Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 3, 631–635

COMPARATIVE RESULTS OF KINETIC DATA OBTAINED WITH DIFFERENT METHODS FOR COMPLEX DECOMPOSITION STEPS

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A comparative kinetic analysis on the thermal decomposition of tartaric acid and potassium tartrate under non-isothermal conditions was performed. The non-isothermal kinetic parameters were determined by the following four methods: integral isoconversional method suggested by Flynn–Wall–Ozawa (FWO method); differential isoconversional method suggested by Friedman; Budrugeac–Segal method and Non-Parametric-Kinetic (NKP) method suggested by Sempere and Nomen and modified by Vlase and Doca. The comparison of the results obtaining by these methods leads to interesting conclusions. The experimental data were obtained in dynamic nitrogen atmosphere at heating rates of 5, 7, 10, 12 and 15 K min^{-1}. The less speculative kinetic analysis was possible by the NPK method.

Keywords: *non-isothermal kinetics, potassium tartrate, tartaric acid*

Introduction

The mechanism of thermal decomposition in condensed phase is very often too complex to be described by a simple kinetic model [1, 2]. These reactions often occur in multiple steps that have different temperature and conversion functions. Therefore a suitable data processing is required in order to separate these steps even as formal kinetics [3].

In some recent papers [4–7] we applied different data processing strategies to the decomposition under non-isothermal conditions of compounds and materials like pharmaceuticals, food additives, catalyst precursors, organic intermediates. The results were rather encouraging, especially regarding to a less speculative interpretation of kinetic data.

The aim of this paper is to extend these studies in order to try the ability of different data processing methods in describing a complex reaction. As a test reaction the decomposition under non-isothermal conditions of tartaric acid and potassium tartrate were used. These two compounds were selected due to almost the same structure, however with a difference in the carboxyl group. This difference, i.e. the presence or absence of the hydroxyl group is expected to have a significant influence on the decomposition/dehydration mechanism.

Experimental

Reagent grade of tartaric acid (TA) and potassium tartrate (TK) were used.

The TG/DTG data were obtained on a Perkin Elmer TGA 7 thermobalance, in nitrogen dynamic atmosphere and heating rates of 3, 5, 7, 10 and 12°C min^{-1}. See example in Fig. 1.

Data processing

According to the aim of this paper, the strategy of data processing is of relevance. Therefore, it will be detailed here.

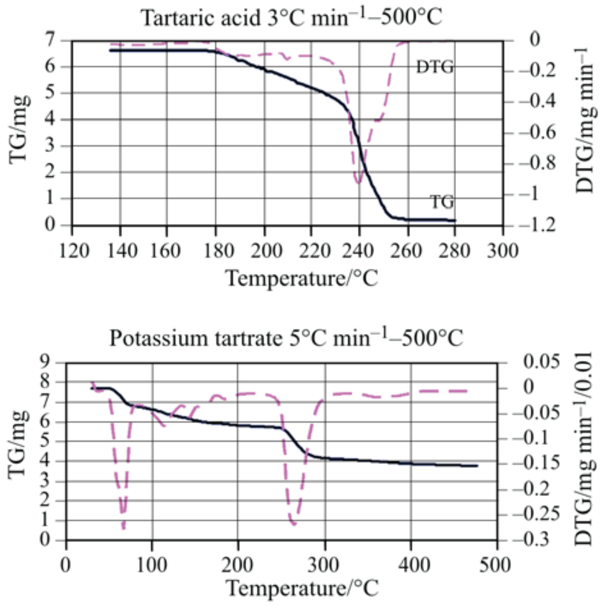

Fig. 1 Thermoanalytical curves of tartaric acid and potassium tartrate

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1388–6150/$20.00

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The integral method of Flynn–Wall–Ozawa [8, 9]

Considering isoconversional conditions, i.e. for the same α_i, the corresponding temperature T_i at different heating rates, the plot of left member of Eq. (1) *vs.* $1/T_i$ give a straight line; from its slope, the activation energy can be calculated.

$$\ln\beta=\ln\frac{A}{Rg(\alpha)}-5.331-1.052\frac{E}{RT} \qquad (1)$$

where: $g(\alpha)=\int_0^\alpha\frac{d\alpha}{f\alpha}$ is the integral conversion function.

From the start, the method of Flynn–Wall–Ozawa furnishes the activation energy for each conversion degree, when the data at different heating rates were processed. And with this, the question of the variation *E vs.* α is opened.

The differential-isoconversional method of Friedman [10]

At constant conversion, the differential form of the reaction is:

$$\left(\beta\frac{d\alpha}{dT}\right)_\alpha=f(\alpha)A\exp\left(-\frac{E}{RT}\right) \qquad (2)$$

or the equivalent

$$\ln\left(\beta\frac{d\alpha}{dT}\right)=\ln[Af(\alpha)]-\frac{E}{RT} \qquad (3)$$

At a certain conversion, the slope and the intercept of the straight line of $\ln(\beta d\alpha/dT)$ *vs.* $1/T$ give the activation energy and the product $Af(\alpha)$ respectively.

Due to its relative simplicity and independence in respect to the kinetic model, the Friedman's method is recommended for obtaining the value of the activation energy. By simple single-step processes, this is usually enough, the obtained *E* values being invariant in respect to α. A monotonous variation of *E vs.* α is a sign of a complex multi-step processes, and more sophisticated methods are necessary.

The Budrugeac–Segal method [11–13]

This method is often useful for description and simulation of complex processes. It is, logical, a continuation of the Friedman's method and is based on a particular variation of the activation energy obtained with this method:

i) the dependence of *E vs.* α is described by:

$$E=E_0+E_1\ln(1-\alpha) \qquad (4)$$

ii) there is a compensation effect, i.e.

$$\ln[Af(\alpha)]=aE+b \qquad (5)$$

with Eqs (4) and (5), considering a conversion function

$$f(\alpha)=(1-\alpha)^n \qquad (6)$$

Equation (3) became:

$$\ln\left(\beta\frac{d\alpha}{dT}\right)=\left(b+aE_0-\frac{E_0}{RT}\right)+ \\ +\left(aE_1-\frac{E_1}{RT}+n\right)\ln(1-\alpha) \qquad (7)$$

The correct value of *n* will be the one that gives a correlation coefficient closest to 1 for the straight line represented by $\ln(\beta d\alpha/dT)$ *vs.* $\ln(1-\alpha)$, the constants E_0, E_1, *a* and *b* being obtained from Eqs (4) and (5) respectively.

According to our previous experience [4–7], with Eq. (7) rather good results by simulation tests were obtained.

The Non-Parametric Kinetic (NPK) method by Sempere and Nomen [14–16]

This more sophisticated method allows the separation of two or more simultaneous processes of a decomposition reaction.

The reaction rates, $r=d\alpha/dt$, obtained at different heating rates, are represented in a 3D coordinate system (r, T, α), based on the general hypothesis:

$$r=f(T)g(\alpha) \qquad (8)$$

By a proper interpolation algorithm, the so obtained experimental points are simulated as a continuous reaction rate surface and then discretizated into a square matrix *M*.

According to Eq. (8), each element of this matrix is:

$$r_{ij}=f(T_i)g(\alpha_j) \qquad (9)$$

If the decomposition process is a result of two simultaneous steps, 1 and 2, it means that:

$$r=r_1+r_2=f_1(T_i)g_1(\alpha_j)+f_2(T_i)g_2(\alpha_j) \qquad (10)$$

respectively the matrix *M* became:

$$M=M_1+M_2 \qquad (11)$$

The NPK method uses the Singular Value Decomposition (SVD) algorithm [17] to decompose the matrix *M* according to:

$$M=U(\mathrm{diag}.S)V^T \qquad (12)$$

A vector u_1 given by the first column of the matrix *U* is analyzed *vs.* α to determine the conversion function. For this we suggest the Šesták–Berggren [18] equation:

$$g(\alpha)=\alpha^m(1-\alpha)^n \qquad (13)$$

Table 1 The variation of activation energy (kJ mol^{-1}) *vs.* conversion degree (Flynn–Wall–Ozawa)

α Sample	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	$\overline{E}$
TA	112.2±52.4	114.4±59.7	112.7±79.7	110.1±59.8	106.9±58.5	101.4±57.1	95.7±60.0	96.5±58.8	93.5±56.3	104.8±32.3
KT	160.8±37.5	177.0±22.3	170.5±31.5	197.5±66.6	156.6±37.8	151.8±59.1	136.9±68.4	118.4±77.5	115.4±75.2	153.9±52.1

Table 2 The variation of activation energy (kJ mol^{-1}) *vs.* conversion degree (Friedman)

α Sample	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	$\overline{E}$
TA	150.8±39.5	118.7±31.2	102.7±44.5	85.4±34.9	72.9±34.3	67.8±32.8	65.9±35.1	81.8±25.2	73.0±22.7	91.0±37.2
KT	171.1±34.3	180.3±25.8	167.2±39.7	152.9±38.8	130.0±43.6	116.5±52.1	91.4±56.4	79.1±56.3	96.6±35.1	131.7±52.0

A similar vector v_1, corresponding to the matrix V, is checked for an Arrhenius type temperature dependence.

In case of a multi-step process (according to Eqs (10) and (11)), the contribution of each step to the observed process is expressed by the explained variance λ so that $\lambda_1+\lambda_2=100\%$.

By applying this data processing strategy, a separation of complex processes and discrimination between the contributions of the physical (m) or the chemical (n) phenomenon are expected.

Results and discussion

Flynn–Wall–Ozawa method

In Table 1, a suggestive dependence of E *vs.* α is observed. Neglecting this dependence, an average values of E=104.8 kJ mol^{-1} for TA and E=154.0 kJ mol^{-1} for KT are obtained.

The differences are enough significant to explain the better thermal stability of KT in comparison for TA. Unfortunately there is rather all the information available. Considering different conversion functions $f(\alpha)$, a series of values for the preexponential factor should be obtained, but this is rather a mathematical exercise but not a kinetic analysis.

Friedman's methods

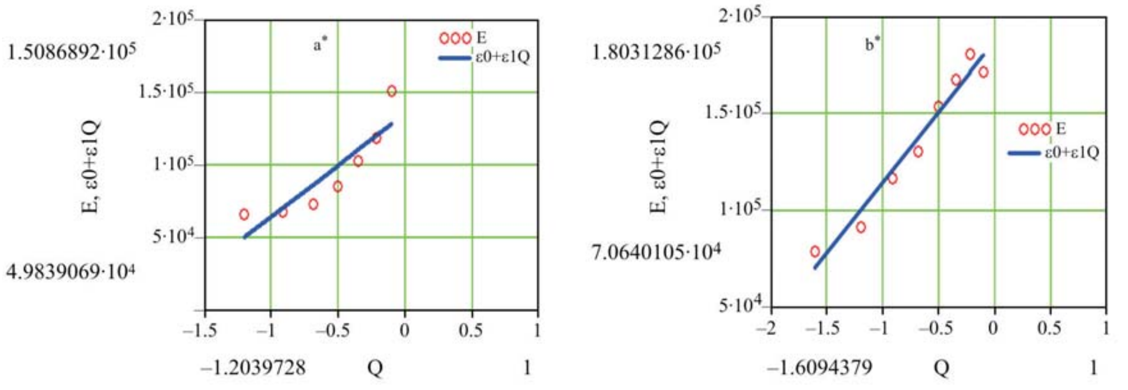
The data obtained according to Eq. (3) are systematized in Table 2.

For each individual conversion degree, the values of E for KT are significant higher than that for TA, an already monotonous variation of E *vs.* α is a first sign of a complex process.

Budrugeac–Segal method

In order to apply the Budrugeac–Segal method, the variation of the activation energy according to Eqs (4) and (5) are checked in Figs 2 and 3.

The kinetic constants according to Eq. (7) are systematized in Table 3.



*a tartaric acid

*b potassium tartrate

Fig. 2 Variation of the activation energy according to Eq. (4); ○ – E, —– $\varepsilon_0+\varepsilon_1$; $Q=\ln(1-\alpha)$

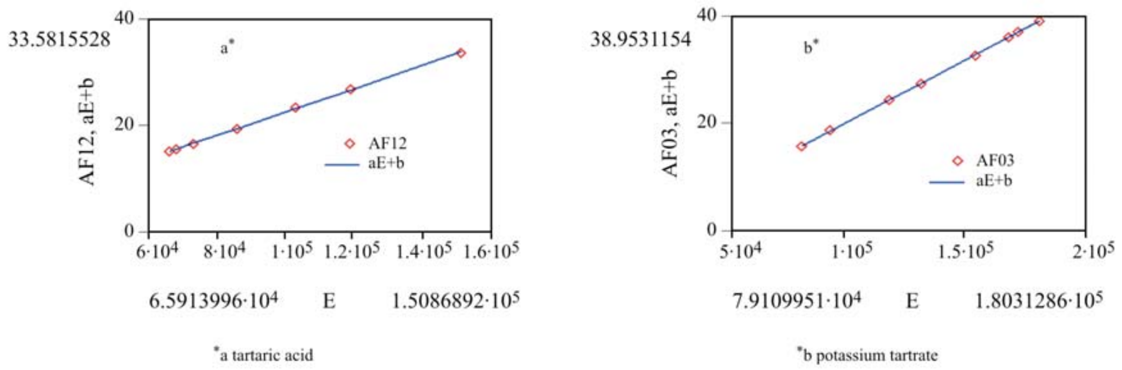


Fig. 3 Compensation effect according to Eq. (5); ◇ – AF12 and AF03, –– – *aE*+*b* (F12=$(1-\alpha)^{1.2}$, F03=$(1-\alpha)^{0.3}$)

Table 3 The kinetic constants by Budrugeac–Segal method

Sample	E_0/kJ mol^{-1}	E_1/kJ mol^{-1}	a	b	n	Corr. coeff.
TA	135.8±24.5	71.4±16.1	$2.2\cdot10^{-4}\pm1.2\cdot10^{-6}$	0.512±0.26	1.2	0.9999
KT	186.7±14.5	72.1±6.1	$2.3\cdot10^{-4}\pm5.1\cdot10^{-7}$	–2.631±0.20	0.3	0.9999

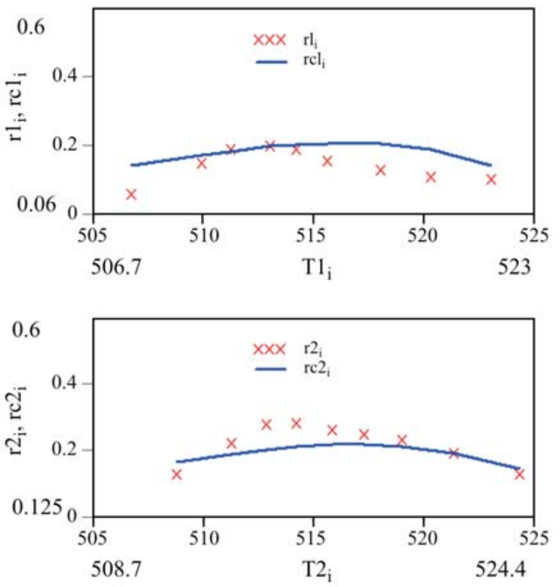


Fig. 4a Reactions rate (x) and regenerated reactions rate (––); Tartaric acid at 5 and 10 deg min^{-1}

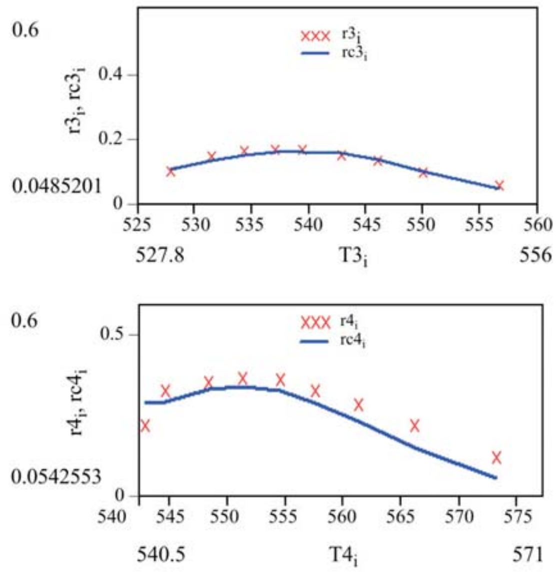


Fig 4b eactions rate (x) and regenerated reactions rate (––);Potassium tartrate at 5 and 10 deg min^{-1}

By inspecting the data in Table 2, some observations are to be underlined:

- the invariant part of the activation energy remains higher for KT in comparison to TA. The difference is bigger than the values obtained by Friedman's method.
- The sensitivity in respect to temperature is the same for both compounds (see the values of E_1). This is also in connection with the similar values of the constant a (Eq. 5).

The constants of Budrugeac–Segal method are useful especially for simulations, a few examples being depicted in Fig. 4.

The NPK method

The results of data processing are systematized in Table 4.

By inspecting the data in Table 4 a parallel variation of *A* and *E* is found. This compensation effect is illustrated in Fig. 5. A first and obvious significance of this effect consists in the same decomposition mechanism, at least regarding the first step. A supplementary argument is the isokinetic temperature of both reactions, in the range 520–530 K.

Table 4 Kinetic parameters of NPK method

Sample	λ/%	E_1/kJ mol^{-1}	A/min^{-1}	m	n	Corr.coeff.
TA	93.3	42.3±8.1	$4.8\cdot10^{5}\pm23.7$	1	2	0.968
	5.8	137.6±25.5	$1.63\cdot10^{13}\pm1$	0	1/2	0.999
KT	97.8	64.1±3.6	$2.52\cdot10^{5}\pm8.7$	0	2/3	0.999
	2.1	110.1±17.7	$7.97\cdot10^{9}\pm1$	0	0.1	0.984

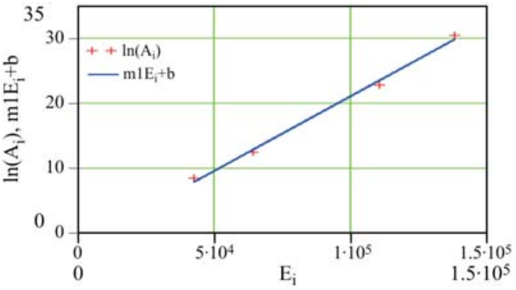


Fig. 5 Compensation effect xx – ln(Ai), — – $m1E_i+b$

Conclusions

For a deep and less speculative understanding of processes involved by thermal decomposition under non-isothermal conditions of similar compounds, a kinetic analysis using different data processing strategies is necessary. A set of experimental data at different heating rates (minimum five) is also an obvious necessity.

The kinetic analysis is recommended to begin with Friedman`s method, due to its relative simplicity and independence in respect to the kinetic model. By single-step processes the obtained value of the activation energy is invariant in respect of the conversion degree.

By multi-step processes some sophisticated methods are necessary. The one of Budrugeac and Segal, based on an initial Friedman analysis, furnish parameters useful for simulations. The NPK method allows a separation between the temperature, respective the conversion dependent part of a rate equation and at the same time an objective analysis of the relevance of the two or more elementary steps of a complex process.

The compensation effect observed for both tartaric acid and potassium tartrate is interpreted as an argument for a similar decomposition mechanism.

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DOI: 10.1007/s10973-006-8019-y