Thermochimica Acta, 236 (1994) 1-13
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01600-8

Conversion dependence of activation energy for model DSC curves of consecutive reactions

S. Vyazovkin [1]

Institute for Inorganic Chemistry, The Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

(Received 3 May 1993; accepted 12 September 1993)

Abstract

This paper discusses the problem of extracting kinetic information on a complex process comprising consecutive reactions from thermal analysis (TA) data. As the real rates of the single reactions forming the process are not available from the TA data, information on the process mechanism can be obtained by analysing the dependence of the effective activation energy E on the conversion w. Using model DSC data, different cases of the process were considered and the corresponding $E-w$ dependences were found. It is shown that the shape of the $E-w$ dependence reflects adequately the kinetic regularities of the process being investigated. The activation energy of the component reactions can be estimated from the effective activation energy of the process.

INTRODUCTION

The most popular thermal analysis (TA) methods, such as differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermal analysis (DTA), measure extensive properties of a system as a function of temperature. As these properties have an additive nature, it is not possible to extract information about the real rate of the single reactions forming a process from TA data. Only the overall process rate is available from TA measurements. However, the rate equation generally accepted for kinetic processing of TA data

$$\mathrm{d}w/\mathrm{d}t = A \exp(-E/RT)f(w)$$

where w is the conversion, t the time, T the temperature, A the pre-exponent, E the activation energy, R the gas constant, and $f(w)$ the reaction model, is an equation for a single-step chemical reaction. Thus the Arrhenius parameters (AP) calculated by means of the above equation should be considered as effective values. Because such values are not related to any

---

[1] On leave from the Institute for Physico-Chemical Problems, Byelorussian University, Minsk 220080, Belarus.

single reaction, they can vary with changing temperature and conversion. The shape of this dependence is conditioned by the change in the contributions of single chemical reactions to the overall rate during a process. The change in these contributions, in turn, depends on the process mechanism. Therefore, by analysing the conversion dependence of the effective activation energy for the process, it is possible to understand the process kinetics without the knowledge of the real rates of the single chemical reactions. Based on this idea, an approach to the kinetic analysis of TA data [1] was successfully applied to study the mechanism of real complex processes [2-7]. The aim of this paper is to study the non-isothermal kinetics of the model process comprising consecutive reactions using the above approach.

It should be mentioned here that the studying of the overall kinetics of consecutive reactions has a special place in the kinetics of solid thermolyses. This is because its theoretical description is applicable not only to processes for which the existence of consecutive reactions is proven [8-10], but also to many other solid-state thermolyses processes. In particular, Rakic et al. [11] and Vyazovkin [12] have shown that the processes comprising chemical reactions complicated by diffusion or desorption can be formally considered as a system of consecutive reactions.

Analysis of the papers published over the years shows that approaches to kinetic analysis of consecutive reactions are not sufficiently developed. We can point out only two papers where an attempt was made to clarify the kinetic regularities for some of the consecutive reactions: ref. 8, from simultaneous DTG and DSC data; and ref. 13, from TG data. In addition, we found a description of the three methods for calculating the AP of such processes. One of these methods [14] is applicable only when the second step of the process begins substantially later than the first. The problems relating to the other two methods [15-17] are discussed below.

MODELLING DATA

All kinetic regularities will be analysed on model DSC curves. The DSC signal characterises the total heat flow of all reactions proceeding at one time. In the case of the simplest consecutive reactions $A \rightarrow P \rightarrow B$, the total heat flow is determined by the rates and thermal effects of the steps comprising the process

$$I(T) = Q_1(-\mathrm{d}[\mathrm{A}]/\mathrm{d}t) + Q_2(\mathrm{d}[\mathrm{B}]/\mathrm{d}t) \qquad (1)$$

Although the thermal effects define the ratio of the partial heat flows, this ratio keeps constant during the process and does not depend on the process mechanism. Thus to make the interrelation between the total heat release and the kinetic regularities of the consecutive reactions more evident, we assume that the thermal effects are the same (41.8 kJ mol^{-1}). In addition, we accept that the $I(T)-T$ dependence is the DSC signal required. The

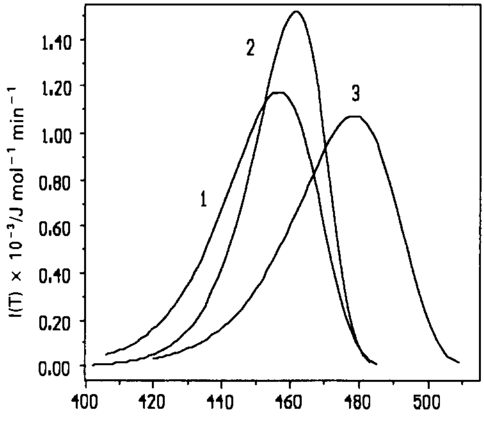

Fig. 1. DSC curves for the single reactions: curve 1, $E = 125.4$ kJ mol^{-1}, $A = 2 \times 10^{14}$ min^{-1}; curve 2, $E = 167.2$ kJ mol^{-1}, $A = 1 \times 10^{19}$ min^{-1}; curve 3, $E = 125.4$ kJ mol^{-1}, $A = 4 \times 10^{13}$ min^{-1}, at the heating rate of 12 K min^{-1}.

conversion at any temperature is the ratio of the DSC curve area corresponding to this temperature to the complete DSC curve area.

To model the DSC curves one should know the temperature dependence of the rate of consumption of the original substance and of the rate of product formation, with a linear increase in temperature at the heating rate $q = dT/dt$. The kinetics of first-order consecutive reactions is described by the following system of differential equations [18]

$$\begin{aligned} -d[A]/dt &= k_1(T)[A] \\ d[P]/dt &= k_1(T)[A] - k_2(T)[P] \qquad (2) \\ d[B]/dt &= k_2(T)[P] \end{aligned}$$

In accordance with the last equation of system (2), the rate of product formation is proportional to the concentration of the intermediate. Its concentration can be found at any time and temperature as a solution of the first two equations of the above system which we solved by the Runge–Kutta method [19] at the heating rates 8, 12 and 16 K min^{-1}. The initial conditions were set: $[A]_0 = 1$, $[P]_0 = 0$. The temperature at which $[A] = 0.9999$ was selected as the initial temperature.

Figure 1 shows the model DSC curves for the single reactions whose AP were set so that the reactions proceed within approximately the same temperature interval. Therefore, the contributions of the reactions to the total heat release will be comparable when these reactions are the components of the process. We now consider six cases of the complex process comprising consecutive reactions (Table 1).

TABLE 1

The Arrhenius parameter values for different cases of the consecutive reactions

Case	E_1/kJ mol^{-1}	A_1/min^{-1}	E_2/kJ mol^{-1}	A_2/min^{-1}
1	125.4	2×10^{14}	167.2	1×10^{19}
2	125.4	4×10^{13}	167.2	1×10^{19}
3	167.2	1×10^{19}	125.4	2×10^{14}
4	167.2	1×10^{19}	125.4	4×10^{13}
5	125.4	2×10^{14}	125.4	4×10^{13}
6	125.4	4×10^{13}	125.4	2×10^{14}

The method of estimating the activation energy

The conversion dependence of the effective activation energy was computed by means of KinTool software, the details of which can be found in ref. 20. The basis of KinTool is the isoconversional method which allows the activation energy to be estimated from the slope of the linear dependence of $\ln(q/T_w^2)$ against $1/T_w$, where T_w is the temperature corresponding to the same conversion at the different heating rates.

RESULTS AND DISCUSSION

Case 1

The process starts with the reaction having the faster rate in an isolated state (Fig. 1) and the smaller activation energy. The DSC curve for the

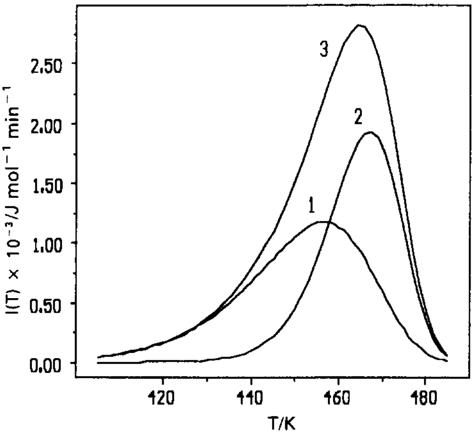

Fig. 2. Heat release of the component reactions (curves 1 and 2) and the DSC curve (3) for the overall process of case 1, heating rate 12 K min^{-1}.

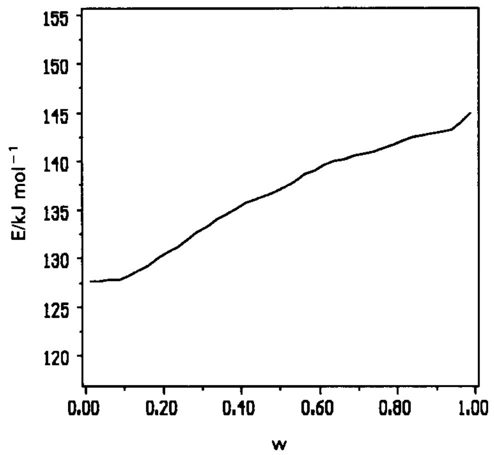

Fig. 3. The conversion dependence of the activation energy for the process in case 1.

process is depicted in Fig. 2. It is seen from the figure that up to 430 K, the DSC curve coincides with the heat release curve of the first reaction. This means that at the very beginning of the process the intensity of the heat release is conditioned by the rate of formation of the intermediate. The intermediate accumulates to approximately 458 K, after which the rate of disappearance of the intermediate becomes higher than its rate of formation. As a result, the contribution of the second reaction becomes determining and this remains the case until the process ends.

Figure 3 displays the conversion dependence of the effective activation energy for the process being considered. At the start of this dependence, the activation energy does not seem to depend on the conversion. Thus the process rate at the very beginning is determined by the single reaction [1], with an activation energy of 127.5 kJ mol^{-1} that can be reliably estimated as a minimum value of the effective one. The final part of the dependence is not flat which indicates that the reaction contributions to the total heat release have become comparable. Thus the maximum value of the effective activation energy (145.1 kJ mol^{-1}) is the average of the activation energies of the single reactions. Evidently such a value can be considered only as a rough estimate of the activation energy of the second step.

Case 2

The process begins with the reaction that has the slower rate in the isolated state (Fig. 1) and the smaller activation energy. The DSC curve for the process is shown in Fig. 4. One can see that at first (420–440 K) the intensity of the total heat release of the process is almost equal to the intensity of the heat released for the reaction forming the intermediate. At higher temperatures (440–475 K), the process proceeds with an increasing

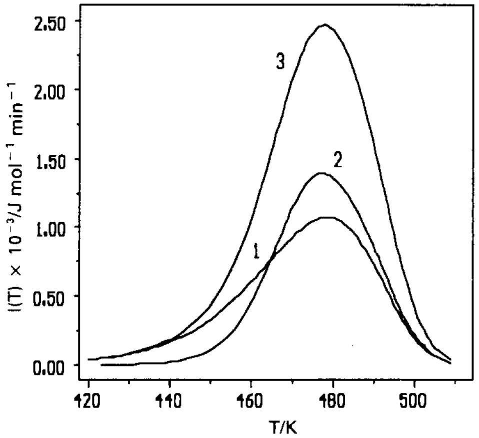

Fig. 4. Heat release of the component reactions (curves 1 and 2) and the DSC curve (3) for the overall process of case 2, heating rate 12 K min^{-1}.

heat-release contribution from the reaction in which the intermediate is consumed. The contribution of this reaction becomes determining after 465 K when the accumulation of intermediate ceases. But, as seen from Fig. 4, after 475 K there is a relative decrease in the heat released from the reaction in which the intermediate disappears. Therefore the intensity of the total heat release of the process is largely determined by the first reaction, at the beginning, then by the second, and then by the first again.

The conversion dependence of the effective activation energy for the process is depicted in Fig. 5. The obtained dependence begins at the activation energy value corresponding to the reaction for the formation of

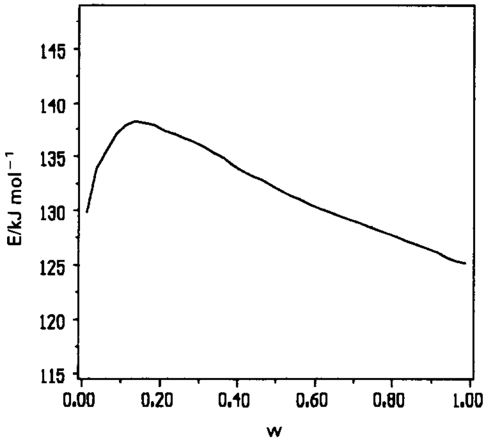

Fig. 5. The conversion dependence of the activation energy for the process in case 2.

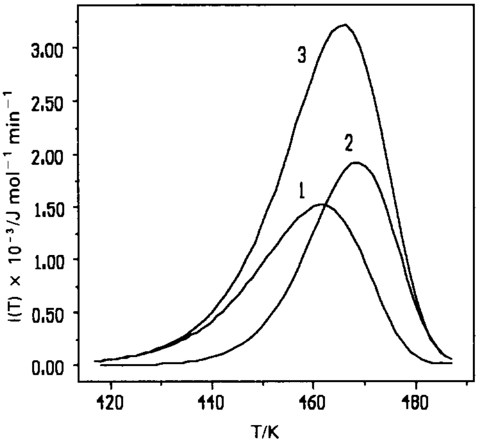

Fig. 6. Heat release of the component reactions (curves 1 and 2) and the DSC curve (3) for the overall process of case 3, heating rate of 12 K min^{-1}.

the intermediate. The ascending part of the dependence indicates that the reaction with the higher activation energy makes a growing contribution to the heat release. Having reached the maximum, the dependence becomes descending because of the relatively decreasing contribution of the reaction with the higher activation energy.

Estimates of the single-reaction activation energies can be obtained as the maximum and minimum values of the effective activation energy. The minimum value (125.4 kJ mol^{-1}) lies at the end of the dependence, where there is no flat trend indicative of a simple (one-stage) process. Thus, it cannot be suggested that such an estimate is close to the true activation energy of one of the reactions. The maximum value of the effective activation energy (138.4 kJ mol^{-1}) is also an approximation. Hence, by analysing the dependence in Fig. 5 we can only estimate approximately the activation energies of the single reactions, but cannot say how close they are to the true values.

Case 3

The process starts with the reaction with the slower rate in the isolated state (Fig. 1) and the higher activation energy. The DSC curve for this process is shown in Fig. 6, from which we can see that the total heat release of the process at the beginning (up to 430 K) is largely determined by the intermediate formation. The accumulation of the intermediate continues until the approximate temperature of 462 K. Then the intensity of the total heat release becomes limited by the reaction of the intermediate transformation. The limiting role of this reaction is kept up to the end of the process.

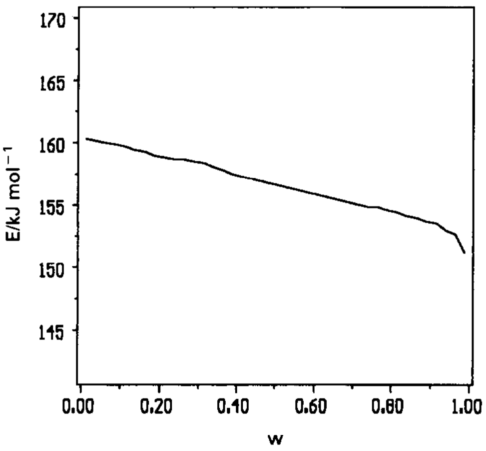

Fig. 7. The conversion dependence of the activation energy for the process in case 3.

Figure 7 indicates that the conversion dependence of the effective activation energy has a descending shape. This suggests that the reaction with the smaller activation energy has a constantly increasing contribution to the total heat release. The activation energies of the single reactions can be estimated as the extreme values of the effective activation energy, i.e. 160.5 and 151.7 kJ mol^{-1}, respectively. But, as in the preceding case, we cannot judge how accurate these estimates are.

Case 4

The process begins with the reaction having the faster rate in the separated state (Fig. 1) and the higher activation energy. The DSC curve for this process is shown in Fig. 8. Comparing the heat release of the whole process and of the single reactions, we see that up to 435 K the total heat release is almost completely conditioned by the reaction of the formation of intermediate. The intermediate accumulates until 470 K. It should be noted that, unlike the previous cases, here the accumulation of intermediate ceases after reaching the maximum rate of its formation (465 K). This means that for this process the reactions of the formation and disappearance of the intermediate are more separated in time from each other than in the previous cases. Therefore, the DSC curve shows a noticeable doubling.

Figure 9 provides the conversion dependence of the effective activation energy for the process. The descending trend of the curve testifies to a constantly decreasing contribution of the reaction with the higher activation energy to the total heat release. For this reaction, the higher activation energy can be estimated as the maximum value of the effective activation energy, 166.4 kJ mol^{-1}, which lies at the start of the dependence. It has already been mentioned that the absence of the conversion dependence of

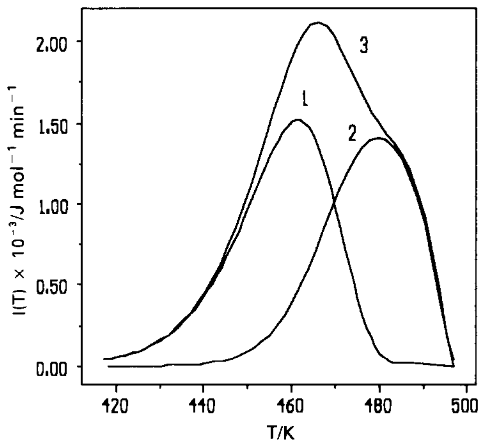

Fig. 8. Heat release of the component reactions (curves 1 and 2) and the DSC curve (3) for the overall process of case 4, heating rate 12 K $\min^{-1}$.

the activation energy indicates that the process rate is conditioned by only one reaction. Thus the value obtained is a fairly reliable estimate of the first reaction activation energy. Because of the double DSC curve, it can be expected that the second reaction makes the main contribution to the total heat release in the final stage. Thus, the minimum value of the activation energy (127.5 kJ mol^{-1}) is expected to be very close to the true value.

Cases 5 and 6

Here we consider two specific cases of the process when the activation energies of both steps are equal. In case 5 the process starts with the

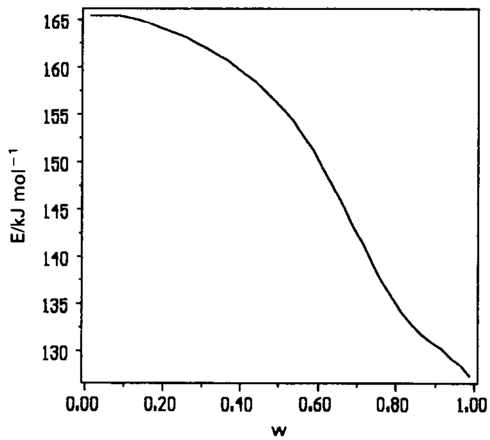

Fig. 9. The conversion dependence of the activation energy for the process in case 4.

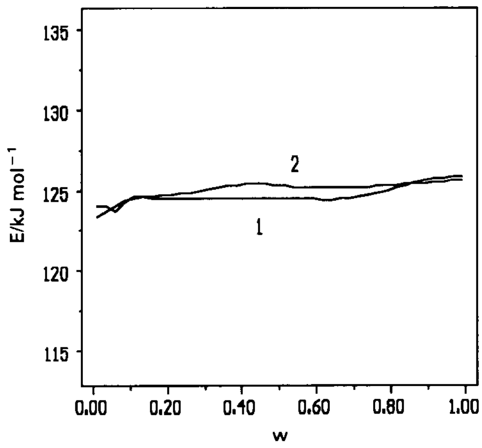

Fig. 10. The conversion dependence of the activation energy for the process in cases 5 (curve 1) and 6 (curve 2).

reaction with the faster rate in the separated state (Fig. 1). In case 6, the process starts with the reaction having the slower rate in the separated state.

These processes reveal no new kinetic regularities in comparison with those considered above. In particular, the DSC curves, characterising the total heat release and the heat release of the component reactions are the same, as depicted in Fig. 8 (case 5) and Fig. 4 (case 6). The conversion dependences of the effective activation energy for these processes are depicted in Fig. 10. Because both dependences are flat we can conclude that the temperature dependence of the overall process rate is governed by one activation energy. In such a case the effective activation energy can be considered a very close estimate for the activation energy of the limiting reaction. From Fig. 10, the effective activation energies of both processes maintain a constant level of about 125 kJ mol^{-1}, which is the activation energy of the component reactions.

It should be noted that the independence of the effective activation energy of the conversion for the cases being considered follows directly from eqn. (1) which, taking into consideration eqn. (2), can be transformed into

$$I(T) = (Q_1A_1[\mathrm{A}] + Q_2A_2[\mathrm{P}])\exp(-E/RT) = A^*f(w^*)\exp(-E^*/RT) \quad (3)$$

where E^* is the effective activation energy, A^* is the effective pre-exponent, w^* is the overall conversion, and $f(w^*)$ is a formal model of the overall process. It is seen from the eqn. (3) that $E^* = E$. Thus, the conversion dependence no longer contains information on the complex process kinetics. All information concerning the contributions of the component reactions to the kinetics of the total heat release is now contained in the conversion dependence of $A^*f(w^*)$, although it cannot be extracted from this term. The problem is that the reaction model $f(w^*)$ can be established from this dependence [21, 22] but only in the case of simple (single-step) processes. For a complex process, when each component reaction obeys its own model, such a dependence shape is simultaneously governed by not only these models, but also by the type (mechanism) of the complex process. Because these factors (the type of complex process and the models of the component reactions) are inseparable, information on the complex process mechanism is not available from the conversion dependence of the $A^*f(w^*)$ term.

The cases considered demonstrate clearly that some of the complex processes can reveal the independence of E^* on w^*. Thus, the independence of the calculated E^* on w^* does not guarantee a single-step (simple) process, and a complex process may also take place. This must be borne in mind when analysing the real macrokinetics of solid-state thermolyses.

GENERALISATION OF THE RESULTS

The above conversion dependences of the activation energy were obtained assuming that the thermal effects of both steps are equal. However, these results can easily be extended to a general case. In particular, from the above we can conclude that the shape of the $E-w$ dependence, as well as the quality of estimating the activation energy, is conditioned by the contributions of component reactions to the total heat release. These contributions, in accordance with eqn. (2), depend not only on the kinetic regularities of the process, but also on the thermal effects of the component reactions. This means that if Q_1 is higher than Q_2, the corresponding $E-w$ dependences have a more pronounced flat portion (cases 1 and 4) at low conversion and the effective activation energy at low conversion is closer to the activation energy of the first reaction (cases 1 and 4). Analogously, an increase in Q_2 leads the final part of the $E-w$ dependence towards the value of the activation energy of the second reaction. Therefore, in the case of non-equal thermal effects, the shape of the obtained $E-w$ dependences will not change substantially.

Nevertheless, as a limiting case, the situation may occur in which the thermal effect of one of the reactions is much higher than that of another. In such a situation, if $Q_1 \gg Q_2$, the DSC curves will only yield information on the $A \rightarrow P$ reaction, i.e. the $E-w$ dependence will be flat and the effective activation energy will be equal to the activation energy of the first reaction. If $Q_1 \ll Q_2$ and the first reaction is faster than the second, the DSC curves will yield information on the $P \rightarrow B$ reaction only, and the effective activation energy will be independent of conversion and equal to the activation energy of the second reaction. But if $Q_1 \ll Q_2$ and the first reaction is limiting, i.e. slower than the second, the DSC curves will describe the overall process and the $E-w$ dependence will correspond to a change from the activation energy of the first reaction to that of the second.

CONCLUSION

Having considered the conversion dependences of the activation energy for the different consecutive reactions, we can conclude the following. Firstly, the shape of such dependences reflects adequately the kinetic regularities of the process. An exception is the specific case when the activation energy of the component reactions are equal. Secondly, the values of the effective activation energy can be used to estimate the activation energy of the individual component reactions. The quality of such an estimate depends on the relative values of the component reaction contributions to the total heat release.

More accurate estimates of the AP could be obtained using the methods of refs. 15-17, as mentioned above. However, these methods are based on the questionable assumption that the model (mechanism) of a complex process is known a priori. But in practice the most frequent case is the absence of any knowledge about the process mechanism. This means that these methods will always confront the perennial problem of the ambiguous identification of the process model. Thus, the high certainty of the above methods merely disguises the AP errors resulting from this ambiguity. This is especially dangerous if the calculated AP are used [16] to solve applied kinetic problems related to predicting the behaviour of a substance under conditions differing from the experimental ones. Algorithms requiring no information about the complex process mechanism to solve applied problems are more safe and reliable [23].

ACKNOWLEDGEMENTS

The author thanks Dr. Wolfgang Linert, Institute of Inorganic Chemistry, The Technical University of Vienna, for his valuable remarks. The support of the Austrian Scientific Foundation (project No. M0055-CHE) is gratefully acknowledged.

REFERENCES

1 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 165 (1990) 273.
2 S.V. Vyazovkin, A.I. Lesnikovich and V.A. Lyutsko, Thermochim. Acta, 165 (1990) 17.
3 S.V. Levchik, E.E. Bolvanovich, A.I. Lesnikovich, O.A. Ivaskevich, P.N. Gaponik and S.V. Vyazovkin, Thermochim. Acta, 168 (1990) 211.
4 S.V. Vyazovkin, V.V. Bogdanova, I.A. Klimovtsova and A.I. Lesnikovich, J. Appl. Polym. Sci., 42 (1991) 2095.
5 S.V. Vyazovkin, V.V. Bogdanova, I.A. Klimovtsova and A.I. Lesnikovich, J. Appl. Polym. Sci., 44 (1992) 2157.
6 C.A. Strydom and D. de Waal, J. Therm. Anal., 38 (1992) 943.
7 S. Vyazovkin, V. Goryachko, V. Bogdanova and V. Guslev, Thermochim. Acta, 215 (1993) 325.
8 D. Skala, M. Sikic, J. Tomic and H. Kopsch, J. Therm. Anal., 35 (1989) 1441.
9 N. Eisenreich and W. Engel, J. Therm. Anal., 35 (1989) 577.

10 F. Paulik, J. Paulik and M. Arnold, Thermochim. Acta, 200 (1992) 195.
11 V. Rakic, V. Dondur and Dj.M. Misljenovic, Thermochim. Acta, 194 (1992) 275.
12 S. Vyazovkin, Thermochim. Acta, 223 (1993) 201.
13 R.K. Agrawal, Thermochim. Acta, 203 (1992) 111.
14 J. Mentel and H. Anderson, Thermochim. Acta, 187 (1991) 121.
15 N.I. Vaganova, V.I. Rozenband and V.V. Barzykin, J. Therm. Anal., 34 (1988) 71.
16 E. Kaiserberger and J. Opfermann, Thermochim. Acta, 187 (1991) 151.
17 J. Opfermann and E. Kaiserberger, Thermochim. Acta, 203 (1992) 167.
18 R. Shmid and V.N. Sapunov, Non-Formal Kinetics, Verlag Chemie, Weinheim e.a., 1982.
19 G.A. Korn, T.M. Korn, Mathematical Handbook, McGraw-Hill, New York, 1968.
20 S. Vyazovkin and V. Goryachko, Int. Labmate, 17 (1992) 21.
21 V.T. Gontkovskaya, N.S. Gordopolova, N.I. Ozerkovskaya and N.I. Peregudov, Khim. Fiz. (Russ. J. Chem. Phys.), 7 (1988) 214.
22 J. Malek, Thermochim. Acta, 200 (1992) 257.
23 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 203 (1992) 177.