# Thermal decomposition kinetics of sodium perborate tetrahydrate to sodium metaborate by using model-fitting and model-free methods

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**Abstract**−Model-free and model-fitting methods have been applied to data for nonisothermal and isothermal decomposition of sodium perborate tetrahydrate to sodium metaborate. The kinetic triplet (f(a), A and E) of sodium perborate tetrahydrate was found by model fitting method defined with a single step reaction, which has an excellent fit for nonisothermal data and obeys different kinetic models and yields highly uncertain values of Arrhenius parameters. The isothermal and nonisothermal data for thermal decomposition of sodium perborate tetrahydrate to sodium perborate monohydrate and sodium metaborate were evaluated by model-free isoconversional method. The complex nature of multi-step process of sodium perborate tetrahydrate to sodium metaborate was more easily indicated by using wide temperature range in nonisothermal isoconversional method.

Key words: Sodium Perborate Tetrahydrate, Thermal Decomposition, Coats-redfern Method, Isothermal Kinetics, Non-isotehermal Kinetics

## INTRODUCTION

Boron and its compounds have wide fields of application in industry and are found in nature under different names, such as Borax decahydrate ($Na_2B_4O_7 \cdot 10H_2O$), colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), ulexite ($NaCaB_5O_9 \cdot 8H_2O$), kernite ($Na_2B_4O_7 \cdot 4H_2O$), probertile ($NaCaB_5O_9 \cdot 5H_2O$). Boron compounds are generally hydrated compounds found with alkaline-earth metals such as Na, K, Ca, Mg and Li. But pure borates cannot be found in nature and produced by the reaction of boron compounds with ammonia, sodium, potassium and lithium. One of the most used boron compounds is sodium perborate; it is used in the detergent industry as a bleaching agent action, which results from active oxygen release in aqueous media. Three different hydrates of sodium perborate with the general formula $NaBO_3 \cdot XH_2O$ (x=1, 3 and 4) are known. Only monohydrate and tetrahydrate form have a commercial importance. Sodium perborate tetrahydrate containing 10.4 weight% active oxygen is stable crystal form at ordinary conditions [1].

The structure of sodium perborate tetrahydrate and sodium perborate monohydrate is given in Fig. 1. Unlike sodium percarbonate and perphosphate, the sodium perborates are not simply addition compounds of hydrogen peroxide, but contain a cyclic anion with



Fig. 1. (a) Sodium perborate tetrahydrate (b) sodium perborate monohydrate.

peroxide bridges and do not contain the $BO_3$ ion [2]. This makes the material more stable, safer for handling and storage. The formula of sodium borate mono and tetrahydrates can be written as $Na_2B_2O_8H_4$ (anhydrous) and $Na_2B_2O_8H_4 \cdot 6H_2O$, respectively [3].

Sodium perborate monohydrate theoretically contains 16.03 weight% active oxygen and has an increasing commercial interest in recent years. The main advantage of sodium perborate monohydrate to tetrahydrate form is a higher content of available oxygen, a higher heat stability and higher dissolution rate into water. Its porous structure gives it higher bleaching action at early stages of the washing process. The dehydration of sodium perborate tetrahydrate to sodium perborate monohydrate can be described as a thermal decomposition of solid substance. The stoichiometric expression for the decomposition is:

$$NaBO_2H_2O_2 \cdot 3H_2O_{(s)} \rightarrow NaBO_2H_2O_{2(s)} + 3H_2O_{(g)} \tag{1}$$
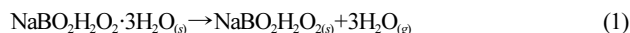
The thermal decomposition of sodium perborate tetrahydrate to monohydrate is about 336 K [1]. The sodium perborate monohydrate is not a very stable substance. Thus, the decomposition of sodium perborate monohydrate to sodium metaborate can be given by the following equation:

$$NaBO_2H_2O_{2(s)} \rightarrow NaBO_{2(s)} + H_2O_{(g)} + 1/2O_{2(g)} \tag{2}$$
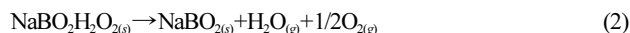
The use of sodium metaborate has increased in recent years, since sodium metaborate is a raw material in the production of sodium borohydrate utilized in a huge number in industrial process including organic and pharmaceutical synthesis, waste water treatment paper bleaching and generation hydrogen gas via hydrolysis reaction [4,5]. The thermal dehydration kinetics of sodium metaborate tetrahydrate was studied under non-isothermal condition by using Coats-Redfern method [6].

As a result, the thermal decomposition kinetics and mechanism of sodium perborate tetrahydrate to sodium metaborate are important in various industrial applications such as detergent and sodium
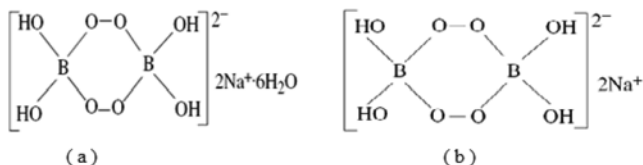
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borohydride production. Although many studies have been done [7-13] on decomposition of boron compound, we have not noticed any studies on the kinetics of sodium perborate tetrahydrate done by non-isothermal analysis method. Therefore, a number of attempts have been made to study the decomposition kinetics of sodium perborate tetrahydrate to sodium metaborate by thermogravimetric analysis.

## 1. Kinetic Procedure

Different methods have been proposed in the literature to calculate activation energy and kinetic parameters of decomposition reactions from analysis of termogravimetric (TG) curve.

The decomposition reaction of sodium perborate tetrahydrate to sodium metabroate can be described as thermal decomposition of a solid substance. This type of reaction can be formulated as

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)} \tag{3}$$

The rate of decomposition of this type reaction based on a single step kinetic equation can be expressed as [14]

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{4}$$

Where t is the time, T is the temperature, a is the extent of conversion, and $f(\alpha)$ is the reaction model. The temperature-dependence of the rate constant is introduced by replacing k(T) with the Arrhenius equation [15]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \tag{5}$$

where A (the pre-exponential factor) and E (the activation energy) are the Arrhenius parameters and R is the gas constant. Arrhenius parameters (A, E), together with the reaction model, $f(\alpha)$ are called the kinetic triplet. In case of nonisothermal conditions, $d\alpha/dt$ in Eq. (5) is substituted with $\beta(d\alpha/dT)(\beta=(T-T_o/t))$ giving,

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \tag{6}$$

where $\beta$ is the heating rate.

By separation of variable and integration, the following equation is obtained:

$$g(\alpha) = \int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = \frac{A}{\beta} \int_{T_o}^T \exp\left(-\frac{E}{RT}\right) dT \tag{7}$$

For nonisothermal conditions, there are several relationships used to compute Arrhenius parameters, each of which is based on an approximate form of the temperature integral [14].

One approximation is given by Coats-Redfern [16] as follows:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right)\left(1 - \frac{2R\overline{T}}{E}\right) - \frac{E}{RT} \tag{8}$$

where $\overline{T}$ is the mean experimental temperature. This method is reported [17] to be one of the most frequently used to evaluate nonisothermal data. Arrhenius parameters are determined from the plot $\ln((g(\alpha))/T^2)$ vs. 1/T. This kind of calculation of kinetic triplet is called model-fitting method.

If the thermal kinetics of studied compounds has complex structure, it is possible to obtain several steps having different energies involved. In this case, the relative contributions of these steps to the overall reaction rate will vary with both temperature and extent of conversion. The model fitting is usually unsuccessful to determine a clean separation between the temperature dependence, k(T) and the reaction model, $f(\alpha)$ since the overall reaction rate contributed by different substeps will change both temperature and extent of conversion. Thus, Eqs. (6) and (8) cannot be used to determine the reaction model that does not represent multi-step kinetics. According to the above, almost any reaction model, $f(\alpha)$ can satisfactorily obey the data at the cost of drastic variation in the Arrhenius parameters compensation effects. Thus, a single heating rate data for the calculation kinetic parameters must be avoided. The problem related to the complex nature of the mechanism of reaction involving solids can be overcome by the use of isoconversional method [18,19], since these methods enable one to determine the activation energy as a function of the extent of conversion and/or temperature, and the activation energy can be determined without making any assumptions about the reaction model [20].

The experimental data can be analyzed by other models different from model fitting approximation such as temperature integral method, isoconversional method and model-free method, since the integral of Eq. (7) on the right-hand side has not any exact analytical solution. In all mentioned approximations, the value of the integral between 0 and $T_o$ is negligible, since the starting temperature is near room temperature and the activation energy is not too low. In this case Eq. (7) becomes

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \tag{9}$$

Eq. (9) can be rewritten by taking x=E/RT

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A \cdot E}{\beta R} \int_x^\infty \frac{\exp(-x)}{x^2} dx = \frac{A \cdot E}{\beta R} \cdot p(x) \tag{10}$$

The P(x) function on the right-hand side is generally termed as temperature integral [21] which can be approximated in different ways.

The most common of P(x) function is

$$p(x) = \frac{\exp(-x)}{x^2} \cdot Q(x) \tag{11}$$

where Q(x) is a function with several particular forms. Q(x) can be considered as the series expansion as follows:

$$Q(x) = 1! - 2!\frac{RT}{E} + 3!\left(\frac{RT}{E}\right)^2 - 4!\left(\frac{RT}{E}\right)^3 \dots\dots \tag{12}$$

Q(x) function can also be expressed in the ratio of two fourth-order polynomials [22] as given below:

$$Q(x) = \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{13}$$

All P(x)-linear isoconversional methods involve the plotting of 1/T versus a logarithmic function which depends on the heating rate and temperature. The Q(x) function shows an approximation for the temperature integral which is different for used different P(x)-linear isoconversional methods. Therefore, the approximation of the temperature integral is the key to understanding the different methods. The linear isoconversional method equation used in this study can be obtained by combining Eqs. (10)-(11) at constant fraction transformation as given below:

$$g(\alpha) = \frac{ART^2}{\beta E} Q(x) \cdot \exp(-x) \qquad (14)$$

For constant $g(\alpha)$, Eq. (14) becomes

$$\frac{\beta}{T^2 Q(x)} = \frac{AR}{E \cdot g(\alpha)} \exp\left(-\frac{E}{RT}\right) \qquad (15)$$

Taking the logarithm of both side gives

$$\ln\left(\frac{\beta}{T^2 Q(x)}\right) = \ln\left(\frac{AR}{E \cdot g(\alpha)}\right) - \frac{E}{RT} \qquad (16)$$

In this study, the first three terms in Eq. (12) were considered as $Q(x)$ function.

Iterative procedure is used to approach the exact value of E in Eq. (15) as in the following:

• Plotting $\ln(\beta/T^2 Q(x))$ vs. $1/T$ under the assumption of $Q(x)=1$ to determine the initial value of $E_1$.

• Using $E_1$ to calculate the value of $Q(x)$ function, then plotting $\ln(\beta/T^2 Q(x))$ vs. $1/T$ to calculate a new value of $E_2$ in slope.

• Comparing step $E_1$ with $E_2$; when $E_n - E_{n-1} < 0.01$ Kcal/mole, the last value of $E_n$ is the exact value of activation energy.

This kind of approximation has been applied by Guan and et al. [23].

In this paper, we examine applying the model-fitting and model-free methods to yield kinetics characteristics of thermal decomposition sodium perborate tetrahydrate to sodium perborate monohydrate and sodium metaborate by using isothermal and nonisothermal experimenst. This kind of characterization is very important, since the thermal kinetics of sodium perborate tetrahydrate to sodium metaborate is valuable in some industrial applications.

## EXPERIMENTAL

Pure sodium perborate tetrahydrate used in all experiments was analytical grade and purchased from Merck. The experimental procedure was performed in a SETARAM TG/DTA/DSC-16 instrument. The thermal dehydration of sodium perborate tetrahydrate to sodium metaborate test was performed under nitrogen flow of 0.850 $cm^3 \cdot s^{1-}$ and a constant heating rate of 1, 3, 5 and 7 °Cmin$^{1-}$.

The initial amount of sodium perborate tetrahydrate used was approximately 5 mg to assure no diffusion problems. Both isothermal and dynamic experiments were performed. The isothermal experiment was started by a heating rate of 25 °Cmin$^{1-}$ to the desired temperature. In case of isothermal condition, predetermined experimental temperature was kept constant through the dehydration or decomposition process and the experiment was considered to be finished until no mass loss observed.

## RESULTS AND DISCUSSION

### 1. Crystallizaiton of Sodium Perborate Tetrahydrate and Metaborate

Commercial preparation of sodium perborate tetrahydrate ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$) can be produced by the reaction of borax pentahydrate, sodium hydroxide and hydrogen peroxide followed by the crystallization of sodium perborate tetrahydrate [24]. The crystal habit of both sodium perborate tetrahydrate and sodium metaborate is very important, since it affects the rheological properties, the filtration, the centrifugation and the bulk density of solid [25].

Fig. 2(a)-(b) shows the sodium perborate tetrahydrate and sodium metaborate crystals obtained at saturated solution by evaporation of water at room temperature, respectively. But, a typical solution of sodium tetraborate tetrahydrate at room temperature is unstable and loss of active oxygen unless stabilizers are added either before or after crystallization stage to improve storage and in-pack stability. The main suitable stabilizers include magnesium sulfate and alkali or alkali earth metal silicate [26].

It can be seen from Fig. 2(a) that the crystal habit of sodium perborate tetrahydrate in presence of $Mg_2SO_4$ (50 ppm) impurity is spherical, whereas the crystal habit of sodium metaborate is hexagonal elongated growth in the vertical direction yield like a needle.

### 2. Thermal Dehydration of Sodium Perborate Tetrahydrate to Monohydrate

Some properties of sodium perborate tetrahydrate are very important in industrial applications and packages of dried form such as degree of drying, bulk density and particle shape. To investigate the changes of sodium perborate tetrahydrate particles with temperature, 10 g of sodium perborate tetrahydrate with particle size of $-600+550$ μm was taken and dried in an oven at three different constant temperatures: 42, 55 and 60 °C. The bulk density of pure sodium



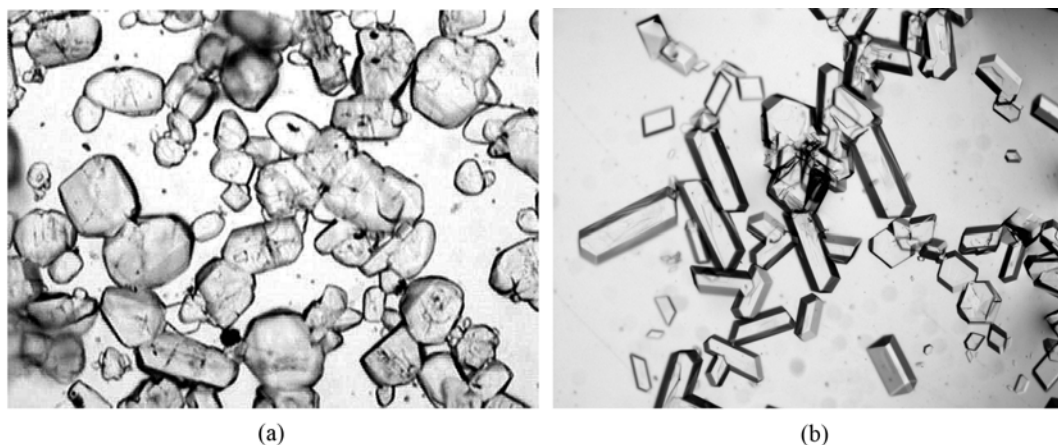|          (a)          |          (b)          |

**Fig. 2. Crystallization of sodium perborate tetrahydrate in the presence of MgSO$_4$ (a) and sodium metaborate (b).**

perborate tetrahydrate and sodium perborate monohydrate was measured by the method similar to ISO 3424(1975) [27].
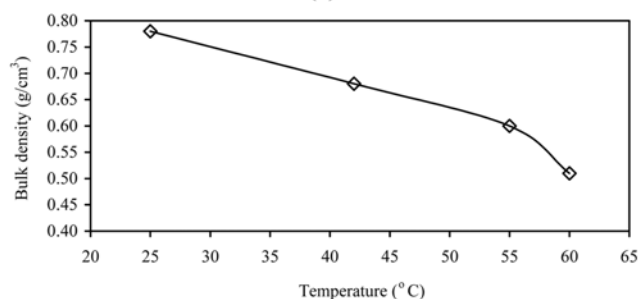
The microscopic photographs of pure sodium perborate tetrahydrate and sodium perborate monohydrate produced from sodium perborate tetrahydrate by drying at 60 °C during 120 min. are given in Fig. 3. Sodium perborate tetrahydrate particles produced by drying of sodium perborate tetrahydrate at 60 °C were puffed as the
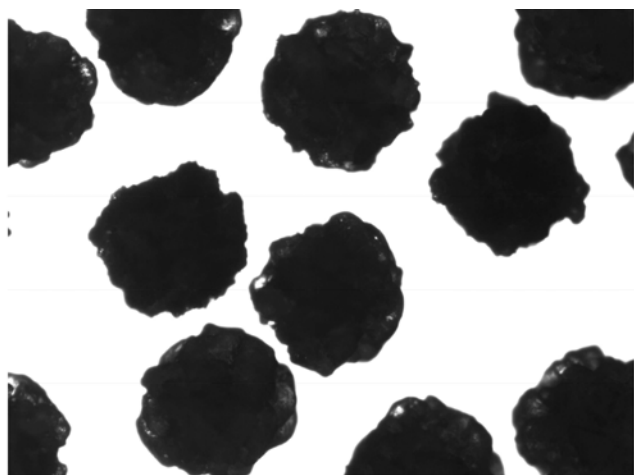


(a)
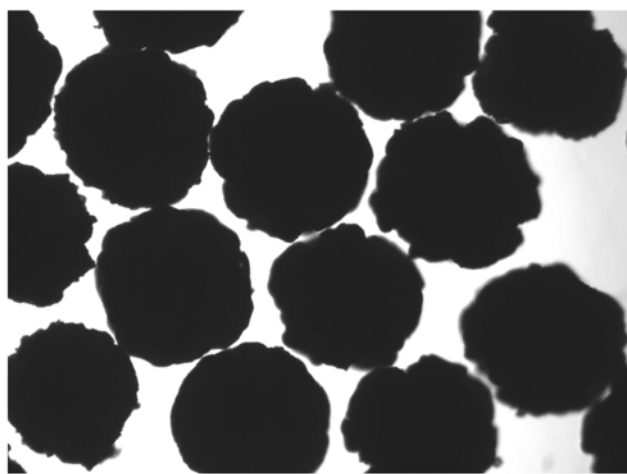


(b)



(c)

Fig. 3. Microscopic photographs of sodium perborate tetrahydrate with the initial particle size of +500−710 μm. (a) initial crystal; (b) puffed particles calcinated at 60 °C; (c) bulk density changes of sodium perborate tetrahydrate to monohydrate with temperature.
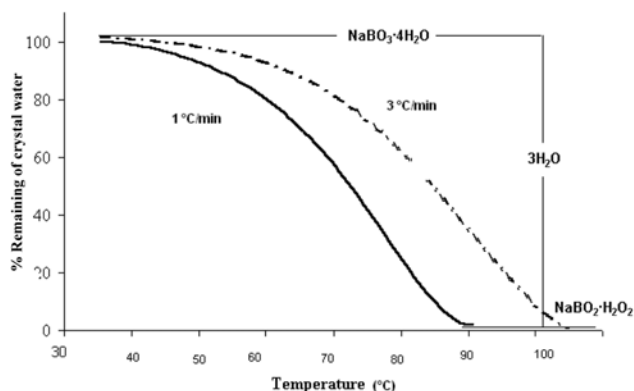


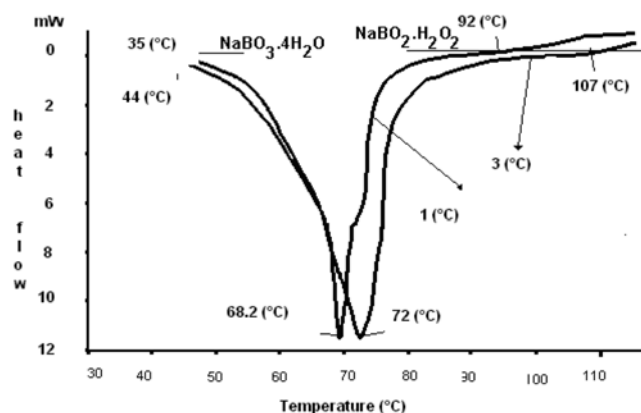Fig. 4. TG curves for sodium perborate tetrahydrate to sodium metaborate.



Fig. 5. DSC curves for sodium perborate tetrahydate to sodium metaborate.

bulk density was decreased from 0.78 to 0.50 g·cm$^{3-}$ as shown in Fig. 3(c). As a result, in order to avoid the puffing problem the production of sodium perborate monohydrate from sodium perborate tetrahydrate, the drying must be done at the temperature below 60 °C.

TG and DSC curves for sodium perborate tetrahydrate are presented in Fig. 4 and Fig. 5. The TG curves in Fig. 4 show the percentage mass loss of sodium perborate tetrahydrate to monohydrate for different temperature and heating rates. Fig. 5 shows DSC curves of the same material having same heating rate with TG. TG curves with 1 °C·min$^{1-}$ and 3 °C·min$^{1-}$. heating rates represent a gradual mass loss starting from 35 °C and ending 92 °C and 107 °C with peak of 68.2 °C and 72.1 °C, respectively. These curves are corresponding to separation of three moles of crystal water. The behavior of TG is identical with the behavior of DSC.

2-1. Nonisothermal Study

For nonisothermal conditions there are several suggested methods to compute Arrhenius parameters [14] and each of them is based on the approximation form of the temperature integral and integration of Eq. (7). One of these methods frequently used to evaluate non isothermal data is Coats-Redfern method [17,28]. Inserting various g($\alpha$) functions into Eq. (8) results in a set of Arrhenius parameters calculated from the plot ln(g($\alpha$)/T$^2$) vs 1/T. The set of Arrhenius parameters obtained by using the best four reaction models for the thermal dehydration of sodium perborate tetrahydrate to sodium

**Table 1. The kinetic parameters for sodium perborate tetrahydrate to sodium perborate monohydrate**

| Model | | Heating rate (°C/min) | | | |
|---|---|---|---|---|---|
| | | 1 | 3 | 5 | 7 |
| A2 | E (kJ/mol) | 91.3426 | 72.5687 | 57.3559 | 55.2565 |
| | A | $2.7259.10^9$ | $1.3424.10^6$ | $4.131.10^3$ | $1.476.10^3$ |
| | $R^2$ | 0.996 | 0.996 | 0.995 | 0.997 |
| D2 | E (kJ/mol) | 38.0340 | 29.4782 | 22.5666 | 21.5566 |
| | A | 7.4640 | 0.2336 | 0.0168 | 0.0104 |
| | $R^2$ | 0.995 | 0.992 | 0.986 | 0.986 |
| R2 | E (kJ/mol) | 180.1161 | 143.4322 | 115.564 | 109.902 |
| | A | $8.4497.10^{22}$ | $3.0342.10^{16}$ | $7.2831.10^{11}$ | $5.7728.10^{10}$ |
| | $R^2$ | 0.968 | 0.970 | 0.963 | 0.974 |
| n=1 | E (kJ/mol) | 188.1322 | 150.7108 | 120.3871 | 116.2629 |
| | A | $5.8965.10^{24}$ | $1.5057.10^{18}$ | $1.4703.10^{13}$ | $1.9283.10^{12}$ |
| | $R^2$ | 0.996 | 0.997 | 0.995 | 0.998 |

**Table 2. Decomposition kinetics of sodium perborate monohydrate to sodium metaborate step II**

| Kinetic models | Heating rate (°C/min) | E (kJ/mole) | A | $R^2$ |
|---|---|---|---|---|
| n=1 | 1 | 81.5981 | $2.7639.10^4$ | 0.904 |
| | 3 | 95.7752 | $9.0991.10^5$ | 0.904 |
| | 5 | 138.1078 | $8.6429.10^{10}$ | 0.981 |
| | 7 | 131.5307 | $9.7779.10^{10}$ | 0.974 |
| n=2 | 1 | 138.7357 | $4.0656.10^{11}$ | 0.979 |
| | 3 | 172.2636 | $2.2149.10^{15}$ | 0.997 |
| | 5 | 195.3784 | $8.5596.10^{17}$ | 0.993 |
| | 7 | 208.1829 | $1.7848.10^{19}$ | 0.998 |
| n=2/3 | 1 | 68.8701 | $6.8200.10^2$ | 0.865 |
| | 3 | 81.6513 | $1.6135.10^4$ | 0.869 |
| | 5 | 111.4648 | $5.0329.10^7$ | 0.946 |
| | 7 | 112.1066 | $4.3064.10^7$ | 0.951 |
| A2 | 7 | 38.8929 | 0.1650 | 0.967 |
| | 1 | 37.1582 | 0.1396 | 0.886 |
| | 3 | 44.2024 | 0.7913 | 0.888 |
| | 5 | 65.3551 | $2.4300.10^2$ | 0.979 |
| | 7 | 62.0524 | $8.1426.10^1$ | 0.971 |

The difference between $R^2$ values for A2 (nucleation and growth, Avrami Eq. (1)), D3 (three-dimensional diffusion, Jander equation), R2 (phase boundary controlled reaction) and first-order kinetics (n= 1) models illustrated in Table 1 is very small, but the apparent activation energy values changes by a factor 2 or more, as given in literature by Vyazovkin [29].

2-2. Model-free Isoconversional Method for Isothermal and Nonisothermal Data of Thermal Decomposition of Sodium Perborate Tetrahydrate to Sodium Metaborate

To calculate kinetic parameters by using isothermal TG curves a set of temperature T and t values obtained for fixed values of conversion, Eq. (4) can be integrated as

$$\frac{g(\alpha)}{t} = k(T) = A \cdot \exp\left(-\frac{E}{RT}\right) \tag{17}$$

This equation can be rearranged in the form of the integration isoconversional method [30,31]

$$-\ln(t) = \ln\frac{A}{g(\alpha)} - \frac{E}{RT} \tag{18}$$

A plot of $-\ln(t)$ versus $1/T$ yields activation energy, $E_\alpha$ for given conversion. Where t is the isoconversional time, A is the pre-exponential factor, $E_\alpha$ is the activation energy. The basic assumption of this method is that $g(\alpha)$ at constant conversion does not vary with temperature [25].

The thermal dehydration of sodium perborate tetrahydrate to sodium perborate monohydrate at four different temperatures as a function of time is given in Fig. 6. As can be seen in Fig. 6 in isothermal study, the reaction is very slow at the low temperatures. At higher temperatures the reaction will be very fast and short.

Fig. 7 shows the change in $E_\alpha$ values in isoconversional isothermal method obtained by using Eq. (18) for the isothermal decomposition of sodium perborate tetrahydrate to sodium perborate monohydrate (step I) and sodium metaborate (step II). For isoconversional isothermal method related to step I, the activation energy value decreases from 104 to 76 kJ·mol$^{1-}$ in the 0.05 to 0.95 range extent of conversion.

For step II, the activation energy value increases from 112 to 188 kJ·mol$^{1-}$ in the 0.1-0.4 range of extent of conversion and takes a

perborate monohydrate and sodium metaborate is shown in Tables 1 and 2. For each model the heating rate, the goodness of fitting is estimated by the correlation coefficient, $R^2$. As can be seen from Tables 1 and 2 the nonisothermal kinetics parameters obtained by Coats-Redfern method for dehydration of sodium perborate tetrahydrate to sodium perborate monohydrate and sodium metaborate can be best represented by one or more different kinetics models with respect to correlation coefficient, but both the apparent activation energy and frequency factor values are different for each best fitting model. A single pair of E and A was then taken commonly for each step of thermal decomposition of sodium perborate tetrahydrate corresponding to a reaction model that gives the maximum correlation coefficient. On the other hand, according to the data given in Table 1 there is no adequate criterion for distinguishing the best set of kinetic parameters at nonisothermal condition.
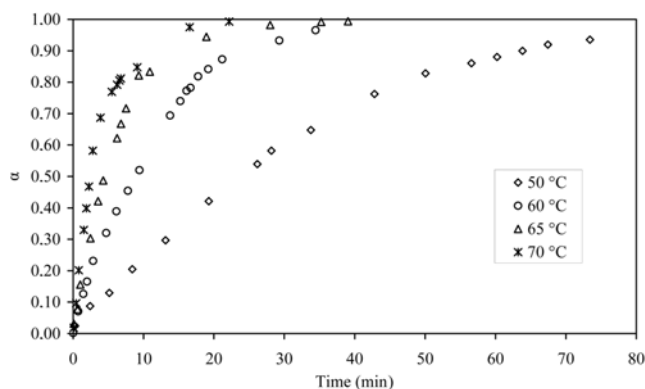
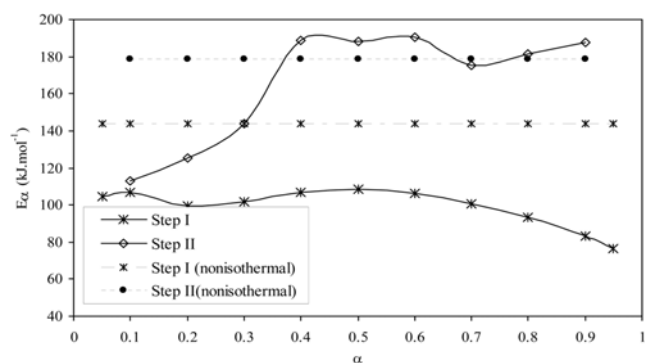Fig. 6. Effect of temperature on dehydration of sodium perborate tetrahydrate.



Fig. 7. Dependence of the activation energy on extent of sodium perborate tetrahydrate to sodium perborate monohydrate (step I) and sodium metaborate (step II). The dashed lines indicate the average values obtained by model-fitting method from nonisothermal data (for first and second order kinetics).
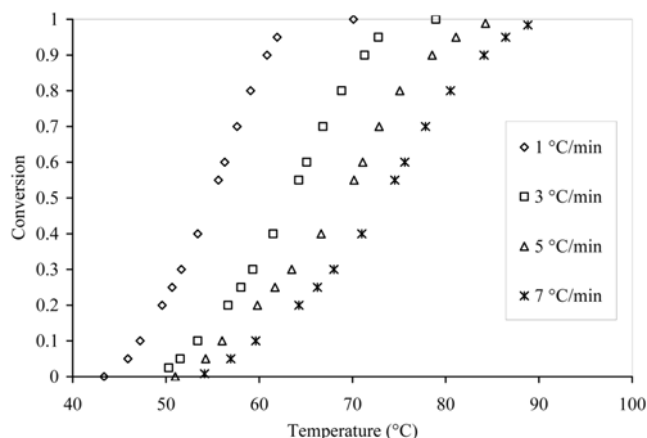


Fig. 8. Changes of dehydration of sodium perborate tetrahydrate to sodium metaborate with temperature.



Fig. 9. Changes of dehydration of sodium perborate monohydrate to sodium metaborate with temperature.

constant value of 188 in the 0.4-0.6 range of conversion and decreases from 188 to 181 kJ·mol$^{-1}$ in the 0.6-0.9 range of conversion.

In the 0.05-0.95 range of conversion degree for the first step of dehydration process (Fig. 7), the $E_\alpha$ dependencies are completely different from the model-free isoconversional isothermal method experiments done in wide range of temperature (40-90 °C) than these of isothermal method experiments (50-70 °C). All these results show us the occurrence of more than one reaction in the both decomposition of sodium perborate tetrahydrate to sodium perborate monohydrate (step I) and sodium metaborate (step II)

2-3. Model-free Linear Isoconversional Method for Thermal Dehydration of Sodium Perborate Tetrahydrate to Sodium Perborate Monohydrate

The main disadvantage of the model-fitting method is validated for a single step of global Arrhenius parameters for the whole process, and therefore it is unable to reveal this type of complexity in solid state reaction. The values calculated in such way are averages that do not represent changes in mechanism and kinetics with the temperature and extent of conversion. The model-free isoconversional method allows for unmistakable detecting multi-stage kinetics as dependence of the activation energy on extending conversion. Furthermore, it was shown that revealing the dependence of the ac-

tivation energy on the conversion not only helps to disclose the complexity of a process, but also helps to identify its kinetics schema. Thus, it is possible to obtain any information about the mechanism of a process and predict its kinetics without knowledge of both the reaction model and the pre-exponential factor.
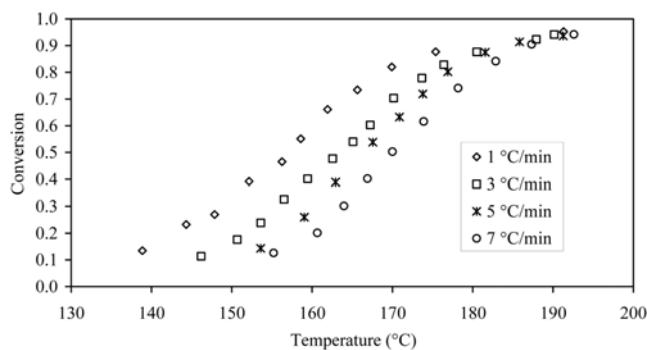
To apply model-free isoconversional method for non-isothermal data, the conversion of sodium perborate tetrahydrate to sodium perborate monohydrate and sodium metaborate is given in Figs. 8 and 9 realized at different heating rates. For a set of experiments done at different heating rates, the activation energy E can be calculated at any particular value of $\alpha$ by using model-free isoconversional method represented with Eq. (16).

Fig. 10 shows the change of activation energy for the dehydration of sodium perborate tetrahydrate to sodium perbroate monohydrate (step I) and sodium metaborate (Step II). For model-free isoconversional method related to the first dehydration step (step I) of sodium perborate tetrahydrate, the activation energy value decreases from 151 kJ·mol$^{-1}$ to 76 kJ·mol$^{-1}$ in the 0.05 to 0.95 range extent of conversion. For the second decomposition step (step II), the activation energy increases from 151 kJ·mol$^{-1}$ to 281 kJ·mol$^{-1}$ in the 0.1-0.9 range extent. As a general result for thermal dehydration of sodium perborate tetrahydrate to sodium perborate monohydrate and sodium metaborate, variation in the value of activation energy obtained by isoconvesional isothermal and non-isothermal method may be a hint of change in reaction mechanism with reac-
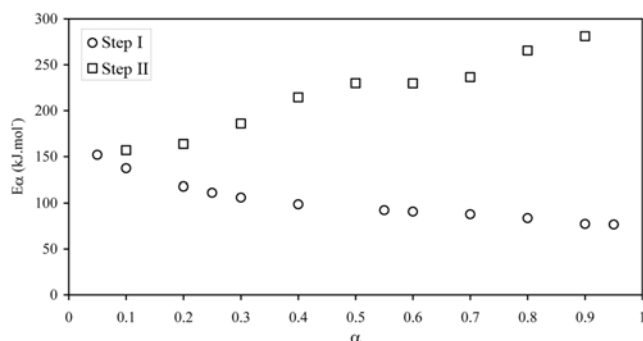
Fig. 10. Changes of activation energy of sodium perborate tetrahydrate to sodium perborate monohydrate (step I) and sodium metaborate (step II) with conversion.

tion progressing or more complex situation such as mutually independent multiple, competitive or consecutive reaction system and reversible reaction [32-34].

## CONCLUSIONS

The thermal decomposition of sodium perborate tetrahydrate to sodium perborate monohydrate and sodium metaborate is realized in multi-step and therefore model-free method is not suitable for non-isothermal data. The application of isothermal data gives us logical and reliable results to solve the kinetics complexity. An alternative common for the model-fitting method is the model-free isoconversional method. By applying the free isoconversional method to the data of isothermal and nonisothermal, the complex nature and change in the activation energy of decomposition of sodium perborate tetrahydrate to sodium perborate monohydrate and sodium metaborate were determined for all range of conversion and decomposition process.

It was also determined that the crystal habits of sodium perborate tetrahydrate and sodium metaborate are spherical and hexagonal.

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