Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 229–236

ADVANCED KINETIC TOOLS FOR THE EVALUATION OF DECOMPOSITION REACTIONS

Determination of thermal stability of energetic materials

B. Roduit[1*], *Ch. Borgeat*[1], *B. Berger*[2], *P. Folly*[2], *B. Alonso*[3], *J. N. Aebischer*[3] *and F. Stoessel*[4,5]

[1]Advanced Kinetics and Technology Solutions AKTS AG http://www.akts.com, TECHNO-Pôle, 3960 Siders, Switzerland
[2]armasuisse, Science and Technology Centre http://www.armasuisse.ch, 3602 Thun, Switzerland
[3]University of Applied Sciences of Western Switzerland http://www.eif.ch, 1705 Fribourg, Switzerland
[4]Swiss Institute for the Promotion of Safety and Security (SWISSI) http://www.swissi.ch, 4002 Basel, Switzerland
[5]Swiss Federal Institute of Technology (EPFL), Institute of Process Sciences http://www.epfl.ch, 1015 Lausanne, Switzerland

An advanced kinetic study on the thermal behaviour of pyrotechnic ignition mixtures has been carried out by differential scanning calorimetry using different B/KNO_3 mixtures (50:50, 30:70, 20:80) as a model reaction. The experimental conditions applied (isochoric conditions/closed crucibles and isobaric conditions/open crucibles) as well as the composition of the mixtures noticeably influences the relative thermal stabilities of the energetic materials. The kinetic study focused on the prediction of the thermal stability of the different mixtures both in extended temperature ranges and under temperature conditions at which ordinary investigation would be very difficult. Using advanced numerical tools [1], thermal ageing and influence of the complex thermal environment on the heat accumulation conditions were computed. This can be done for any surrounding temperature profile such as isothermal, non-isothermal, stepwise, modulated, shock, adiabatic conditions and additionally for temperature profiles reflecting real atmospheric temperature changes (yearly temperature profiles of different climates with daily minimal and maximal fluctuations). Applications of accurate decomposition kinetics enabled the determination of the time to maximum rate under adiabatic conditions (TMR_{ad}) with a precision given by the confidence interval of the predictions. This analysis can then be applied for the examination of the effects of the surrounding temperature for safe storage or transportation conditions (e.g. determination of the safe transport or storage temperatures).

Keywords: *ageing, decomposition kinetics, energetic materials, pyrotechnic ignition, runaway reactions, thermal hazards, time to maximum rate,* TMR_{ad}

Introduction

To get an ideal ignition of rocket motors containing composite or double base propellant it is very important to use igniter compositions with an excellent performance concerning the production of hot gases, glowing reaction particles in a short reaction time. On the other hand, igniter compositions for rocket motors should not be sensitive towards environmental influences. To use such compositions to ignite LOVA propellants of insensitive munitions their ignition level must be quite high. Additionally such compositions should not age too fast under normal conditions. Today the pyrotechnic materials 'black powder' or boron/potassium nitrate mixtures are commonly used.

Typical composition of 'black powder':

• charcoal	75 mass%
• sulfur	10 mass%
• potassium nitrate	15 mass%

Typical composition of boron–potassium nitrate ignitor:

• boron	30 mass%
• potassium nitrate	70 mass%

The investigations of the decomposition process and determination of the aging properties of igniters can be carried out by applying thermoanalytical methods such as differential scanning calorimetry (DSC) or thermogravimetry (TG).

Experimental

The DSC data were collected on Mettler Toledo, type 821 thermoanalyzer, Switzerland. The DSC measurements were performed in closed crucibles with a lid having three small holes and in fully closed high pressure gold crucibles. The applied heating rates were 1, 2, 3, 5 and 10 K min^{-1}. Figure 1 shows the DSC signal at 10 K min^{-1} of a boron/potassium mixture (30:70) under isobaric conditions.

The DSC plot (Fig. 1) shows at a temperature of 134°C an endothermal event resulting from the phase

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[*] Author for correspondence: b.roduit@akts.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

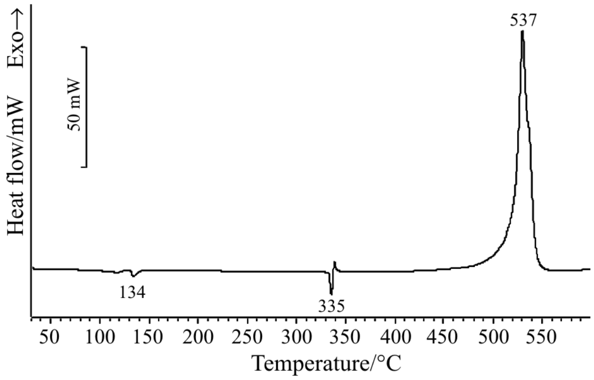

Fig. 1 DSC plot of a boron/potassium nitrate composition 30:70 mass%, crucible closed with a perforated lid

transition of potassium nitrate (literature data 129°C). The endo-peak at 335°C is due to the melting of KNO_3 (literature data 334°C) [2]. The rate of exothermal redox reaction between boron and potassium nitrate has the maximum at temperature of 537°C. After baseline subtraction and normalization, these exothermal peaks obtained by different heating rates were used for the simulations with the AKTS-Thermokinetics software [1].

Calculation methods

Determination of the baseline

The selection of the evaluation range of the baseline should contain the part of the signals before and after the occurrence of the thermal effects. Generally the application of straight-line form for the baseline is incorrect [3]. The recorded signal results not only from the heat of the reaction but is additionally affected by the change of the specific heat of the mixture reactant-products during the progress of the reaction.

$$S(T)_{\text{normed}} = \frac{S(T)}{\int_{T_0}^{T_{\text{end}}}[S(T)-B(T)]\mathrm{d}T} = \frac{\text{mW mg}^{-1}}{(\text{mW mg}^{-1})\text{K}} = \frac{1}{\text{K}} \Rightarrow [\text{units of } S_{\text{normed}}(T)=(1/\text{K})] \qquad (1)$$

with $B(T)$ the baseline, $S(T)$ the differential signal, the reaction progress $x(T)$ can be expressed as

$$x(T) = \frac{\int_{T_0}^{T}[S(T)-B(T)]\mathrm{d}T}{\int_{T_0}^{T_{\text{end}}}[S(T)-B(T)]\mathrm{d}T} \qquad (2)$$

The tangential area-proportional baseline is the mostly applied type because of its correction possibilities. It is created at $x(T)\to 0$ and at $x(T)\to 1$ by the appropriate tangents at the beginning or the end of the measured DSC signal. It allows compensation of not only changes of the c_p values of the reactant and product, but also of changes in their temperature dependency. This type of baseline can be described by the following equation:

$$B(T)=[1-x(T)](a_1+b_1T)+x(T)(a_2+b_2T) \qquad (3)$$

with (a_1+b_1T) – tangent at the beginning of the signal $S(T)$; (a_2+b_2T) – tangent at the end of the signal $S(T)$.

$B(T)$ can be calculated iteratively. The convergence is achieved as soon as the relative average deviations between two iterations are smaller than an arbitrarily chosen value (e.g. 1E-6). Presented in Fig. 2 an area-proportional baseline has been calculated using arbitrarily chosen 300 iteration loops.

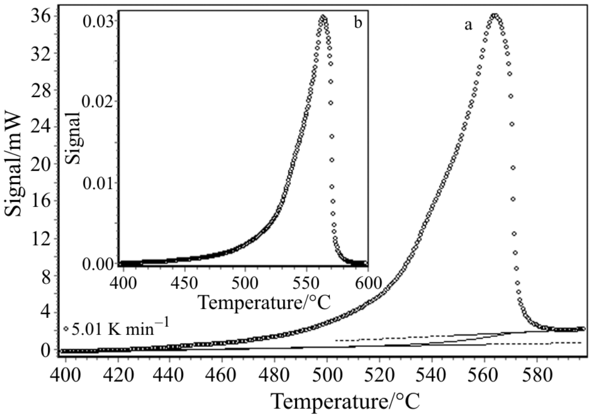

Fig. 2 a – DSC heat flow curve and the baseline calculated for the heating rate of 5 K min^{-1} (open crucibles/isobaric conditions B/KNO_3 20:80 mixture); [Units of $S(T)$=(mW mg^{-1})], b– inset: DSC heat flow curve after baseline subtraction and normalization

It is obvious that the baseline determination can significantly influence the determination of the kinetic parameters of the reaction. Moreover, the correct baseline determination should be intimately combined with the computation of the kinetic parameters for the investigated reaction. Advanced mathematical procedures are therefore necessary for an objective calculation of the most appropriate baseline for each DSC signal.

Kinetic parameters

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 introducing the ‘multi-curve’ methods over the past few years: see e.g. the International ICTAC kinetics project [4–7]. Only series of non-isothermal measurements carried out at different heating rates can give a data set which generally contains the necessary amount of information required for full identification of the complexity of a process. This data set usually contains:

- the relationship between specific conversion degree, x_i, and temperatures for different heating rates (non-isothermal mode)
- the relationship between specific conversion, x_i, and time for different temperatures (isothermal mode)

Commonly applied isoconversional methods are known as methods of Friedman [8] and Ozawa–Flynn–Wall [9].

Friedman analysis, based on the Arrhenius equation, applies the logarithm of the conversion rate dx/dt as a function of the reciprocal temperature at different degrees of the conversion.

$$\ln\left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_{x_i} = \ln A - \frac{E}{RT_{i,j}} + \ln[f(x_i)] \qquad (4)$$

with i – index of conversion, j – index of heating rate, $f(x)$ the function dependent on the decomposition mechanism.

As $f(x)$ is assumed to be constant at each conversion degree x_i, the dependence of the logarithm of the reaction rate over $1/T$ is linear with the slope of $m=E/R$. If the decomposition follows a single mechanism then the reaction can be described in terms of a single pair of Arrhenius parameters and the commonly used set of reaction models (Table 1). In such cases the reaction rate can be described by the following expression:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT(t)}\right)f(x) \qquad (5)$$

However, this approach is not fulfilled during most of the decomposition reactions because, as presented in Fig. 3 for the examined B/KNO$_3$ samples, the activation energy is often strongly dependent on the reaction progress. Decomposition reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and the commonly applied set of reaction models. As a general rule, these reactions demonstrate profoundly multi-step characteristics. They can involve several processes with different activation energies and mechanisms. In such situations the reaction rate can be described only by complex equations, where the activation energy term is no longer constant but is dependent on the reaction progress x(E≠const. but E=E(x)) [8, 9]. Thus, a simplified kinetic analysis can no longer lead to an accurate description of the experimental data. For multistage, overlapped reactions the prediction of the thermal behavior under any new temperature profile, without taking into account the dependence of the activation energies E(x) on the conversion degree x, is of little value. The accurate determination of the kinetic parameters under experimental conditions applied which enables the correct fit of the experimental data is a prerequisite for prediction of the reaction progress under any new temperature profile. When solving the complicated interrelation between the baseline, the kinetic parameters of the reaction and reaction progress, two important points have to be considered:

Table 1 The forms of the $f(x)$ function dependent on the reaction model and their commonly used abbreviations

Autocatalytic: $(1–x)^n x^m$	A1.5: $1.5(1–x)[–\ln(1–x)]^{1/3}$ A2: $2(1–x)[–\ln(1–x)]^{1/2}$ An: $n(1–x)[–\ln(1–x)]^{1–1/n}$
F1: $1–x$ F2: $(1–x)^2$ F3: $(1–x)^3$ Fn: $(1–x)^n$	R2: $2(1–x)^{1/2}$ R3: $3(1–x)^{2/3}$ Rn: $n(1–x)^{1–1/n}$
P1: x^0 P2: $2x^{1/2}$ P3: $3x^{2/3}$ P4: $4x^{3/4}$ Pn: $nx^{1–1/n}$	D1: $1/2x$ D2: $[–\ln(1–x)]^{–1}$ D3: $1.5[1–(1–x)^{1/3}]^{–1}(1–x)^{2/3}$ D4: $1.5[(1–x)^{–1/3}–1]^{–1}$

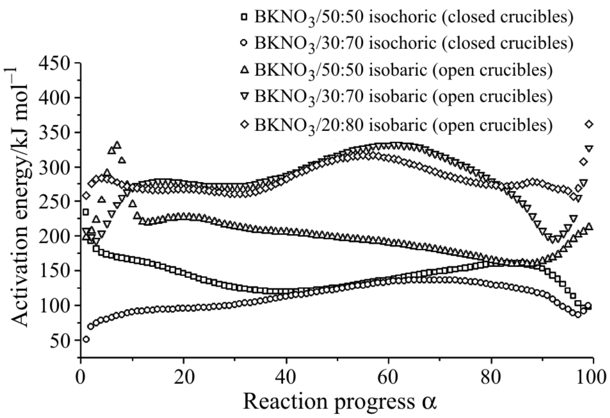

Fig. 3 Activation energy of the B/KNO$_3$ samples as a function of the reaction progress for closed and open crucibles. The activation energy is strongly dependent on the reaction progress. It can be observed that the different composition of the mixtures influences strongly the dependence of the activation energy on the reaction extent. These differences will strongly influence the prediction of decomposition progress for other temperature profiles

(*i*) The dependence of the reaction rate on temperature should follow the Arrhenius equation.

(*ii*) When measuring the progress of a reaction, one tries to eliminate the systematic errors so that only accidental errors have to be taken into account. In that case the measured values will spread around the average value for each heating rate, in a form of the Gaussian-type curve. The Gaussian distribution results from a summation of several events, e.g. overlapping reactions, noise, drift, artefacts, uncertainties in the baseline construction, etc. During the optimization, the true information has to be extracted taking into account the requirement of the point (1). Once, the optimization is finished, the reliability of the predictions depends on the sum of all possible sources of errors. Therefore, under consideration of all heating rates the mathematical approach has to determine for each heating rate the 'best value' or 'central tendency' of the signal, for which the chance of the good reproducibility on subsequent measurements is maximal.

Fulfilling both above conditions (I – Arrhenius type reaction rate, and II – Gaussian-type distributed errors) makes possible the iterative calculation and objective determination of the correct baseline for each signal measured under different heating rates. Baselines are no more arbitrarily chosen by the users but objectively optimized taking into account:

- statistics, for the consideration of the experimental noise and shape of the signals
- kinetic parameters, for the consideration of reaction rates following Arrhenius relationship

Results

The kinetic parameters calculated from the non-isothermal experiments then make possible the prediction of the reaction progress for any other heating rate and more generally for any temperature mode. In the following Figs 4–8 the results of computations performed with AKTS-Thermokinetics software [1] are shown for the different B/KNO_3 mixtures.

- top graphs in all figures present the reaction rates (normalized DSC-signals after correctly calculated baselines and kinetics) as a function of the temperature for the various B/KNO_3 mixtures under isobaric and isochoric conditions. Experimental data are represented as symbols; solid lines represent the calculated signals. The values of the heating rate in K min^{-1} are marked on the curves

$$S(T)_{\mathrm{rate}}=S(T)_{\mathrm{normed}}\beta(t)=S(T)_{\mathrm{normed}}(\partial T/\partial t)=$$

$$=(1/\mathrm{K})(\mathrm{K/s})=1/\mathrm{s}\Rightarrow[\text{units of } S_{\mathrm{rate}}(T)=(1/\mathrm{s})]=$$

$$=\text{conversion rate}$$

- bottom graphs show the reaction progress as a function of time under isothermal conditions. The values of the temperature in °C are marked on the curves. Results of some experiments done under isothermal conditions (temperatures 320°C) are presented as symbols together with the predicted relationships (Figs 4 and 5)

Decomposition reactions generally involve different reactions with various activation energies. They are thus influenced in different ways by the temperature. This is illustrated by the fact that, according to the temperature range taken into consideration, it is one of the reactions that will dominate. In fact, a mistake about the energy of activation can have dramatic consequences as far as the safety of a process is concerned. It is thus strongly recommended to verify the results according to an isothermal measurement achieved directly in the temperature range taken into consideration as illustrated in Figs 4 and 5. This is particularly important for the safety analysis of storage and transport of potentially reactive materials.

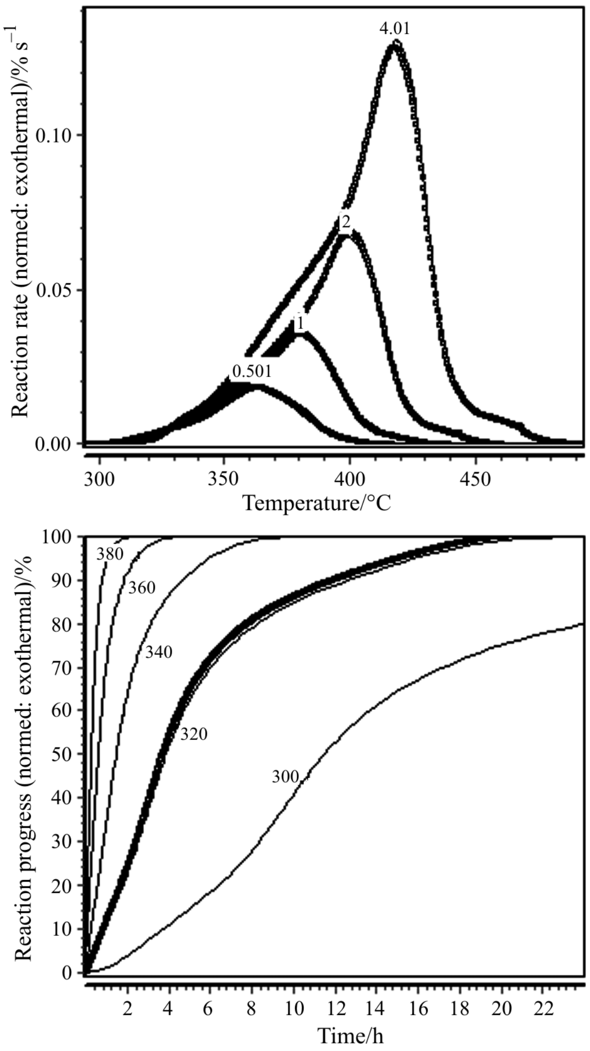

Fig. 4 B/KNO_3 50:50 (closed crucibles/isochoric conditions)

Thermal risks: calculation of adiabatic thermal transformation and heat accumulation from non-isothermal DSC measurements

The precise prediction of reaction progress under adiabatic conditions is necessary for the safety analysis of many technological processes [10–12]. Calculations of an adiabatic temperature-time curve of the reaction progress can also be used to determine the decrease of

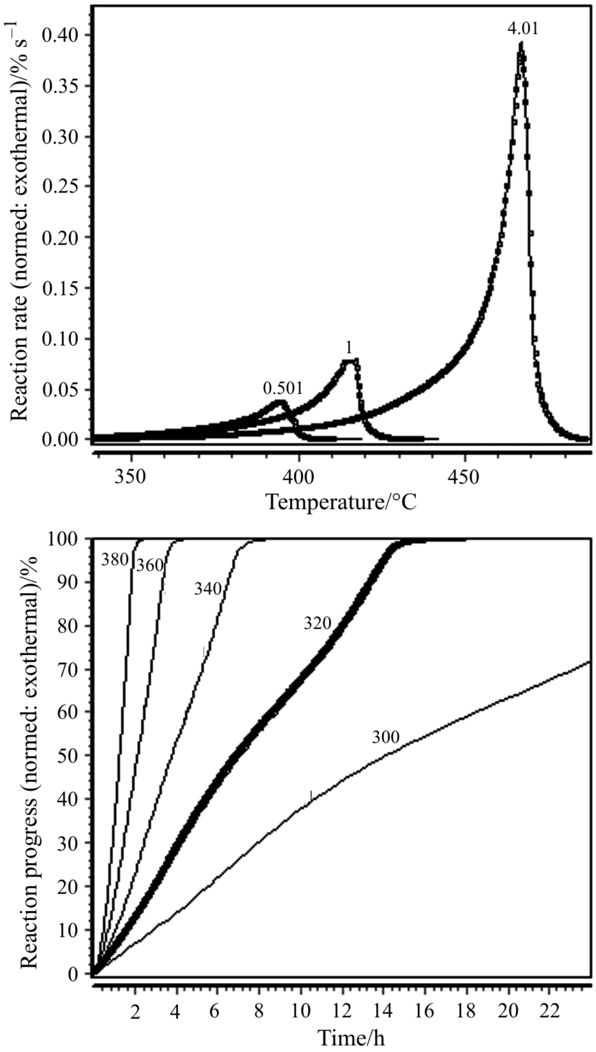

Fig. 5 B/KNO$_3$ 30:70 (closed crucibles/isochoric conditions)

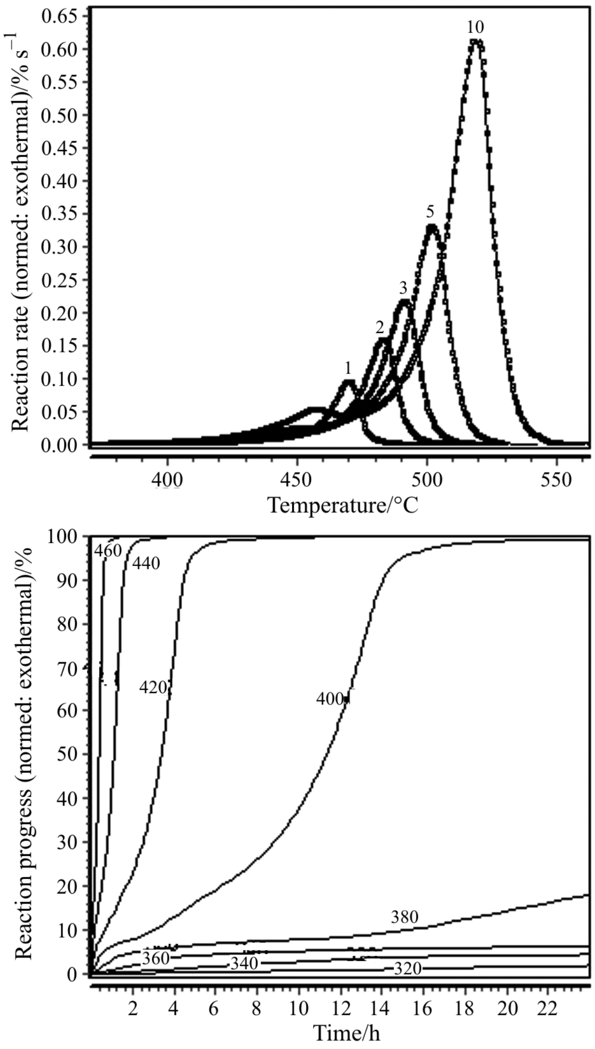

Fig. 6 B/KNO$_3$ 50:50 (open crucibles/isobaric conditions)

the thermal stability of materials during storage at temperatures near the threshold temperature for triggering the reaction. Due to limited thermal conductivity, a progressive temperature increase in the sample can easily take place, resulting in rapid decomposition or an explosion [13].

A commonly used approach for the determination of the time to maximum rate under adiabatic conditions TMR$_{ad}$ [14] applies the following formula with the arbitrarily chosen zero-order reaction [15]:

$$\mathrm{TMR_{ad}}=c_pRT_0^2/(q_0E_a) \qquad (6)$$

where c_p (J kg^{-1} K^{-1}) – specific heat, T_0 (K) – initial temperature of the runaway, q_0 (W kg^{-1}) – maximum specific heat flux measured during an isothermal exposure at the temperature T_0, E_a (J mol^{-1}) – activation energy of the reaction, R (=8.31431 J mol^{-1} K^{-1}) – gas constant.

However, when applying the above approach to predict the TMR$_{ad}$ the only one, simplified zero-order kinetic equation is used by fitting the reaction/decomposition exotherms by the Arrhenius relationship. This method unfortunately gives a very rough approximation of the TMR$_{ad}$ due to the severe assumptions made concerning both the kinetics and the constancy of the value of the activation energy. As presented in Fig. 3, the activation energy is strongly dependent on the reaction progress for the considered compounds. In addition, it can be observed that the different compositions of the mixtures as well as the different experimental conditions (isochoric/isobaric) strongly influence the dependence of the activation energy on the reaction extent. The solution of the problem should therefore be achieved numerically. The computations have to consider the dependence of the activation energy on the reaction progress and the optimization of the baselines. For predictions with a certain level of accuracy, advanced kinetic analysis is therefore required because most decomposition reactions are complex combinations of several steps.

The potential damages due to a loss of control of the reaction are also related to the quantity of heat re-

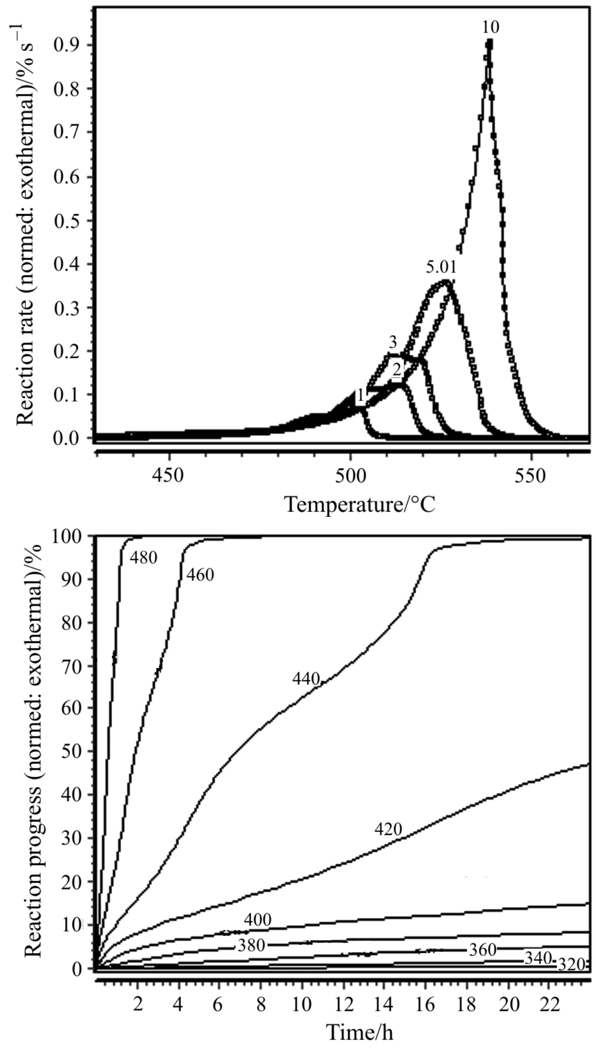

Fig. 7 B/KNO_3 30:70 (open crucibles/isobaric conditions)

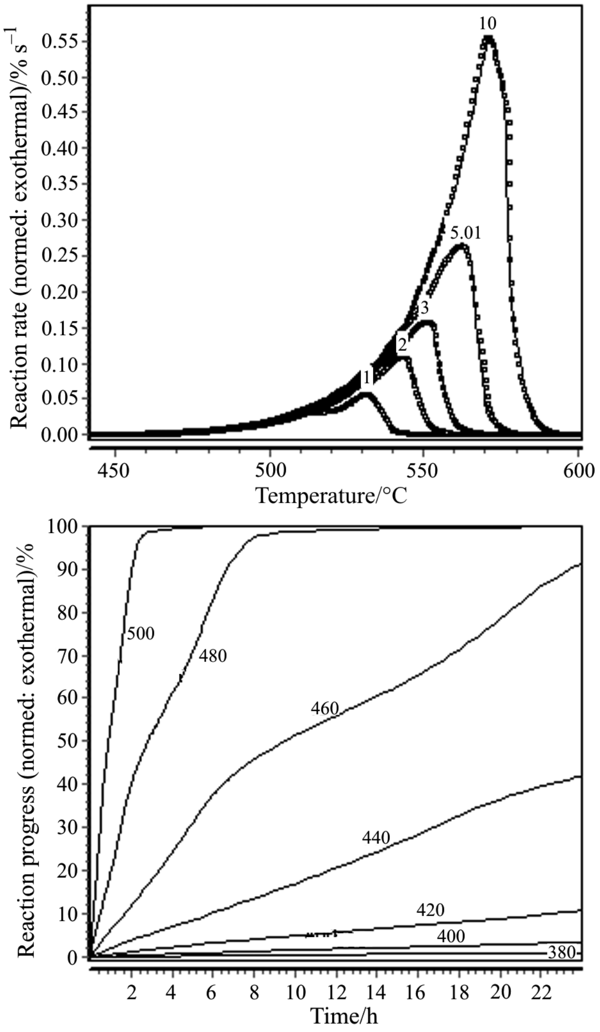

Fig. 8 B/KNO_3 20:80 (open crucibles/isobaric conditions)

leased. The heat of reaction is one of the key data required for correct evaluation of the potential risks. Estimating the thermal risks involves the evaluation of the severity and the probability to generate a runaway reaction. In order to find and elaborate the appropriate measures that will reduce the risks, it is crucial to evaluate in which part the severity and the probability play the role in the case of thermal risks. The thermal risk related to a chemical reaction is the risk of loss of control of a reaction and its possible consequences such as, e.g, a runaway risk. It is thus essential to understand how a reaction can shift from its normal course to a runaway scenario [16]. For all exothermic reactions, the heat of reaction is a factor of severity. It gives a direct measure of consequences which result from a runaway destruction potential. A more common and easier value to use and understand is the adiabatic temperature rise. The adiabatic rise can be calculated by dividing the heat of reaction by the specific heat.

Using the reaction heat ΔH_r presented in Table 2 and a specific heat c_p of 1.62 J g^{-1} °C^{-1} for the various B/KNO_3 mixtures under isochoric and isobaric conditions, one can calculate the reaction progress due to self-heating for the different ΔT_{ad} (with $\Delta T_{ad}=\Delta H_r/c_p$). Figure 9 and Table 2 present the results of such calculations for a starting temperature of 370°C. The results illustrate how the thermal stability may be investigated using DSC experiments and advanced kinetic analysis.

As for the determination of the correct course of the baseline, the predictions of the reaction progress will spread (with Gaussian distribution) around an average value. The predictions of the reaction progress for a given temperature profile will give the 'central tendency', for which the chance of the good reproducibility on subsequent measurements is maximal. The illustration of these remarks for the investigation of the B/KNO_3 mixture with ratio 20:80 under isobaric conditions for a starting temperature of 370°C is presented in Fig. 10a. The mean value of the TMR_{ad} pre-

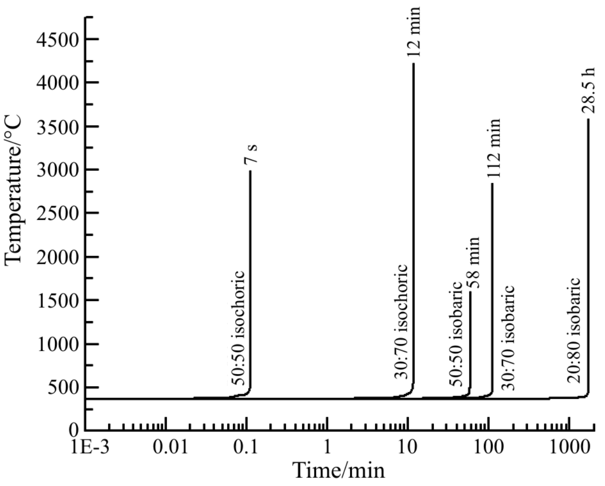

Fig. 9 Adiabatic runaway curves for the various B/KNO_3 mixtures under isochoric and isobaric conditions for a starting temperature of 370°C. The different B/KNO_3 composition ratios as well as the TMR_{ad} are marked on the curves. Under isochoric conditions the B/KNO_3 mixtures are thermally by order of magnitude less stable than under isobaric conditions. Similar behaviour is observed when comparing the different compositions of B/KNO_3 mixtures. It can be observed that mixtures with equimolar ratios have both, for the experimental conditions considered, shorter TMR_{ad} (or lower thermal stability) and smaller ΔT_{ad} (or lower heat of reaction)

diction is about 28.5 h. The lower and upper limits of the confidence intervals are 21.7 and 37.4 h, respectively. These values indicate that there is a 95% probability that the mean TMR_{ad} is greater than 21.7 h and lower than 37.4 h. Figure 10b and Table 3 present the relationship between the starting temperature and corresponding adiabatic induction time TMR_{ad}. The confidence interval was determined for 95% probability. Depending on the decomposition kinetics and ΔT_{ad}, the choice of the starting temperatures strongly influences the adiabatic induction time and, therefore, the boundary conditions valid for achieving necessary safety (e.g. storage or transport of self-reactive substances).

The adiabatic induction time is defined as the time which is needed for self-heating from the starting temperature to the time of maximum rate (TMR_{ad}) under adiabatic conditions. Depending on the decomposition

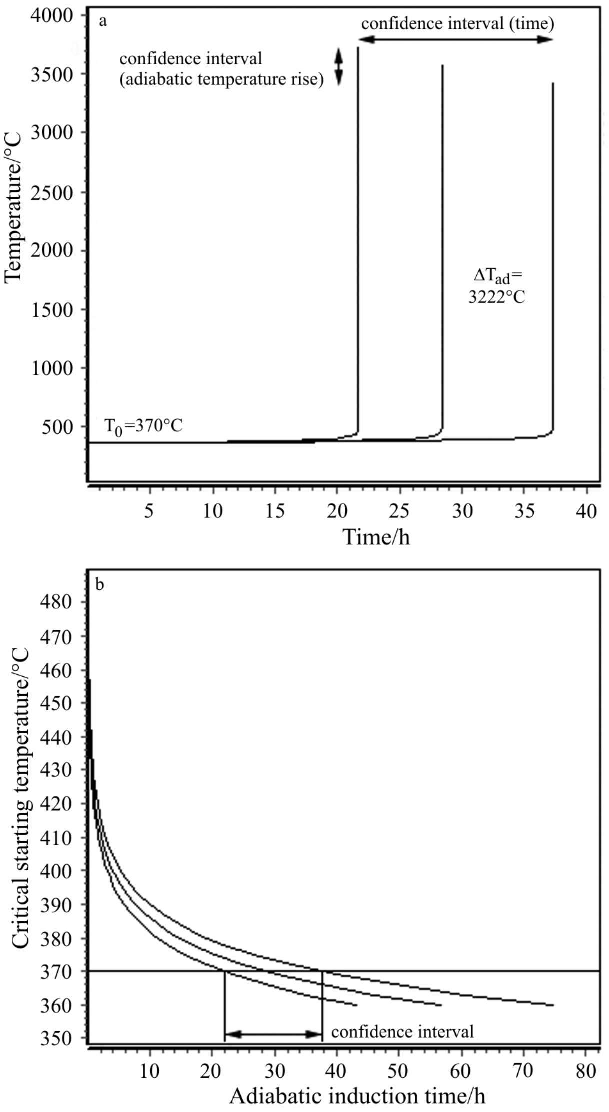

Fig. 10 a – Adiabatic runaway curves for the B/KNO_3 mixture (20:80) under isobaric conditions showing the confidence interval for the prediction (T_{begin}=370°C and $\Delta T_{ad}=\Delta H_r/c_p$=3222±152.6°C). The confidence interval was determined for 95% probability; b – starting temperature and corresponding adiabatic induction time TMR_{ad} relationship of the mixture with ratio 20:80 under isobaric conditions. The choice of the starting temperatures strongly influences the adiabatic induction time (Confidence interval: 95% probability)

Table 2 ΔH_r, $\Delta T_{ad}=\Delta H_r/c_p$ (c_p=1.62 J g^{-1} $°C^{-1}$) and TMR_{ad} of the different B/KNO_3 mixtures for a starting temperature of 370°C

Compounds	ΔH_r/J g^{-1}	$\Delta T_{ad}=\Delta H_r/c_p$/°C	TMR_{ad}
B/KNO_3 – isochoric conditions:			
50:50	4248±119.9	2622±74	7 s
30:70	6291±245.3	3883±151.4	12 min
B/KNO_3 – isobaric conditions:			
50:50	2010±161.6	1240±99.7	58 min
30:70	4021±246	2482±151.8	112 min
20:80	5221±247.3	3222±152.6	28.5 h

Table 3 Starting temperature and corresponding adiabatic induction time TMR_{ad} relationship of the B/KNO_3 mixture with ratio 20:80 under isobaric conditions. The choice of the starting temperatures strongly influences the adiabatic induction time (Confidence interval: 95% probability)

T/°C	TMR_{ad}		
	lower limit	mean value	upper limit
360	43.08 h	56.67 h	74.76 h
365	30.51 h	40.04 h	52.71 h
370	21.72 h	28.44 h	37.36 h
375	15.54 h	20.31 h	26.62 h
380	11.18 h	14.57 h	19.06 h
385	8.08 h	10.51 h	13.72 h
390	5.86 h	7.62 h	9.92 h
395	256.97 min	5.55 h	7.21 h
400	188.38 min	243.66 min	5.26 h

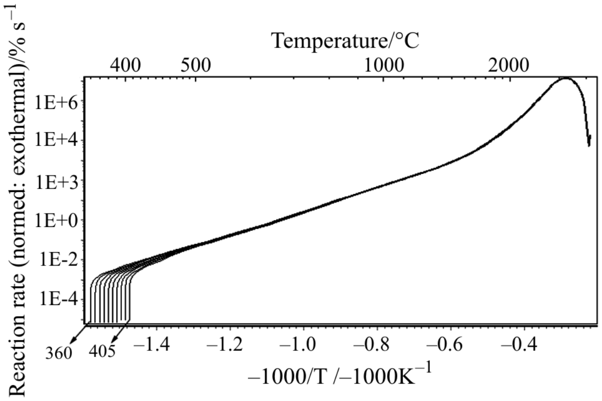

Fig. 11 Heat rate curves *vs*. temperature for the B/KNO_3 mixture with ratio 30:70 under isochoric conditions

kinetics and ΔT_{ad}, the choice of the starting temperatures strongly influences the time to explosion but also the rate of the decomposition process under adiabatic conditions. Figure 11 presents the heat evolution rate curves of the B/KNO_3 mixture with ratio 30:70 under isochoric conditions for different starting temperatures.

Conclusions

Based on the decomposition of different B/KNO_3 mixtures under isobaric and isochoric conditions, the discussion shows how advanced numerical techniques can be applied for the interpretation of the measured signals. The main challenge is the prediction of the reaction progress both in extended temperature ranges and at the temperature conditions for which experimentation is difficult or impossible. With at least three DSC experiments done under isothermal or non-isothermal conditions it is possible to compute the kinetics of decomposition of the products of interest. Decomposition reactions usually have a multi-step nature; therefore, the accurate determination of the kinetic characteristics strongly influences the ability to correctly describe the progress of the reaction. For self-heating reactions, incorrect kinetic description of the process can be the main source of serious errors in its interpretation. It can be hazardous to develop safety predictive models that are based on simplified kinetic assumptions. The goal of the presented advanced numerical approach of the kinetic analysis is getting a deeper insight into the reaction course for a better control of the examined process. In general, advanced kinetics can be applied for the examination of any type energetic materials allowing better understanding of thermal hazards and an ability to predict safety limits. Finally, kinetics allows not only examination of the thermal behaviour under adiabatic conditions but the prediction of the thermal stability can be extended also to any required temperature profiles, such as isothermal, non-isothermal, stepwise, modulated, shock and additionally temperature profiles reflecting real atmospheric temperature changes (yearly temperature profiles of different climates with daily minimal and maximal fluctuations) [17].

References

1 Advanced Kinetics and Technology Solutions: http://www.akts.com (AKTS-Thermokinetics software and AKTS-Thermal Safety software).
2 R. C. Weast, Handbook of Chemistry and Physics, 53rd Edition, The Chemical Rubber Co.; Cleveland, Ohio, USA.
3 W. F. Hemminger and S. M. Sarge, J. Thermal Anal., 37 (1991) 1455.
4 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.
5 B. Roduit, Thermochim. Acta, 355 (2000) 171.
6 M. Maciejewski, Thermochim. Acta, 355 (2000) 145.
7 A. Burnham, Thermochim. Acta, 355 (2000) 165.
8 H. L. Friedman, J. Polymer Lett., 4 (1966) 323.
9 T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881.
10 D. W. Smith, Chem. Eng., 14 (1984) 54.
11 D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, Plenum Press, New York, London 1969.
12 T. Grewer, Thermochim. Acta, 225 (1993) 165.
13 P. Folly, Chimia, 58 (2004) 394.
14 D. I. Townsend and J. C. Tou, Thermochim. Acta, 37 (1980) 1.
15 R. Gygax, International Symposium on Runaway reactions, Cambridge, Massachusetts, USA, March 7–9, 1989, p. 52.
16 F. Stoessel, Chem. Eng. Progress, October 1993, p. 68.
17 B. Roduit, Thermochim. Acta, 388 (2002) 377.