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Chemical Engineering Journal 139 (2008) 128–135

Chemical Engineering Journal

www.elsevier.com/locate/cej

Kinetic analysis of the nonisothermal decomposition of potassium metabisulfite using the model-fitting and isoconversional (model-free) methods

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Received 11 May 2007; received in revised form 23 July 2007; accepted 24 July 2007

Abstract

The thermal decomposition kinetics of potassium metabisulfite was studied by thermogravimetry using nonisothermal experiments. The complete kinetic analysis was established by the following procedures: isoconversional methods (model-free) (including the Friedman (FR), Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Vyazovkin (V) methods), master-plot method, the artificial isokinetic relationship and in addition the differential composite method. Firstly, it was established that the Friedman's and Vyazovkin's isoconversional methods are the best two methods for describing the dependence of apparent activation energy (E_a) on the degree of conversion (α) for the investigated decomposition process. Secondly, the appropriate conversion model ($f(\alpha)$) of the process were selected by means of the "model-fitting" master-plot method. From the system studied, using the composite differential method we obtained the following kinetic triplet: $f(\alpha) = 2(1-\alpha)^{1/2}$, $E_a = 121.9\,\mathrm{kJ\,mol^{-1}}$, $A = 1.22 \times 10^{12}\,\mathrm{min^{-1}}$. Comparing both experimental and calculated thermoanalytical curves at constant heating rate assessed the adequate consistency of the kinetic triplet. It was concluded that the totally unambiguous choice of the reaction model is practically impossible based solely on the existing kinetic data, and because of this fact, the meaningful conclusions concerning the real mechanism of the investigated decomposition process should be based on additional microscopic observations.

Keywords: Thermal decomposition; Kinetic triplet; Potassium metabisulfite; Contracting area; Isoconversional methods

1. Introduction

Potassium metabisulfite, $K_2S_2O_5$, is a white crystalline powder with a pungent sulfur odour. $K_2S_2O_5$ is also known as potassium pyrosulfite. The main use for the chemical is as an antioxidant (Antiox. group C) or chemical sterilant. It is a sulfite and is chemically very similar to sodium metabisulfite, with which it is sometimes used interchangeably [1]. In addition, potassium metabisulfite is sometimes used in the brewing industry to inhibit the growth of wild yeasts, bacteria, and fungi [1]. This is called 'stabilizing'. It is used both by homebrewers and commercial brewers alike. It is not used as much for brewing beer, because the wort is almost always boiled, which kills most microorganisms anyway. Also, potassium metabisulfite was used as the activator in polymerization process of mechanically strong polymeric materials [2,3].

Potassium metabisulfite has a monoclinic crystal structure and decomposes through the following chemical reaction:

$$K_2S_2O_{5(s)} \rightarrow K_2O_{(s)} + 2SO_{2(g)}\uparrow \tag{1}$$

where the potassium monoxide (K_2O) is a solid salt, whereas the sulfur dioxide (SO_2) is a gas. The complete kinetic analysis (determination of Arrhenius parameters (A and E_a) and reaction model function, $f(\alpha)$) realised by applying the model-fitting and isoconversional (model-free) methods for the investigated process in modern literature has not been performed. However, the decomposition of $K_2S_2O_5$ has been investigated in order to analyze the nature of thermally induced ion-radicals where are samples of $K_2S_2O_5$ subjected to X-ray irradiation [4]. On the other hand, the decomposition of $K_2S_2O_5$ was used for the electron spin resonance study of the sulfur dioxide radical anion ($SO_2{\cdot}^-$) [5].

The objective of this paper was to study the potentials of model-fitting and model-free isoconversional methods to provide clues about the decomposition mechanism of potassium

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doi:10.1016/j.cej.2007.07.085

metabisulfite. The nonisothermal TG data will be treated by model-fitting and model-free methods for evaluating the variation of the apparent activation energy (E_a) with heating rate and/or reaction model and the degree of conversion (α). Also, for checking the correctness of determined reaction model ($f(\alpha)$), the differential composite method was applied.

2. Experimental

Thermal decomposition of $K_2S_2O_5$ (Merck, 99.5%, powder) was carried out in a SDT 2960 simultaneous TGA/DTA unit from TA Instruments Ltd.

The $K_2S_2O_5$ samples were decomposed directly within the thermobalance, in korund pans, under (99.9995 vol.%) nitrogen flowing at a rate of 20 mL min^{-1}. The five different heating rates ($\beta = 2.5$, 5, 10, 15 and 30 °C min^{-1}) were used in this study. All experiments are conducted in the temperature range from an ambient one up to 600 °C. The furnace temperature, which was controlled by a thermocouple, rose linearly according to the preset linear temperature schedules. The mass of samples was about 15 ± 1 mg.

The original mass loss versus temperature (TG) curves obtained at constant heating rate were transformed into the degree of conversion (α) versus temperature curves by means of the following equation:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{2}$$

where m_t represents the mass of the sample at arbitrary time t (or temperature T), whereas m_0 and m_f are the mass of the sample at the beginning and at the end of the process, respectively.

3. Kinetic analysis

3.1. Model-fitting and model-free methods

In kinetic analysis, it is generally assumed that the rate of reaction can be described by two separate functions $k(T)$ and $f(\alpha)$ such that [6]:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{3}$$

where $k(T)$ is the rate constant, A the pre-exponential factor, E_a the apparent activation energy, R the universal gas constant, T the absolute temperature and $f(\alpha)$ is the differential conversion function (reaction model).

When a sample is heated at a constant rate, $\beta = dT/dt$, Eq. (3) is rewritten as

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{4}$$

Solid-state kinetics was developed from reaction kinetics in homogeneous systems (i.e., gases and liquids). The Arrhenius equation (introduced in Eqs. (3) and (4)) relates the rate constant of a simple one-step reaction to the temperature through the apparent activation energy (E_a) and pre-exponential factor (A). It has been generally assumed that the apparent activation energy (E_a) and pre-exponential factor (A) remain constant, however, it has been shown [7–9] in solid-state reactions that these kinetic parameters may vary with the degree of conversion (α). In the solid-state, a variation in apparent activation energy could be observed for an elementary reaction due to the heterogeneous nature of the solid sample or due to a complex reaction mechanism. This variation can be detected by isoconversional (model-free) methods [10]. The efficacy of the isoconversional analysis originates from its ability of disclosing and handling the complexity of the respective processes. As a matter of fact, the isoconversional analysis provides a fortunate compromise between the oversimplified but widely used single-step Arrhenius kinetic treatments and the prevalent occurrence of processes whose kinetics are multi-step and/or non-Arrhenius [10].

Some integral kinetic methods are based on the following relation, which is obtained from Eq. (4) through integration:

$$g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E_a}{RT}\right) dT = \frac{AE_a}{\beta R}\int_{x}^{\infty} \frac{\exp(-x)}{x^2} dx = \frac{AE_a}{\beta R} p(x) \equiv \frac{A}{\beta} I(E_a, T) \tag{5}$$

where $g(\alpha)$ is the integral conversion function (Table 1), $x = E_a/RT$, and $p(x)$ is the temperature integral, which has no analytical solution. To overcome this difficulty, the temperature integral has been solved using approximation methods, series expansions, and numerical solution methods [11].

Kinetic parameters can be obtained by both model-fitting and isoconversional methods. For nonisothermal experiments, model-fitting method involves fitting different models to α–T curves and simultaneously determining E_a and A.

Nevertheless, the use of model-fitting (modelistic) methods has been criticised in nonisothermal studies because regression methods may lead to indistinguishable fits or mathematical expressions with high correlation [12]. As a result, the values of the Arrhenius parameters, obtained for various forms of $g(\alpha)$, are correlated through the relation of compensation effect [12,13].

In contrast, the isoconversional methods, which allow for model-independent estimates of the apparent activation energy at progressive degrees of conversion by conducting multiple experiments at different constant heating rates, are highly recommended in order to obtain a reliable kinetic description of the investigated process [12].

Isoconversional differential methods are frequently called Friedman (FR) methods due to the researcher who first derived this method [14]. The method derives from taking the logarithm of Eq. (4):

$$\ln\left[\beta_i \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln[A_\alpha f(\alpha)] - \frac{E_{a,\alpha}}{RT_\alpha} \tag{6}$$

The apparent activation energy (E_a) is determined from the slope of the plot of $\ln[\beta_i(d\alpha/dT)_{\alpha,i}]$ versus $1/T_\alpha$, at a constant α value. Subscript i is the ordinal number of an experiment performed at a given heating rate. This method is rather accurate because it does not include any mathematical approximations.

Table 1
Set of reaction models applied to describe the reaction kinetics in heterogeneous solid state systems

No.	Symbol	Reaction model	$f(\alpha)$	$g(\alpha)$
1	P1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	P2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	P4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	R2	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
6	R3	Phase-boundary controlled reaction (contracting volume, i.e., tridimensional shape)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
7	F1	First-order (Mampel)	$(1-\alpha)$	$-\ln(1-\alpha)$
8	A2	Avrami–Erofe'ev ($m=2$)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
9	A3	Avrami–Erofe'ev ($m=3$)	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
10	A4	Avrami–Erofe'ev ($m=4$)	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
11	D1	One-dimensional diffusion	$1/2\alpha$	α^2
12	D2	Two-dimensional diffusion (bidimensional particle shape) Valensi equation	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
13	D3	Three-dimensional diffusion (tridimensional particle shape) Jander equation	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
14	D4	Three-dimensional diffusion (tridimensional particle shape) Ginstling-Brounshtein	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

The isoconversional integral methods are based on an approximate form of the temperature integral that results from rearrangement and integration of Eq. (4) (see Eq. (5)).

The Kissinger–Akahira–Sunose (KAS) method [15,16] uses the Coats–Redfern [17] approximation of the temperature integral that leads to

$$\ln\left(\frac{\beta}{T_\alpha^2}\right)=\ln\left(\frac{A_\alpha R}{E_{\mathrm{a},\alpha}g(\alpha)}\right)-\frac{E_{\mathrm{a},\alpha}}{RT_\alpha} \tag{7}$$

Thus, for $\alpha=\mathrm{const.}$, a plot of $\ln(\beta/T_\alpha^2)$ versus $1/T_\alpha$, obtained from thermal curves recorded at several heating rates, is a straight line whose slope allows evaluation of the apparent activation energy and whose intercept allows the value of the pre-exponential factor to be obtained for a known analytical form of the integral function of conversion.

The Flynn–Wall–Ozawa (FWO) method [18,19] uses the Doyle approximation [20] for the temperature integral:

$$\ln p(x)=-5.331-1.052x \tag{8}$$

Relations (5) and (8) lead to

$$\ln\beta_i=\ln\left(\frac{A_\alpha E_{\mathrm{a},\alpha}}{Rg(\alpha)}\right)-5.331-1.052\frac{E_{\mathrm{a},\alpha}}{RT_\alpha} \tag{9}$$

Thus, for $\alpha=\mathrm{const.}$, a plot of $\ln\beta_i$ versus $1/T_\alpha$, obtained from thermal curves recorded at several heating rates, should be a straight line whose slope allows evaluation of the apparent activation energy. As far as, the pre-exponential factor is concerned, its value can be obtained from the intercept if the form of the integral conversion function is known. For $x<20$, Doyle's approximation leads to errors higher than 10%. For such cases Flynn [21] suggested corrections in order to obtain correct activation energy values.

The Vyazovkin (V) method [22–24] represent a advanced isoconversional method that utilizes an accurate, nonlinear, Senum–Yang [25] approximation of $p(x)$ (Eq. (5)), which leads to

$$\Phi=\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_{\mathrm{a},\alpha},T_{\alpha,i})\beta_j}{I(E_{\mathrm{a},\alpha},T_{\alpha,j})\beta_i}\right| \tag{10}$$

where n is the number of heating rates, $I(E_{\mathrm{a},\alpha},T_{\alpha,i})$ the exponential integral ($p(x)$) that results from heating rate β_i while $I(E_{\mathrm{a},\alpha},T_{\alpha,j})$ is the exponential integral from heating rate β_j. The fourth degree Senum–Yang approximation was chosen for this work.

The apparent activation energy (E_a) at a given degree of conversion is the value that minimizes Φ in the above equation. This nonlinear procedure suggested by Vyazovkin shows extremely low errors in the activation energy, which are practically independent on x value [22].

The physico-chemical conversion function ($f(\alpha)$ or $g(\alpha)$) of solid-state reactions can be determined by using the so-called master-plot method. Master plots are reference theoretical curves depending on the kinetic model but generally independent of the kinetic parameters of the process [26]. Essentially the master-plot method is based on the comparison of theoretical master plots, which are obtained for a wide range of ideal kinetic models, with the experimental master plot. This comparison obviously requires the previous transformation of the experimental data into the corresponding master plot. The application of this method usually leads to the selection of the appropriate conversion model for the solid-state reaction investigated [27].

By using a reference at point $\alpha=0.5$ and according to Eq. (5), the following equation is obtained:

$$g(0.5)=\frac{AE_\mathrm{a}}{\beta R}p(x_{0.5}) \tag{11}$$

where $x_{0.5}=E_\mathrm{a}/RT_{0.5}$, and $T_{0.5}$ is the temperature required to attain 50% conversion. When Eq. (5) is divided by Eq. (11), the

Eq. (12) is deduced:

$$\frac{g(\alpha)}{g(0.5)} = \frac{p(x)}{p(x_{0.5})} \tag{12}$$

Plotting $g(\alpha)/g(0.5)$ versus α corresponds to theoretical master plots of various $g(\alpha)$ functions. Both the conversion–temperature profile (α–T) and the value of E_a for the process should be known in advance in order to draw the experimental master plots of $p(x)/p(x_{0.5})$ versus α from experimental data obtained at a given heating rate. To draw the experimental master plots of $p(x)/p(x_{0.5})$ versus α obtained under different β's, an approximate formula [25] of $p(x)$ was used. Thus, Eq. (12) indicates that, for a given α, the experimental value of $p(x)/p(x_{0.5})$ and theoretically calculated values of $g(\alpha)/g(0.5)$ are equivalent when an appropriate conversion model is used. Consequently, this integral "model-fitting" master-plot method can be used to determine reaction models for solid-state reactions.

4. Results and discussion

The TG and DTG curves of the decomposition process of potassium metabisulfite samples obtained at different heating rates (2.5, 5, 10, 15 and 30 °C min^{-1}) are shown in Fig. 1(a) and (b).

The observed thermogravimetric curves show an asymmetric character (Fig. 1a) and were moves to higher temperatures with increase in heating rate.

The kinetic models of some thermal decomposition reactions can be obtained through Dollimore's approach, which is based on the "sharpness" of the onset (T_i) and final (T_f) temperatures of the TG/DTG and its asymmetry (Fig. 1(a) and (b)) [28–30]. The investigation of some parameters that describe this asymmetry can thereby indicate the probable kinetic mechanism expressed through the function $f(\alpha)$. When the thermal decomposition reaction is not complex, the quantitative approach may be obtained using parameters such as α_{max} (α_{max} is the degree of conversion at the maximum rate), peak temperature (T_p), half-width (HW) from DTG curves, HiT and LoT, the higher and lower temperature ends of the half-width, respectively.

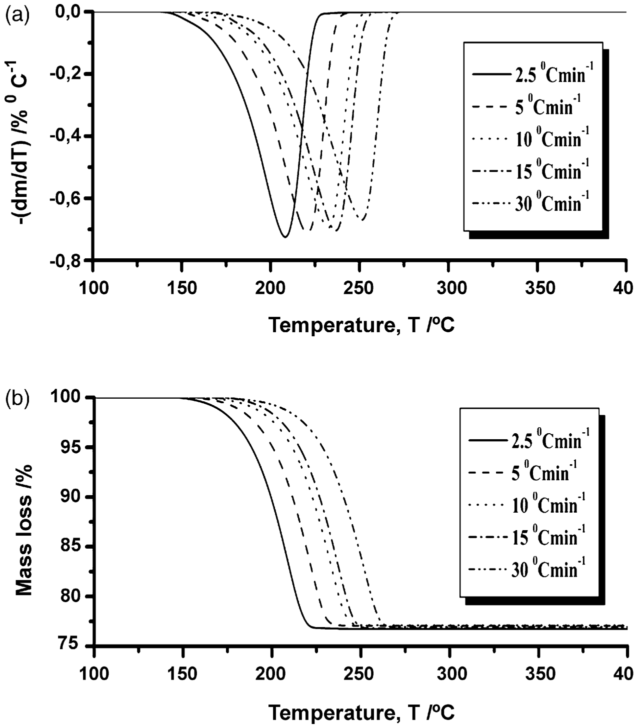

Fig. 1. TG (a) and DTG (b) curves for the thermal decomposition process of potassium metabisulfite samples in nitrogen atmosphere.

Table 2
Data from TG and DTG curves for decomposition process of potassium metabisulfite at different heating rates

β (°C min^{-1})	α_{max}	HiT (°C)	LoT (°C)	Half-width peak, HW
2.5	0.73	219.4	188.4	31.0
5	0.73	230.3	201.3	29.0
10	0.74	241.2	212.2	29.0
15	0.74	246.7	215.7	31.0
30	0.74	261.3	228.3	33.0
Expected values $\geq 0.7 - < 0.8$ to R2 kinetic model[a]				24–34

[a] T_i: diffuse; T_f: sharp.

Dollimore's procedure is applied on TG/DTG curves (Fig. 1) whose asymmetry observed between the onset T_i and the final T_f in DTG curves, may be associated with the parameters as the degree of conversion at rate of maximum decomposition, α_{max}, peak temperature, T_p, and HW = HiT–LoT which is the difference between the high-temperature and low-temperature at half-width of the DTG peak (Fig. 1(b)).

The above-mentioned parameters from Dollimore′s method, obtained for decomposition process of potassium metabisulfite at different heating rates, are presented in Table 2.

Table 2 indicates the R2 model ($f(\alpha) = 2(1-\alpha)^{1/2}$) corresponding to the phase-boundary controlled reaction (contracting area). This approach is useful for basic classification of possible kinetic model but it is not sufficient for an unambiguous determination of true kinetic model function, $f(\alpha)$.

The nonisothermal decomposition process of potassium metabisulfite was analyzed by Friedman (FR), Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Vyazovkin (V) isoconversional methods. For all the sets of α values, the linear isoconversional plots of FR, KAS, FWO and V methods result in a correlation coefficient (r^2) higher than 0.9950. The dependence of apparent activation energy (E_a) on the degree of conversion (α) (E_a–α curve) for nonisothermal decomposition process of potassium metabisulfite ($K_2S_2O_5$) obtained by isoconversional methods is presented in Fig. 2.

From Fig. 2 one can notice the same shapes of the curves E_a versus α corresponding to the considered isoconversional methods. Also, from the same figure, it can be seen that the values of apparent activation energy (E_a) calculated by KAS and FWO integral methods are lower than values of E_a calculated by FR differential and V nonlinear methods. The average values of E_a for KAS and FWO methods obtained in the range $0.05 \leq \alpha \leq 0.95$ are also lower than average values of E_a obtained

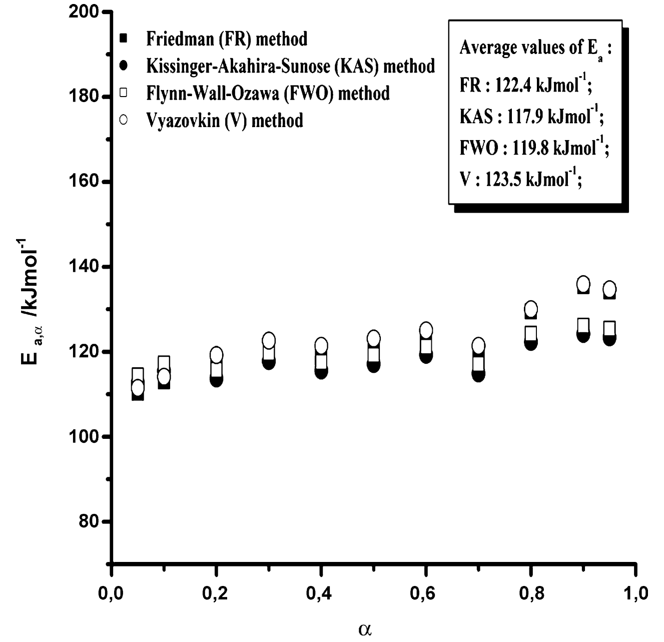

Fig. 2. The dependence of apparent activation energy (E_a) on the degree of conversion (α) for nonisothermal decomposition process of potassium metabisulfite according to Friedman (FR), Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Vyazovkin (V) isoconversional methods. The average values of E_a calculated for different methods in the range $0.05 \leq \alpha \leq 0.95$ are given in the inset.

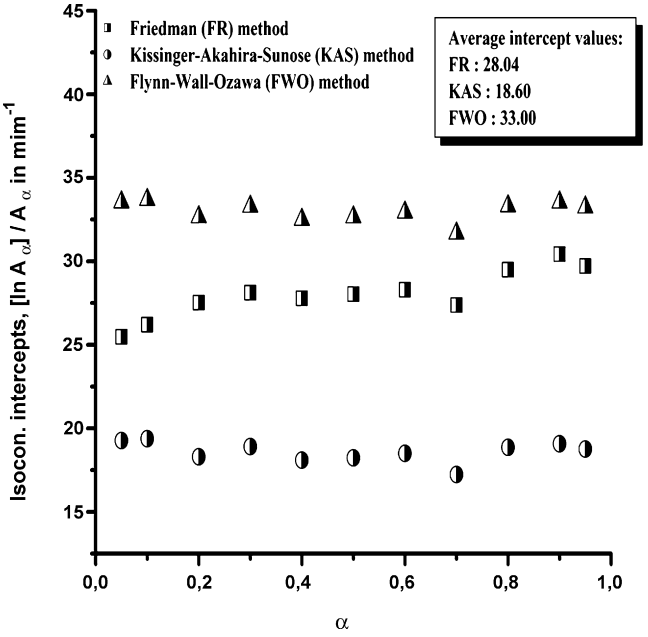

Fig. 3. The dependence of isoconversional intercepts (FR, KAS and FWO methods) on the degree of conversion (α) for nonisothermal decomposition process of potassium metabisulfite. The average values of isoconversional intercepts for corresponding methods in the range $0.05 \leq \alpha \leq 0.95$ are given in the inset.

for FR and V methods (see the inset in Fig. 2). Some of the differences observed between the values of E_a obtained using various linear integral methods (KAS and FWO) can be assigned to the different approximations of the temperature integral. On the other hand, the existence of significant differences between $E_{a,FR}$, $E_{a,V}$ and E_a calculated using all of the integral methods described above, are due to the way in which the relations that form the basis of the integral methods are derived. It can be observed that the calculated average values of apparent activation energy for FR and V methods are very similar (Fig. 2). The Eqs. (8) and (10) are derived assuming a constant apparent activation energy. This assumption introduces a significant systematic error for a process whose apparent activation energy strongly varies with the degree of conversion [31]. Such an error does not appear in the differential isoconversional FR method. The nonlinear Vyazovkin method uses integration as a part of the procedure for estimating the apparent activation energy. Compared to linear integral procedures, nonlinear V method was found to be a very accurate method with relative errors in E_a which are practically independent of E_a/RT. For the system under investigation, the nonlinear V and differential FR methods appears to be the best compromise between the stability of calculations (not attained with FR method) and obtaining valid values of actual activation energies in the above-considered range of α. The dependence of isoconversional intercepts (FR, KAS and FWO) on the degree of conversion (α) is presented in Fig. 3.

It can be seen from Fig. 3, that the isoconversional intercept values does not show the significant dependence on the degree of conversion. The average values of isoconversional intercepts for FR, KAS and FWO methods in the conversion range $0.05 \leq \alpha \leq 0.95$ are presented in the inset of Fig. 3. Fig. 3 shows that the highest average value of isoconversional intercept is observed for FWO method.

The above results indicates that there exists a high probability for the presence of a single-step reaction [32,33]. Therefore, it allows to estimate the most probable kinetic model.

4.1. Determination of the conversion model and the pre-exponential factor (A)

As said previously, the knowledge of α as a function of temperature and the value of the apparent activation energy are essential in order to calculate the experimental masterplot of $p(x)/p(x_{0.5})$ against α from experimental data obtained under a linear heating rate (Eq. (12)).

Fig. 4 shows the experimental masterplots of $p(x)/p(x_{0.5})$ against α constructed from experimental data under different heating rates. The theoretical masterplots corresponding to the $g(\alpha)$ functions for R2, R3, D2, D3 and D4 models (Table 1) are also shown in Fig. 4.

It is shown that the all experimental masterplots of decomposition process at 2.5, 5, 10, 15 and 30 °C min^{-1} are consistent with theoretical masterplot for R2 kinetic model. The comparison of the experimental masterplots with theoretical ones revealed that the kinetic process for the decomposition process of potassium metabisulfite was most probably described by the R2 (phase-boundary) model, $g(\alpha) = [1 - (1 - \alpha)^{1/2}]$ with kinetic exponent $n = 2$.

The accommodated model [34] of R_n with integral exponent $n = 2$ was used for estimating the pre-exponential factor (A). The expression of R2 is introduced into Eq. (5), and the following

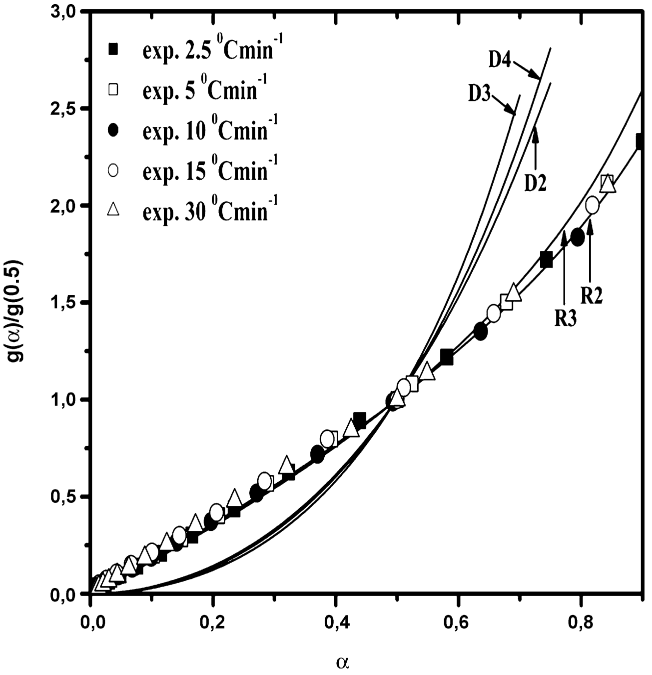

Fig. 4. Master plots of theoretical $g(\alpha)/g(0.5)$ vs. α for R2, R3, D2, D3 and D4 reaction models and experimental master plots for the decomposition process of potassium metabisulfite at a heating rates of 2.5, 5, 10, 15 and 30 °C min^{-1}.

equation was obtained:

$$1-(1-\alpha)^{1/2}=\frac{AE_a}{\beta R}p(x) \tag{13}$$

where E_a in Eq. (13) represent the average value of the apparent activation energy obtained by Friedman's method ($E_{a,av}=122.4\,\mathrm{kJ\,mol^{-1}}$).

Fig. 5 shows the plot of $[1-(1-\alpha)^{1/2}]$ versus $E_a p(x)/\beta R$ for investigated decomposition process at various heating rates, using linear least square fitting procedure.

For R2 kinetic model with $n=2$ and $E_a=122.4\,\mathrm{kJ\,mol^{-1}}$, the pre-exponential factor was found to be $A=1.37\times10^{12}\,\mathrm{min^{-1}}$ ($\ln A=27.95$). All the values are within the limit of error. The obtained value of $\ln A$ is in good agreement with average value of isoconversional intercept estimated by FR method (Fig. 3).

For checking the correctness of determined conversion function ($f(\alpha)$), the differential composite method [35] was used. This method is based on the following equation:

$$\ln\left[\frac{\beta(\mathrm{d}\alpha/\mathrm{d}T)}{f(\alpha)}\right]=\ln A-\frac{E_a}{RT} \tag{14}$$

where β is the heating rate and $\mathrm{d}\alpha/\mathrm{d}T$ is the nonisothermal differential rate of investigated process. The data for different heating rates must be grouped together in a single relation, from which a single set of parameters, A and E_a, is obtained.

The curves $\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)]$ versus $1/T$ for the $f(\alpha)$ corresponding to R2 kinetic model, and all used heating rates were drawn. All points are placed around/on the same line only for R2 kinetic model (phase-boundary controlled reaction (contracting area, i.e. bidimensional shape)) (Fig. 6).

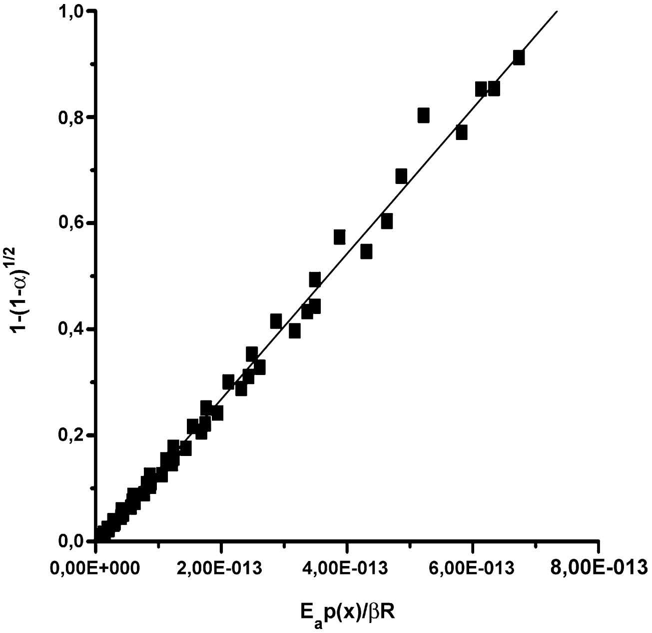

Fig. 5. Plotting $[1-(1-\alpha)^{1/n}]$ vs. $E_a p(x)/\beta R$ at $n=2$ for the decomposition process of potassium metabisulfite at various heating rates (β) and their linear-fitting drawning (solid line).

From the parameters of this straight line the Arrhenius parameters were evaluated obtaining $\ln A=27.83$ ($A=1.22\times10^{12}\,\mathrm{min^{-1}}$) and $E_a=121.9\,\mathrm{kJ\,mol^{-1}}$ ($r=-0.9980$). The values of Arrhenius parameters obtained by the differential composite method are in good agreement with values of Arrhenius parameters obtained by FR and V isoconversional methods (except for KAS and FWO methods, Fig. 2).

The isoconversional (model-free) method does not, by itself, permit an analysis of pre-exponential factor and the reaction model. The reaction model can be reconstructed by a method that

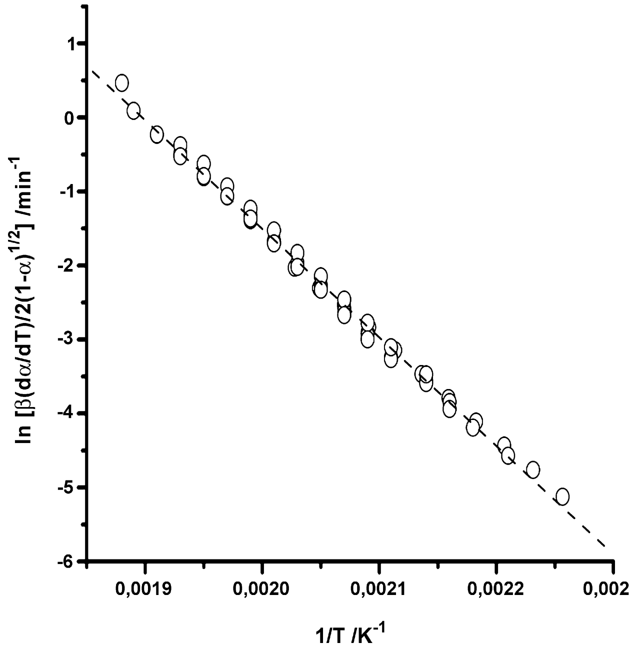

Fig. 6. The straight line $\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)/2(1-\alpha)^{1/2}]$ vs. $(1/T)$ for the thermal decomposition process of potassium metabisulfite at all the used heating rates.

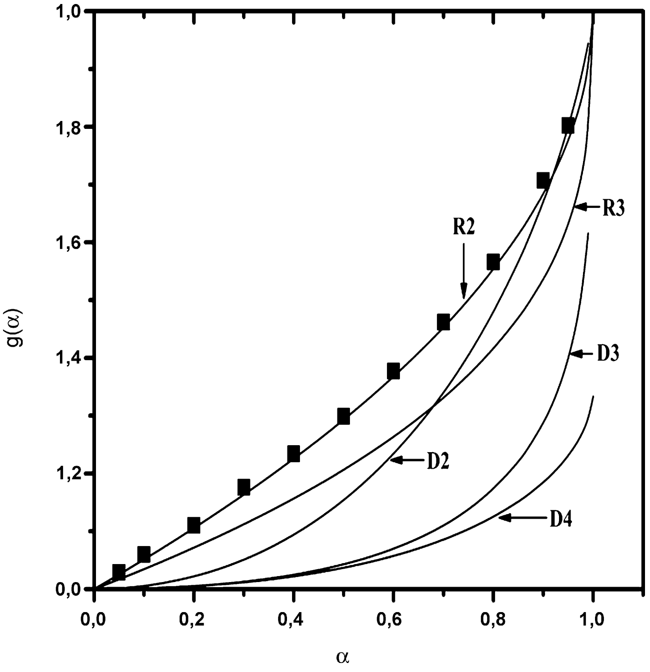

Fig. 7. Reconstruction of $g(\alpha)$ vs. α plots from the model-free analysis (FR method) (solid lines are calculated from R2, R3, D2, D3 and D4 models). The data designated with full squares (■) represents the values calculated for decomposition process of potassium metabisulfite, from the E_a and A values derived from model-free (FR) analysis.

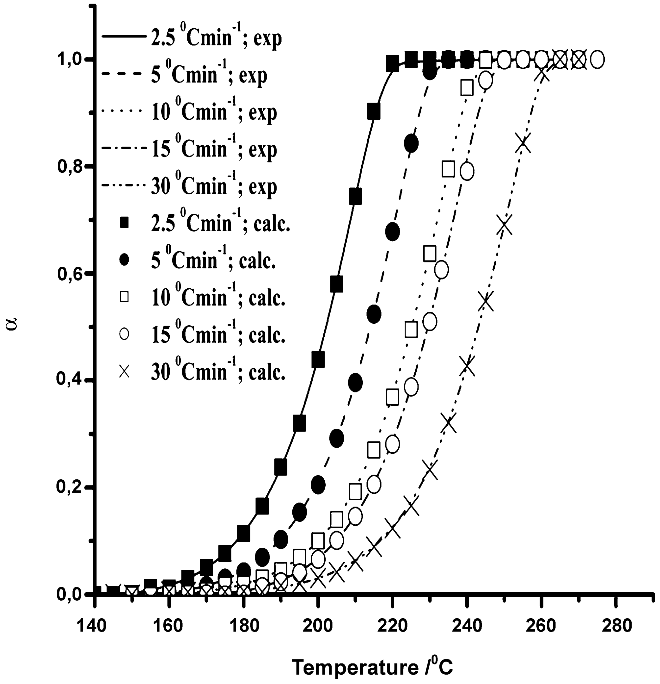

Fig. 8. The experimental and reconstructed $\alpha = \alpha(T)$ curves for the kinetic model R2, $E_a = 121.9\,\text{kJ mol}^{-1}$ and $\ln A = 27.83$ (A expressed in min^{-1}).

makes use of an artificial isokinetic relationship [36–38]. Using cited method, we can numerically evaluated the integrated form of reaction model ($g(\alpha)$ function in Eq. (5)), taking into account the experimentally obtained dependence of E_a on α. Fig. 7 shows a comparison of $g(\alpha)$ function obtained from nonisothermal TG data (at average heating rate, 15 °C min^{-1}) with R2, R3, D2, D3 and D4 reaction models listed in Table 1.

From Fig. 7, we can see that the experimental kinetic function follows the R2 model in considered range of α. From the above kinetically procedure, we can conclude that the model-free analysis clearly supports the two-dimensional phase boundary reaction. On the other hand, we can see that the evaluated kinetic function is complete consistent with kinetic function introduced in differential composite method.

Fig. 8 shows comparatively the experimental and reconstructed $\alpha = \alpha(T)$ curves using kinetic triplet $\ln A = 27.83$ (A expressed in min^{-1}), $E_a = 121.9\,\text{kJ mol}^{-1}$ and R2 model. It comes out that a satisfactory agreement among the experimental and reconstructed $\alpha = \alpha(T)$ curves exist.

From the results given above follows that the unambiguously chosen reaction model can not help in drawing an unambiguous mechanistic conclusion because of the ambiguous association of the kinetic equation with the mechanistic model of a process [39]. Jacobs and Tompkins [40] emphasized that a posterior agreement between the theoretical rate equations and experimental results does not necessarily confirm the basis on which these equations are derived. This statement is rather obvious if we take into account that the same equation can be derived for totally different mechanistic models and the same mechanistic model can give rise to several different equations [41]. For example, Pysiak [42] demonstrated that the equation of contracting sphere can be derived from three different mechanistic concepts. Accordingly, the phase boundary model:

$$g(\alpha) = 1 - (1-\alpha)^{1/n} \tag{15}$$

which is associated with an inward advancement of the reaction interface from the crystal's edges (with $n = 2$ for reactions spreading in two dimensions), the probably represent the most reliable reaction model, which best describes the investigated decomposition process of potassium metabisulfite. However, a totally unambiguous choice of the reaction model is practically impossible based solely on the existing kinetic data [12], and additional high resolution microscopy studies would be necessary to validate the assigned mechanism. From the results given in this paper, we can concluded, that the alternative approach for the kinetic analysis of potassium metabisulfite decomposition process, which avoids the ambiguity and subjectivity associated with the model-fitting methods is the isoconversional method. The values of apparent activation energy obtained using the Friedman's and Vyazovkin's advanced isoconversional methods are generally comparable with value of E_a calculated by the differential composite method.

5. Conclusions

The kinetics of the nonisothermal decomposition of potassium metabisulfite was accurately determined from a series of thermoanalytical experiments at different constant heating rates. The apparent activation energy (E_a) was calculated by four different isoconversional methods (one differential (FR), two linear (KAS and FWO) and one nonlinear (V) methods) without previous assumption regarding the conversion model fulfilled by the reaction. It was established that the Friedman's and Vyazovkin's isoconversional methods are the best two methods for describing the dependence of apparent activation energy on the degree of conversion (α) for the investigated decomposition process. The apparent activation energy was practically constant in the considered α range (for $0.05 \leq \alpha \leq 0.95$), and this suggesting that the investigated decomposition was a single-step process with an average values of $E_a = 122.4\,\mathrm{kJ\,mol^{-1}}$ and $E_a = 123.5\,\mathrm{kJ\,mol^{-1}}$ obtained by Friedman and Vyazovkin methods, respectively. The master-plot method revealed that the conversion model $g(\alpha) = 1 - (1 - \alpha)^{1/n}$ (with $n = 2$) best described the kinetics of the process. The same reaction mechanism, that of the contracting area geometrical model (R2), was observed at all heating rates. The artificial isokinetic relationship was used for numerical reconstruction of the experimental kinetic function. It was established that the numerically reconstructed experimental function follows the R2 reaction model in the considered range of α, taken from the model-free analysis. Also, it was concluded, that the alternative approach for the kinetic study of decomposition process, which avoids the ambiguity and subjectivity associated with the model-fitting methods is the isoconversional (model-free) method.

The obtained kinetic triplet $E_a = 121.9\,\mathrm{kJ\,mol^{-1}}$, $A = 1.22 \times 10^{12}\,\mathrm{min^{-1}}$ and $f(\alpha)$ given by geometry model equation with $n = 2$ was used for calculation of α versus T curves. A satisfying agreement of these calculated curves with those experimentally obtained was put in evidence.

However, it was established, that the totally unambiguous choice of the reaction model is practically impossible and therefore, it seems that meaningful conclusions concerning the real mechanism of the decomposition process should be based on the other types of complementary evidence, including microscopic observations together with all other relevant informations.

Acknowledgements

The investigation was partially supported by the Ministry of Science and Environmental Protection of Serbia, under the following Projects 142025.

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