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UP-SCALING OF DSC DATA OF HIGH ENERGETIC MATERIALS
Simulation of cook-off experiments

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Differential scanning calorimetry (DSC) carried out with few heating rates was applied in the studies of the thermal properties of four energetic materials: EI® propellant, high explosive PBXW-17, pyrotechnic mixtures with composition B/KNO_3 (50:50) and B/KNO_3 (30:70). DSC signals, after optimization of the baseline, were used for the calculation of the kinetic parameters (KP) of the decomposition process applying advanced kinetic software designed by AKTS. The determination of the kinetic parameters was based on the differential iso-conversional method of Friedman. The correctness of the estimation of KP was checked by the comparison of the experimental and predicted courses of the decomposition.

The slow cook-off experiments of above mentioned energetic materials were carried out with a heating rate of 3.3°C h^{-1}. For the simulation of the experimental results, the heat balance based on the finite element analysis (FEA) was applied together with the advanced kinetic description of the reaction. The comparison of the experimental and simulated data indicates that applied procedure resulted in a very good prediction of the temperature of the ignition. Application of commonly used, simplified assumptions concerning the mechanism of the decomposition (such as 1st or *n*th order mechanisms) led to significantly worse prediction of the cook-off temperatures.

Keywords: *adiabatic runaway, cook-off, ignition, kinetics, safety, thermal ageing, thermal hazards, TMR_{ad}*

Introduction

The prediction of the thermal stability of energetic materials is difficult due to the multi-step character of their decomposition and distinct thermal effects influencing significantly the decomposition kinetics. This prediction is even more complicated in typical cook-off experiments carried out with masses of the samples few order of magnitude larger than those usually investigated in thermoanalytical (TA) experiments. The proper solution of the problem requires both: correct kinetic description of complicated decomposition process and application of finite element analysis (FEA) for the calculation of the correct heat balance in large-scale samples.

The application of the TA signals such as thermogravimetry (TG), differential scanning calorimetry (DSC) or evolved gas analysis (EGA) e.g. mass spectrometry or infrared spectroscopy for the prediction of the thermal stability of solids requires determination of the kinetic parameters (KP) of the reaction. The knowledge of the activation energy (E), pre-exponential factor in the Arrhenius equation (A) and the function $g(\alpha)$, depending on the formal reaction mechanism, is the prerequisite of the simulation of the reaction progress under conditions different from those applied during kinetic measurements. However, the commonly applied procedure has two main drawbacks, especially when applied for energetic materials:

- It is generally assumed that the reaction progress can be described by one set of KP, moreover, that they are constant during the course of the reaction.
- The predictions are based on the experiments in which the thermal effects (endo- or exothermic) are relatively small due to the small size of the samples commonly used in conventional TA experiments. During highly exothermic reactions the heat evolved can distinctly change the sample temperature what, in turn, will change the course of the reaction. Kinetic predictions obtained without considering the heat transfer, especially for larger samples, can be of little value.

The application of thermal analysis for the characterization of the energetic materials has been many times reported, see e.g. [1–6]. In the present paper we propose the procedure which allows avoiding errors leading to oversimplified conclusions concerning the thermal properties of the energetic materials. Our method is based on the correct description of the kinetics of the process without simplified assumptions concerning the stability of the KP during the reaction course [3–10] and on application of FEA enabling the correct introduction of the problem of the heat transfer into prediction procedure.

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Theoretical

The method of the evaluation of the kinetic parameters

The kinetic parameters were evaluated by the isoconversional method. This is a numerical method which involves 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). The isoconversional integral method is based on the equation:

$$g(\alpha)=\int_{0}^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_{\alpha=0}}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (1)$$

where the $f(\alpha)$ – reaction model, (also called the conversion function), $g(\alpha)$ – integral reaction model, T – temperature, R – the gas constant. The isoconversional integral method with the integration over low ranges of α and, respectively, temperature, is based on the equation:

$$g(\alpha-\Delta\alpha,\alpha)=\int_{\alpha-\Delta\alpha}^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha}}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (2)$$

by supposing that in the range of the variation of the conversion extent $\Delta\alpha$, E can be assumed as constant. The use of such an approach leads to a determination of the dependence of E and A on the α. However, the dependence of the E on the α looks like a stair function, in which, the low ranges of $\Delta\alpha$, where E keeps a constant values, are clearly marked. The number of stairs depends directly on the size of $\Delta\alpha$.

In order to evaluate the integrals from the previous equation, one can use the theorem of the average value:

$$\frac{1}{f(\alpha_{\xi})}\Delta\alpha=\frac{A}{\beta}\exp\left(-\frac{E}{RT_{\xi}}\right)\Delta T \qquad (3)$$

where $(\alpha-\Delta\alpha)<\alpha_{\xi}<\alpha$, $(T_{\alpha-\Delta\alpha}-T_{\alpha})<T_{\xi}<T_{\alpha}$ and $\Delta T=T_{\alpha}-T_{\alpha-\Delta\alpha}$.

Since the number of stairs (where the E is assumed to be constant) depends directly on the range of chosen $\Delta\alpha$, an unlimited number of stairs can be obtained by taking $\Delta\alpha$ infinitesimal for calculating the dependence of the E on α at each conversion degree. For $\Delta\alpha\Rightarrow 0$, we have $T_{\alpha}\Rightarrow T$ and $f(\alpha_{\xi})\Rightarrow f(\alpha)$. As a consequence, the previous equation turns into its differential form:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (4)$$

used in the isoconversional differential methods. One of commonly used differential isoconversional methods is the Friedman approach [11] which is applied in the present study. In more general cases, the conversion rate expression can be adapted to an arbitrary chosen variation of temperature (as well as to isothermal conditions) by replacing $\beta(\mathrm{d}\alpha/\mathrm{d}T)$ with $\mathrm{d}\alpha/\mathrm{d}t$. The Friedman analysis applies the logarithm of the conversion rate $\mathrm{d}\alpha/\mathrm{d}t$ as a function of the reciprocal temperature at different extents of the conversion. Thus, the function dependent on the reaction model $f(\alpha)$ becomes a constant at each conversion degree $\alpha_{i,j}$ and the dependence of the logarithm of the reaction rate over $1/T$ has a slope equal to E_i/R (with i – index of the conversion, j – index of the heating rate). The activation energy and pre-exponential factor as a function of the reaction extent under isochoric conditions (DSC closed crucibles) can thus be calculated by applying the following equation:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}\bigg|_{\alpha_i}=\ln(A_i f(\alpha_{i,j}))-\frac{E_i}{RT_{i,j}} \qquad (5)$$

with i – index of conversion, j – index of the curve and $f(\alpha_{i,j})$ the function dependent on the reaction model that is constant for a given reaction progress $\alpha_{i,j}$ for all curves j.

Temperature profiles and heat balances in the multi-layers: generalized heat balance over a layer volume element

In order to consider the change of the temperature inside the layer a heat balance over a volume element (Fig. 1) can be made as follows:

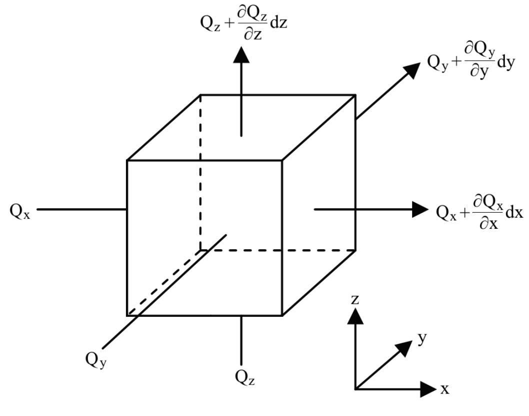

Fig. 1 Generalized heat balance over a volume element

input=output+accumulation+reaction

$$Q_x+Q_y+Q_z=\left(Q_x+\frac{\partial Q_x}{\partial x}\mathrm{d}x\right)+\left(Q_y+\frac{\partial Q_y}{\partial y}\mathrm{d}y\right)+\left(Q_z+\frac{\partial Q_z}{\partial z}\mathrm{d}z\right)+\frac{\mathrm{d}(\rho c_v T)}{\mathrm{d}t}\mathrm{d}V+Q_r\mathrm{d}V \qquad (6)$$

where Q, ρ, c_v, V, T mean: heat flow, density, specific heat, volume and temperature, respectively.

With

$$\mathrm{d}V=\mathrm{d}x\mathrm{d}y\mathrm{d}z$$

and

$$\begin{aligned}
Q_{\mathrm{x}} &= -\lambda \mathrm{d}y\mathrm{d}z\frac{\partial T}{\partial x}\\
Q_{\mathrm{y}} &= -\lambda \mathrm{d}x\mathrm{d}z\frac{\partial T}{\partial y}\\
Q_{\mathrm{z}} &= -\lambda \mathrm{d}x\mathrm{d}y\frac{\partial T}{\partial z}
\end{aligned} \tag{7}$$

where λ is the thermal conductivity, we can write:

$$\begin{aligned}
c_{\mathrm{v}}\rho\frac{\mathrm{d}T}{\mathrm{d}t}\mathrm{d}x\mathrm{d}y\mathrm{d}z=&\left[\frac{\partial}{\partial x}\left(-\lambda\mathrm{d}y\mathrm{d}z\frac{\partial T}{\partial x}\right)\mathrm{d}x+\right.\\
&\left.\frac{\partial}{\partial y}\left(-\lambda\mathrm{d}x\mathrm{d}z\frac{\partial T}{\partial y}\right)\mathrm{d}y+\frac{\partial}{\partial z}\left(-\lambda\mathrm{d}x\mathrm{d}y\frac{\partial T}{\partial z}\right)\mathrm{d}z\right]-\\
&Q_{\mathrm{r}}\mathrm{d}x\mathrm{d}y\mathrm{d}z
\end{aligned} \tag{8}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t}=\frac{\lambda}{c_{\mathrm{v}}\rho}\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}\right)-Q_{\mathrm{r}} \tag{9}$$

Using the above approach and considering different cylindrical pre-defined geometries of the reactors applied in the cook-off experiments, we can write:

$$\begin{aligned}
&\frac{\partial T}{\partial x}>>\frac{\partial T}{\partial z}\Rightarrow\frac{\partial^2 T}{\partial x^2}>>\frac{\partial^2 T}{\partial z^2}\quad\text{and}\\
&\frac{\partial T}{\partial y}>>\frac{\partial T}{\partial z}\Rightarrow\frac{\partial^2 T}{\partial y^2}>>\frac{\partial^2 T}{\partial z^2}
\end{aligned} \tag{10}$$

the heat balance reads now:

$$\frac{\mathrm{d}T}{\mathrm{d}t}=\frac{\lambda}{c_{\mathrm{v}}\rho}\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}\right)-Q_{\mathrm{r}} \tag{11}$$

Considering cylindrical coordinates and generalizing the above equation we can write for a recipient:

$$\frac{\mathrm{d}T}{\mathrm{d}t}=\frac{\lambda}{c_{\mathrm{v}}\rho}\left(\frac{\partial^2 T}{\partial r^2}+\frac{J}{r}\frac{\partial T}{\partial r}\right)-Q_{\mathrm{r}} \tag{12}$$

where J is a geometry factor which is dependent on the type of recipient: J=0 for an infinite plate of thickness r; J=1for an infinite cylinder of radius r; J=2 for a sphere of radius r; c_{p} the specific heat and Q_{r} the heat generation rate.

$$Q_{\mathrm{r}}=\frac{\Delta H_{\mathrm{r}}}{c_{\mathrm{p}}}\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\Delta T_{\mathrm{ad}}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{13}$$

The rate of the reaction in the above equation can be expressed by the Arrhenius type equation as those applied in Friedman analysis.

The balance of Q_{r} has to be considered for each layer where the reaction heat is evolved during the decomposition and, in turn, the temperature profile has to be considered for all layers. In each layer the initial temperatures at t=0 have to be introduced. If the layer is perfectly insulated on its left or right side, the boundary conditions is derived from the symmetrical properties of the temperature profile at the wall surface. The other boundary conditions are derived from comparison of the heat transfers through the interface between the different layers. We have:

- Boundary (I): Symmetry axis

$$\left.\frac{\partial T}{\partial x}\right|_{\mathrm{U}}=0\ \text{(if perfect insulation)} \tag{14}$$

- Boundary (II): At contact surfaces between a fluid and a solid wall, there is always a thin layer of fluid through which the heat is transferred by conduction. Whenever there is an appreciable movement of the fluid, conduction heat transfer in fluid may be neglected compared with convection heat transfer. The heat transfer from the solid surface to the fluid can be described by Newton's law. It states that the heat transfer, dQ/dt, from a solid surface of area S, at a temperature T_{s}, to a fluid of temperature T_∞, is:

$$\left.\frac{\partial Q}{\partial x}\right|_{\mathrm{U}}=h(T_{\mathrm{s}}-T_\infty)S\ \text{or}\ \lambda\left.\frac{\partial T}{\partial x}\right|_{\mathrm{U}}=h(T_{\mathrm{s}}-T_\infty) \tag{15}$$

where h is the heat transfer coefficient and λ the thermal conductivity.

- Boundary (III): Considering the 'left' and 'right' side of one interface, we can write at the interface between two layers:

$$Q_{\mathrm{x}}\Big|_{\mathrm{layer_U}}=Q_{\mathrm{x}}\Big|_{\mathrm{layer_{U+1}}}\Leftrightarrow\lambda_{\mathrm{layer_U}}\left.\frac{\partial T}{\partial x}\right|_{\mathrm{U}}=\lambda_{\mathrm{layer_{U+1}}}\left.\frac{\partial T}{\partial x}\right|_{\mathrm{U+1}} \tag{16}$$

The above equations for the boundary conditions can be now solved from r=0 (centre of recipient) to r=R (surface of the recipient) with AKTS – Thermal Safety Software [12].

Experimental

The following finely ground energetic materials (source of the samples: armasuisse and Nitrochemie Wimmis AG) were investigated: propellant EI®, explosive PBXW-17 and pyrotechnic materials with composition B/KNO_3 (50:50) and B/KNO_3 (30:70). DSC experiments were carried out on Mettler DSC-821e. The sample masses were in the range of 0.5–2 mg, the applied heating rates range from 0.5 to 5°C min^{-1}. The experiments were carried out in gold sealed crucibles. The decomposition was investigated in the atmosphere of nitrogen and the gas flow applied was 100 mL min^{-1}. The slow cook-off experiments were carried out in cylindrical reactor (armasuisse in-house construction) with the diameter of 47 mm equipped with three thermoelements as depicted in the inset in Fig. 6. The applied heating rate was 3.3°C h^{-1} according to STANAG 4382. The geometry of the samples investigated by DSC was chosen as close as possible to those applied during up-scaling experiments (cook-off). The ignition temperature was determined as the point of the beginning of the vertical dependence in the *T–t* plot.

Results and discussion

DSC experiments

The DSC signals of four investigated samples are presented in Fig. 2. The heating rates (in °C min^{-1}) are marked on the curves. The plots show the experimental results (symbols) after normalization and subtraction of the baselines and predictions of the reaction rates (solid lines).

Figure 3 depicts the results of the Friedman analysis of four investigated energetic materials. The conversion rates dα/dt measured at different extents of the conversion for different (three or four) heating rates (straight lines on the diagrams) allowed determination of the kinetic parameters A and E for investigated reactions as a function of the reaction extent what is presented in Fig. 4.

The results presented in Fig. 4 clearly show that the decomposition of all investigated energetic materials does not follow a single mechanism because the determined activation energies and pre-exponential factors are not constant during the course of the reactions. Clearly visible is the dependence of the kinetic parameters on the reaction extent. This observation indicates that the decomposition of the examined energetic materials is a complex reaction which cannot be described in terms of a single pair of Arrhenius parameters and commonly used set of reaction models.

In order to check how the simplified method of the determination of the kinetic parameters influences the prediction of the reaction extent, the experimental results presented in Fig. 2 were compared to the reaction rates calculated with the assumption that the mechanism of the decomposition is constant and follows the 1st order equation. The following kinetic parameters were applied for calculations: propellant EI$^{®}$: pre-exponential factor A=8.49E17 s^{-1}, activation energy E=181 kJ mol^{-1}; explosive PBXW-17: A=5.37E20 s^{-1}, E=221 kJ mol^{-1}; the pyrotechnic mate-

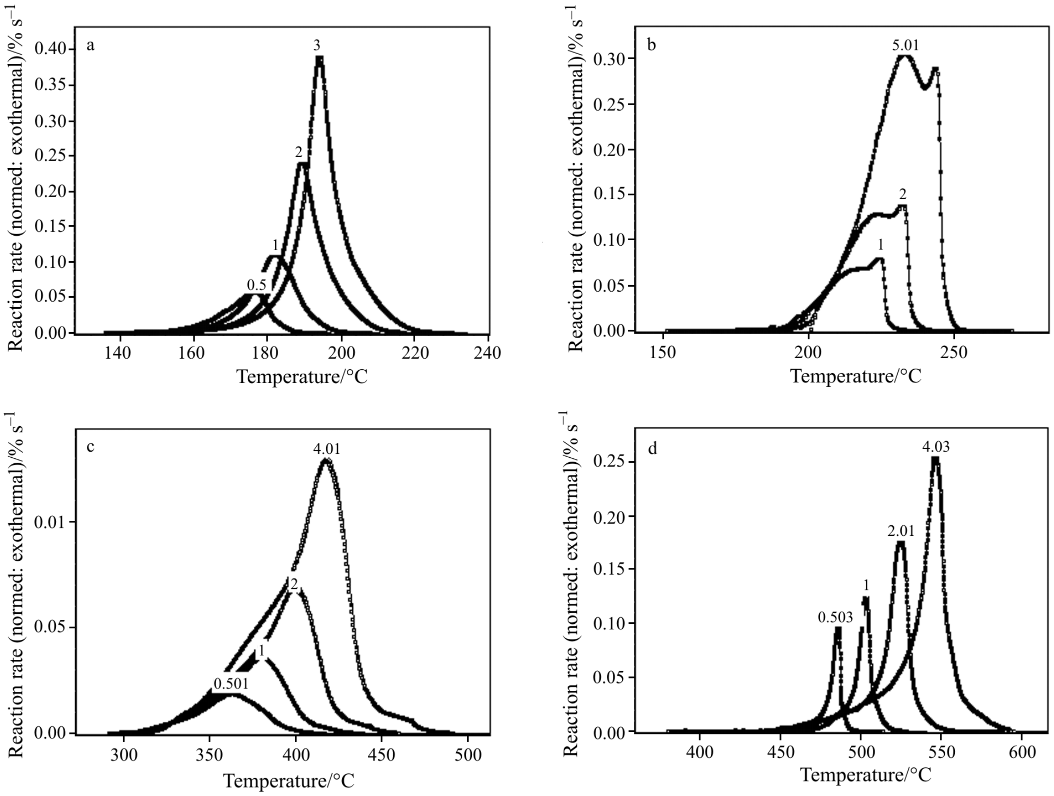

Fig. 2 Advanced kinetic description of normalized non-isothermal DSC-signals as a function of the temperature for the decomposition of a – propellant EI$^{®}$, b – explosive PBXW-17, c – pyrotechnic mixtures B/KNO$_3$ (50:50) and d – B/KNO$_3$ (30:70). Experimental data are represented as symbols, solid lines represent the calculated signals. The values of the heating rate in °C min^{-1} are marked on the curves

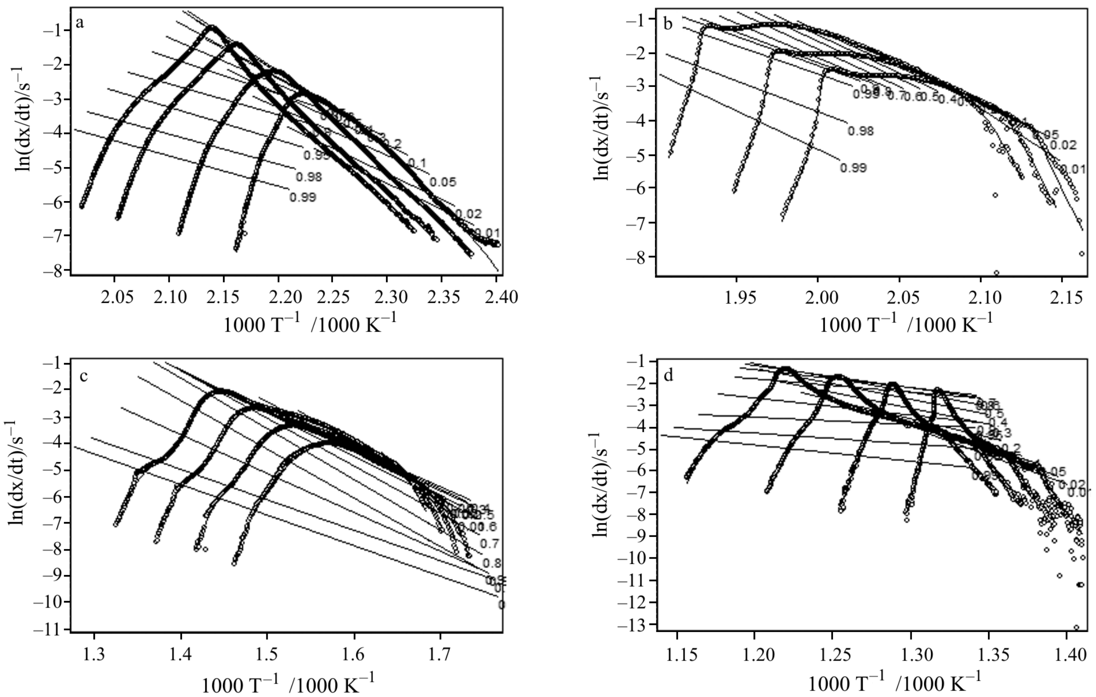

Fig. 3 Friedman analysis for the decomposition of a – propellant EI®, b – explosive PBXW-17, c – pyrotechnic mixtures B/KNO$_3$ (50:50) and d – B/KNO$_3$ (30:70)

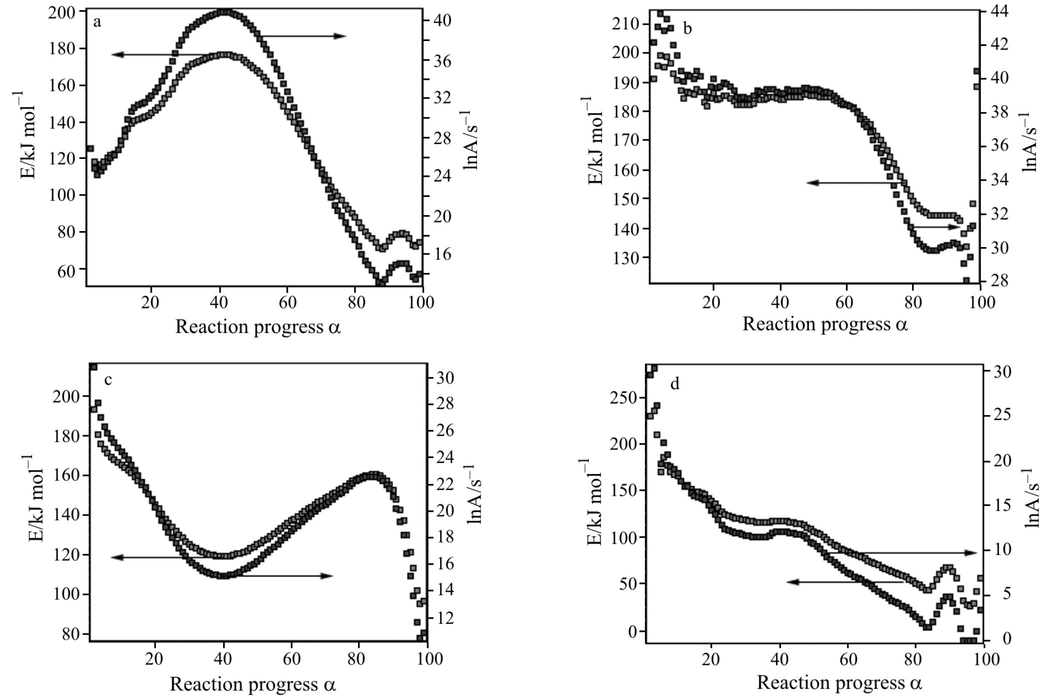

Fig. 4 Activation energy and pre-exponential factor determined by Friedman analysis as a function of the reaction progress for the decomposition of a – propellant EI®, b – explosive PBXW-17, c – pyrotechnic mixtures B/KNO$_3$ (50:50) and d – B/KNO$_3$ (30:70)

rial B/KNO$_3$ (50:50): A=3.5E8 s^{-1}, E=146 kJ mol^{-1} and B/KNO$_3$ (30:70) A=5.15E10 s^{-1}, E=202 kJ mol^{-1}. The results presented in Fig. 5 indicate that commonly used method of the prediction of the reaction rates based on the assumption of the constancy of the reaction mechanism cannot lead to the proper description of the process. In some case, especially for lower heating rates, the simplified methods do not introduce large errors but, for higher heating rates, the prediction of the reaction progress is generally very bad.

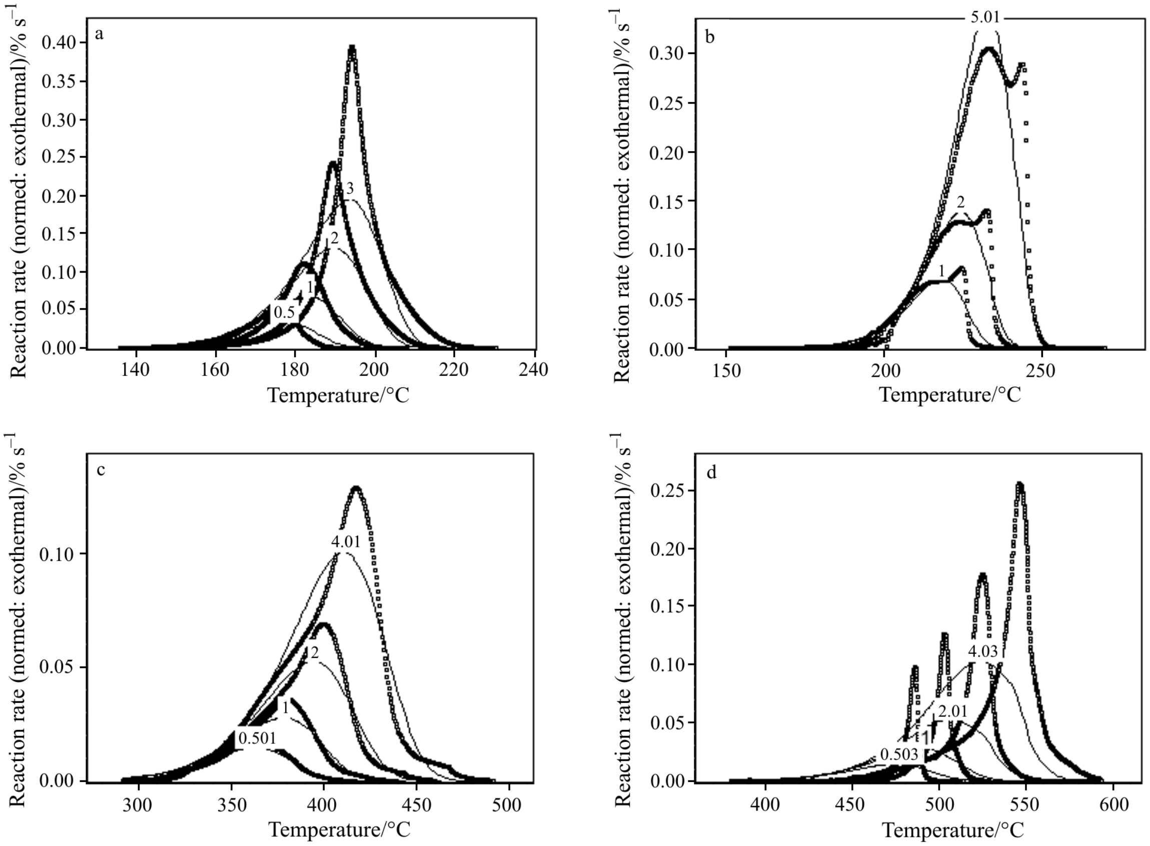

Fig. 5 Simplified kinetic description (model: 1st order reaction) of normalized non-isothermal DSC-signals as a function of the temperature for the decomposition of a – propellant EI®, b – explosive PBXW-17, c – pyrotechnic material B/KNO_3 50:50 and d – B/KNO_3 30:70

Cook-off experiments

The results of slow cook-off experiments (heating rate 3.3°C h^{-1}) are shown in Fig. 6. The experimentally determined ignition temperatures were 126°C (propellant EI®), 177°C (PBXW-17), 318°C (B/KNO_3 50:50) and 436°C (B/KNO_3 30:70).

The simulation results of slow cook-off experiments for the four energetic materials are presented in Table 1. In these simulations the kinetic parameters determined by the Advanced Kinetics Software [12] were applied together with the heat balance based on FEA. For the simulations, the following parameters were used: T_{initial}=40°C during 6 h followed by a heating rate of 3.3°C h^{-1}.

The simulation results obtained from the Advanced Kinetics Software show very good agreement with the experimentally found values as presented in

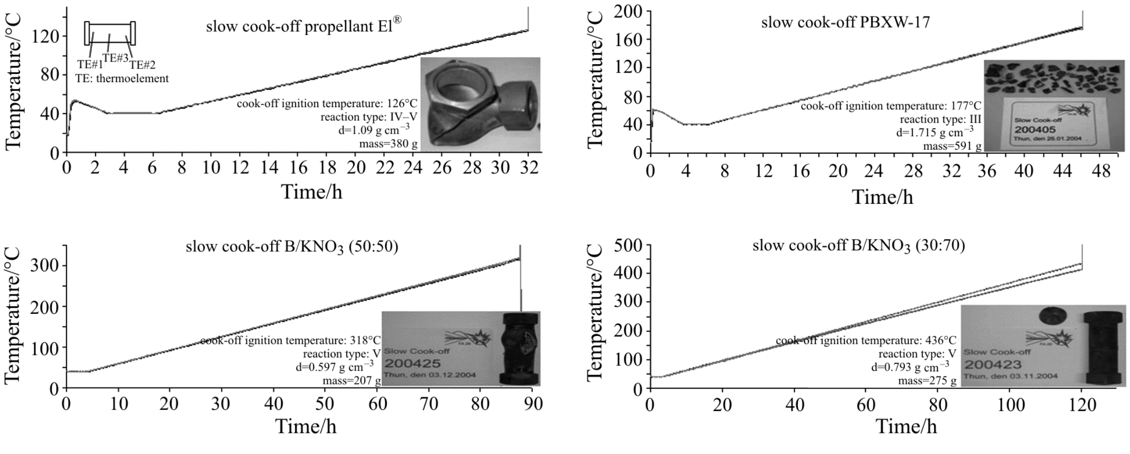

Fig. 6 Slow cook-off experiments. The change of temperature of the energetic materials with a heating rate of 3.3°C h^{-1}

Table 1 The experimental details of cook-off experiments and comparison of experimental and simulated data for four energetic materials

Parameter	Propellant El®	PBXW-17	B/KNO$_3$ 50:50	B/KNO$_3$ 30:70
Density/g cm^{-3}	1.09	1.715	0.597	0.793
c_p/J g^{-1} K^{-1}	1.54	1.15	1.62	1.62
Recipient thickness/mm	4	4	4	4
Recipient thermal diffusivity/cm^2 s^{-1}	0.166	0.166	0.166	0.166
Energetic layer radius/mm	23.5	23.5	23.5	23.5
Sample thermal diffusivity/cm^2 s^{-1}	0.01	0.01	0.001	0.001
Heat of reaction/J g^{-1}	3875	2572	4248	5273
Experimental slow cook-off temperature/°C	126	177	318	436
Simulated slow cook-off T/°C (adv. kinetics)	128	180.5	313	437
Simulated slow cook-off T/°C (1st order)	126	160.5	271	376
Simulated slow cook-off T/°C (nth order)	118	151	270	351

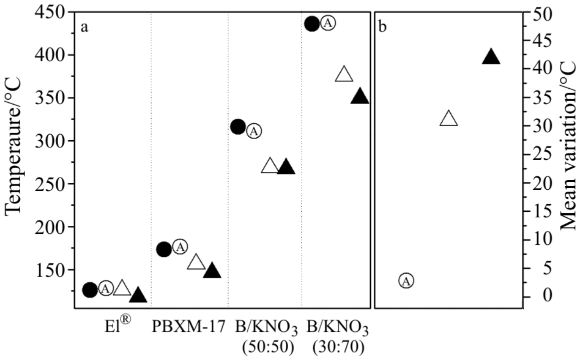

Fig. 7 a – Temperatures of the ignition during simulated cook-off experiments: circles with ‘A’ – applying advanced kinetics AKTS software, △ – assuming 1st order mechanism and ▲ – nth order mechanism. Experimental results are marked by filled circles; b – mean variations of the temperature difference between experimental and simulated values of the ignition temperatures for differently calculated kinetic parameters (the meaning of the symbols is the same as in plot A)

Table 1. The difference between the predicted and measured cook-off temperature can be refined by adjusting slightly the thermal diffusivity in order to take into account the possible deviations due to the simplified geometries applied for the simulation (infinite cylinder instead of a drum shape).

The results of the additional simulation of the cook-off experiment but with the application of simplified kinetics (assuming first order and nth order mechanisms, constant during the course of the decomposition) are presented in Table 1 and in Fig. 7a. Figure 7b depicts the mean variations of simulated data for three applied methods: (*i*) an advanced kinetics calculated by AKTS software, (*ii*) by an assumption first- and (*iii*) by an assumption of the nth order mechanism i.e, two, commonly applied simplified kinetic descriptions of the reaction. The weak correlation between experimental and predicted data when applied oversimplified kinetic parameters confirms clearly that without the correct kinetic description of the decomposition process the prediction of the cook-off is of a little value.

Conclusions

The results of the kinetic analysis of four energetic materials clearly indicate that their decomposition cannot be described by the simplified kinetics with the assumption of the constant value of the activation energy E and the pre-exponential factor A during the full range of the decomposition. These both kinetic parameters vary during the reaction and the exact knowledge of their dependence on the reaction progress α is the prerequisite for the proper simulation of the material properties. The kinetic parameters calculated from the results obtained in non-isothermal DSC experiments were used for the prediction of the slow (3.3°C h^{-1}) cook-off experiments. Due to the fact that the sample mass in the real cook-off experiment was ca. four orders of magnitude larger than in the thermoanalytical investigations the prediction of the ignition temperature required additionally the precise evaluation of the heat transfer. This goal was achieved by the application of finite element analysis (FEA). The results of the simulations compared with the experimental values indicated that the proper kinetic description of the thermal decomposition of energetic materials and the application of detailed heat balance calculated with the FEA allowed very good simulation of the time to self-ignition. Obtained in this case, the similarity of the predicted and experimentally found temperatures of the ignition was not achieved when applying the simplified kinetics, being the procedure commonly reported in the literature.

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