Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 1, 163–173

ADVANCED KINETICS-BASED SIMULATION OF TIME TO MAXIMUM RATE UNDER ADIABATIC CONDITIONS

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An adiabatic calorimeter is very often used for the investigation of runaway of exothermic reactions. However the ideal adiabatic environment is a theoretical state which during laboratory scale testing cannot be obtained but may only be approached. Deviation from the fully adiabatic state comes from (*i*) the thermal inertia of the test system or heat lost into the sample container and (*ii*) the loss of heat from the container itself to the environment that reflects the 'operational adiabaticity' of the instrument. In addition to adiabatic testing, advanced kinetic approach based on the kinetic parameters determined from DSC data performed under different heating rates can be applied. It enables to simulate what may happen on a large scale by testing and up-scaling results obtained with a small amount of the sample.

The present study describes the method of the evaluation of kinetic parameters of the coupling reaction of aniline with cyanamide in water/HCl from the DSC signals measured in non-isothermal experiments carried out with the rates of 0.5–8 K $\min^{-1}$. The reaction rate and reaction progress in adiabatic conditions were predicted after introducing the kinetic description of the reaction into the heat balance equations. It enabled to calculate the thermal safety diagram depicting the runaway time as a function of the process temperature. The influence of thermal inertia of the system, expressed by the Φ-factor, on the reaction course in concentrated and diluted reactant solutions was determined and discussed.

Keywords: *adiabatic conditions, aniline, cyanamide, DSC, Φ-factor, thermal decomposition kinetics, thermal runaway, time to maximum rate (TMR)*

Introduction

It is known that the DSC signals monitoring progress of the reactions can be used not only for the qualitative and quantitative analysis but for the kinetic description of the process as well [1]. After determination of the kinetic parameters of the investigated reaction the main challenge is the prediction of the thermal stability of the substance in both: extended temperature ranges and at the temperature conditions for which the collection of the experimental data is difficult or impossible. These difficulties are prevalent at low temperatures (requiring very long investigation times), and under specific temperature profiles such as modulated temperature changes or experiments containing simultaneous isothermal and non-isothermal temperature modes. In all these DSC experiments carried out with mg-scale samples the heat evolved or consumed in the reaction is fully exchanged with the environment, thus not influencing the reaction rate. This is not the case when the investigations are carried out with the samples in kg or Mg-scale where part of, or, in an ideal adiabatic system, all heat stays in the sample. Therefore, during up-scaling two important factors have to be considered: (*i*) the application of advanced kinetics, which properly describes the complicated, multistage course of the decomposition process, (*ii*) the effect of heat accumulation in the energetic system, as the sample mass is increased by a few orders of magnitude compared to the thermoanalytical experiments.

The application of the kinetic parameters for the description of the thermal behaviour of larger amount of substance is possible because the kinetics of any reaction does not depend on the sample mass and is the same for ten milligrams of substance and for one ton.

Experimental

During the synthesis of an intermediate product required in the production of an active pharmaceutical ingredient (API) a 50 mass/mass% of the aqueous solution of cyanamide is mixed with the aniline and heated up to 60°C. At that point, the hydrochloric acid is dosed to the reaction mixture, what leads to the

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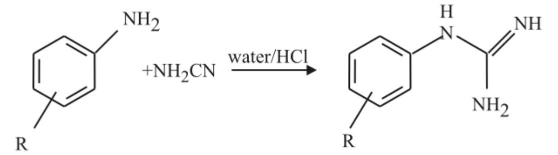

Fig. 1 Scheme of coupling reaction of the aniline with cyanamide in water/HCl

desired coupling reaction. The reaction scheme is given in Fig. 1. This reaction proceeds relatively fast with a high yield of high purity product. One of the reactants, the cyanamide, is very unstable and starts to decompose slowly already above the ambient temperature. Due to the high exothermicity of the coupling reaction, dosing of hydrochloric acid needs to be done slowly, resulting in relatively long reaction times, typically more than ca. 4 h. In this timeframe, the decomposition of the cyanamide takes already place with a considerable rate what leads to the competition between the main, coupling reaction and the undesired decomposition of the reactant. Since the decomposition of the cyanamide is very exothermic as well, this results in a serious safety problem. In the hazard analysis, the most credible runaway scenario was deemed to originate from a cooling failure right before the start of the reaction, when the temperature of the reaction mixture has reached already 60°C and hydrochloric acid has not been added yet. In this scenario, the cyanamide would start to decompose, at first slowly, but then faster as the decomposition proceeds almost under adiabatic conditions. Key issue in this scenario is the heat generation at the reflux temperature. If this heat generation is too high, flooding of the vapour lines could lead to the possible subsequent ejection of the reaction mixture. The detailed evaluation of the decomposition reaction of the cyanamide is therefore a very important factor in the safety analysis of this coupling reaction.

In the laboratory scale, the process was investigated with two, concentrated and diluted reaction mixtures. At room temperature, the reaction mixture is heterogeneous and changes to homogeneous at temperatures around 60°C. The specific heat, determined from a Mettler RC1 experiment (Quickcal procedure), was 2.7 J g^{-1} K^{-1} (at 65°C) and 3.4 J g^{-1} K^{-1} (at 60°C) for the concentrated and diluted mixtures, respectively. The adiabatic calorimeter experiments were performed with glass cans having a Φ-factor of about 1.25 for the aqueous solutions. DSC data used for the determination of the kinetic parameters of the reaction were supplied by Janssen Pharmaceutica (Belgium). Experiments were performed in gold plated 20 μL high pressure sealed crucibles [2] at different heating rates ranging from 0.5 to 8 K min^{-1} with a sample mass between 10 and 20 mg in range of 30 to 300°C. Figure 2a shows the DSC signals recorded at heating rates of 0.5, 1, 2, 4 and 8 K min^{-1}. Experiments were also performed in a C80 calorimeter with the high pressure vessels at lower rates (0.1, 0.2, 0.5 and 1 K min^{-1}) and with larger sample mass in the range of 1 g. The adiabatic experiments were performed in a HEL Phi-Tec calorimeter. Glass cans with magnetic stirring were used.

Elaboration of the experimental data

Selection of the evaluation range and determination of the baseline

The key issue for receiving meaningful kinetic parameters is the correct determination of the dependence of the reaction progress α on time (t) or temperature (T). This is relatively easy task if the process is investigated by thermogravimetry (TG) when the recorded mass changes reflect the course of the reaction. However, the problem is much more complicated when α–T or α–t dependences have to be extracted from the DTA or DSC data. This procedure requires the integration of the signals which may be significantly influenced by the improper construction of the baseline [3]. Before the determination and optimization of the course of the baseline in DSC experiments, one has to select the evaluation range which should contain the certain amount of the experimental points just before and just after the occurrence of the measured thermal event. For safety issues, the experiments should be run in ‘closed high pressure sealed crucibles’ (isochoric conditions) in order to consider the influence of the pressure on strongly pressure dependent reactions [2]. The DSC runs should be continued to the temperatures laying slightly after the end of the reaction, because the thermokinetic approach requires the knowledge of the baseline after the final peak for the determination of the heat of the reaction. It is obvious that the integration of DSC signal is influenced by the method chosen for the determination of the baseline as it was discussed in our previous paper [4].

The construction of the baseline for the DSC signal recorded with a heating rate of 4 K min^{-1} is depicted in the Fig. 2b. It can be seen that the course of the baseline can significantly influence the determination of the heat of the reaction and the estimation of the α–T dependence what, in turn, will significantly influence the determination of the kinetic parameters. Since, generally, we do not know the value of the heat of reaction we are measuring, its standard deviation may help in estimation how reliable our measurements and baseline construction are. If the isoconversional principle applies to the

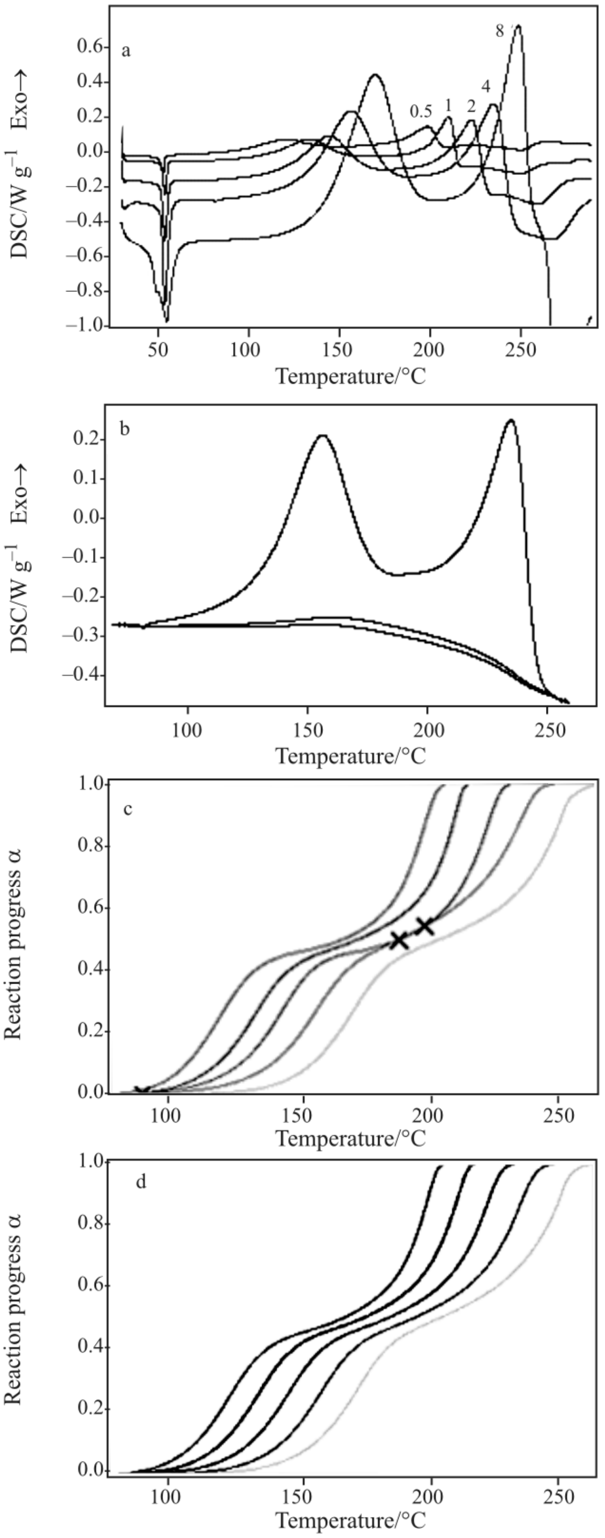

Fig. 2 a – As-received DSC curves of the examined material recorded under different heating rates (marked on curves in K min^{-1}). The signals after selection of the evaluation range required before the construction of the baseline; b – the construction of the baseline can significantly influence the determination of the heat of the reaction and c – the estimation of the α–*T* dependence; d – α–*T* dependence after the optimization of all baselines

examined reaction, the heat of reaction should be independent of the heating rate and therefore the same for all considered thermoanalytical curves. Depending on the quality of the measured data, the additional adjustment of the baseline construction enables a better estimation of the average heat of reaction for all curves. The values of the reaction heat used later for the kinetic evaluation should have the maximal standard deviation lower than 10% (ΔH_r±10%). In addition, a kinetically dependent relationship should be retrieved when plotting the reaction progress as a function of the temperature. Consequently, when increasing heating rate one should observe the shift of α–*T* dependences into the direction of the higher temperatures. The crossing curves, as those observed in Fig. 2c, indicates the necessity of the correction of the shape of the baseline and confirms the improper relationship α–*T*. To avoid crossing curves three procedures should be applied:

- slight modification of the tangents at the beginning or at the end of the signals
- minor change of the temperature range of the selected of thermal analysis curves
- new measurements when necessary.

The very important feature of the AKTS-Thermokinetics Software [1] is the possibility of the optimization of the baseline for all experiments collected at different heating rates (or temperatures) so that the random errors in the various baseline constructions for all heating rates will 'average themselves out'. This will result in the correct course of the α–*T* dependences as this one presented in Fig. 2d.

Determination of the kinetic parameters

It is generally accepted that only series of non-isothermal measurements carried out at different heating rates can give a data set which contains the necessary amount of information required for full identification of the complexity of a process [4, 5]. The noticeable weakness of the 'single curve' methods (determination of the kinetic parameters from single run recorded with one heating rate only) has led to the introduction of the 'multi curve' methods over the past few years, as discussed in the International ICTAC Kinetics project [6–9].

The following equation relating reaction rate and reaction progress is commonly used in the heterogeneous kinetics:

$$d\alpha/dt = K(T)f(\alpha) \qquad (1)$$

where $f(\alpha)$ is the reaction progress function dependent on the reaction mechanism, T is temperature and K the rate constant which dependence on the temperature is assumed to follow the Arrhenius equation:

$$K = A\exp\,(-E/RT) \qquad (2)$$

where A – pre-exponential (or 'frequency') factor, E – activation energy and R – gas constant.

Combination of these two equations results in the expression:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT(t)}\right)f(\alpha) \qquad (3)$$

There are two general methods of the determination of the kinetic parameters based on the above equation: (*i*) so-called 'model fitting' methods applying the f(α) function which has to be known or arbitrarily assumed before calculations. All three kinetic parameters i.e. E, A and the form of the function $f(\alpha)$ are assumed to be constant during the course of the reaction. (*ii*) isoconversional methods in which the assumption concerning the reaction mechanism is not required and E and A can vary during the reaction.

Because decomposition reactions usually have a multi-step nature, the isoconversional analysis enables a more accurate determination of the kinetic characteristics than simplified kinetic approaches which states that kinetics of complicated processes may be correctly described by just one value of the A, E and that the $f(\alpha)$ function can be applied in the form of zero- or first- or n^{th} order expressions.

Isoconversional methods

These methods of the determination of the kinetic parameters are based on so-called isoconversional principle saying that the reaction rate at constant reaction progress α is only a function of temperature. They allow determination of the activation energy (or dependence E on α) without assuming the explicit form of $f(\alpha)$. The kinetic parameters are not assumed to be constant during the course of the reaction. All isoconversional methods are based on the determination of temperatures corresponding to a certain, arbitrarily chosen values of the conversion extent α recorded in the experiments carried out at different heating rates β or at different temperatures.

There are three main modifications of the isoconversional method:

- differential (Friedman) [10]
- integral (Flynn–Ozawa–Wall) [11, 12]
- advanced integral based on non-linear procedure (Vyazovkin) [13].

One has to mention the method based also on the isoconversional principle namely ASTM E698 [14].

A detailed analysis of the differential and integral isoconversional methods for the determination of the activation energy has been reported by Budrugeac [15]. The convergence of the activation energy values obtained by means of a differential method like Friedman [10] with those resulted from using integral methods with integration over small ranges of reaction progress α comes from the fundamentals of the differential and integral calculus. In other words, it can be mathematically demonstrated that the use of isoconversional integral methods for too large ranges of the reaction progress can yield systematic errors. These errors depend directly on the size of Δα over which the integration is performed and can be avoided by using infinitesimal ranges of reaction progress Δα. As a result, the isoconversional integral methods turn into the differential isoconversional method formerly proposed by Friedman [10].

Differential method of Friedman

The results of isoconversional differential Friedman method are depicted in Fig. 3 for concentrated (left) and diluted (right column) reactant mixtures. The figure presents the dependence of the reaction rate on the reciprocal temperature (Fig. 3a), dependence of E and A on the reaction progress (Fig. 3b) and comparison of the experimental and calculated reaction rates (Fig. 3c).

The Friedman analysis, based on the Arrhenius equation, applies the logarithm of the conversion rate $\mathrm{d}\alpha/\mathrm{d}t$ as a function of the reciprocal temperature at different degrees of the conversion α:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}\bigg| = \ln[A_{\mathrm{i}}f(\alpha_{\mathrm{i,j}})] - \frac{E_{\mathrm{i}}}{R}\frac{1}{T_{\mathrm{i,j}}} \qquad (4)$$

with i: index of conversion, j: index of the curve and $f(\alpha_{\mathrm{i,j}})$ the function dependent on the reaction model that is constant for a given reaction progress $\alpha_{\mathrm{i,j}}$ for all curves j. As $f(\alpha)$ is constant at each conversion degree α_{i}, the method is so-called 'isoconversional'. The ratio $-E_\alpha/R$ and $\ln[A_\alpha f(\alpha)]$ are the slope and the intercept with the vertical axis of the plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t_\alpha)$ *vs.* $1/T_\alpha$, respectively. It is then possible to make kinetic predictions at any temperature profile $T(t)$, from the values of E_α and $[A_\alpha f(\alpha)]$ extracted directly from the Friedman method by using the following expression:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t_\alpha} = [A_\alpha f(\alpha)]\exp\left(-\frac{E_\alpha}{RT(t_\alpha)}\right) \qquad (5)$$

where t_α, $T(t_\alpha)$, E_α and A_α are the time, temperature, apparent activation energy and preexponential factor, respectively, at conversion α.

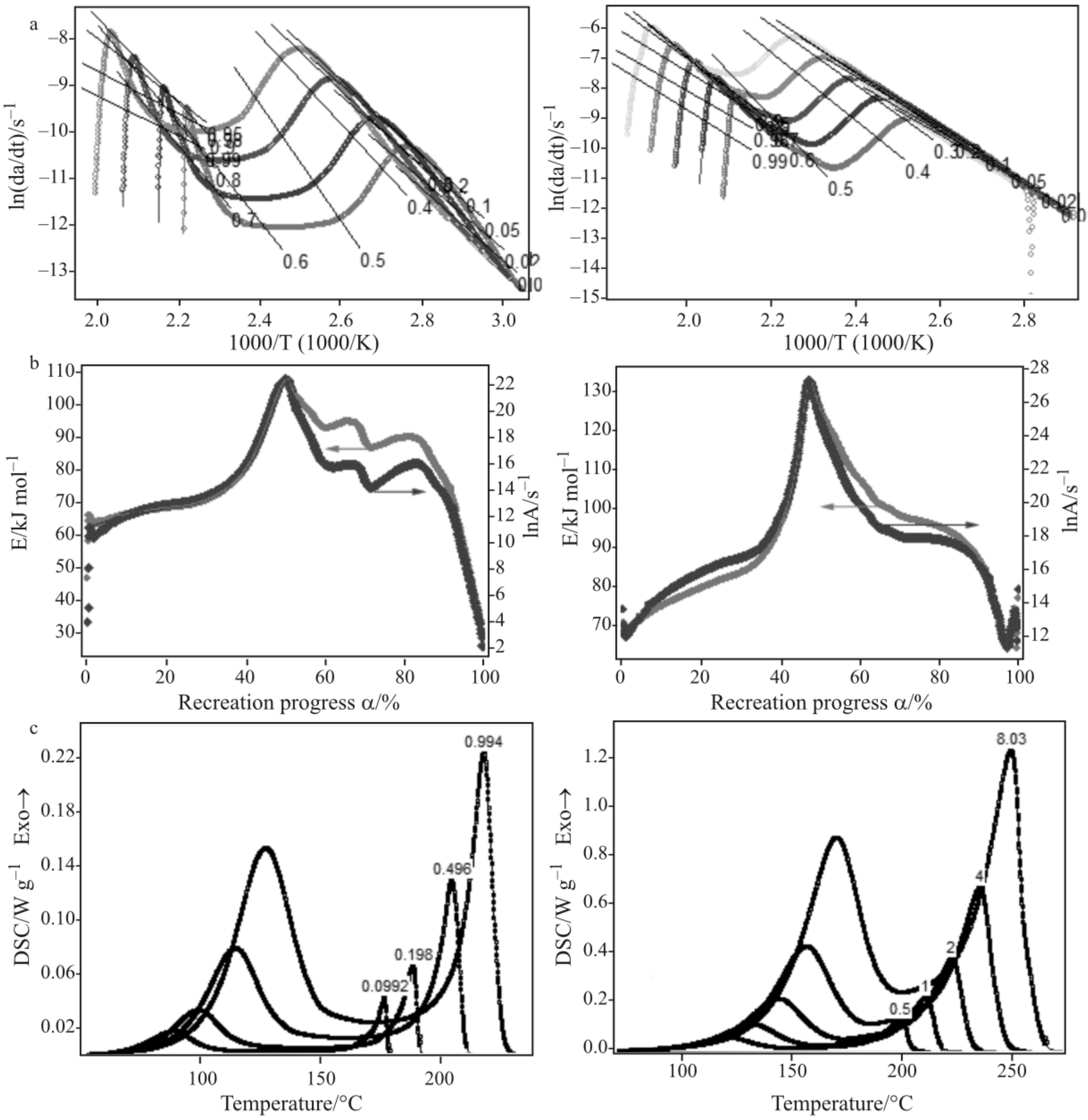

Fig. 3 a – Friedman analysis: The logarithm of the reaction rates is presented as a function of the reciprocal temperature. The Friedman method allows finding the Arrhenius dependence for any, arbitrarily chosen decomposition progress. Left column (C80): concentrated, right column (DSC): diluted solution; b – activation energy and pre-exponential factor as a function of the reaction progress; c – reaction rates (normalized DSC-signals simulated with the use of the kinetic parameters obtained from the experimental data after baseline optimization). Experimental data are represented as symbols, solid lines represent the calculated signals. The values of the heating rates are marked on the curves

No specification of the reaction model term, $f(\alpha)$, is necessary for the kinetic prediction since it requires (Eq. (5)), along with E_α, only the product term, $[A_\alpha f(\alpha)]$, which is experimentally extracted from the kinetic experiment according to Eq. (4). However, nothing can be inferred about the pre-exponential factor, A_α, unless $f(\alpha)$ is assumed to have some particular form (first-order reaction, nucleation-growth, etc.). And when $f(\alpha)$ is associated with a specific reaction model, still the experimentally extracted product term $[A_\alpha f(\alpha)]$ remains unchanged. AKTS-Thermokinetics Software and AKTS-Thermal Safety Software [1] take advantage of this unique property of the Friedman method of the isoconversional kinetics evaluation and enable determination and displaying, in arbitrarily chosen form, the apparent 'first-order pre-exponential factor', A_α (Fig. 3b).

Kinetics at milligram scale

Prediction of the reaction progress under any temperature mode

The kinetic parameters calculated from the non-isothermal experiments validated by the very good fit of

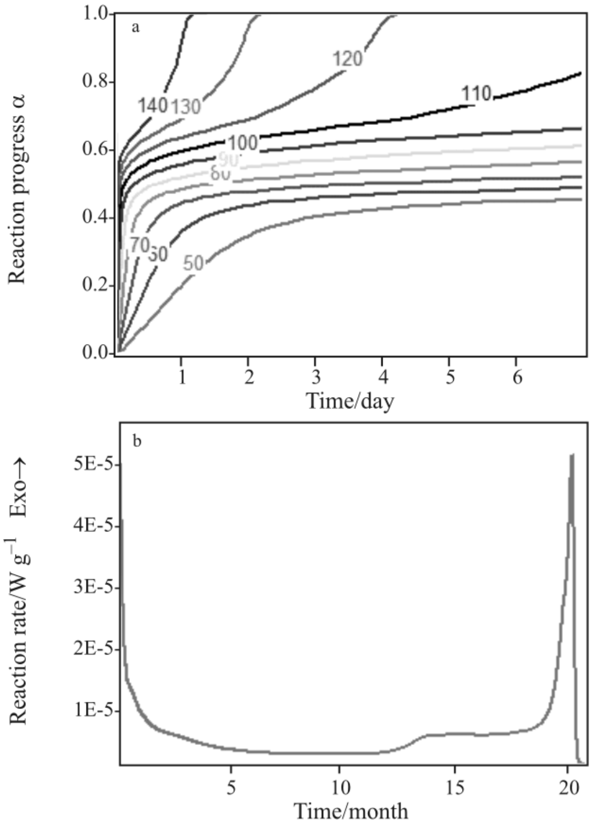

Fig. 4 Isothermal temperature mode; a – calculated reaction progress (normalized signals) as a function of time (temperatures in °C are marked on the curves); b – calculated reaction rate at 60°C. The shape of the curve reflects a 'non self-accelerating reaction type' at the beginning of the decomposition process followed by a strongly 'self-accelerating reaction type' but only after ca. 20 months at that temperature

the simulated and experimental data, as depicted in Fig. 3c, can now be applied for the prediction of the reaction progress at any temperature mode [1]. The prediction of the reaction progress at different constant temperatures is illustrated in Fig. 4. The decomposition reaction clearly involves at least two reaction steps: the first depicting a non-self-accelerating effect and the second one demonstrating a strong self-acceleration typical for autocatalytic reactions.

Kinetics at tones scale

Prediction of adiabatic behaviour from the results of non-isothermal DSC measurements

Above presented results illustrate the possibility of the prediction of the course of the thermal degradation of the investigated material if the sample mass is in the range of few milligrams as in conventional DSC experiments, where it is possible to accurately control the temperature of the examined material. Due to the ideal heat transfer in isothermal or non-isothermal experiments all heat evolved during reaction (let us consider the exothermic reaction) is exchanged with surroundings and decomposition takes place at the constant temperature or under constant heating rate. The situation is radically different if we perform the reaction with the sample e.g. in Mg scale (ton-scale). We should consider here the adiabatic conditions that are usually assumed when working with more than one cubic meter of the substance. Such a situation represents e.g. the scenario of the cooling failure of the batch reactor. Under adiabatic conditions all heat evolved during reactions is accumulated in the system what leads to, firstly very slow, and later, very fast increase of the sample temperature and self-heat rate which can result in runaway process. The adiabatic induction time is defined as the time which is needed for self-heating of the sample from the starting temperature to the time of maximum rate (TMR_{ad}) under adiabatic conditions. The key parameters characterising the adiabatic process are: ΔT_{ad}: the adiabatic temperature rise, TMR_{ad}: time to maximum rate, and Max SHR: maximum self-heat rate. The precise determination of the time to maximum rate under adiabatic conditions is necessary for the safety analysis of many technological processes [16–19].

Taking into account the heat evolved during the reaction and considering its influence on the reaction rate calculated from the kinetic parameters obtained from the data collected by means of DSC it is possible to simulate the behaviour of an adiabatic calorimeter. Additionally, one has to take into considerations the thermal inertia (characterized by the Φ-factor) i.e. the heat lost into the reaction vessel.

Heat balance over the sample inside the vessel may be expressed by the equation:

$$M_{\mathrm{s}}C_{\mathrm{p,s}}\frac{\mathrm{d}T_{\mathrm{s}}}{\mathrm{d}t}+M_{\mathrm{c}}C_{\mathrm{p,c}}\frac{\mathrm{d}T_{\mathrm{c}}}{\mathrm{d}t}+M_{\mathrm{x}}C_{p,x}\frac{\mathrm{d}T_{\mathrm{x}}}{\mathrm{d}t}= \\ =UA(T_{\mathrm{env}}-T_{\mathrm{c}})+M_{\mathrm{s}}\Delta H\frac{\mathrm{d}\alpha}{\mathrm{d}t} \qquad (6)$$

with M: mass, C_{p}: specific heat, T: temperature, U: heat transfer coefficient, A: contact surface between the solution and the container, ΔH: heat release, indices c, s, x and env: container (or bomb in the adiabatic calorimeter experiment), sample, solvent and environment, respectively. The specific case when the dissociation of the dissolved compound is different than those of pure substance is not considered here, being out of the scope of the presented paper. In a fully operationally adiabatic environment all the heat released goes to the solution and the container (this is the case when $T_{\mathrm{env}}=T_{\mathrm{c}}$ or $U=0$). If there is thermal equilibrium within the solution and the bomb, i.e.:

$$T(t) = T_c(t) = T_s(t) = T_x(t) \rightarrow \frac{dT}{dt} = \frac{dT_c}{dt} = \frac{dT_s}{dt} = \frac{dT_x}{dt}$$

then the whole system will have the same temperature rise and we can simplify Eq. (6) to:

$$\frac{dT}{dt} = \frac{M_s C_{p,s}}{M_c C_{p,c} + M_s C_{p,s} + M_x C_{p,x}} \frac{\Delta H}{C_{p,s}} \frac{d\alpha}{dt} \tag{7}$$

that can be rewritten as

$$\frac{dT}{dt} = \frac{1}{\Phi} \Delta T_{ad.real} \frac{d\alpha}{dt} \tag{8}$$

with:
the adiabatic temperature rise:

$$\Delta T_{ad,real} = \frac{\Delta H}{C_{p,s}} \tag{9}$$

the Φ factor:

$$\Phi = \frac{M_c C_{p,c} + M_s C_{p,s} + M_x C_{p,x}}{M_s C_{p,s}} \tag{10}$$

the reaction rate:

$$\frac{d\alpha}{dt} \tag{11}$$

When applying isoconversional analysis which allows the variation of E and A during the reaction course, the rate of the reaction at any specific reaction progress α can be expressed as:

$$\frac{d\alpha}{dt_\alpha} = [A_\alpha f(\alpha)] \exp\left(-\frac{E_\alpha}{RT(t_\alpha)}\right) \tag{12}$$

Using the presented above equation (Eq. (8)) describing the heat balance under experimental conditions and kinetic description of the process (Eq. (12)) one can now predict the reaction progress $\alpha(t)$ and the rate $d\alpha/dt$ as well as the development of the temperatures $T(t)$ and dT/dt and, finally, the adiabatic induction times at any selected starting temperatures.

It comes from the above equations that the value of the Φ-factor influences the simulation of an adiabatic calorimeter experiment and the prediction of the thermal behaviour of the batch reactor. The problem of matching Φ-factor of the experimental system to that of full-scale system and the review of the Φ-factor during runaway conditions have been reported by Townsend *et al.* [19] and Wilcock *et al.* [20], respectively.

The change of Φ factor influences the ΔT_{ad} (measured) due to the relationship:

$$\Delta T_{ad}\ (\text{measured}) = \frac{1}{\Phi} \Delta T_{ad}\ (\text{real}) \tag{13}$$

- the maximum self-heat rate (max SHR)
- and the TMR_{ad}, differently, depending on the decomposition kinetics.

Commonly applied, the standard method of correcting the TMR_{ad} due to the imperfect adiabatic conditions in the reaction vessel is based on the equation

$$TMR_{ad}\ (\text{real}) = \frac{1}{\Phi} TMR_{ad}\ (\text{measured}) \tag{14}$$

However, this relationship is only a very general approximation. The precise correction of the effects of the thermal inertia of the system on the results of the adiabatic calorimetric experiments should be rather performed by applying advanced kinetic description of the process with a heat balance as proposed in this section.

The application of the DSC data for the simulation of the adiabatic measurements seems to be, for the first glance, not obvious. However, the closer look on the differences and similarities of the processes occurring under different conditions of the heat exchange allows to understand that the adiabatic properties such as self-heating rate or time to maximum rate can be correctly determined from the DSC results obtained or isothermally, or better, at different heating rates. The main difference between DSC run and fully adiabatic process lays in the conditions of the heat exchange. Due to the fact that in the thermoanalytical experiments the heat evolved during reaction is fully exchanged with the environments, the heating rates under which the experiment are carried out can be arbitrarily chosen. In turn, after determination of the kinetic parameters from the results of few experiments done with different heating rates, one can predict the reaction rate under any temperature ramp. Such a simulation was presented in Fig. 3c.

In adiabatic conditions the heating rate of the process (called now self-heating rate) cannot be controlled anymore, being dependent only on the kinetics, adiabatic temperature rise and Φ-factor. However, even in this case we can simulate the reaction rate. The scheme of the general idea of this procedure is presented in Fig. 5.

Let us assume that the temperature increase under adiabatic conditions in the coordinates time–temperature can be presented schematically as in Fig. 5 in the form of four sequences of the short periods of time Δt in which the heating rate is constant. In time periods 0–t_1, t_1–t_2, t_2–t_3 and, finally, t_3–t_4, the heating rates are β_1, β_2, β_3 and β_4, respectively. As shown previously in Fig. 3c and in the

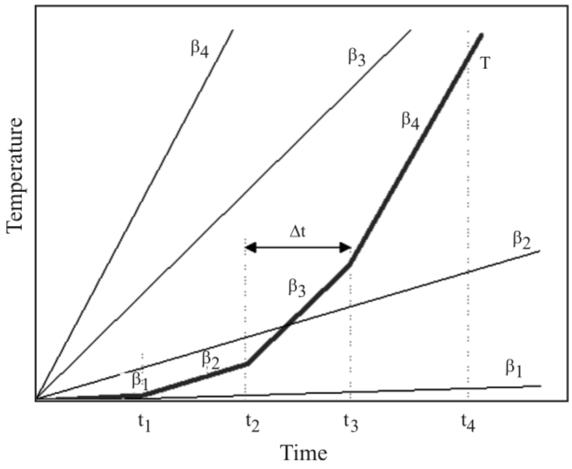

Fig. 5 Scheme of the presentation of the adiabatic temperature rise in the form of four sequences of the time periods Δt in which the heating rates are constant and amount in turn to β_1, β_2, β_3 and β_4

section ‘Kinetic in milligram scale’ one can easily predict the reaction rate under any β value. During the temperature change schematically presented in Fig. 5, the reaction course can therefore be calculated as a sequence of processes occurring at known heating rates β_1– β_4. Using the infinitesimal Δt values for the description of the self-heating rate one can, using the Eq. (8) and procedure applied in DSC experiments, predict the reaction course under the adiabatic temperature change. The process occurring under adiabatic temperature rise is expressed as a succession of an infinite number of processes occurring at constant heating rates which can now be easily calculated by described method.

Thermal safety diagram: runaway time as a function of process temperature under adiabatic conditions ($TMR_{ad}=f(T)$)

The time to maximum rate under adiabatic conditions for any starting temperatures can be determined from the Eq. (8) applying: (*i*) kinetic data obtained from DSC results and (*ii*) heat balance under adiabatic conditions.

In other words, one can predict, for an arbitrarily chosen starting temperature, after which time a runaway reaction will occur assuming the ideal adiabatic conditions (U=0) without any heat transfer to or from the investigated material. After solving both above presented differential equations we will obtain the thermal stability diagram, depicting the dependence of the adiabatic induction time TMR_{ad} on the starting temperature (Fig. 6a). A TMR_{ad} of 24 h is reached for starting temperatures of 37°C. The data used for the calculations were following: heat release determined from C80 experiments ΔH= 554.3±53.7 J g^{-1}, the heat capacity (C_P=2.7 J g^{-1} K^{-1} at 60°C). Due to the fact that the value of the heat release applied in these calculations has been determined with the standard deviation of ca. 10%, the confidence interval (determined for 95% probability) for 37°C is laying between 18 and 34 h.

The simulation of the sample temperature (confidence interval for 95% probability, the same ΔH and C_P) under adiabatic conditions for the starting temperature of 37°C is presented in Fig. 6b. Depending on the decomposition kinetics and ΔT_{ad}, the choice of the starting temperature strongly influences the adiabatic induction time.

In practice, it is very difficult to perform real adiabatic measurements with a Φ-factor close to unity. The current approach enables however to perform simulations of virtually any adiabatic runaway scenario and for any Φ-factor. By varying the heat transfer coefficient U or the Φ-factor, it is

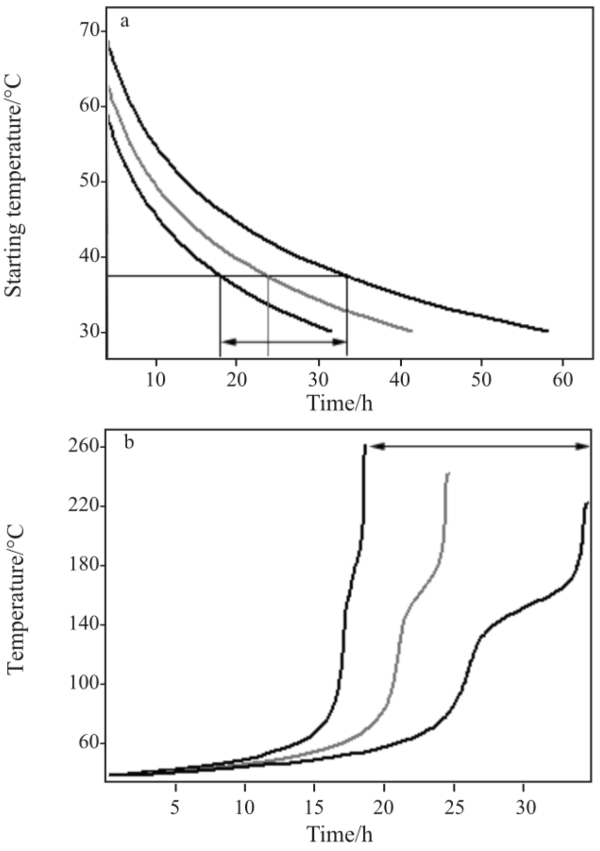

Fig. 6 a – thermal safety diagram of the concentrated solution: Dependence of adiabatic induction time TMR_{ad} on starting temperature calculated for the following parameters: ΔH=554.3±53.7 J g^{-1} and $\Delta T_{ad}=\Delta H/C_P/\Phi$= 205±19.8°C for Φ=1 and C_P=2.7 J g^{-1} K^{-1}. (Confidence interval is marked by an arrow); b – change of the sample temperature (confidence interval is marked by an arrow) under adiabatic conditions for starting temperature T_{begin}=37°C and the same simulation parameters

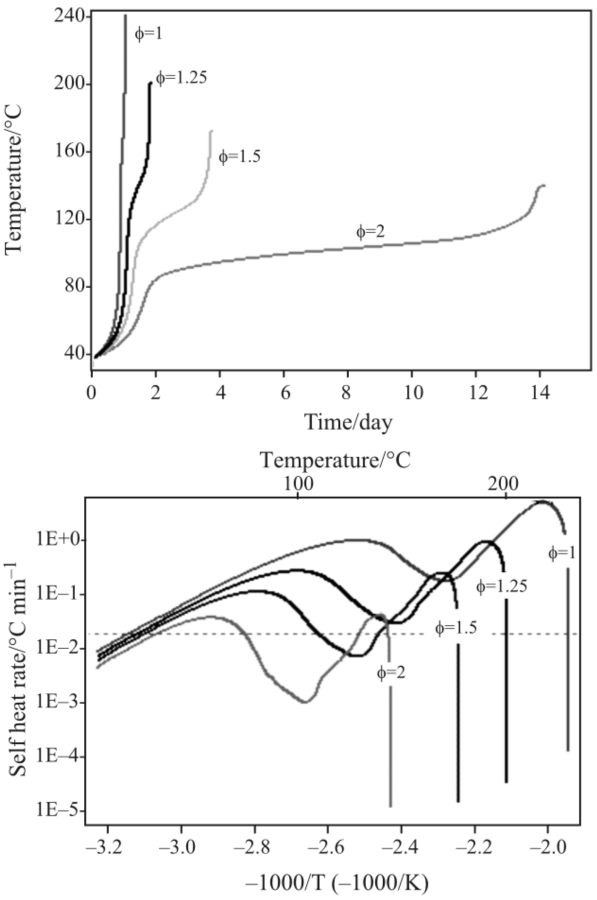

Fig. 7 Simulation of the thermal behaviour under adiabatic conditions of the concentrated solution for different Φ-factors calculated for the following parameters: T_{begin}=37°C, ΔH=554.3±53.7 J g^{-1}, C_P=2.7 J g^{-1} °C^{-1}; a – adiabatic runaway curves; b – self-heat rate curves. ΔT_{ad} for Φ factors of 1; 1.25; 1.5 and 2 amounted to 205±19.8; 164±15.9; 136±13.2 and 102±9.9°C, respectively

possible to reproduce the non-adiabatic conditions or the thermal runaway as observed in an adiabatic calorimeter experiment. Figures 7a and b present such calculations performed for different Φ-factors with the same starting temperature of 37°C and the same simulation parameters as before (see caption of Fig. 6). One can note the very strong influence of the Φ-factor on the TMR$_{\text{ad}}$ and maximum SHR.

Note that the isothermal conditions can be retrieved by setting an exceptionally low value for ΔT_{ad}. If $\Delta T_{\text{ad}} \to 0$°C

$$\text{then } \frac{\mathrm{d}T}{\mathrm{d}t} \cong 0$$

$$\text{and } T(\alpha = 0) \cong T(\alpha = 1) \cong T_{\text{isothermal}}$$

Since the considered process should be run at 60°C (Experimental), the thermal safety diagram for the concentrated solution depicted in Fig. 6a indicates that the use of the concentrated solution results in a TMR$_{\text{ad}}$ shorter than 24 h. In such a situation, the process is considered as not sufficiently safe and therefore not acceptable for introduction in the production. An approach was therefore needed to change the process in such a manner that it would become intrinsically safe, without interfering with the high yield and quality of the obtained product. This was achieved by diluting the mixture of the reactants with an additional amount of the solvent, in this case water. The rough approximation applying a Φ-factor= 1.5 (chosen for the simulation of the diluted system) leads to a TMR$_{\text{ad}}$ of 46 h. This dilution acts as a heat sink for the heat generated decreasing therefore the adiabatic temperature rise. However, since a lower overall concentration of the reactants results in a decrease the reaction rate, it was than necessary to perform new set of DSC experiments in order to determine the influence of the dilution on the reaction kinetics (results presented in the right column of Fig. 3). In addition, the same reaction conditions were tested in an adiabatic calorimeter for the concentrated and diluted solutions to confirm the effect of the dilution on the resulting TMR$_{\text{ad}}$, and to confirm experimentally the expected decrease in severity of the runaway reaction. The reaction was started at 73°C, a final temperature of 165°C was reached after 160 min for the concentrated solution (Fig. 8a) and 170°C after 11.5 h for the diluted solution (Fig. 8b). Both experiments were conducted in a glass test cell with a Φ-factor of 1.25. Due to the evolution of the gaseous products (confirmed by pressure experiments) occurring during the second stage of the decomposition, the reaction process was aborted after the first stage, in order to prevent triggering the second decomposition stage. Such a decomposition reaction could result in rupture of the test cell. The results presented in Fig. 4b indicated also that reaction rate of the second stage is self-accelerating. The simulations, together with confidence intervals, were calculated for conditions similar to those as applied during the test in the adiabatic calorimeter (same starting temperature, Φ-factor). For the model prediction, an upper and lower confidence interval was calculated as well. Figures 8a and b show the good agreement of the experimental curves (open circles) with the simulated results. Part of the difference between the experimental curves and the predicted ones can originate from the difficulties to accurately determine the Φ-factor of the glass test cells used, and/or from the fact that the heat capacity and the Φ-factor are kept constant throughout the entire temperature range in the simulations, whereas, in reality, they are the functions of the temperature.

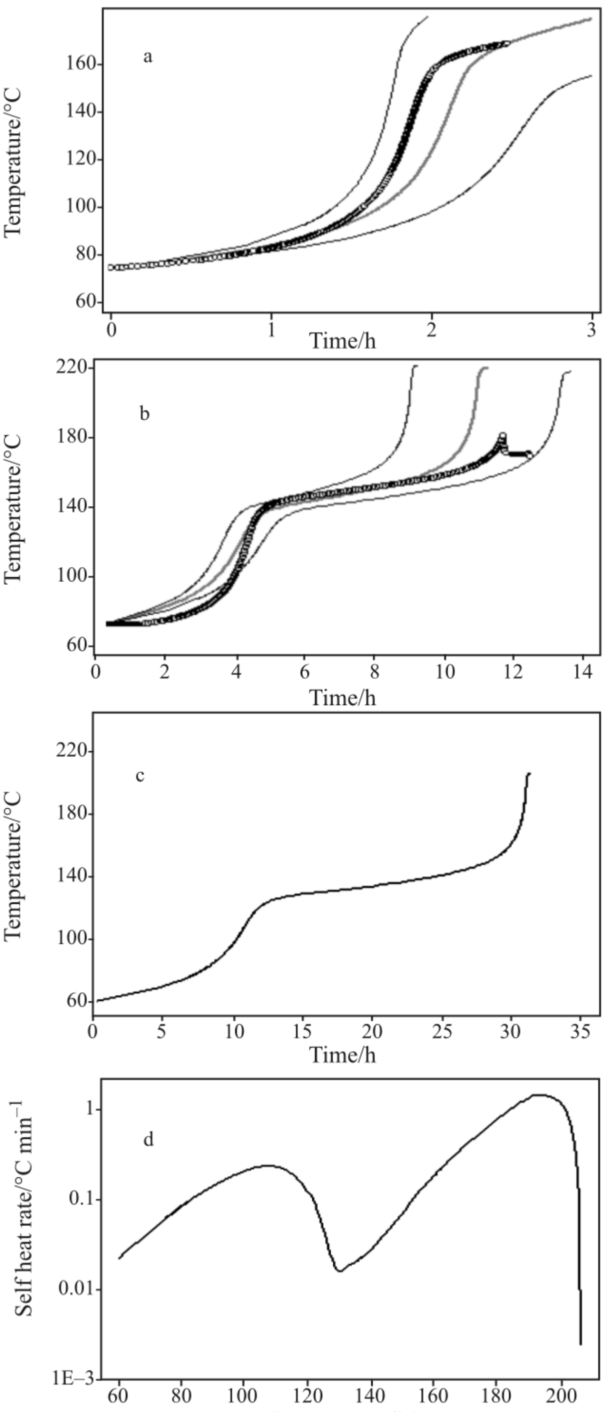

Fig. 8 a – change of the sample temperature (95% confidence intervals, thin lines) under adiabatic conditions and the experimental adiabatic run (open circles, Φ=1.25) carried out with the concentrated solution (starting temperature T_{begin}=74°C) and b – with the diluted solution (T_{begin}=73°C). c – simulations of the temperature profiles of the diluted solution (starting temperature 60°C, Φ=1, C_P=3.4), d – corresponding self-heat rate curve, note the logarithmic scale of the *Y*-axis

Presented simulations of the process which is going to be carried out in the industrial scale at 60°C clearly indicate that the severity of a possible runaway scenario is now acceptable for the diluted solution (Figs 8c and d). Firstly, the first and the second parts of decomposition are clearly distinguishable (Fig. 8c). Secondly, the self-heating rates during the decomposition are low (Fig. 8d). The first part of the decomposition is not accompanied by any pressure build-up (apart from the increase of vapour pressure with increasing temperature), whereas the second part of the decomposition is accompanied by the significant gas generation leading to the distinct increase of the pressure. It would therefore be unacceptable, from a safety point of view, to take any risk to trigger the second stage of the decomposition reaction. Because both steps of the decomposition are sufficiently separated the risk of triggering the second part of the decomposition is significantly limited. The experimental results of the adiabatic testing, being in a good agreement with the simulation, confirmed that the reaction in diluted solution is safe and acceptable for introduction in the production.

Conclusions

The presented results illustrate the possibility of the successful simulation of the thermal behaviour of the energetic substances in: (*i*) mg-scale, as usually applied in conventional (DSC, DTA) experiments when the temperature in the sample can be perfectly controlled due to ideal heat transfer to, or from, surroundings. (*ii*) ton-scale, when reactions occur almost under adiabatic conditions and the reaction heat, accumulated in the sample, influences the course of the reaction.

The correct simulation of the thermal behaviour of the investigated material in mg- and ton-scales requires: (*i*) the knowledge of the kinetic parameters of the process describing the rate of the reaction and, therefore, the rate of the heat generation. (*ii*) and careful heat balance in the system describing the accumulation of the heat under adiabatic conditions.

The application of the advanced kinetic approach enables the determination of the kinetic parameters from the results of the conventional thermal analysis. Once combined with the heat balance it allows the successful simulation of the thermal behaviour under adiabatic conditions such as e.g. the determination of the time to maximum rate $\mathrm{TMR}_{\mathrm{ad}}$ for any, arbitrarily chosen, starting temperature. The presented method of simulation enables also investigation of the influence of thermal inertia of the system (Φ-factor) on the course of the reaction. The calculations were verified by comparison with the results obtained by means of DSC and adiabatic calorimetry.

When applying the advanced kinetic based method:

- it is not necessary to perform several adiabatic calorimetric experiments. One only for the verification is sufficient.
- it is not necessary to perform heat wait search adiabatic experiments to find out the detection limit as it can be read from the calculated self-heat rate curves.
- it is possible to quantify the influence of the Φ-factor on: (*i*) the ΔT_{ad} (measured) because ΔT_{ad} (measured)$=\frac{1}{\Phi}\Delta T_{ad}$ (real). (*ii*) the maximum self heat rate. (*iii*) and the measured time to maximum rate.

Consequently, the application of advanced kinetics-based simulation for determination of the TMR_{ad} is based on the three following steps:

- Carrying out few DSC experiments with different heating rates and determining from them the kinetic parameters using the isoconversional analysis of Friedman.
- Performing one isothermal or non-isothermal DSC experiment or one adiabatic calorimeter experiment lasting few hours to validate the kinetic based simulation done by the Thermokinetics Software.
- Once the all verifications are done, the advanced kinetic based simulation approach enables to predict the thermal behaviour of the substance under any type of circumstances, independent of its mass (mg or ton), for any kinetics (*n*th order or autocatalytic) of the decomposition and heat accumulation conditions.

References

1 Advanced Kinetics and Technology Solutions: http://www.akts.com (AKTS-Thermokinetics software and AKTS-Thermal Safety software)
2 Swiss Institute of Safety and Security: http://www.swissi.ch/index.cfm?rub=1010.
3 W. F. Hemminger and S. M. Sarge, J. Thermal Anal., 37 (1991) 1455.
4 B. Roduit, Ch. Borgeat, B. Berger, P. Folly, B. Alonso, J. N. Aebischer and F. Stoessel, J. Therm. Anal. Cal., 80 (2005) 229.
5 M. E. Brown, J. Therm. Anal. Cal., 82 (2005) 665.
6 M. Maciejewski, Thermochim. Acta, 355 (2000) 145.
7 M. E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H. L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H. O. Desseyn, C.-R. Li, T. B. Tang, B. Roduit, J. Malek and T. Mitsuhashi, Thermochim. Acta, 355 (2000) 125.
8 A. Burnham, Thermochim. Acta, 355 (2000) 165.
9 B. Roduit, Thermochim. Acta, 355 (2000) 171.
10 H. L. Friedman, J. Polym. Sci, Part C, Polymer Symposium (6PC), 183 (1964).
11 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
12 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Standards, 70A (1966) 487.
13 S. Vyazovkin, J. Comput. Chem., 22 (2001) 178.
14 ASTM Standard E 698, 1999 (2005), ‘Standard Test method for Arrhenius Kinetic Constants for Thermally Unstable Materials’, ASTM International, West Conshohocken, PA, www.astm.org.
15 P. Budrugeac, J. Therm. Anal. Cal., 68 (2002) 131.
16 A. Keller, D. Stark, H. Fierz, E. Heinzle and K. Hungerbüler, J. Loss Prev. Proccess Ind., 10 (2000) 31.
17 J. Pastré, U. Wörsdörfer, A. Keller and K. Hungerbühler, J. Loss Prev. Proccess Ind., 13 (2000) 7.
18 B. Roduit, C. Borgeat, B. Berger, P. Folly, H. Andres, U. Schädeli and B. Vogelsanger, J. Therm. Anal. Cal., 85 (2006) 195.
19 D. I. Townsend and J. C. Tou, Thermochim. Acta, 37 (1980) 1.
20 E. Wilcock and R. L. Rogers, J. Loss Prev. Process Ind., 10 (1997) 289.

DOI: 10.1007/s10973-007-8866-1