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Thermochimica Acta 391 (2002) 119–127

thermochimica acta

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Model-free analysis of thermoanalytical data-advantages and limitations

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Received 3 September 2001; received in revised form 28 February 2002; accepted 7 March 2002

Abstract

Model-free kinetic analysis is a powerful tool to estimate the activation energy of processes, investigated by various isothermal or dynamic measurements. On the basis of real measurements and simulations we demonstrate that limitations of application exist. Conditions are listed under which estimated values of activation energy could be incorrect.

Keywords: DSC; TGA; Kinetics; Model-free analysis; Model-fit; Non-linear regression

1. Introduction

Kinetic investigations are, today, one of the most important application of thermal analysis. Under the methods summarized by thermal analysis, differential scanning calorimetry (DSC) and thermogravimetry (TGA) have outstanding significance. The common advantage of both these techniques compared to many other analytical methods is the ease of sample preparation. In addition, the conditions of activation can be easily varied. The fact that thermodynamic (reaction enthalpy) and kinetic (activation parameters and kinetic model) parameters can be determined simultaneously, is one of the major advantages of the DSC method. In contrast to TGA, the DSC method is always applicable because nearly all reactions produce or consume heat.

In the past, single scan analysis methods were dominant. Drastic and different simplifications were used sometimes. Together with different calculation methods they frequently resulted in extremely scattered kinetic parameters when one and the same reaction was examined in different laboratories. One of the most important conclusions to be taken from the "ICTAC kinetics project, 2000" has been formulated by Burnham [1] as follows: "With the ready availability of . . . good analysis programs, kinetic analysis using single heating rate methods should no longer be considered in the thermal analysis community." Of course, techniques have existed over many decades (Friedman [2], Ozawa [3], Flynn and Wall [4]) that determine the activation energies from the common analysis of multiple curves measured at different heating rates or at different isothermal temperatures. Those were the isoconversional methods. Using the differential isoconversional method according to Friedman, the logarithm of the conversion rate $\ln(d\alpha/dt)$ is recorded vs. $1/T$ for a series of measurements with

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PII: S0040-6031(02)00169-7

heating rates β. In contrast, when using the integral isoconversional method according to Ozawa–Flynn–Wall (OFW) for a selected degree of reaction α_j, in the case of dynamic measurements $\ln(\beta)$ is recorded vs. $1/T$ and for isothermal measurements $\ln(t)$ is recorded vs. $1/T$. In both the above methods the activation energy is determined from the slope of isoconversional lines. The pre-exponential factor can also be estimated if a reaction model $f(\alpha)$—valid for the whole range of the reaction—is assumed for the investigated reaction.

In the past, the model-free analysis of thermoanalytical data got a non-expected boost. A considerable contribution was furnished by the works of Vyazovkin [6–11]. Thanks to him that, due to new ideas, the available methodology has been extended for versatile application. To avoid inaccuracies of the conventional isoconversional methods, Vyazovkin and Sbirrazzuoli [11] calculate for a set of n experiments carried out at different heating rates the minimum of the function

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

with

$$I(E_\mathrm{A},T_\alpha)=\int_0^{T_\alpha}\exp\left(-\frac{E_\mathrm{A}}{RT}\right)\mathrm{d}T$$

Assuming the simple additive superposition of the individual reactions for a possible multi-step mechanism, they obtain conversion-dependent formal activation energies. This concept is not generally accepted in chemistry. Furthermore, in the meantime a number of problems show that its application has fundamental limits in spite of all advantages of the model-free analysis. The following examples demonstrate where the model-free analysis must fail in principle. It is thought as warning of a non-critical use of this easy and fast technique. We use another concept [12,13] and assume that the overall reaction is the sum of individual reaction steps (formal or true steps) with constant activation parameters as generally accepted in chemistry. Our kinetic analysis using model fitting with non-linear regression is free of any limits. In the following we compare for some critical cases our results with those of the isoconversional method.

The transformation (1) of the differential or the integral signal into the general variable reaction degree α is the center of model-free kinetic analysis.

For differential signals, like DSC, DTA

$$\alpha(t)=\frac{\int_{t_\mathrm{S}}^{t}[\mathrm{DSC}(t)-\mathrm{Baseline}(t)]\,\mathrm{d}t}{\int_{t_\mathrm{S}}^{t_\mathrm{F}}[\mathrm{DSC}(t)-\mathrm{Baseline}(t)]\,\mathrm{d}t} \tag{1a}$$

For integral signals, like TGA, DIL

$$\alpha(t)=\frac{m(t_\mathrm{S})-m(t)}{m(t_\mathrm{S})-m(t_\mathrm{F})} \tag{1b}$$

where t is the actual time, t_S the starting time of the reaction, t_F the time at the end of the reaction, m the mass, DSC the differential scanning calorimetry signal, and Baseline the baseline signal belonging to the reaction peak.

Due to the transformation (1) all measurements have the value $\alpha=0$ at the start $t=t_\mathrm{S}$, and the value $\alpha=1$ at the end of the reaction ($t=t_\mathrm{F}$). The restriction $0\leq\alpha\leq1$ is valid for all α values, but this restriction is still too weak. The precondition must be fulfilled that the reaction degree α is an increasing monotonic function of time [14]. This condition automatically includes the restriction $\alpha\geq0$. The monotonic increase is absolutely necessary, otherwise the correlation of the activation energy E to a reaction degree α would be ambiguous.

2. Examples

2.1. Combination of exothermal and endothermal signals

This condition of a monotonic increase of the reaction degree α in model-free kinetic analysis means that the total signal must not result from a superposition of exothermal and endothermal signals, when using DSC measurements as an example. Clearly, this means a great restrictions for the application of model-free kinetics. The cross-linking of powder paints (Fig. 1) is a typical example.

Here the endothermal melting process and the exothermal cross-linking reaction overlap significantly. The enthalpy of the cross-linking reaction is higher than the enthalpy of the melting process. Therefore, the partial area is negative at the beginning and only becomes positive later (Fig. 2).

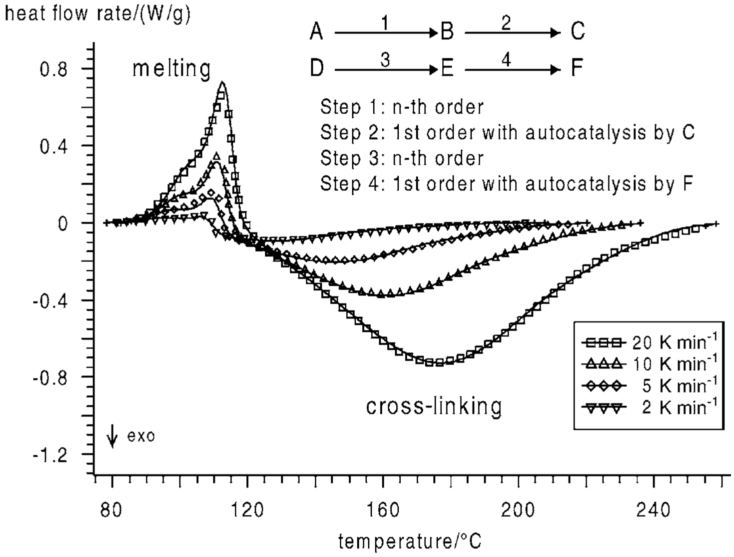

Fig. 1. Melting process and cross-linking reaction as two overlapping processes in a powder point. Symbols—experimental values; solid lines—calculated values.

The melting process is excluded from the model-free analysis because only the range can be considered where $\alpha \geq 0$. Therefore, both the model-free analysis and the predictions based thereon have a restricted range of application; other kinetic evaluation methods have to be applied for better reliability of the resulting parameters and predictions.

2.2. Reactions with competing reaction paths

The transformation made in (1) is linked to an additional condition: the same final product must always be achieved at the end of the reaction. Otherwise the transformation is ambiguous. If thermoanalytical measurements prove that either the mass loss

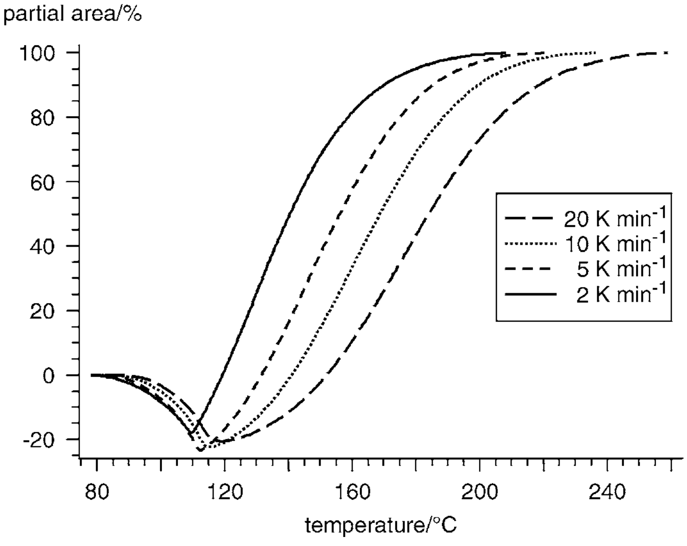

Fig. 2. Partial area, calculated for both the melting process and the cross-linking reaction.

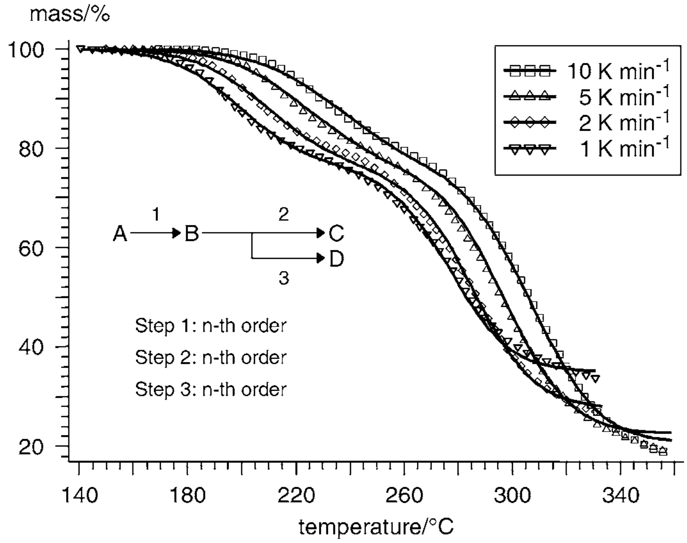

Fig. 3. Thermal decomposition of α-D-glucose. Symbols—experimental points; solid lines—calculations. The residual mass strongly depends on the heating rate.

(thermogravimetric measurements) or the peak area (DSC measurements) or the total shrinkage (dilatometric measurements [15]) depend on the heating rate, then this is a clear indication that concentrations of final products are dependent on the heating rate. Then the model-free analysis fails.

Fig. 3 shows the thermal decomposition of α-D-glucose [16]. It is noticeable that the mass loss in thermogravimetric measurements depends strongly on the heating rate. By the transformation (1) to the range of values $0 \leq \alpha \leq 1$, this specific behavior of the measurements is lost, i.e. one loses the dependence of the total mass loss on the heating rate. Therefore, the model-free analysis cannot provide a prediction that also calculates different mass losses at different heating rates.

The different activation energies for the reaction paths 2 and 3 of $E_{A,2} < 3$ kJ mol^{-1} and $E_{A,3} = 163$ kJ mol^{-1} act as a soft switch (Fig. 4). At 210 °C the product C will be dominant, while at 280 °C, the product D is favored.

In a second example [17a], the actual concentrations of reactants and individual rate constants are used to describe the course of reaction. This method,

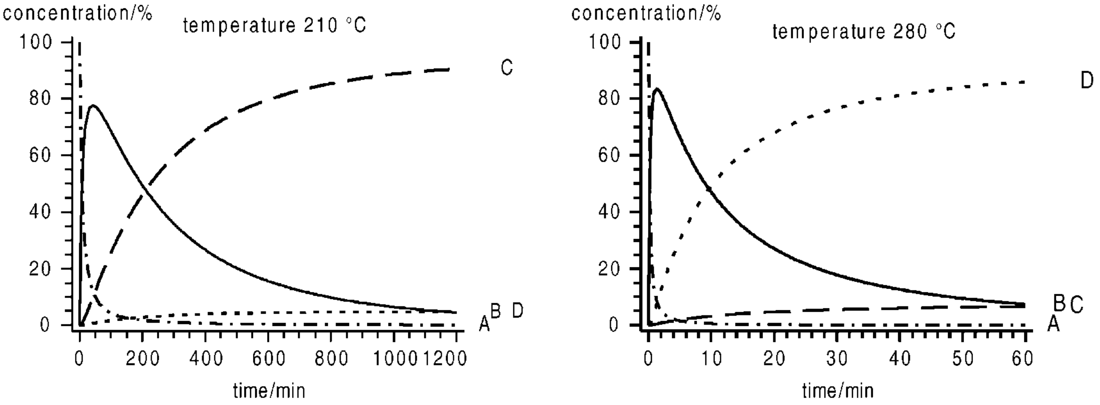

Fig. 4. Prediction of isothermal decomposition of α-D-glucose.

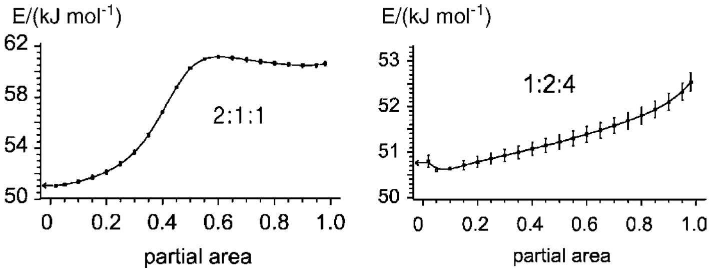

Fig. 5. Activation energies estimated using the model-free isoconversional method according to OFW. Different initial stoichiometries for a mechanism with two competing reactions.

the so-called 'component kinetics', also allows the simultaneous evaluation of reaction curves with different initial stoichiometries of the reactants. First, we have calculated error-free DSC curves for the two second-order competitive reactions:

$$A + B \xrightarrow{k_1} X, \qquad A + C \xrightarrow{k_2} Y \tag{2}$$

The simulation is based on $\log A_1 = 5.0\ (\mathrm{mol/l})^{-1}\ \mathrm{s}^{-1}$, $E_{A,1} = 50\ \mathrm{kJ\ mol}^{-1}$ and $\log A_2 = 5.5\ (\mathrm{mol/l})^{-1}\ \mathrm{s}^{-1}$, $E_{A,2} = 60\ \mathrm{kJ\ mol}^{-1}$. Let us now consider two possible initial concentration ratios of the reactants $c_A{:}c_B{:}c_C = 2{:}1{:}1$ and $c_A{:}c_B{:}c_C = 1{:}2{:}4$. Our non-linear regression method exactly reproduces the assumed log A and E_A couples for any initial concentrations. The deviations from the theoretical values are found in the fourth digit after the decimal point. Of course, this is valid only if the correct model is used during the nonlinear regression. All other combinations of elementary steps yield not only poorer fits, but above all they can be unambiguously excluded using statistical tests. If on the other side, the model-free analysis is used, the calculated activation energies and their errors (Fig. 5) show great differences for the two cases.

Activation energies determined for the mixture $c_A{:}c_B{:}c_C = 2{:}1{:}1$ are close to the used basis data. At the same time, only small errors could be observed. Activation energies of the mixture $c_A{:}c_B{:}c_C = 1{:}2{:}4$ have no visible connection to the basis data and their errors have thus dramatically increased. This result is surprising as the simulations were carried out with the same kinetic model. However, if one looks at the course of reaction in more detail, one sees that, in the mixture $c_A{:}c_B{:}c_C = 2{:}1{:}1$, the reaction step 1 ($A + B \rightarrow X$) is nearly finished before reaction step 2 ($A + C \rightarrow Y$) starts. In contrast, both reaction steps take place simultaneously in the mixture $c_A{:}c_B{:}c_C = 1{:}2{:}4$ (Fig. 6).

The following conclusion can thus be reached if—using certain initial concentration ratios—two reaction steps take place simultaneously in one process and if the weight of both these reaction steps shifts (this is always the case when the activation energies are different), then the results of the model-free estimation of the activation energy are meaningless. Completely irrational results are obtained if data sets belonging to reaction curves with different stoichiometries are combined, analyzed by isoconversional methods.

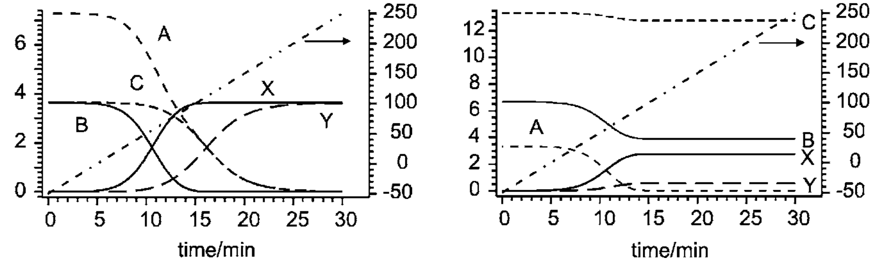

Fig. 6. Simulation of concentrations, using various stoichiometries for the initial reactants, heating rate = 10 K min^{-1}.

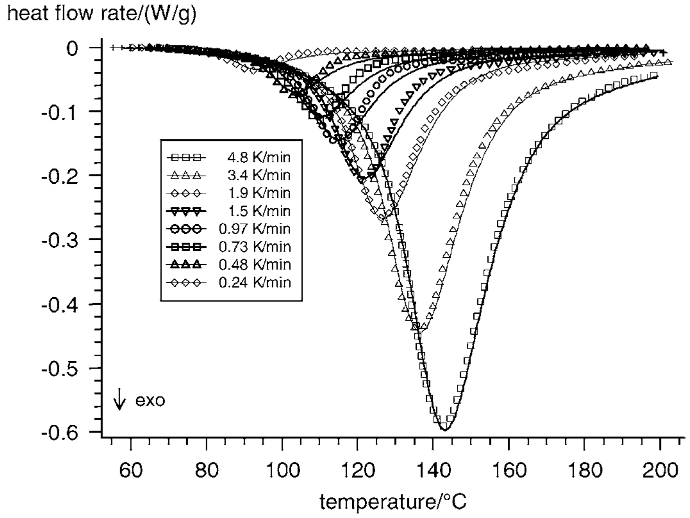

Fig. 7. Curing of epoxy resin with partial diffusion control. Symbols—experimental points; solid lines—calculations; diffusion control is taken into account.

2.3. Reactions with partial diffusion control

It is common knowledge [17b–e,19] that, during the curing of epoxy resins the problem of partial diffusion control arises as soon as the glass transition temperature approaches the reaction temperature. This becomes particularly evident at low heating rates or when using a constant temperature and $T \leq T_g$. Fig. 7 demonstrates this for seven different heating rates [18]. By combining kinetic control and diffusion control in one model, it is possible to describe all measurements with heating rates between 0.24 and 4.87 K min^{-1}.

The model-free analysis according to OFW [3,4], which is essentially identical to Vyazovkin's technique, shows two things (Fig. 8): firstly, as long as

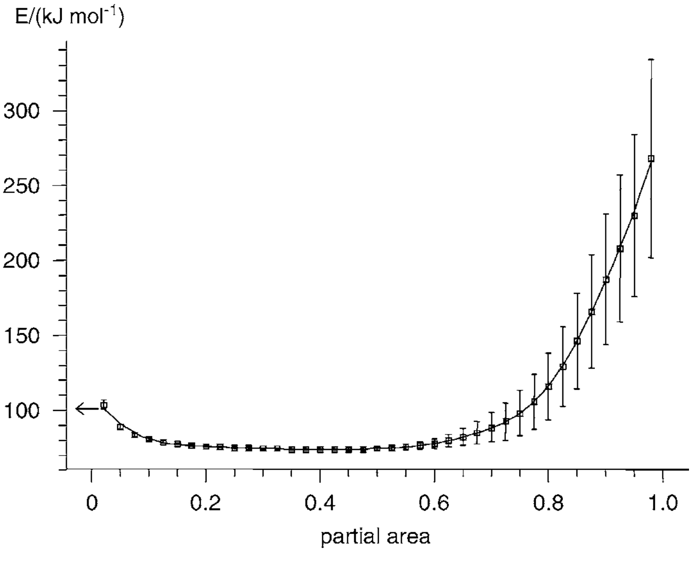

Fig. 8. Curing of epoxy resin with partial diffusion control model-free analysis according to OFW.

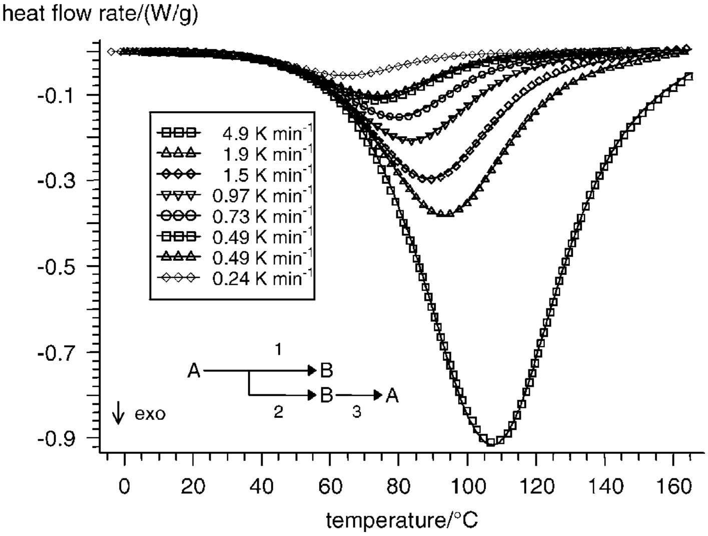

Fig. 9. DSC measurements of dimerization of CPD. Symbols—experimental points; solid lines—calculations, based on kinetic model including back reaction.

diffusion control has no influence—as in the present example for a reaction degree below 0.7—the activation energy is close to 75 kJ mol^{-1}. The error found for the activation energy is always below 2 kJ mol^{-1}.

Secondly, the activation energy increases rapidly at the beginning of diffusion control. However, the marked increase of the error in the activation energy values above a reaction degree of $\alpha > 0.7$ is much more important (Fig. 9). This great increase in error is due to the fact that the diffusion control violates the assumptions of the OFW analysis.

2.4. Processes with back reactions

Experiments should be carried out taking care that no back reactions can occur. However, these back reactions cannot always be excluded. Another limitation of the model-free analysis comes to light here.

At the end of the signal, it is always assumed that all starting reactants have been changed into the final product [5], and that here the reaction degree $\alpha = 1$. In the case of the participation of a back reaction, $\alpha = 1$ can never be achieved. The Diels–Alder type dimerization of cyclopentadiene (CPD) [17a,19] is shown as an example (Fig. 9). Two forward reactions run parallel, a simple second-order reaction and a reaction that is autocatalyzed by the formed dimer DCPD. The kinetic analysis using non-linear regression (Fig. 10) gives activation energies of 69.4 ± 1.0 and 73.8 ± 2.4 kJ mol^{-1} for the two forward reactions. For the back reaction, which can be noticed above 120 °C, an activation energy of 142 ± 8 kJ mol^{-1} has been determined. In contrast to the above, using the model-free analysis, no value of activation energy higher than 75 kJ mol^{-1} can be found in the full range of partial area. A decrease of the activation energy can be seen just at the end of the peak (high values of the partial area, the range with a high portion of back reaction), whereas the non-linear regression provides a high value activation energy. This means that the model-free analysis fails in processes with back reaction because here, too, the assumptions of this analysis method are violated.

The objection could be raised that these examples were selected to present a choice only of more exceptional cases. It is true that all examples originate from the practical application. In no case should the impression be given that model-free analysis has no significance for kinetic analysis or always leads to wrong information. In our experience, the significance of model-free analysis lies in its function as the preliminary stage of non-linear regression.

The determination of kinetic parameters by means of non-linear regression is an iterative process.

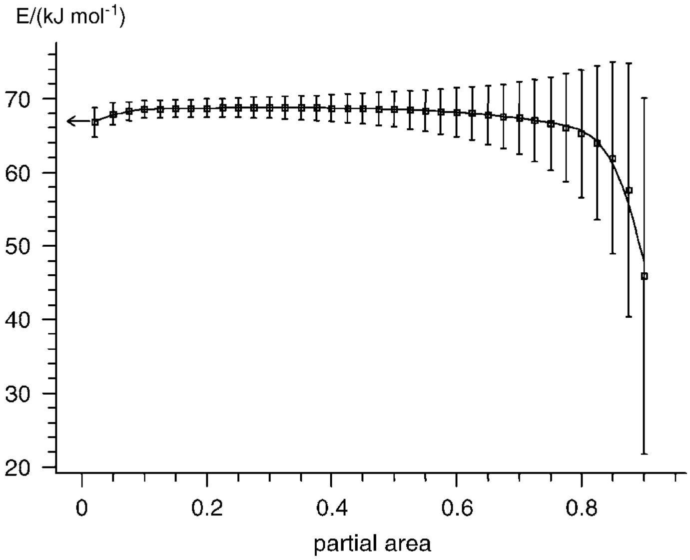

Fig. 10. Model-free analysis (Friedman) concerning DSC measurements of dimerization of CPD.

Initial values must be set for the parameters, but this is generally viewed as a great disadvantage. The model-free estimation of the activation energy is of great help to the non-linear regression by being able to provide what is needed. In addition, and as a rule, one can also detect the multiple-step nature of a process from the dependence of the activation energy on the reaction degree.

3. Conclusions

The experience gained from both analysis methods, the model-free analysis according to Friedman, OFW or Vyazowkin, and the analysis based on non-linear regression, allows the following conclusion: the great advantage of the model-free analysis is founded on its simplicity and on the avoidance of errors connected with the choice of a kinetic model. Constant activation energies can only be expected for single-step reactions. If one accepts the formal description of multi-stage processes by conversion-dependent E_A's, it is also possible to make predictions of the reaction behavior for isothermal conditions within the tested temperature range. But the presented examples in this paper clearly show that prior to using model-free analysis, one must check that the processes under investigation fulfill the conditions required for the application of this technique.

Up to now one knows that the following conditions should not be present:

- combination of signals with opposite signs, e.g., the combination of exothermal and endothermal signals in DSC measurements;
- processes with branched reaction paths (competing reactions);
- processes with partial diffusion control;
- processes with back reaction;
- distinct variations of the stoichiometries for curves belonging to a common data set.

These restrictions are not valid for kinetic analysis using non-linear regression and model-fit. The necessity of defining a model and of presetting starting values for the kinetic parameters is sometimes described as a disadvantage of this technique. This disadvantage is now clearly minimized if the model-free analysis is used as a preliminary step. The necessary starting values can nearly always be obtained from the model-free analysis. In addition, it also provides information about possible reaction types. Seen as a whole, non-linear regression is more universal than model-free analysis. It is also characterized by a higher degree of data reduction, combined with a greater confidence in predictions for ranges that are not covered by the measurements.

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