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A critical evaluation of three non-isothermal kinetic techniques

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Abstract

A systematic evaluation was conducted of three different methods to obtain kinetic information from non-isothermal thermogravimetric data. The methods evaluated were those of Zimmerman, Abou-Shaaban and Simonelli, and Reich and Stivala. It was established that none of these methods was entirely appropriate for use in the study of calcium oxalate monohydrate desolvation.

INTRODUCTION

Many techniques have been presented in the literature which utilize non-isothermal thermogravimetric analysis to obtain kinetic information. These methods have been summarized in several review articles [1–6]. Unfortunately, there has been little or no consensus as to which method yields the most meaningful results. This study was undertaken to evaluate systematically three of the published techniques in order to determine which, if any, of them is appropriate to study desolvation.

The problem of obtaining kinetic information from non-isothermal thermogravimetric data is a difficult one. The major difficulty is in transforming the general non-isothermal kinetic equation

$$\frac{d\alpha}{dT} = \frac{K(T)}{a} f(\alpha) \tag{1}$$

where α = fraction converted, $f(\alpha)$ is some function of α, and $K(T)$ is some function of temperature. In order for this expression to be useful, a value for $f(\alpha)$ must be found and the expression must be manipulated so that the activation energy can be calculated from weight loss data.

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The three methods which were evaluated were selected because they represent a variety of approaches to the selection of an appropriate value for $f(\alpha)$ and to the manipulation of the general non-isothermal kinetic equation (eqn. (1)).

EXPERIMENTAL

Materials

Calcium Oxalate Monohydrate was obtained from Eastman Organic Chemicals.

Methods

The TGA data were collected using a Perkin–Elmer TGS-2 Thermogravimetric Analyzer connected to a Perkin–Elmer model 3600 Data Station. Data were recorded in a computer file on the data station and transferred to a floppy disk at the end of the experimental run. Data were collected at various heating rates and a constant nitrogen purge was maintained throughout each run.

Weight loss was calculated using the TADS TGA standard program. Weight loss was measured from the temperature at which the thermogram departed from the baseline to the temperature at which the new baseline was established.

EVALUATION OF PUBLISHED TECHNIQUES

Zimmerman method

The first published technique evaluated was that of Zimmerman [7]. His method uses the following non-isothermal kinetic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\alpha^{a}(1-\alpha)^{b}[-\ln(1-\alpha)]^{c} \exp(-E_a/RT) \tag{2}$$

Taking the natural logarithm of each side of eqn. (2) leads to

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln\left(\frac{A}{\beta}\right) + a \ln(\alpha) + b \ln(1-\alpha) + c \ln[-\ln(1-\alpha)] - \frac{E_\mathrm{a}}{RT} \tag{3}$$

This expression can be used in matrix form in order to make it amenable to solution as a system of linear equations. The resulting matrix equation is

$$\begin{bmatrix} a \\ b \\ c \\ E_a \end{bmatrix} = \begin{bmatrix} \ln\dfrac{\alpha_1}{\alpha_2} & \ln\dfrac{(1-\alpha_1)}{(1-\alpha_2)} & \ln\dfrac{\ln(1-\alpha_1)}{\ln(1-\alpha_2)} & \dfrac{1}{T_2}-\dfrac{1}{T_1} \\ \ln\dfrac{\alpha_3}{\alpha_4} & \cdot & \cdot & \cdot \\ \ln\dfrac{\alpha_5}{\alpha_6} & \cdot & \cdot & \cdot \\ \ln\dfrac{\alpha_7}{\alpha_8} & \cdot & \cdot & \cdot \end{bmatrix}^{-1} \cdot \begin{bmatrix} \ln\dfrac{D_1}{D_2} \\ \ln\dfrac{D_3}{D_4} \\ \ln\dfrac{D_5}{D_6} \\ \ln\dfrac{D_7}{D_8} \end{bmatrix} \tag{4}$$

where $D = \mathrm{d}\alpha/\mathrm{d}t$. To perform the evaluation, eight data sets (α, $\mathrm{d}\alpha/\mathrm{d}T$, T) are collected for each TGA run. The matrices are then solved and a, b, c and E_a are determined.

There are two major theoretical advantages to this technique. Firstly, there are no assumptions made about the mechanism of the solid-state process being investigated. Values for a, b, and c are calculated directly from the data. Clearly, once a, b, and c are known the most likely mechanism can be selected. Secondly, this method requires no approximations or complex transformations of the data. This could potentially result in a more accurate calculation of activation energy.

In order to evaluate this method, a computer program was written for the Hewlett–Packard (HP) 86B computer which would perform the matrix solution and determine the values for the kinetic parameters.

The first step in the evaluation was to consider the simulated data presented in Zimmerman's thesis which was generated using a fourth-order Runge–Kutta method. Zimmerman's simulations and evaluations were performed on Texas Instruments TI-58 and TI-59 programmable calculators. The values used for his simulations and the results of the calculations performed using the HP program are summarized in Table 1.

The results of the calculation using the HP 86B program are clearly not in agreement with the input parameters and the results of the Zimmerman calculation. This is possibly because the data were not simulated and evaluated on the same computer/calculator. To investigate this possibility, a computer program was written for the HP 86B which would simulate kinetic data using a fourth-order Runge–Kutta method. The simulated data were evaluated using the HP 86B kinetic program. The results of this calculation appear in Table 2. These indicate that the round-off error and, ultimately, variability in the TGA data will have a significant effect on the calculated results using this method.

TABLE 1

Calculated values of empirical parameters using Zimmerman's method

		Parameters for simulation	Zimmerman calculation	HP program calculation
Trial 1	a	1/3	0.333	0.329
	b	1/3	0.333	0.335
	c	1/3	0.333	0.337
	E_a (kJ mol^{-1})	100.0	99.99	100.0
Trial 2	a	0	−0.001	−0.109
	b	4/3	1.342	1.507
	c	0	−0.031	−0.600
	E_a (kJ mol^{-1})	100.0	103.8	86.86
Trial 3	a	1/3	0.333	0.348
	b	2/3	0.665	1.344
	c	0	−0.012	6.063
	E_a (kJ mol^{-1})	100.0	101.9	−179.9

Extended Zimmerman method

The Zimmerman method can be easily extended to use more than eight sets of data for a given experimental run. Considering eqn. (3), if $d\alpha/dT$, $1/T$ and the three functions of α are fitted to the equation, it should be straightforward to obtain a, b, c and E_a from the coefficients of the multiple linear regression fit. To evaluate this approach, a computer

TABLE 2

Calculated values of empirical parameters using Zimmerman's method: data simulated and calculated on HP 86B

		Parameters for simulation	HP program calculation
Trial 1	a	1/3	0.333
	b	1/3	0.333
	c	1/3	0.333
	E_a (kJ mol^{-1})	100.0	100.0
Trial 2	a	0	9.9E−8
	b	4/3	1.333
	c	0	2.7E−7
	E_a (kJ mol^{-1})	100.0	100.0
Trial 3	a	1/3	0.333
	b	2/3	0.666
	c	0	−1.6E−6
	E_a (kJ mol^{-1})	100.0	100.0

TABLE 3

Extended Zimmerman evaluation of calcium oxalate monohydrate desolvation data

	Calculated kinetic parameters			
	a	b	c	E_a (kcal mol^{-1})
Trial 1	15.28	−3.77	−11.96	24.5
Trial 2	5.67	−1.82	−5.57	39.3
Trial 3	−15.80	8.08	23.04	122.0

program was written for the Perkin–Elmer TADS system which would perform this multiple linear regression for TGA data generated on the Perkin–Elmer TGS-2. This program was used to evaluate data generated in the course of non-isothermal desolvation. Data from three different dehydration runs for calcium oxalate monohydrate were evaluated. The results of this evaluation appear in Table 3. Each of the TGA runs was performed under identical conditions.

It is clear from the results of these evaluations that no meaningful results can be obtained using this particular computational technique. The values for a, b, c and E_a differ significantly from run to run and cannot be related to any meaningful kinetic expression. This analytical technique was more thoroughly evaluated by varying the method used to calculate the derivative of the weight loss curve as well as the number of points used for the analysis. In all cases the results were similar to those tabulated in Table 3.

Abou-Shaaban and Simonelli method

Abou-Shaaban and Simonelli [8] also introduced a technique for performing non-isothermal TGA kinetic evaluations. They derived kinetic expressions for several different processes involving weight loss or gain. The general non-isothermal kinetic expression which they used for desolvation processes was

$$\frac{\mathrm{d}(A_t)}{\mathrm{d}T} = -\frac{Z}{a}\exp\left(\frac{-\Delta H_a}{RT}\right)(A_t)^1 \tag{5}$$

where A = amount of reactant, Z = the pre-exponential factor and ΔH_a = the enthalpy of activation. A key assumption made in all their derivations is that the rate law for all processes is first-order. This simplifying assumption is potentially valuable when comparing kinetic information calculated for different compounds. Clearly, using the same rate law for the calculations makes a comparison more straightforward.

This kinetic expression can be transformed to

$$\ln\frac{[-\mathrm{d}W(\mathrm{obs})_t/\mathrm{d}T]}{[W(\mathrm{obs})_t - W(\mathrm{obs})_0/r]} = \ln\frac{Z}{a} - \frac{\Delta H_\mathrm{a}}{RT} \tag{6}$$

where $W(\mathrm{obs})_t$ = the weight at time t, $W(\mathrm{obs})_0$ = the initial weight, and r = the molecular weight of the reactant divided by the molecular weight of the product. This transformation makes it possible to obtain kinetic parameters from the TGA weight loss data by plotting the left-hand side versus $1/T$. The enthalpy of activation (ΔH_a) can then be calculated from the slope of the line. Using this kinetic expression should yield parameters which are unaffected by experimental variables. Abou-Shaaban and Simonelli claim that procedural effects on kinetic parameters are due to a thermal gradient in the sample, the effect of which is eliminated by dividing the derivative of the weight loss curve by a function of sample weight.

In order to evaluate the effectiveness of their technique, a program was written for the Perkin–Elmer Data Station which could evaluate TGA data using this method. The decomposition of calcium oxalate monohydrate was used as a model process.

The activation energies calculated using this technique were found to be in good agreement with literature values and were shown to be relatively free from procedural effects as presented by Abou-Shaaban and Simonelli.

Another aspect of their method requiring investigation is their claim that all processes can be modeled as first-order. To evaluate this, the desolvation of calcium oxalate monohydrate was evaluated isothermally. Clearly, the results determined isothermally should be in good agreement with those determined non-isothermally. For isothermal desolvation, the kinetic expression derived by Abou-Shaaban and Simonelli is

$$\ln[W(\mathrm{obs})_t - W(\mathrm{obs})_0/r] = -kt + \ln\{[W(\mathrm{obs})_0/r](1-r)\} \tag{7}$$

Data from isothermal studies conducted at 140°C, 170°C and 200°C were evaluated using this expression. The calculated rate constants for each trial are summarized in Table 4. The calculated activation energy from this data is 16.68 kcal mol^{-1} and the correlation coefficient for the calculation is -0.943. This calculated activation energy differs significantly from 24.8 kcal mol^{-1} which was calculated non-isothermally using this model. Additionally, there is a wide scatter in the results calculated for replicate trials at the same temperature, and a poor correlation coefficient for the Arrhenius regression, suggesting that the data do not fit the first-order model well.

This model proposed by Abou-Shaaban and Simonelli has some serious shortcomings. Clearly, the assumption that all solid-state kinetic processes can be described by a first-order rate law is an oversimplification. This assumption implies one of two mechanisms on a molecular level — either

TABLE 4

Results of isothermal kinetic evaluation of calcium oxalate monohydrate dehydration

Temperature (°C)	k (min^{-1})
140	2.791E−3
140	1.272E−3
140	1.921E−3
170	1.460E−2
170	4.986E−3
170	7.438E−3
200	3.691E−2
200	2.588E−2
200	1.619E−2

each molecule has the same probability of being tranformed, independent of its location in a particle, or the rate-limiting step is the formation of one reaction nucleation site per particle. Either of these assumptions may be appropriate for a given transformation, but it seems unlikely that all solid-state reaction mechanisms would follow this model.

The studies conducted isothermally on calcium oxalate monohydrate indicate that this transformation fits this rate law poorly, suggesting that the model proposed by Abou-Shaaban and Simonelli is not universally applicable to all solid-state reactions.

The Reich and Stivala method

A technique proposed by Reich and Stivala [9] for performing kinetic evaluations makes no assumptions about the form of the rate law prior to calculation. They use an integral solution to the general non-isothermal kinetic expression

$$\ln\left[\frac{g(\alpha)}{T}\bigg/\left(\frac{E_a}{RT}+2\right)\right]=\ln\frac{Z}{a}-\frac{E_a}{RT} \qquad (8)$$

where $g(\alpha)=\int \mathrm{d}\alpha/f(\alpha)$. Rate laws corresponding to ten different solid-state mechanisms are evaluated. The goodness-of-fit of the data to each model is assessed by determining which model results in the lowest standard deviation in delta or B where

$$\mathrm{delta}=\left\{\sum\left[B(i)-\bar{B}\right]^2/N\right\}^{1/2} \qquad (9)$$

and

$$B=\log(ZE_a/Ra) \qquad (10)$$

The correct activation energy is determined to be the one calculated for the mechanism which has the lowest delta value. They presented a com-

TABLE 5

An evaluation of the kinetics of calcium oxalate monohydrate dehydration using the Reich and Stivala method

Trial	Heating rate ($K min^{-1}$)	Sample size (mg)	E_a (kcal mol^{-1})	Mechanism
1	5	11.5	25	D1
2	5	11.3	25	D3
3	10	11.5	23	D4
4	10	11.4	27	D3
5	10	10.9	25	D4
6	10	10.9	26	D3
7	10	10.1	27	D3
8	20	11.3	30	D3
9	20	11.2	20	D2
10	10	10.0	27	D3
11	10	10.2	26	D3

puter algorithm for this method which was adapted for the Perkin–Elmer Data Station.

In their method, delta is calculated for each mechanism for values of E_a between 20 and 60 kcal mol^{-1}. At the end of the calculation, the mechanism and E_a pair which result in the lowest delta value are considered to be the most appropriate for the process.

This technique was used to analyze several different sets of data for calcium oxalate monohydrate dehydration collected under varying experimental conditions. The results of this evaluation are summarized in Table 5.

Although the calculated value for the activation energy does not vary widely for the different trials, there is no clear indication as to which mechanism and corresponding rate law is the most appropriate. The dehydration should occur by the same mechanism for all repetitions of the same process. Although the D3 mechanism is selected most often, other diffusional mechanisms are indicated as well. However, when mechanisms other than D3 are selected the lowest delta value may not be significantly smaller than delta for D3.

The failure of this technique may be due to several factors. The most probable mechanism for a given activation energy is selected, but this activation energy may not be the correct one for the mechanism. Consider the data from trial No. 2. The results from this program indicate that D3 is the most appropriate mechanism and 25 kcal mol^{-1} is the correct activation energy. If the activation energy is calculated for this run using the Coats and Redfern integral approach [10] and a rate law corresponding to mechanism D3, the value obtained is 45.3 kcal mol^{-1}. Additionally, the program requires that the activation energy be between 20 and 60 kcal

mol^{-1}. This is not necessarily the case for every process of interest. Lastly, the program uses an un-normalized standard deviation (i.e., delta) and thus, as the value for the activation energy term increases, so will the value for delta. Therefore this method is not generally applicable.

CONCLUSION

In this evaluation, three different types of non-isothermal kinetic techniques were evaluated: the Zimmerman method, the Abou-Shaaban and Simonelli method, and the Reich and Stivala method. The Zimmerman method appears attractive because it requires no transformations and approximations in the use of the general non-isothermal kinetic equation, and it requires no *a priori* assignment of a rate law. Unfortunately, the extracted parameters are too dependent upon the method of calculation to make the approach useful. The Abou-Shaaban and Simonelli method uses a linearized differential form of the non-isothermal kinetic expression which was shown to give kinetic parameters which were free from procedural effects. Unfortunately, their simplifying assumption that a first-order rate law is appropriate for all processes was shown to be erroneous. It is important that the data fit the proposed model well to facilitate comparison with data collected for other samples. The Reich and Stivala method uses an integral form of the general non-isothermal kinetic equation and fits data to several different rate laws. This should result in knowledge about both the kinetic parameters and the mechanism. Unfortunately, the computational technique results in inconsistent calculation of activation energy and selection of reaction mechanism.

The identification of a good technique for obtaining kinetic information from non-isothermal TGA data is difficult, and the significance of the calculated results is unclear. A good technique should be relatively free from procedural effects and provide meaningful, reproducible kinetic data. None of the three methods evaluated in this study meets these criteria.

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