermal decomposition kinetics of boric acid has been investigated. The film growth rate increased continuously with further increase in substrate temperature in an H_2 atmosphere, indicating an extension of a kinetic-controlled regime compared to that of Ar and N_2 atmospheres.

EXPERIMENTAL

Boric acid was obtained from Bandýrma Boron and Acid Plants Works of Eti Bor A.Ş. The chemical analysis of boric acid is given in Table 1. B_2O_3 analysis was made by the volumetric method. A sulfate analysis was performed by using a UV-VIS Spectrophotometer (Shimadzu UV-160A), and the other impurities were determined by atomic absorption spectrometer (Varian SpectrAA-300). The particle size of boric acid was between 0.12-0.5 mm. TG experiments were carried out with a SETARAM Labsys 3.0 simultaneous DTA-TG System. Thermal experiments were conducted with a sample size of 20 mg in the temperature range 20-600 °C. The sample was put into a platinium crucible and its dehydration was recorded at a constant heating rate of 3 K min^{-1} under flowing nitrogen atmosphere with a flow rate of 25 ml/min and a purge time of 20 min. The thermobalance measured mass to 0.001 mg, with an accuracy of ±1%.

KINETIC ANALYSIS

For a kinetic analysis employing thermal decomposition data, various approaches have been developed and two of them, based on TG, were used in the present study and therefore briefly explained below:

1. Coats-Redfern Method

In this method, the decomposition reaction of a solid can be defined as thermal decomposition of the solid and the reaction type can be expressed as below:

$$aA_{solid} \longrightarrow bB_{solid} + cC_{gas} \quad (1)$$

The decomposition rate of the solid material, A_{solid}, can be expressed as

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (2)$$

Where α is the conversion fraction, t is time, k is the rate constant and n is the reaction order. If the heating rate s expressed as q=dT/dt, and the rate constant $k=k_o\exp(-E/RT)$, Eq. (2) can be expressed as

$$\frac{d\alpha}{dT} = \frac{k_o}{q}(1-\alpha)^n \exp\left(\frac{-E}{RT}\right) \quad (3)$$

Where k_o is the frequency factor, T is the absolute temperature, E is the activation energy and R is the universal gas constant. Integration of Eq. (3) with the boundary conditions $0 \rightarrow \alpha$ for the conversion fraction and $T_o \rightarrow T$ for the temperature gives the following expression:

$$\frac{1-(1-\alpha)^{1-n}}{(1-n)} = \frac{k_o}{q}\int \exp\left(\frac{-E}{RT}\right) dT \quad (4)$$

The right hand-side of this equation has no exact integral, but the following equation can be obtained when the right-hand side of the equation is expanded into an asymptotic series and the higher-order terms are ignored:

$$\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \frac{k_o R}{qE}\left(1-\frac{2RT}{E}\right)\exp\left(\frac{-E}{RT}\right) \quad (n \neq 1) \quad (5)$$

Where k_oR/qE is constant for any definite value of n and of heating rate. Assuming that $2RT/E \ll 1$, Eq. (5) reduces to

$$\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \frac{k_o R}{qE}\exp\left(\frac{-E}{RT}\right) \quad (n \neq 1) \quad (6)$$

For n=1, the following equation can be obtained from Eq. (3) with the same assumptions:

$$\frac{-\ln(1-\alpha)}{T^2} = \frac{k_o R}{qE}\exp\left(\frac{-E}{RT}\right) \quad (n = 1) \quad (7)$$

If the following functions are defined:

$$f(\alpha) = \frac{1-(1-\alpha)^{1-n}}{(1-n)} \quad (n \neq 1) \quad (8)$$

$$f(\alpha) = -\ln(1-\alpha) \quad (n = 1) \quad (9)$$

the following general equation can be written:

$$\ln\frac{f(\alpha)}{T^2} = \ln\left(\frac{k_o R}{qE}\right) - \left(\frac{E}{RT}\right) \quad (10)$$

A plot of $\ln(f(\alpha)/T^2)$ vs. 1/T gives a straight line of slope –E/R. The frequency factor can be calculated from the intercept of this straight line.

2. Suzuki Method

In this method, first order kinetics is assumed as a first approximation. A conversion vs. temperature plot obtained from TGA data is used to obtain kinetic parameters. The temperature corresponding to 50% conversion, $T_{1/2}$, and ΔT, which is the slope of the plot at the point of 50% conversion, is determined by using this plot. The following function is then defined.

$$\xi = \frac{\Delta T}{T_{1/2}} = \frac{2}{\ln 2}\varphi\left(\frac{E}{RT_{1/2}}\right) \quad (11)$$

where

$$\varphi\left(\frac{E}{RT_{1/2}}\right) = 1 - [ze^{z}E_1(z)] \quad (12a)$$

$$E_1(z) = \int_0^{\infty}\left[\frac{\exp(-z)}{z}\right]dz \quad (12b)$$

Where $z=E/RT_{1/2}$. To calculate the activation energy of the process, ξ is obtained from the conversion vs. temperature plot, and the term φ is then calculated from Eq. (11). For estimation of the value z, the graph prepared by Suzuki [Suzuki et al., 1978] is used. The frequency factor is obtained from the following equation:

$$k_0 = \frac{2q}{\Delta T}\exp\left(\frac{E}{RT_{1/2}}\right) \quad (13)$$

RESULTS AND DISCUSSION

In the study of dehydration kinetics of boric acid from thermogravimetric data, three different heating rates have been used in the calculations: 3, 5 and 10 °C·min^{-1}. In the study, for the heating rate 3 °C·min^{-1}, the calculations have been determined and the graphs have been drawn. For the other heating rates (5 and 10 °C·min^{-1}) the same process has been applied. TGA analysis of boric acid powder demonstrated 43.68% weight loss between 20-600 °C, which is consistent with theoretical weight loss of 43.67% (Fig. 1). The peak temperature values in DTA are also consistent with the values given in the literature [Marano and Shuster, 1969; Pişkin, 1983]. The major peak value at around 159 °C is due to the first dehydration of boric acid and the second peak value at around 181 °C is due to the second dehydration and subsequent boiling of the sample. In addition, the endothermic peak values, which were observed above 181 °C, are related with melting and bubbling of the sample. Two TG peaks and two DTA regions with different nominal mass loss rates revealed that the dehydration process takes place in two steps (Fig. 1).

The r-square values obtained from DTA-TGA curves fitted first order kinetic model. As can be seen from the TG curve, the mass loss increases with temperature. Conversion fractions were calculated as the ratio of the mass loss at a given temperature to the total mass loss at the end of the process. In order to determine the kinetic parameters, Coats-Redfern and Suzuki methods were applied and the results were compared. It was determined that the Coats-Redfern method gives more reliable results than the Suzuki method since it can be applied to both regions successfully.

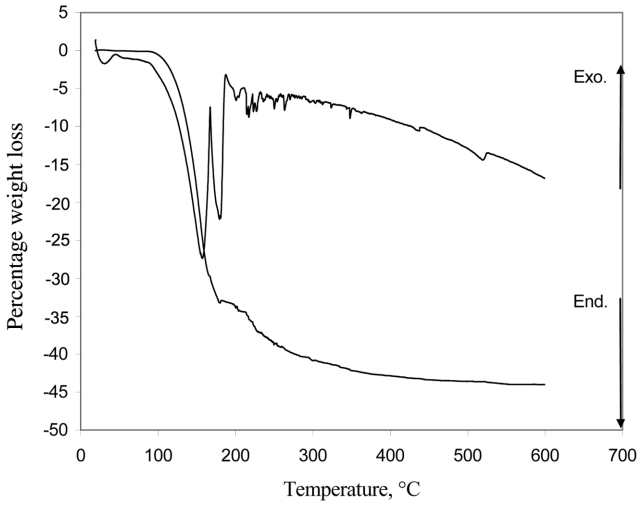

Fig. 1. Differential thermal and thermogravimetric analysis curves of boric acid.

Kinetic parameters for the thermal degradation of solids can be determined from thermogravimetric data by using different methods. In the present study, the Coats-Redfern method is used to determine the kinetic parameters of a reaction with the following type:

$$aA_{solid} \longrightarrow bB_{solid} + cC_{gas}$$

The reaction order was determined from the plot $\ln(f(\alpha)/T^2)$ vs. (1/T). As can be seen from Fig. 2, it would be more suitable to take two dissimilar regions into account in the calculations of kinetic parameters. Therefore, the Coats-Redfern method was applied to both regions separately. $\ln(f(\alpha)/T^2)$ vs. (1/T) plots for the two regions were drawn and given in Fig. 2. After application of the method, the regions were determined as below and the calculations were made accordingly.

Region I; mass loss: 3-28%, temperature range: 118-162 °C

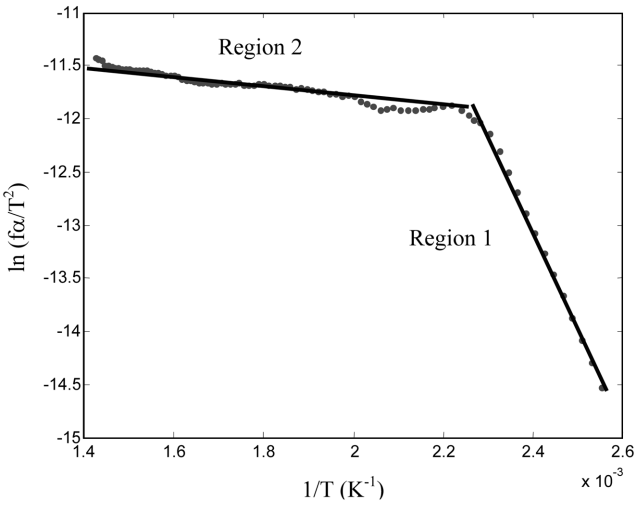

Fig. 2. Coats-Redfern treatment for boric acid dehydration.

Table 2. r-square values for different orders calculated according to the Coats-Redfern method

	Region I	Region II
Order	r-square	r-square
1. Order	0.9613	0.9998
0. Order	0.9416	0.9947
1/3. Order	0.8646	0.9974
1/2. Order	0.7247	0.9984
2/3. Order	0.0940	0.9991
3/4. Order	0.2988	0.9994
3/2. Order	0.9502	0.9991
2. Order	0.9347	0.9967
5/2. Order	0.9299	0.9930
3. Order	0.9294	0.9882

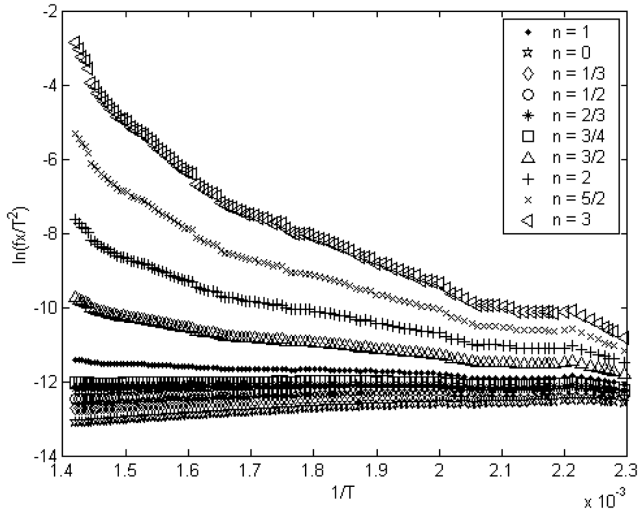

Fig. 3. Coats-Redfern treatment for boric acid dehydration in the first region.

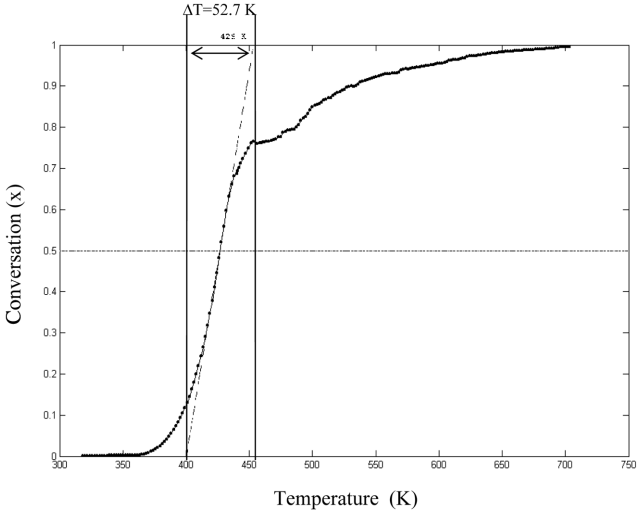

Fig. 4. Suzuki Method treatment for boric acid dehydration.

Table 3. Frequency factor and activation energy values which are evaluated by the Coats-Redfern method for both two regions

Heating rate ($^{o}C \cdot min^{-1}$)	For Region I		For Region II	
	k	E ($kJ \cdot mol^{-1}$)	k	E ($kJ \cdot mol^{-1}$)
3	63718.71	79.85	4.045×10^{-5}	4.7939
5	1094132.94	83.50	1.532×10^{-5}	7.8863
10	703214.95	84.14	1.315×10^{-5}	8.1127

Region II; mass loss: 28-43.15%, temperature range: 162-430 °C

For the first and second regions, the results showed that the reaction fit a first-order kinetic model and the activation energy and frequency factor were calculated from the slopes of straight lines and Eq. (10), respectively, as 4.79 $kJ \cdot mol^{-1}$ and 4.04×10^{-5} for the first region and 79.85 $kJ \cdot mol^{-1}$ and 3.82×10^{5} for the second region; r-square values for the other orders were calculated according to the Coats-Redfern method and the results are given in Table 2 and shown in Fig. 3. In Table 3, the activation energies and frequency factors which were calculated at different heating rates due to the Coats-Redfern method have been shown.

According to these results, the dehydration of boric acid probably occurs in two steps as given below:

$$2H_3BO_3 \longrightarrow 2HBO_2 + 2H_2O \quad \text{(Region I)}$$

$$2HBO_2 \longrightarrow B_2O_3 + H_2O \quad \text{(Region II)}$$

To apply the Suzuki method [Suzuki et al., 1978], the plots of conversion fraction vs. temperature were constructed (Fig. 4). ξ, was obtained from slope of Fig. 4 and φ was calculated by using Eq. (11). For estimation of the value z, the graph, which was prepared by Suzuki, was used. The frequency factor was obtained from Eq. (13). The values of ΔT and $T_{1/2}$ obtained from these plots were 426 K and 52.7 K, respectively. The activation energy and frequency factor calculated according to the Suzuki method were found as 4.45 $kJ \cdot mol^{-1}$ and 4.08×10^{8} min^{-1} respectively. The activation energies and frequency factors which were calculated for the other heating rates with this method are shown in Table 4. From the evaluated results it has seen that the activation energy had been increased balanced with the heating rate. This result is expected because the dehydration of boric acid is an endothermic reaction. Finally, to verify the appropriateness of the results obtained from this work, the kinetic parameters reported in the literature are summarized in Table 4, which shows that the proposed method gave reliable kinetic parameters for thermal decomposition of polyethylene.

Table 4. Frequency factor and activation energy values which are evaluated by the Suzuki method

Heating rate ($^{o}C \cdot min^{-1}$)	k	E ($kJ \cdot mol^{-1}$)
3	4.081×10^{-8}	4.45
5	1.451×10^{-10}	5.18
10	3.354×10^{-9}	5.38

CONCLUSIONS

A kinetic analysis using the various analytical methods showed the tremendous variations depending upon the mathematical approach taken in the analysis. Because of the wide variations in the kinetic parameters obtained with the single heating rate experiments, the use of a multiple heating rate technique was felt to represent more realistically the thermal decomposition of boron. By using our method, the kinetic parameters of the thermal decomposition of boric acid have been investigated by using TGA data. More reliable results have been determined by the use of the Coats-Redfern method with comparison to the Suzuki method because of the successful applications of it to both regions. It was also determined that decomposition kinetics of boric acid occurred in two steps and both regions suitably fit a first-order kinetic model. The activation energies and frequency factors calculated according to the Coats-Redfern method were found as 79.85 $kJ \cdot mol^{-1}$ and 3.82×10^{4} min^{-1} for region I and 4.79 $kJ \cdot mol^{-1}$ and 4.045×10^{-5} min^{-1} for region II, respectively. The activation energy and frequency factor calculated according to the Suzuki method were found as 4.45 $kJ \cdot mol^{-1}$ and 4.08×10^{8}

min^{-1} respectively. It can be stated that the obtained results agree reasonably with those given by Ersahan et al. [1994].

NOMENCLATURE

E : activation energy [kJ mol^{-1}]
K : rate constant [s^{-1}]
k_o : frequency factor [s^{-1}]
n : reaction order
Q : heating rate [K s^{-1}]
R : universal gas constant [8,314 $kJmol^{-1}K^{-1}$]
T : temperature [K]
α : fraction reacted

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