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Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data

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Abstract

The model-free and model-fitting kinetic approaches have been applied to data for nonisothermal and isothermal thermal decompositions of HMX and ammonium dinitramide. The popular model-fitting approach gives excellent fits for both isothermal and nonisothermal data but yields highly uncertain values of the Arrhenius parameters when applied to nonisothermal data. These values cannot be meaningfully compared with the values derived from isothermal measurements, nor they can be used to reasonably predict the isothermal kinetics. On the other hand, the model-free approach represented by the isoconversional method yields similar dependencies of the activation energy on the extent of conversion for isothermal and nonisothermal experiments. The dependence derived from nonisothermal data permits reliable predictions of the isothermal kinetics. The use of the model-free approach is recommended as a trustworthy way of obtaining reliable and consistent kinetic information from both nonisothermal and isothermal data. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Isothermal; Nonisothermal; Activation energy; Arrhenius parameters; Thermal decomposition; Solids; Energetic materials; HMX; Ammonium dinitramide; TGA

1. Introduction

Kinetic analysis of solid state decompositions is usually based on a single step kinetic equation [1]

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (1)$$

where t is the time, T is the temperature, α is the extent of conversion, and $f(\alpha)$ is the reaction model. The reaction model may take various forms, some of which are shown in Table 1. The explicit temperature dependence of the rate constant is introduced by replacing

$k(T)$ with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right)f(\alpha), \quad (2)$$

where A (the pre-exponential factor) and E (the activation energy) are the Arrhenius parameters and R is the gas constant. The Arrhenius parameters, together with the reaction model, are sometimes called the kinetic triplet. Under nonisothermal conditions in which a sample is heated at a constant rate, the explicit temporal dependence in Eq. (2) is eliminated through the trivial transformation

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right)f(\alpha), \quad (3)$$

where $\beta = dT/dt$ is the heating rate.

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Table 1

Set of reaction models applied to describe thermal decomposition in solids

	Reaction model	$f(\alpha)$	$g(\alpha)$
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$1/2\alpha^{-1}$	α^2
6	Mampel (first-order)	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
11	Contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}$

Compared with isothermal experiments, non-isothermal runs are more convenient to carry out because it is not necessary to perform a sudden temperature jump of the sample at the beginning. However, Arrhenius parameters obtained from non-isothermal data are often reported to disagree with the values derived from isothermal experiments. In our opinion, there are two major reasons for this disagreement. The first is a result of the prevalent use of kinetic methods that involve force fitting of nonisothermal data to hypothetical reaction models. Following this “model-fitting approach”, Arrhenius parameters are determined by the form of $f(\alpha)$ assumed. Because in a nonisothermal experiment both T and α vary simultaneously, the model-fitting approach generally fails to achieve a clean separation between the temperature dependence, $k(T)$, and the reaction model, $f(\alpha)$. As a result, almost any $f(\alpha)$ can satisfactorily fit data at the cost of drastic variations in the Arrhenius parameters, which compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown reaction model. For this reason, the model-fitting methods tend to produce highly uncertain values of Arrhenius parameters.

The second major reason for this disagreement arises from the fact that isothermal and nonisothermal experiments are necessarily conducted in different temperature regions. If decomposition involves several steps with different activation energies, the contributions of these steps to the overall decomposition rate measured in a thermal analysis experiment will

vary with both temperature and extent of conversion. This means that the effective activation energy determined from thermal analysis experiments will also be a function of these two variables. However, the usual implementation of model-fitting methods is aimed at extracting a single value of the activation energy for an overall process. The value obtained in such a way is in fact an average that does not reflect changes in the reaction mechanism and kinetics with the temperature and the extent of conversion.

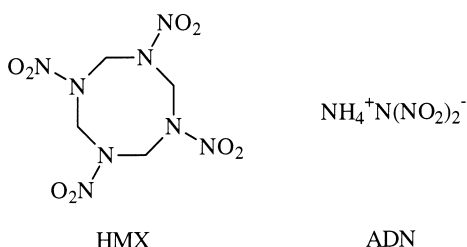
The aforementioned drawbacks of model-fitting can be avoided with the use of isoconversional methods [2–4]. Firstly, these methods allow the activation energy to be determined as a function of the extent of conversion and/or temperature. Secondly, this dependence is determined without making any assumptions about the reaction model. Because the model-free isoconversional methods eliminate the causes of the aforementioned disagreement, they are likely to produce consistent kinetic results from isothermal and nonisothermal experiments.

In this paper, we explore an opportunity of employing model-fitting and model-free methods to produce consistent kinetic characteristics from isothermal and nonisothermal experiments. Analysis of isothermal kinetic experiments is traditionally believed to be more reliable because the one variable (T) is held constant during each experiment, thereby reducing the number of kinetic parameters that are determined simultaneously by fitting. Therefore, the results of nonisothermal experiments are expected to agree with

the isothermal data. As a definitive test for such agreement we consider the capability of predicting isothermal kinetics from nonisothermal data.

2. Experimental

As experimental examples we have chosen thermal decompositions of two energetic materials, 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and ammonium dinitramide (ADN). The Thiokol Corporation kindly supplied a sample of ADN. The material was used without further purification. An HMX sample was received from the Army Research Laboratory at Aberdeen Proving Grounds, MD. The sample was used after recrystallization from acetone.



The thermogravimetric analysis (TGA) experiments were carried out using a Rheometric Model 1000M TGA instrument. To reduce thermal gradients and exothermic self-heating, the experiments were performed on small (~ 0.5 mg) samples. The sample temperature, which is controlled by a thermocouple, did not exhibit any systematic deviation from the preset linear temperature programs. Samples of energetic material were placed in aluminum pans and heated in a flowing atmosphere of nitrogen (100 ml min^{-1}). For experiments carried out under nonisothermal conditions, the instrument was programmed to heat the sample from room temperature at a constant heating rate. After an initial period of nonlinear heating (< 5 min), the programmed linear heating rates were established. The actual heating rates used in the kinetic analysis were calculated from temperature measurements made during the actual period of a material decomposition. For the thermal decomposition of HMX the heating rates were 0.17, 0.34, 0.51, 0.68, and $0.84^\circ\text{C min}^{-1}$. For ADN experiments, the heating rates were 1.5, 4.0, 5.5, 7.8, and $9.50^\circ\text{C min}^{-1}$.

For isothermal experiments, the temperature program was optimized to reach the preset isothermal temperature within 1.5 min without overshooting. During the next 1.5 min, the sample temperature was regulated to within $\pm 1^\circ\text{C}$ of the set point. For the remainder of each run, the sample temperature was maintained within $\pm 0.05^\circ\text{C}$. The thermal decomposition of HMX was studied at the temperatures of 230, 235, 240, 245, and 250°C . ADN was decomposed under the temperatures of 132, 138, 143, 147, and 150°C .

3. Kinetic computations

3.1. Model-fitting method

Rearrangement and integration of Eq. (1) for isothermal conditions gives

$$g_j(\alpha) = k_j(T)t, \quad (4)$$

where $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$ is the integrated form of the reaction model (Table 1). The subscript j has been introduced to emphasize that substituting a particular reaction model into Eq. (4) results in evaluating the corresponding rate constant, which is determined from the slope of a plot of $g_j(\alpha)$ versus t . For each reaction model selected, the rate constants are evaluated at several temperatures, T_i , and the Arrhenius parameters are determined in the usual manner using the Arrhenius equation in its logarithmic form,

$$\ln k_j(T_i) = \ln A_j - \frac{E_j}{RT_i}, \quad (5)$$

Arrhenius parameters evaluated for the isothermal experimental data by the model-fitting method are presented in Tables 2 and 3.

To choose an appropriate reaction model, one can plot α as a function of a reduced time variable t/t_α , where t_α is the time required to reach a specified conversion (e.g., $\alpha = 0.9$). The method is broadly used in solid state kinetics [1]. The reduced time plots for the thermal decomposition of HMX and ADN are shown in Figs. 1 and 2, respectively. For each model, the goodness of fit can be estimated by using the residual sum of squares

$$S_j^2 = \frac{1}{n-1} \sum_{i=1}^n \left(\frac{t_i}{t_{0.9}} - \frac{g_j(\alpha_i)}{g_j(0.9)} \right)^2. \quad (6)$$

Table 2

Arrhenius parameters for isothermal decomposition of HMX determined using the model-fitting approach

Model ^a	$F = S^2/S_{\min}^2$	E (kJ mol ⁻¹)	$\log(A/\text{min}^{-1})$
1	43.89	120.9	10.0
2	27.45	122.0	10.2
3	9.10	123.9	10.5
4	16.41	132.7	11.5
5	32.33	136.0	11.8
6	32.34	158.1	14.7
7	16.96	137.1	11.9
8	5.37	139.7	12.3
9	1.00	144.6	13.0
10	69.84	158.9	13.9
11	17.80	144.4	12.6
12	12.25	139.2	12.1
13	90.02	362.4	37.5

^a Enumeration of the models is given in Table 1.

Table 3

Arrhenius parameters for isothermal decomposition of ADN

Model ^a	$F = S^2/S_{\min}^2$	E (kJ mol ⁻¹)	$\log(A/\text{min}^{-1})$
1	592.12	126.0	13.2
2	454.32	126.1	13.3
3	266.55	126.4	13.5
4	2.38	127.7	13.7
5	16.88	128.2	13.8
6	22.81	129.5	14.5
7	332.84	127.4	13.6
8	197.99	127.6	13.8
9	56.67	128.1	14.0
10	126.04	130.3	13.7
11	1.00	128.4	13.7
12	1.26	128.1	13.75
13	217.93	289.9	36.8

^a Enumeration of the models is given in Table 1.

Statistics constructed as

$$F_j = \frac{S_j^2}{S_{\min}^2}, \quad (7)$$

where S_{\min}^2 is the minimum value of all S_j^2 , have the F -distribution [5–7]. According to the F -test, only those reaction models for which $F_j > F_{1-p,n-1,n-1}$ should be discriminated as giving S_j^2 that are significantly larger than S_{\min}^2 (and therefore not belonging to the set of “best fit” models). All other reaction models fit experimental data as accurately as the model that gives the minimum residual sum of squares, S_{\min}^2 .

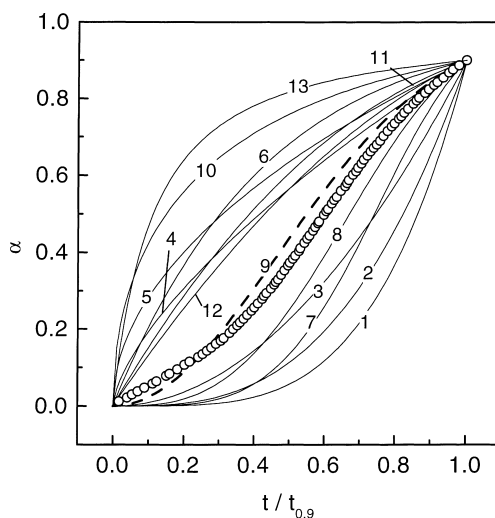


Fig. 1. Reduced time plots for the reaction models (solid curves, as enumerated in Table 1) and isothermal experimental data for HMX decomposition. Circles correspond to data that are the average of five isothermal experiments performed at 230, 235, 240, 245, and 250°C. The dashed curve for model 9 designates the best fit.

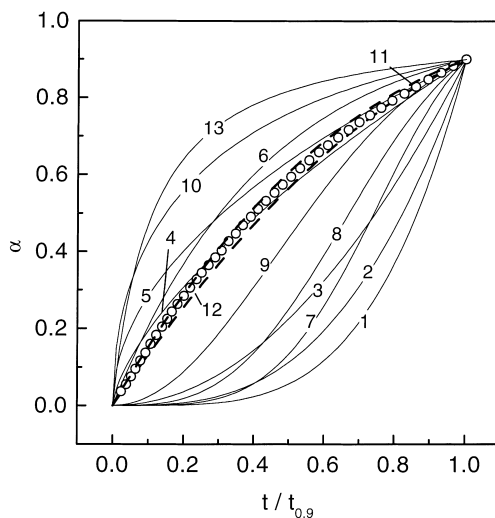


Fig. 2. Reduced time plots for the reaction models (solid curves, as enumerated in Table 1) and isothermal experimental data for ADN decomposition. Circles correspond to data that are the average of five isothermal experiments performed at 132, 138, 143, 147, and 150°C. The dashed curves for models 11 and 12 designate the best fits.

The value $F_{1-p,n-1,n-1}$ is a percentile of the F -distribution for $(1-p)100\%$ confidence probability [5–7]. Tables 2 and 3 provide the values of F_j for various

reaction models as applied to the thermal decompositions of HMX and ADN.

For nonisothermal conditions there are several relationships used to compute Arrhenius parameters, [1] each of which is based on an approximate form of the temperature integral that results from rearrangement and integration of Eq. (3)

$$g(\alpha) = \frac{A}{\beta} \int_0^{T_\alpha} \exp\left(\frac{-E}{RT}\right) dT = \frac{A}{\beta} I(E, T_\alpha). \quad (8)$$

One such approximation gives rise to the Coats–Redfern equation [8]

$$\ln \left[\frac{g_j(\alpha)}{T^2} \right] = \ln \left(\frac{A_j R}{\beta E_j} \right) \left(1 - \frac{2R\bar{T}}{E_j} \right) - \frac{E_j}{RT}, \quad (9)$$

where \bar{T} is the mean experimental temperature. This method is reported [9] to be one of the most frequently used to evaluate nonisothermal data. Inserting various $g_j(\alpha)$ into Eq. (9) results in a set of Arrhenius parameters determined from the plot $\ln[g_j(\alpha)/T^2]$ against T^{-1} . The sets of Arrhenius parameters for the thermal decompositions of HMX and ADN are shown in Tables 4 and 5, respectively. For each model, the goodness of fit is customarily estimated by a coefficient of linear correlation, r_j . A single pair of E and A is then commonly chosen as that corresponding to a reaction model that gives rise to the maximum absolute value of the correlation coefficient, $|r_{\max}|$ [10–13]. This popular routine ignores the fact that the correla-

Table 4
Arrhenius parameters for nonisothermal decomposition of HMX at $0.17^\circ\text{C min}^{-1}$ determined using the Coats–Redfern equation

Model ^a	E (kJ mol ⁻¹)	$\log(A/\text{min}^{-1})$	$-r$
1	21.3	-0.6	0.9327
2	31.0	0.5	0.9424
3	50.4	2.7	0.9501
4	167.0	14.8	0.9582
5	225.3	20.7	0.9591
6	125.9	10.8	0.9444
7	25.6	0.0	0.9205
8	36.7	1.3	0.9299
9	59.0	3.7	0.9378
10	246.1	22.2	0.9536
11	119.1	9.5	0.9508
12	116.2	9.4	0.9530
13	152.6	14.0	0.9073

^a Enumeration of the models is given in Table 1.

Table 5

Arrhenius parameters for nonisothermal decomposition of ADN at $5.5^\circ\text{C min}^{-1}$ determined using the Coats–Redfern equation

Model ^a	E (kJ mol ⁻¹)	$\log(A/\text{min}^{-1})$	$-r$
1	24.5	1.7	0.9783
2	35.1	3.0	0.9813
3	56.2	5.5	0.9837
4	182.9	20.1	0.9862
5	246.2	27.3	0.9865
6	139.4	15.5	0.9928
7	29.5	2.4	0.9903
8	41.7	3.9	0.9913
9	66.1	6.9	0.9921
10	269.1	29.3	0.9928
11	131.0	13.9	0.9924
12	127.6	13.6	0.9910
13	177.8	20.5	0.9436

^a Enumeration of the models is given in Table 1.

tion coefficient (and other statistical measures) is subject to random fluctuations, and its uncertainty must be taken into account in the form of confidence limits. Within these limits, all the models are equally probable. Therefore, the maximum value of $|r|$ or the minimum value of S^2 does not necessarily indicate “the most probable” reaction model.

The above-mentioned F -test takes proper account of the uncertainty in S^2 , and there are similar tests for the correlation coefficient [6,7,14]. They all start from Fischer’s transformation,

$$z = \frac{1}{2} \ln \frac{1+r}{1-r}, \quad (10)$$

which allows one to obtain a variable that has a normal distribution with the standard deviation $\sigma = 1/\sqrt{n-3}$ where n is the sample size. Let us now determine z_0 , which is the smallest value of z that does not violate the statistical hypothesis $z_0 = z_{\max}$ where z_{\max} and z_0 are Fisher’s transformations for $|r_{\max}|$ and $|r_0|$, respectively. This can be done with the help of the following statistics [14]

$$U = \frac{z_{\max} - z_0}{(1/\sqrt{n-3})} \quad (11)$$

that has a standard normal distribution. For 95% confidence probability, the percentage point of the normal distribution is 1.645. By substituting this value into Eq. (11), we can determine z_0 . Then the inverse

Table 6

Best kinetic triplets for nonisothermal decomposition of HMX at various heating rates determined using the Coats–Redfern equation

β ($^{\circ}\text{C min}^{-1}$)	Model	$g(\alpha)$	E (kJ mol $^{-1}$)	$\log(A/\text{min}^{-1})$	$-r$
0.17	4	$\alpha^{3/2}$	167.0	14.8	0.9582
	5	α^2	225.3	20.7	0.9591
0.34	4	$\alpha^{3/2}$	166.0	14.6	0.9326
	5	α^2	224.0	20.4	0.9340
	10	$[1-(1-\alpha)^{1/3}]^2$	236.5	20.9	0.9312
	12	$1-(1-\alpha)^{1/2}$	112.6	9.0	0.9281
0.51	4	$\alpha^{3/2}$	154.5	13.3	0.9548
	5	α^2	208.7	18.6	0.9558
0.68	4	$\alpha^{3/2}$	144.7	12.2	0.9304
	5	α^2	195.6	17.1	0.9320
0.84	4	$\alpha^{3/2}$	146.1	12.5	0.9501
	5	α^2	197.5	17.4	0.9513

Fisher's transformation gives the value of r_0

$$r_0 = \frac{\exp(2z_0) - 1}{\exp(2z_0) + 1}. \quad (12)$$

Therefore, we can discriminate only those reaction models for which $|r_j| < |r_0|$ as having inferior linear correlations. All other models are as good fits of experimental data as the model that gives the maximum absolute value of the correlation coefficient, $|r_{\max}|$. Tables 6 and 7 show “the best” (statistically equivalent) reaction models with the corresponding values of Arrhenius parameters.

Sometimes, fitting various reaction models is replaced with solely fitting the reaction order model. In this method the reaction order, n , is varied to determine the best fit (e.g., the maximum of $|r|$) and thereby determine the best kinetic triplet [13].

This procedure is not statistically valid unless the uncertainty in r_{\max} is taken into account. Again, we have to evaluate r_0 as given in above. As seen in Fig. 3, the value of r_0 determines a confidence interval for n as well as for Arrhenius parameters. The results shown in Fig. 3 were obtained by substituting the reaction order model into the Coats–Redfern equation (9).

The statistically equivalent kinetic triplets determined from nonisothermal data using the model-fitting method (Tables 6 and 7) have been used to predict isothermal kinetics as follows:

$$t_\alpha = \frac{g(\alpha)}{A \exp(-E/RT_0)}, \quad (13)$$

where t_α is the time to reach the extent of conversion α at the temperature T_0 . The kinetic triplets obtained from fitting the reaction-order model have also been

Table 7

Best kinetic triplets for nonisothermal decomposition of ADN at various heating rates determined using the Coats–Redfern equation

β ($^{\circ}\text{C min}^{-1}$)	Model	$g(\alpha)$	E (kJ mol $^{-1}$)	$\log(A/\text{min}^{-1})$	$-r$
1.5	10	$[1-(1-\alpha)^{1/3}]^2$	260.9	28.8	0.9939
	11	$1-(1-\alpha)^{1/3}$	127.0	13.4	0.9936
4.0	6	$-\ln(1-\alpha)$	145.6	16.3	0.9946
	9	$[-\ln(1-\alpha)]^{1/2}$	69.3	7.2	0.9941
5.5	6	$-\ln(1-\alpha)$	139.4	15.5	0.9928
	9	$[-\ln(1-\alpha)]^{1/2}$	66.1	6.9	0.9921
	10	$[1-(1-\alpha)^{1/3}]^2$	269.1	29.3	0.9928
	11	$1-(1-\alpha)^{1/3}$	131.0	13.9	0.9924
7.8	6	$-\ln(1-\alpha)$	139.4	15.5	0.9920
	9	$[-\ln(1-\alpha)]^{1/2}$	66.1	6.9	0.9912
9.5	6	$-\ln(1-\alpha)$	158.5	17.7	0.9768
	9	$[-\ln(1-\alpha)]^{1/2}$	75.6	8.1	0.9745

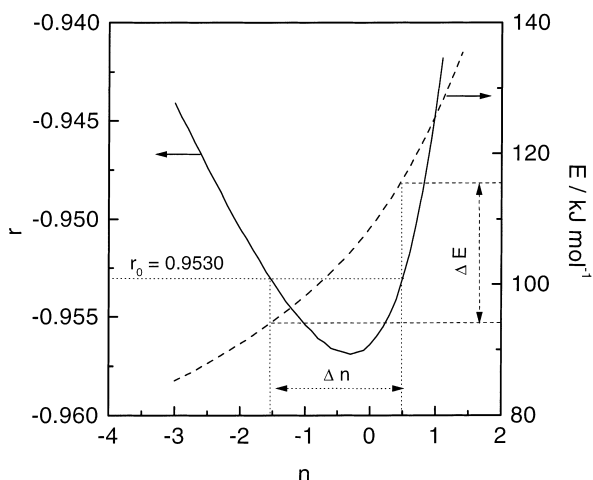


Fig. 3. Nonisothermal decomposition of HMX at $0.17^{\circ}\text{C min}^{-1}$. Variation of the correlation coefficient (solid curve) and the activation energy (dashed curve) with the value of the reaction order, n . The critical value of the correlation coefficient, r_0 , determines the confidence intervals Δn and ΔE for the reaction order and activation energy, respectively.

used to make isothermal predictions by Eq. (13). All these predictions are displayed in Figs. 4 and 5.

3.2. Model-free isoconversional method

The basic assumption of the isoconversional method is that the reaction model, as defined in Eq. (1), is not dependent on temperature or heating rate. Under isothermal conditions, we may combine Eqs. (4) and (5) to obtain

$$-\ln t_{\alpha,i} = \ln \left[\frac{A_{\alpha}}{g(\alpha)} \right] - \frac{E_{\alpha}}{RT_i}, \quad (14)$$

where E_{α} is evaluated from the slope of the plot $-\ln t_{\alpha,i}$ against T_i^{-1} . The E_{α} dependencies obtained for the thermal decomposition of HMX and ADN are shown in Figs. 6 and 7.

For nonisothermal experiments, a nonlinear isoconversional method has been developed [15,16] which avoids inaccuracies associated with analytical approximations of the temperature integral. Because $g(\alpha)$ is independent of the heating rate, for any two experiments conducted at different heating rates, the ratio of the temperature integral $I(E, T_{\alpha})$ to the heating rate β is a constant, as shown by Eq. (8). For a set of n

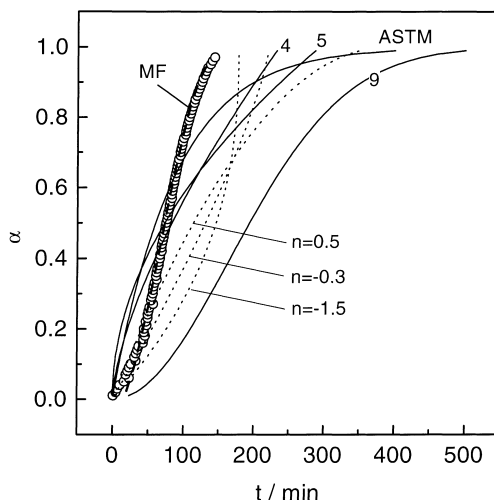


Fig. 4. Predictions of the isothermal decomposition kinetics of HMX at 235°C from nonisothermal kinetic parameters. The solid curves numbered 4, 5, and 9 are calculated using Eq. (13) and the corresponding kinetic triplets in Table 4. The dotted curves are calculated based on kinetic triplets obtained by fitting the reaction order model (the values of n are indicated by each curve). The curve marked ASTM was calculated using Eq. (18), and the dashed curve marked ME is the model-free prediction calculated using Eq. (16). Circles indicate the experimental data.

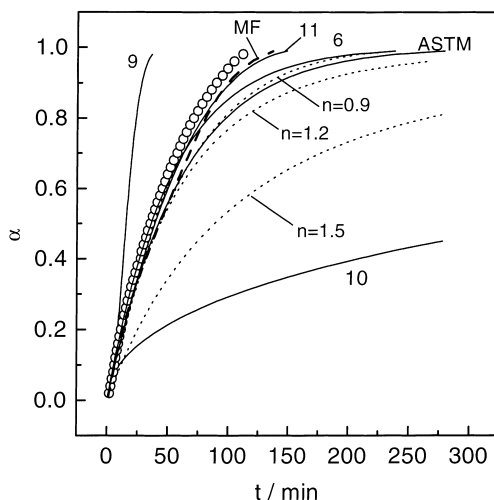


Fig. 5. Predictions of the isothermal decomposition kinetics of ADN at 150°C from nonisothermal kinetic parameters. The solid curves numbered 6, 9, 10 and 11 are calculated using Eq. (13) and the corresponding kinetic triplets in Table 5. The dotted curves are calculated based on kinetic triplets obtained by fitting the reaction order model (the values of n are indicated by each curve). The curve marked ASTM was calculated using Eq. (18), and the dashed curve marked ME is the model-free prediction calculated using Eq. (16). Circles indicate the experimental data.

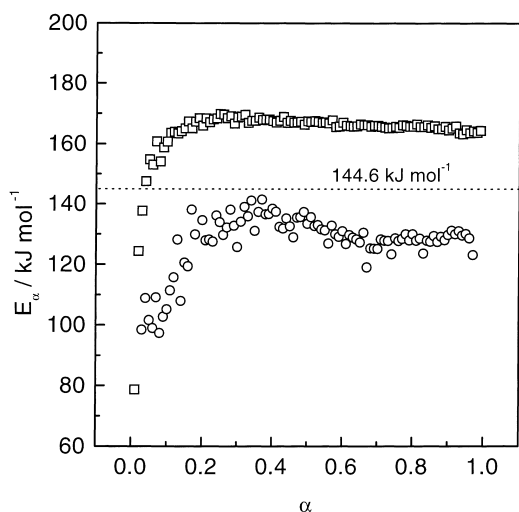


Fig. 6. Dependencies of the activation energy on extent of HMX conversion determined using the model-free isoconversional method for the isothermal data (squares) and nonisothermal data (circles). The dashed line indicates the value obtained by the model-fitting method from isothermal data.

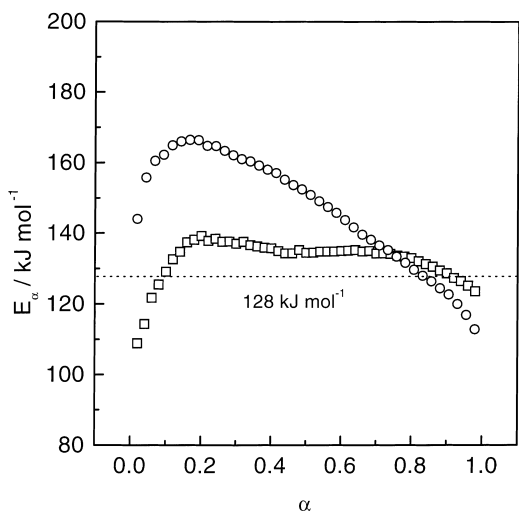


Fig. 7. Dependencies of the activation energy on extent of ADN conversion determined using the model-free isoconversional method for the isothermal data (squares) and nonisothermal data (circles). The dashed line indicates the value obtained by the model-fitting method from isothermal data.

experiments carried out at different heating rates, the activation energy can be determined at any particular value of α by finding the value of E_α for

which the function

$$\sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} \quad (15)$$

is a minimum. The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion. Figs. 6 and 7 provide the E_α dependencies determined for the nonisothermal decompositions of HMX and ADN.

Recently, Vyazovkin [16,17] extended the non-linear isoconversional method to arbitrary heating programs. This method can be effectively used to process data obtained under the conditions of distorted linear (e.g., self-heating/cooling) or purposely non-linear (e.g., temperature modulations) heating.

The sole evaluation of E_α dependence is sufficient to predict the isothermal kinetics from nonisothermal data. This is formalized by Eq. (16)

$$t_\alpha = \frac{\int_0^{T_\alpha} \exp(-E_\alpha/RT) dT}{\beta \exp(-E_\alpha/RT_0)}, \quad (16)$$

which enables the time at which a given conversion will be reached at an arbitrary temperature, T_0 , to be computed. Vyazovkin and Lesnikovich [18] first derived Eq. (16). Because predictions using this method can be made without knowledge of the reaction model (and the pre-exponential factor), they will be referred to as “model-free predictions”. The model-free predictions for isothermal decompositions of HMX and ADN are presented in Figs. 4 and 5. Although the pre-exponential factor and the reaction model are not needed for making predictions, the techniques of their evaluating have been developed [19–21].

3.3. ASTM E698

The ASTM E698 method [22] occupies an intermediate position between the model-fitting and model-free methods. It uses a model-free estimate for the activation energy which is evaluated from Kissinger's plot of $\ln(\beta/T_m^2)$ against T_m^{-1} [23], where T_m is the temperature corresponding to the maximum of $d\alpha/dT$. However, the pre-exponential factor is evaluated on assumption of a first-order

reaction as follows:

$$A = \frac{\beta E}{RT_m^2} \exp\left(\frac{E}{RT_m}\right). \quad (17)$$

Predictions of the isothermal kinetics are also based on the assumption that a reaction obeys first-order kinetics

$$t = \frac{-\ln(1-\alpha)}{A \exp(E/RT_0)}. \quad (18)$$

To determine the values of T_m , we used smoothed numerical derivatives of α over T . The use of the ASTM method yields values of $E = 130.6 \text{ kJ mol}^{-1}$, $\log(A/\text{min}^{-1}) = 11.5$, and $r = -0.9932$ for HMX decomposition. For decomposition of ADN, this method yields $E = 117.2 \text{ kJ mol}^{-1}$, $\log(A/\text{min}^{-1}) = 12.7$, and $r = -0.9991$. Substitution of the E and A values into Eq. (18) gave rise to predictions that are shown in Figs. 4 and 5.

4. Discussion

4.1. Model-fitting method

Examination of Tables 2 and 3 suggests that the Arrhenius parameters determined for the isothermal data using the model-fitting method are rather mildly variable when changing the reaction model. The reduced time plots for isothermal decompositions of HMX (Fig. 1) and ADN (Fig. 2) were subjected to statistical analysis as described above Eqs. (6) and (7). The resulting values of F are given in Tables 1 and 2. The F -test allows the Avrami–Erofeev model (number 9) to be identified as the best description for isothermal decomposition of HMX. The corresponding Arrhenius parameters are $E = 144.6 \text{ kJ mol}^{-1}$ and $\log(A/\text{min}^{-1}) = 13.0$. For the isothermal decomposition of ADN, the statistical analysis of reduced time plots suggests that of the reaction models shown in Table 1, the contracting sphere and contracting cylinder models provide the best fits to experimental data. These two models describe quite similar mechanisms and give rise to practically identical pairs of Arrhenius parameters ($E = 128 \text{ kJ mol}^{-1}$ and $\log(A/\text{min}^{-1}) = 14$). Therefore, the model-fitting method appears to produce quite reasonable kinetic information from isothermal data.

In contrast, the Arrhenius parameters obtained for nonisothermal decompositions of HMX and ADN are highly variable, exhibiting a strong dependence on the reaction model chosen (Tables 4 and 5). As we can see, most of the models give rise to good linear fits as characterized by the values of r . Statistical analysis Eqs. (10)–(12) of the linear correlation coefficients helps to identify “best” (statistically equivalent) reaction models (Tables 6 and 7).

For the nonisothermal decomposition of HMX, models 4 and 5 are the best for all five heating rates. Model 4 gives rise to an activation energy that varies from 146 to 167 kJ mol^{-1} with the heating rate. Model 5 also shows the variation in E from 196 to 225 kJ mol^{-1} . Fitting of the reaction-order model followed by statistical analysis (Fig. 3) resulted in the following confidence limits $-1.5 \leq n \leq 0.5$, $94.3 \leq E \leq 116.2 \text{ kJ mol}^{-1}$, and $7.1 \leq \log(A/\text{min}^{-1}) \leq 9.7$. The kinetic triplet corresponding to the minimum ($r = -0.9569$) is $n = -0.3$, $E = 105.0 \text{ kJ mol}^{-1}$, and $\log(A/\text{min}^{-1}) = 8.3$. According to the statistical test Eqs. (10)–(12) this kinetic triplet is equivalent to the triplets corresponding to models 4 and 5.

Let us now compare the results of model-fitting for nonisothermal and isothermal decompositions of HMX. Although model 9 (Avrami–Erofeev) was uniquely chosen from isothermal decomposition, it did not happen to be among the best fits for nonisothermal data. The mechanisms represented by models 4 and 5 are obviously different from that embodied in model 9. Note that the value of the activation energy corresponding to model 9 is significantly different from the value 144.6 kJ mol^{-1} obtained for this model from isothermal data. The application of models 4 and 5, as well as fitting of the reaction-order model, resulted in markedly different values of the activation energy. Among these three models, only model 4 gives the value of E that is fairly consistent with the value obtained from isothermal data. However, statistical analysis does not allow this model to be chosen to the exclusion of all others. The resulting uncertainty does not permit meaningful comparison of the activation energy derived from nonisothermal data with the value produced from isothermal measurements.

The above kinetic triplets have been used to predict the kinetics of the thermal decomposition of HMX at 235°C. As illustrated in Fig. 4, all these predictions are rather unsatisfactory.

For nonisothermal decomposition of ADN, no single reaction model happened to be the best in all five experiments (Table 7). In four experiments models 6 and 9 were identified as the best descriptions. Models 10 and 11 are the best in two experiments. All four best models are best fits of thermal decomposition of ADN at $5.5^{\circ}\text{C min}^{-1}$. Let us compare the results of this experiment with isothermal data. Again, we encounter the problem of internal inconsistency between kinetic triplets derived from nonisothermal data. The four best models describe qualitatively different mechanisms, and the corresponding Arrhenius parameters span a factor of 4 in activation energy and log A. Therefore the value of the activation energy for nonisothermal decomposition is too uncertain to be meaningfully compared with that value for isothermal process.

In contrast to the results of the experiments with HMX, one of the two best fits of the isothermal data (model 11) ranks with other best models for nonisothermal data. All other best fits of nonisothermal data suggest mechanisms that are qualitatively different from the contracting geometry interface processes represented by models 11 and 12 (best fits of isothermal data). The Arrhenius parameters corresponding to model 11 also show good agreement with the parameters computed for isothermal data. Substitution of the kinetic triplet corresponding to this model into Eq. (13) results in a very good prediction for the isothermal decomposition of ADN at 150°C (Fig. 5). In spite of the obvious viability of model 11, we have to stress that statistical analysis of the nonisothermal experimental data does not allow this model to be preferred over three other models (6, 9, and 10) whose use results in unsatisfactory predictions of the isothermal kinetics.

The kinetic triplets found by fitting the reaction-order model have also been used for the isothermal predictions by Eq. (13). Again, the resulting predictions are unreliable (Fig. 5).

The fact that the use of the model identified from isothermal data allows one to accomplish agreement between nonisothermal and isothermal kinetics calls to mind the method proposed by Tang and Chaudhri [24]. Their idea was to run an isothermal experiment to identify the reaction model and then use it to evaluate Arrhenius parameters of a nonisothermal process. As we can see this method would work well for the thermal decomposition of ADN. Nevertheless,

for the nonisothermal decomposition of HMX, the best model identified from isothermal data gave rise to Arrhenius parameters that were significantly different from the isothermal values (cf. Tables 2 and 4). The prediction of isothermal kinetics based on these parameters was also unsatisfactory (Fig. 4). In other words, this method would obviously fail when applied to the HMX data. Therefore the general applicability of this method is questionable.

4.2. Limitations of statistical analysis as applied to model-fitting

As shown here for ADN and HMX, the application of statistical analyses in model-fitting is most likely to result in several best fits (i.e., kinetic triplets) for the same set of data. The problem with using and interpreting differing kinetic triplets is obvious. But what if the kinetic triplet has been determined unambiguously as in the case of the isothermal decomposition of HMX. There are several problems to be considered in this situation.

Firstly, we can never be sure that the unambiguous choice is actually unambiguous. The reaction model is chosen from the list of arbitrarily (subjectively) compiled models. No matter how comprehensive this list may seem, there is absolutely no guarantee that the adequate model is included in the list. For any process under study, the appropriate model may yet to be invented. However, any arbitrarily compiled list always has a model that gives a better description of the process than other models. Therefore, even an unambiguous choice still can be wrong and yield an inadequate kinetic triplet.

Secondly, even an unambiguously chosen reaction model cannot help in drawing an unambiguous mechanistic conclusion because of the ambiguous association of the kinetic equation with the mechanistic model of a process. Jacobs and Tompkins [25] 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 [26]. For instance, Pysiak [27] demonstrated that the equation of contracting sphere

can be derived from three different mechanistic concepts.

Last but not least, any statistical characteristics rank the reaction models by the goodness of data fit, but not by the physical sense of applying these models to experimental data. Even if a reaction model does not have any physical meaning at all, it may perfectly fit data. For instance, the HMX decomposition data can be successfully fit by the reaction order model with $n = -0.3$ and $|r| = 0.9569$ (Fig. 3). According to statistical analysis this bizarre model fits the data as well as models 4 and 5 (Table 1), which are derived from definite physical models. It should be remembered that the prime objective of kinetic analysis is obtaining physically sound kinetic information. Therefore, statistical methods cannot be used as an ultimate tool of kinetic analysis.

4.3. Model-fitting methods and compensation effect

The reason for the failure of the model-fitting method, as applied to nonisothermal data, is clear. Unlike the isothermal experiments, in which temperature is isolated as an experimental variable, the non-isothermal experiments allow fits that vary the temperature sensitivity $k(T)$ and the reaction model $f(\alpha)$, simultaneously. This extra flexibility in the fitting procedure allows errors in the functional form of the reaction model to be concealed by making compensating errors in $k(T)$ so that a series of approximate equalities

$$\begin{aligned} \frac{d\alpha}{dt} &\cong k_1(T)f_1(\alpha) \cong \dots \cong k_j(T)f_j(\alpha) \\ &\cong \dots \cong k_n(T)f_n(\alpha), \end{aligned} \quad (19)$$

holds true subject to variable temperature. Because for most of the reaction models the variation in $f(\alpha)$ with α is practically negligible as compared to the variation in $k(T)$ with T , we can derive from the logarithmic form of Eq. (19) the following approximate equality

$$\ln k_j(T) \cong \text{const.} \equiv \ln k^0, \quad (20)$$

(here k^0 is the isokinetic rate constant [21,28]) that holds over the experimental temperature region. Eq. (20) can be rewritten as

$$\ln k^0 \cong \ln A_j - (RT)^{-1} E_j. \quad (21)$$

The experiments are typically carried out over a relatively narrow range of temperatures so that

$$T^{-1} \cong \text{const.} \equiv (T^0)^{-1}, \quad (22)$$

where T^0 is the isokinetic temperature [21,28]. Subject to condition (22), Eq. (21) can be rearranged as follows:

$$\ln A_j \cong \ln k^0 + (RT^0)^{-1} E_j. \quad (23)$$

Eq. (23) suggests a linear correlation between the values of E_j and $\ln A_j$ computed for different reaction models (cf. Tables 4 and 5). This correlation is often called “compensation effect” [1].

Eqs. (20) and (22) also suggest that a series of Arrhenius plots related to various reaction models should have a common intersection point at coordinates $(T^0)^{-1}$ and $\ln k^0$. This effect is described as the so-called artificial isokinetic relationship [21,28]. Fig. 8 gives a graphic presentation of this effect for the thermal decomposition of HMX. Although the Arrhenius parameters vary by as much as one order of magnitude (see Table 4), the values of $\ln k_i(T)$ related to various reaction models are virtually equal within the experimental temperature region (Fig. 8).

An interesting consequence of the compensation behavior given by Eq. (19) is that despite the wide

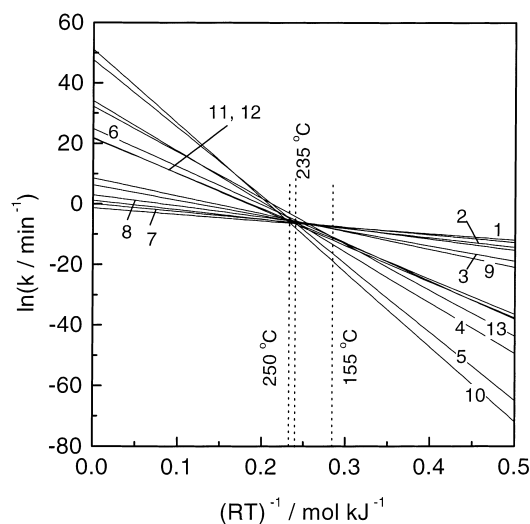


Fig. 8. Arrhenius lines plotted data presented in Table 4 for nonisothermal decomposition of HMX. 155–250 °C is the temperature region of the nonisothermal decomposition of HMX. 235 °C is the temperature for the predictions (Fig. 4) were made.

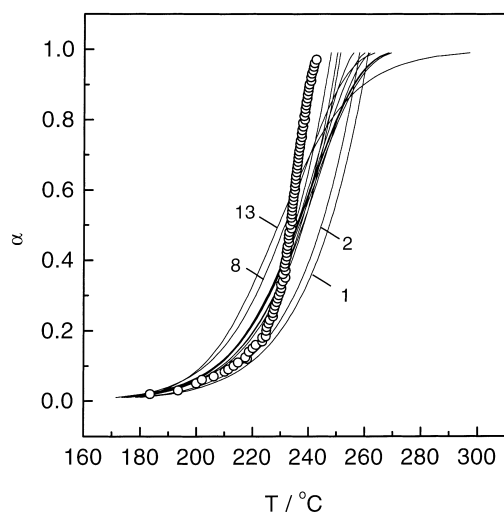


Fig. 9. Predictions of the nonisothermal decomposition of HMX at $0.17^{\circ}\text{C min}^{-1}$. The numbers 1, 2, 8, and 13 indicate the kinetic triplets (Table 4) that resulted in the worst fits. Circles show the actual measurements.

variation in Arrhenius parameters they can be used to fairly reproduce the dependence of α on T from which these parameters were estimated. This is shown in Fig. 9. The α versus T predictions were made by substituting the kinetic triplets (Table 4) into Eq. (24)

$$\alpha = G_j \left[\frac{A_j}{\beta} I(E_j, T) \right], \quad (24)$$

where G_j is the function inverse to $g_j(\alpha)$, so that $G_j[g_j(\alpha)] \equiv \alpha$. The temperature integral in Eq. (24) was replaced with the Senum–Yang approximation [29].

Then, the question arises why these Arrhenius parameters cannot be used to reasonably predict the isothermal kinetics even for the temperatures that lie within the temperature region of a nonisothermal experiment (Fig. 10). As we can see in Fig. 8, the rate constants for different reaction models are almost identical at the temperature for which the predictions are made. It should be remembered that the predictive power of the kinetic triplets derived from nonisothermal data rests upon the compensation of $k(T)$ and $f(\alpha)$ (Eq. (19)) that holds only for the conditions of variable temperature. For this reason, the form of the reaction model is virtually irrelevant when the kinetic triplets are used to reproduce nonisothermal data (Fig. 9).

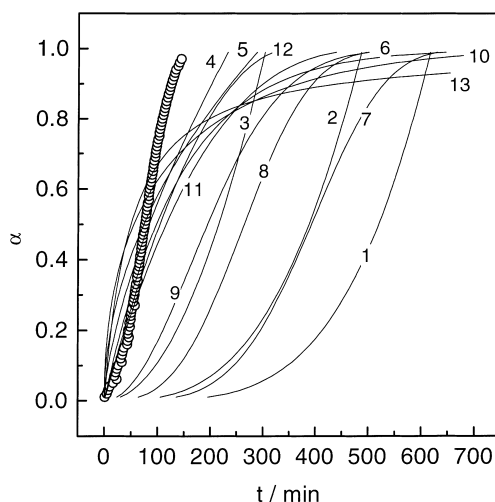


Fig. 10. Predictions of the isothermal decomposition of HMX at 235°C . The numbers indicate kinetic triplets (Table 4) used for predictions by Eq. (13). Circles show the actual measurements.

Because for isothermal predictions the rate constant is invariable, it cannot compensate for the difference between the assumed and true reaction model. As a result the error in choosing the reaction model from nonisothermal experimental data is revealed when those constants are used to predict the results of isothermal experiments (Fig. 10). This fact brings us to the important conclusion that the goodness of nonisothermal data fits does not characterize the ability of the kinetic triplets to predict the isothermal kinetics.

To characterize the quality of isothermal predictions made with various kinetic triplets, we used the average relative deviations determined as follows:

$$\text{ARD} = \frac{100\%}{n} \sum_{i=1}^n \left| \frac{t_{\alpha,i}^{\text{exp}} - t_{\alpha,i}^j}{t_{\alpha,i}^{\text{exp}}} \right|, \quad (25)$$

where $t_{\alpha,i}^{\text{exp}}$ and $t_{\alpha,i}^j$ respectively are the experimentally measured and predicted by j th model (Eq. (13)) times to reach the same extent of conversion. The ARD values were applied to evaluate the predictions of the isothermal decomposition of HMX at 235°C . Fig. 11 shows the ARD values plotted against the correlation coefficients that characterize the kinetic triplets for the nonisothermal decomposition of HMX (Table 4). As we can see, the correlation between these two char-

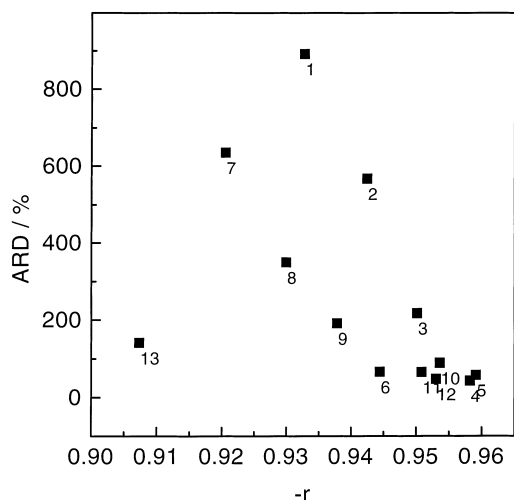


Fig. 11. Average relative deviations (ARD) of the isothermal predictions (Fig. 10) from the actual measurements plotted against the correlation coefficients (Table 4).

acteristics is poor. This emphasizes the point that choosing a kinetic triplet from nonisothermal data on the basis of linear correlation coefficients is not very likely to result in successful prediction of the results of the corresponding isothermal experiment.

4.4. Model-free isoconversional method

Application of Eq. (14) to the isothermal data for HMX reveals the functional dependence of E_α on α (Fig. 6). The activation energy at high extents of conversion is essentially constant, but is somewhat lower in the early stages of the reaction. Unlike the model-fitting method, which yields a single effective value of the activation energy for the whole process ($144.6 \text{ kJ mol}^{-1}$), the isoconversional method has the ability to reveal complexity of the process in the form of a functional dependence of E_α on α . Application of Eq. (15) to the nonisothermal data results in a E_α -dependence that is similar in shape to the isothermal one. The similarity of the dependencies derived from isothermal and nonisothermal measurements suggests that the operative multi-step mechanism is essentially the same for the isothermal and nonisothermal conditions.

The E_α -dependence evaluated from nonisothermal data was employed to predict (by the use of Eq. (16)) the isothermal kinetics of HMX decomposition. This

model-free prediction is in excellent agreement with the actual isothermal measurements (Fig. 4).

For the isothermal decomposition of ADN, the use of Eq. (14) gives rise to an E_α -dependence (Fig. 7) that rises from about 110 kJ mol^{-1} at low conversion to nearly 140 kJ mol^{-1} at $\alpha = 0.2$. At $\alpha > 0.2$ the dependence decreases to about 124 kJ mol^{-1} near the completion of the reaction. As compared to the model-fitting method that gave a single value of the activation energy for the process (128 kJ mol^{-1} in this case), the isoconversional method reveals complexity of the process. Fig. 7 also shows the E_α -dependence for the nonisothermal decomposition of ADN, as computed by the nonlinear isoconversional method Eq. (15). The dependence is similar in shape to the isothermal one. The activation energy increases to a maximum around 168 kJ mol^{-1} at $\alpha \cong 0.2$, then decreases monotonically to 112 kJ mol^{-1} near the end of the reaction. The obtained dependencies unmistakably indicate a multi-step mechanism of both isothermal and nonisothermal decompositions of ADN. Recently we have reported a detailed scheme of this process [30,31].

Fig. 5 demonstrates the ADN isothermal decomposition as predicted by using the E_α -dependence derived from nonisothermal data (Eq. (16)). We can see that the model-free prediction agrees very well with the actual measurements.

The examples considered here demonstrate that the parallel application of model-free isoconversional method to isothermal and nonisothermal data results in obtaining E_α -dependencies that are similar in shape, but not identical. Our theoretical analysis has shown [32] that some difference in the E_α -dependencies produced from isothermal and nonisothermal is rather typical. However, the use of E_α -dependence derived from nonisothermal data has permitted reliable predictions of the isothermal decomposition of HMX and ADN. Therefore, we may conclude that the model-free isoconversional method is capable of producing consistent kinetic information from isothermal and nonisothermal data.

4.5. ASTM E698

The application of model-free Kissinger's method resulted in the values of the activation energy that agree well with the values obtained from isothermal

measurements. The values derived from nonisothermal and isothermal data respectively are 131 and 148 kJ mol⁻¹ for HMX and 117 and 128 kJ mol⁻¹ for ADN. The value of A determined by Eq. (17) and Kissinger's estimate for E were substituted in Eq. (18) to obtain the isothermal predictions that are shown in Figs. 4 and 5. The resulting predictions appear to have intermediate accuracy that is obviously higher than that of the model-fitting predictions but lower than accuracy of model-free predictions. In general, Kissinger's method permits obtaining the values of the activation energy that agree with the values produced from isothermal data. The isothermal predictions made by using the ASTM method (Eq. (18)) are reasonable, but significantly less accurate than the predictions obtained with model-free method Eq. (16). As compared to the authentic isoconversional methods [2–4,15–17] the Kissinger method has a disadvantage of producing a single value of the activation energy for the whole process. As a result, activation energy variations in that may accompany complex (e.g., multi-step) kinetics may not be revealed by this method.

4.6. Model-free versus model-fitting method as applied to multi-step kinetics

Solid state reactions ordinarily demonstrate a tangled interplay of various chemical and physical processes such as solid-state decomposition, reaction of gaseous products with the solid, sublimation, polymorphous transitions, diffusion, melting, evaporation, adsorption, desorption, etc. Therefore, the effective activation energy of a solid state reaction is generally a composite value determined by the activation energies of various processes and by their influence on the overall reaction rate. Even if the temperature is kept constant (single isothermal experiment), the relative contributions of the elementary steps into the overall reaction rate vary with the extent of conversion ultimately resulting in a dependence of the effective activation energy on the extent of conversion [32]. Additionally, the kinetics of solid state reactions are known [33] to be sensitive to pressure, size of crystals, gaseous atmosphere and many other factors which are likely to change during the process.

Model-fitting methods are designed to extract a single set of global Arrhenius parameters for the

whole process and are therefore unable to reveal this type of complexity in solid state reactions. The values obtained in such a way are averages that do not reflect changes in the mechanism and kinetics with the temperature and the extent of conversion. The model-free isoconversional method allows for unmistakably detecting multi-step kinetics as a dependence of the activation energy on the extent of conversion. Furthermore, it was shown [34] that revealing the dependence of the activation energy on conversion not only helps to disclose the complexity of a process, but also helps to identify its kinetic scheme. The shapes of the dependence of E_α on α have been identified from simulated data for competing [34], independent [35], consecutive [36], and reversible [37] reactions, as well as reactions complicated by diffusion [38]. Principles and examples of the mechanistic interpretations of the dependence of E_α on α can be found elsewhere [30,34,39–47].

4.7. Model-fitting method and nonisothermal kinetics, or “why has nonisothermal kinetics gained so bad a reputation?” [48]

As was mentioned above, application of the model-fitting method to nonisothermal data always gives rise to highly ambiguous kinetic triplets. This ambiguity ultimately causes the failures of interpretation and utilization of the kinetic triplets. It should be emphasized that the problem of ambiguity is peculiar to the model-fitting method itself, no matter if it is applied to isothermal or nonisothermal data. In a nonisothermal experiment, the temperature and conversion contributions of the reaction rate are not separated, and this strongly aggravates the problem of ambiguity. That is why this problem is often considered as a specific problem of nonisothermal kinetics, but not a problem of the model-fitting method. Unfortunately, this flawed method has been employed in an overwhelming majority of kinetic analyses. Its failures are sometimes revealed as bizarre results, such as unreasonably small [49,50] or even negative [51] values of the activation energy, or as negative values of the activation entropy for endothermic processes [49,52,53], or as a negative estimated number of collisions [54]. The flood of inconsistent information produced from nonisothermal data with the model-fitting method

provoked an antagonistic attitude towards nonisothermal kinetics as a whole. In our view this attitude is justifiable only as it pertains to the use of the model-fitting approach to the kinetic analysis. The model-free isoconversional approaches provide trustworthy methods of analyzing nonisothermal kinetic data such that the kinetic parameters can be used to predict the results of isothermal experiments.

5. Conclusions

The application of the model-fitting method to nonisothermal data results in highly uncertain kinetic triplets that cannot be meaningfully compared with the triplets evaluated from isothermal measurements. Because of the characteristic uncertainty, the kinetic triplets obtained from nonisothermal data are not capable of reasonably predicting isothermal kinetics. The model-fitting method applied to isothermal data gives rise to unambiguous values of Arrhenius parameters that are likely to conceal multi-step kinetics. A viable alternative to the model-fitting method is the model-free isoconversional method. This method has the attractive attributes that

- it can be used to analyze either isothermal or nonisothermal data;
- results from isothermal and nonisothermal experiments are internally consistent;
- the explicit evaluation of E_a -dependencies can reveal complexities in the reaction kinetics.

Therefore, this model-free approach can be recommended as a trustworthy way of obtaining reliable and consistent kinetic information from both nonisothermal and isothermal data.

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