

THE SIMULATION OF THE THERMAL BEHAVIOR OF ENERGETIC MATERIALS BASED ON DSC AND HFC SIGNALS

B. Roduit^{1*}, L. Xia¹, P. Folly², B. Berger², J. Mathieu², A. Sarbach², H. Andres³, M. Ramin³, B. Vogelsanger³, D. Spitzer⁴, H. Moulard⁴ and D. Dilhan⁵

¹AKTS AG Advanced Kinetics and Technology Solutions, TECHNOArk 3, 3960 Siders, Switzerland

²armasuisse, Science and Technology, 3602 Thun, Switzerland

³Nitrochemie Wimmis AG, 3752 Wimmis, Switzerland

⁴ISL, Institut franco-allemand de recherches de Saint-Louis, 68301 Saint Louis, France

⁵CNES Centre National d'Etudes Spatiales, 31401 Toulouse, France

Two small calibre and four medium calibre types of propellants were investigated non-isothermally ($0.25\text{--}4\text{ K min}^{-1}$) by differential scanning calorimetry (DSC) in the range of RT–260°C and isothermally (60–100°C) by heat flow calorimetry (HFC). The data obtained from both techniques were used for the calculation and comparison of the kinetic parameters of the decomposition process. The application of HFC allowed to determine the kinetic parameters of the very early stage of the reaction (reaction progress α below 0.02) what, in turn, made possible the precise prediction of the reaction progress under temperature mode corresponding to real atmospheric changes according to STANAG 2895. In addition, the kinetic parameters obtained from DSC data enabled determination of self-accelerating decomposition temperature (SADT) and comparison of the predicted ignition temperature during slow cook-off with the experimental results. The study contains also the results of the calculation of the time to maximum rate (TMR_{ad}) of the propellants under adiabatic conditions.

Keywords: *adiabatic conditions, cook-off, DSC, energetic materials, HFC, SADT, thermal decomposition kinetics, TMR_{ad}, time to maximum rate*

Introduction

Independent of the mass of the sample investigated in any thermoanalytical experiment the correct description of the reactions requires the knowledge of two important parameters (*i*) the kinetics of the investigated reaction and (*ii*) the heat balance of the system. Depending on the mass of the sample both these parameters differently contribute to the reaction progress: (*i*) The kinetics of the process, being its intrinsic property, is not dependent on the mass of the substance. The correct determination of the kinetic parameters allows simulation of the reaction progress under any temperature mode independent on the mass of investigated sample. (*ii*) On the other hand, the heat balance in the system strongly depends on the sample mass and therefore has to be considered in adiabatic and semi-adiabatic conditions. One can distinguish following boundary cases:

- in mg scale, i.e. in typical thermoanalytical experiments (DSC, HFC) one assumes the ideal exchange of the reaction heat with the environment, what, in turn, allows to carry on the experiments under isothermal conditions or with constant heating

rates. The reaction heat does not influence the course of the reaction.

- in ton scale one assumes that the reactions proceeds in adiabatic conditions, without any heat exchange with surroundings, therefore all heat evolved during exothermic reactions stays in the sample increasing its temperature. Under certain conditions this self-heating can lead to the runaway reaction therefore the prediction of the reaction course has to take into account not only the kinetics of the reaction but also the temperature increase resulting from the self-heating.
- in kg scale the problem of the heat exchange is more complicated because, depending on the thermal properties of the sample, its mass and type of the reactor (or container), the different amount of heat will be exchanged with the surroundings and some part of it will accumulate in the system. The heat balance in this situation is more complicated and generally can be correctly done only using numerical methods such as e.g. finite element analysis or finite differences.

Above considerations clearly indicate that the correct prediction of the reaction progress or reaction rate is possible only when the correct kinetic descrip-

* Author for correspondence: b.rodut@akts.com

tion of the process and exact heat balance in the system are done. The data collected during conventional thermoanalytical experiments, as e.g. DSC or HFC signals, can be used for determination of the kinetics of the reaction and therefore enable the prediction of e.g. the life-time at any temperature mode. However, it seems to be obvious that the simplified kinetic assumptions such as e.g. that reaction is of the first or *zero*-th order cannot describe correctly the kinetics of the complicated multistage reactions. Therefore the advanced kinetics methods, not assuming any reaction mechanism and allowing changes of the kinetic parameters during the course of the reactions, are required.

General

Application of DSC

The use of DSC allows the monitoring of the full range of the process from $\alpha=0$ to $\alpha=1$ (where α depicts the reaction progress). To apply the heat flow signals monitored by DSC for the kinetic analysis it is necessary to convert them into α -time or α -temperature dependences. The integration of heat flow signal is unfortunately influenced by the course of the baseline.

Often applied the straight-line form of the baseline is incorrect. For DSC signal types, a sigmoid baseline [1] is usually chosen because the recorded DSC signals depends not only on the heat of the reaction but are additionally affected by the change of the specific heat of the mixture reactant-products during the progress of the reaction. The proper construction of the baseline is especially important at the beginning of the reaction, when the heat flow is very low what results in weak DSC signal. Any small deviation in the construction of the tangent at the beginning of the signal leads to the uncertainty in the determination of the reaction progress. Unfortunately, this range between 0–5% of the total decomposition is very important for the prediction of the thermal stability of the material e.g. its service life time.

Summarizing, the relatively fast DSC experiments carried out in the following experimental domain:

$$0\% < \alpha < 100\%$$

$$0.25 < \beta \text{ (heating rate)} < 8 \text{ K min}^{-1}$$

$$0 < t \text{ (measuring time)} < 10 \text{ h}$$

can be used as a screening approach to predict the reaction progress for any temperature profile. However, for the very precise prediction of the changes of the properties of the investigated materials

which occur at the very low reaction progress the second technique, heat flow calorimetry (HFC) is certainly better suited.

Application of HFC

In order to gain better knowledge on the reaction course during the early stage of the decomposition one can determine the kinetic parameters from the results of calorimetric measurements carried out in the following experimental domain:

$$0\% < \alpha < 5\%$$

$$20^\circ\text{C} < T \text{ (isothermal temperature)} < 100^\circ\text{C}$$

$$0 < t \text{ (measuring time)} < 3 \text{ months}$$

Due to the fact that the determination of the reaction progress, being necessary for the kinetic analysis, does not require the construction of the baseline, the results obtained by this technique are more precise, especially for low and very low α values. This fact, in turn, allows the precise prediction of the reaction progress from the data measured at very low conversion degrees. However, for the determination of safety parameters such as the time to maximum rate under adiabatic conditions (TMR_{ad}), or the self-accelerating decomposition temperature (SADT), the DSC technique is superior as is it fast and enables monitoring full range of the process from $\alpha=0$ to $\alpha=1$.

Experimental

The high temperature DSC experiments were carried out in sealed crucibles [2] with heating rates of $0.25\text{--}4 \text{ K min}^{-1}$ in the range $\text{RT--}260^\circ\text{C}$. The low-temperature isothermal microcalorimetric investigations were done with thermal activity monitor (TAM), Thermometric AB, in the range of $60\text{--}100^\circ\text{C}$. The kinetic parameters were calculated using AKTS Thermokinetics software [3, 4]. The presented study contains the results of the evaluation of the kinetics of the decomposition of six propellants: two small calibre types ‘SB-SC1’ (5.56 mm, EI[®]), ‘SB-SC2’ (5.56 mm, single base); and four medium calibre types ‘SB-MC1’ (25 mm, EI[®]); ‘SB-MC2’ (23 mm, single base); ‘EI-MC1’ (30 mm, EI++) and ‘EI-MC2’ (30 mm, EI++).

Determination of the kinetic parameters

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 certain, arbitrarily chosen values of the reaction progress α recorded in the experiments carried out at e.g. different heating rates β or at different temperatures.

There are three main modifications of the isoconversional method: differential (Friedman) [5], integral (Flynn–Ozawa–Wall) [6, 7], advanced integral based on non-linear procedure (Vyazovkin) [8].

One has to mention also the method based on the isoconversional principle namely ASTM E698 analysis [9].

Differential method of Friedman

Based on the Arrhenius equation, Friedman proposed to apply to the commonly used expression in solid state kinetics, the logarithm of the conversion rate $d\alpha/dt$ as a function of the reciprocal temperature at any conversion α :

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT(t)}\right) f(\alpha) \quad (1)$$

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A_\alpha f(\alpha) - \frac{E_\alpha}{R} \frac{1}{T_\alpha} \quad (2)$$

where T , t , A , E and R are temperature, time, pre-exponential factor, activation energy and gas constant, respectively.

As $f(\alpha)$ is a constant in the last term at any fixed α , the logarithm of the conversion rate $d\alpha/dt$ over $1/T_\alpha$ shows a straight line with the slope $m=E_\alpha/R$ and the intercept on y -axis equal to $\ln[A_\alpha f(\alpha)]$.

So, having determined E_α and $A_\alpha f(\alpha)$ we can predict the reaction rate or reaction progress using the following expression:

$$\frac{d\alpha}{dt_\alpha} = A_\alpha f(\alpha) \exp\left(-\frac{E_\alpha}{RT(t_\alpha)}\right) \quad (3)$$

Integral Ozawa–Flynn–Wall method

This method is also based on the use of several dependences α - T measured at different heating rates. Starting from the commonly applied equation:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT(t)}\right) f(\alpha) \quad (4)$$

for the constant heating rate β , $dT/dt=\beta$ =constant and $T(t)=T_0+\beta t$. After integration we obtain:

$$g(\alpha) = \int_{\alpha=0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T(\alpha)} \exp\left(-\frac{E}{RT(t)}\right) dt \quad (5)$$

If T_0 lies below the temperature at which the reaction rate is noticeable, then one can set the lower limit of integration to $T_0=0$, so that the following equation in the logarithm form is obtained after integration:

$$\ln g(\alpha) = \ln(AE/R) - \ln \beta + \ln p(z) \quad (6)$$

with

$$p(z) = \frac{\exp(-z)}{z} - \int_{-\infty}^z \frac{\exp(-z)}{z} dz \text{ and } z = \frac{E}{RT} \quad (7)$$

By using the approximation given by Doyle [10] $\ln p(z) = -5.3305 - 1.052z$ one obtains:

$$\ln \beta = \ln \frac{AE}{R} - \ln g(\alpha) - 5.3305 - 1.052 \frac{E}{RT} \quad (8)$$

With data collected in series of measurements performed with the different heating rates β at a fixed degree of conversion α , it ensues from the above equation that the dependence $\ln \beta$ vs. $1/T$ will be linear with a slope $m = -1.052E/R$.

Advanced integral method of Vyazovkin

According to this method, for a set of n experiments carried out at different arbitrary heating programs $T_i(t)$, the E_α is determined as the value that minimizes the function

$$\phi(E_a) = \sum_{i=1}^n \sum_{j=1}^n \frac{J[E_a, T_i(t_\alpha)]}{J[E_a, T_j(t_\alpha)]} \quad (9)$$

where J denotes the integral

$$J[E_a, T_i(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_a}{RT_i(t)}\right] dt \quad (10)$$

The systematic error is eliminated by carrying out the integral in this last equation over small time intervals. Generally, α varies from $\Delta\alpha$ to $1-\Delta\alpha$ with a step $\Delta\alpha$ which is usually taken to be 0.02.

ASTM method E698

The analysis according to ASTM E698 is based on the assumption that the maximum (e.g. on the DSC or DTG curves) of a single step reaction is reached at the same conversion degree independent on the heating rate. Although this assumption is only partly right, the resulting errors are sometimes low [9]. In this method, the logarithm of the heating rate is plotted over the reciprocal temperature of the maximum. The slope of the yielded straight line is proportional to the activation energy, as in the Ozawa–Flynn–Wall method.

Comparison of the isoconversional methods

A detailed analysis of the differential and integral isoconversional methods for the determination of the activation energy has been reported by Budrugaec [10]. The convergence of the activation energy values obtained by means of a differential method like Friedman [5] with those obtained by 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 can yield systematic errors when determining the activation energies. These

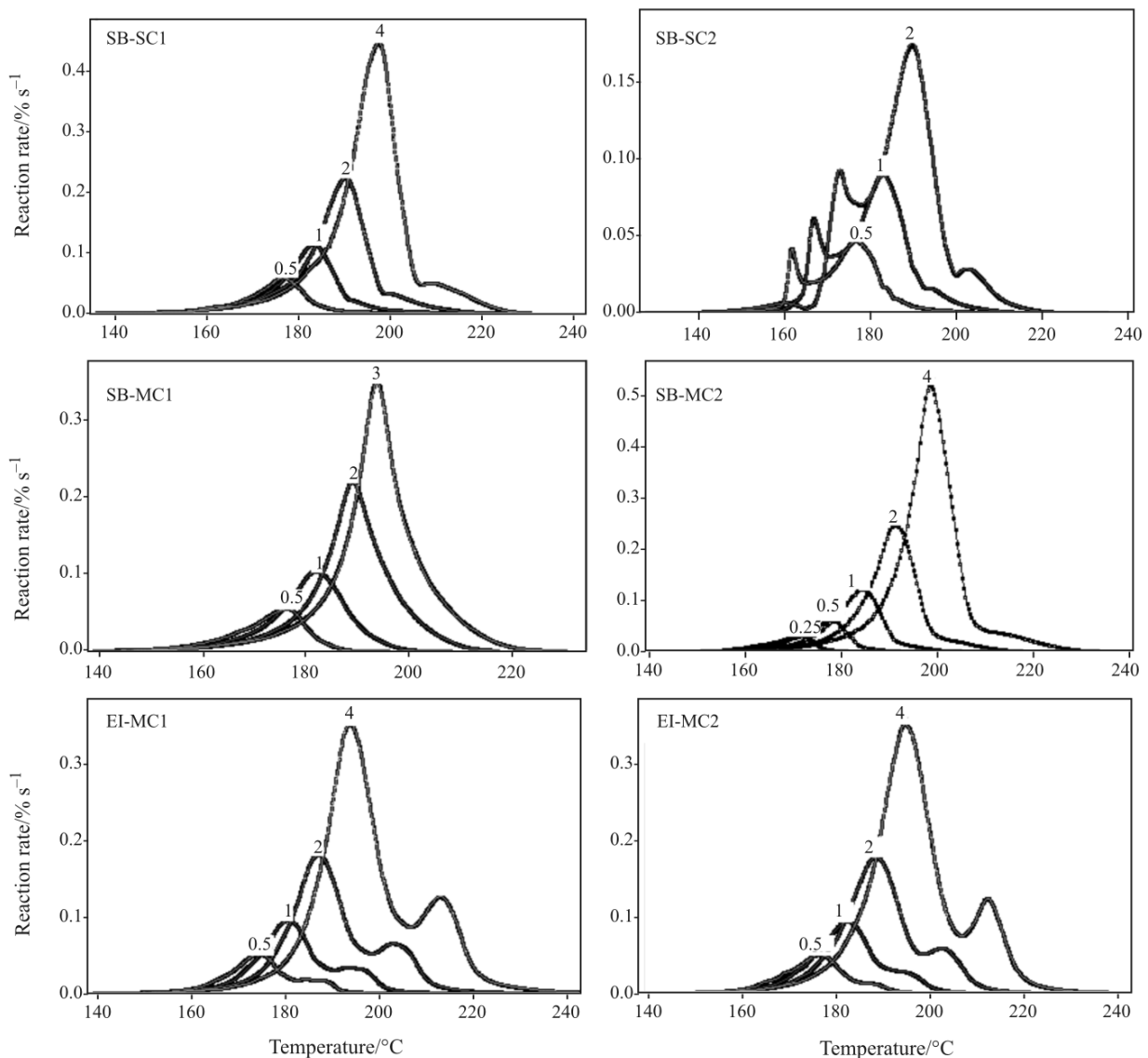


Fig. 1 Normalized DSC signals of propellants as a function of the temperature and heating rate (marked in K min^{-1} on the curves). Experimental data are depicted as symbols, solid lines represent the signals calculated on the basis of kinetic parameters derived from the Friedman analysis. The meaning of the sample labels is given in the section ‘Experimental’

errors depend directly on the size of the small ranges of reaction progress $\Delta\alpha$ over which the integration is performed. These errors can be avoided by using infinitesimal ranges of reaction progress $\Delta\alpha$. As a result, isoconversional integral methods turn back to the differential isoconversional methods formerly proposed by Friedman.

In the current study the kinetic parameters have been calculated by the differential isoconversional method of Friedman using the isothermal data obtained by means of HFC and the non-isothermal data obtained by DSC.

Results and discussion

Kinetic analysis of DSC data

The DSC signals after correction of the baseline were used for the estimation of the reaction progress. The obtained α - T values were applied for the calculation of the E and A kinetic parameters by isoconversional method of Friedman. The DSC signals of investigated samples are presented in Fig. 1 in the form of the normalized reaction rate on the temperature for four heating rates. Kinetic parameters calculated from the DSC traces allowed the simulation of the reaction progress at any heating rate. The comparison of the experimental data (symbols) with the simulated course of the reactions (lines) indicates the very good fit when the advanced kinetic analysis was applied.

Kinetic analysis of HFC data

The heat flow signals recorded by HFC in isothermal runs at 60, 70, 80, 90, 100°C for SB-SC1 and SB-SC2 and at 80, 90 and 100°C for SB-MC1, SB-MC2, EI-MC1 and EI-MC2 are shown in Fig. 2 as a heat flow – time dependences. The reaction progress was calculated from HFC signals by relating cumulative heat after certain time of the decomposition (Q) to the total heat of the reaction ΔH_r measured by DSC as presented in Table 1.

The dependence of the activation energy on the reaction progress calculated from the HFC data is presented in Fig. 3. It is clearly visible that the activation energy changes significantly even in the very narrow range of the reaction progress (between 0 and 1.6%).

The results presented in Fig. 3 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 (not shown) are not constant during the course of the reactions. Clearly visible is the

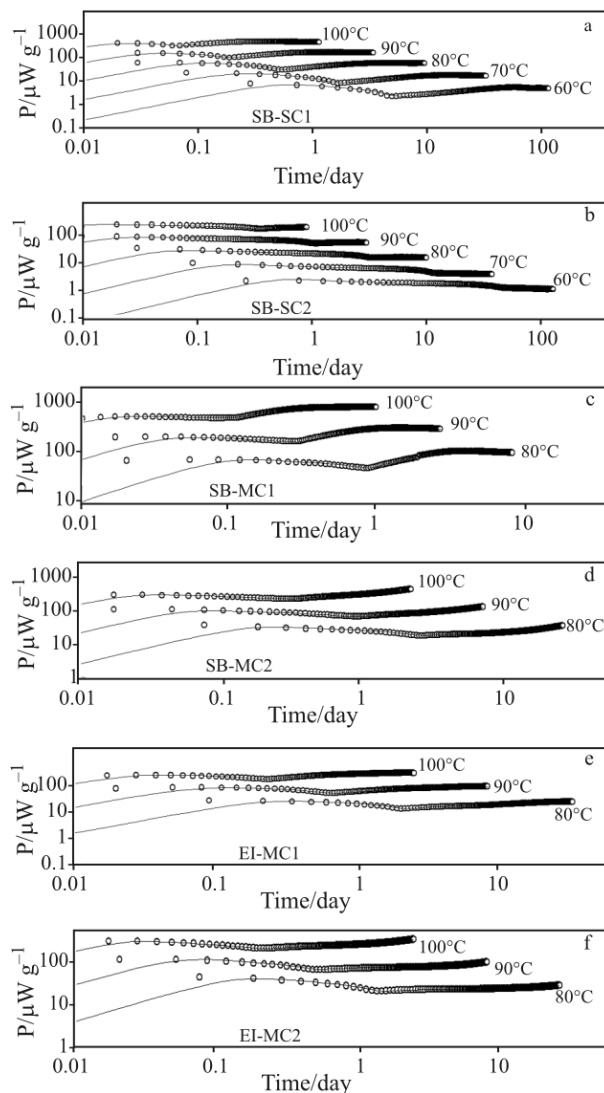


Fig. 2 HFC-signals vs. time at different temperatures a – SB-SC1, b – SB-SC2: 60, 70, 80, 90, 100°C; c – SB-MC1, d – SB-MC2, e – EI-MC1 and f – EI-MC2: 80, 90 and 100°C. Experimental data are depicted as symbols, solid lines represent the signals calculated on the basis of kinetic parameters derived by Friedman method. The reaction progresses for each sample are the same at all temperatures, the values of α are depicted in Table 1

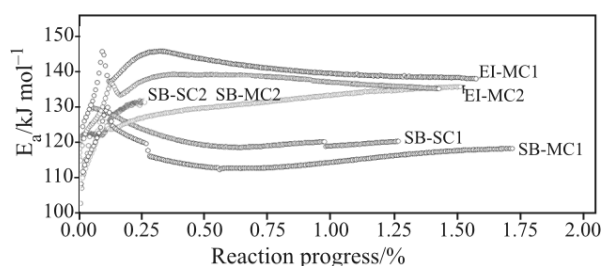
dependence of the kinetic parameters on the reaction extent. This observation indicates that the decomposition of the examined energetic materials is a complex reaction which cannot be described in terms of a single pair of Arrhenius parameters and commonly used set of reaction models.

Application of HFC data for the prediction of the reaction progress under temperature mode corresponding to real atmospheric temperature changes

The important goal for investigating kinetics of thermal decompositions of propellants is the deter-

Table 1 The reaction progress calculated from HFC signals by relating the cumulative heat Q measured by HFC to the heat release ΔH measured by DSC

Sample	$\Delta H/J\text{ g}^{-1}$ DSC	$Q/J\text{ g}^{-1}$ HFC	Reaction progress $\alpha/\%$
SB-SC1	4010	51.58	51.58/4010=1.286
SB-SC2	4137	11.00	11.00/4137=0.266
SB-MC1	3450	59.71	59.71/3450=1.731
SB-MC2	3947	56.49	56.49/3947=1.431
EI-MC1	3870	62.07	62.07/3870=1.604
EI-MC2	3937	59.70	59.70/3937=1.516

**Fig. 3** Activation energy of the decomposition of the propellants as a function of the reaction progress calculated from the HFC data by the Friedman analysis

mination of their thermal stability, i.e. the temperature range over which the substance does not decompose at an appreciable rate. During their production, storage or final usage the propellants often undergo the temperature fluctuations. Due to the fact that the reaction rate varies exponentially with the temperature it is important that predictive tools could enable the simulation of the reaction progress in the real conditions, as a small temperature jump can induce a significant increasing reaction rate. Since the HFC data allow very precise monitoring early stage of the decomposition process, the reaction rate can therefore be predicted very precisely for any temperature profile, such as stepwise variations, oscillatory conditions, temperature shock, or even real atmospheric temperature profiles. To illustrate the importance of the influence of the temperature fluctuations on the reaction rate, the simulations of the reaction progress were carried out for the high temperature climatic category A1 according to the STANAG 2895 [12]. This document describes the principal climatic factors which constitute the distinctive climatic environments found throughout the world and provides guidance on the drafting of the climatic environmental clauses of requirement documents.

The prediction of the influence of the temperatures on the slow decomposition of the propellants requires the knowledge of the diurnal and annual variations of the meteorological and storage/transit temperatures. The meteorological temperature is the

Table 2 Summarized temperature cycles world-wide for climatic category A1

Cycle	$T/^\circ\text{C}$ (meteorological)	$T/^\circ\text{C}$ storage and transit
Zone A1	32 to 49	33 to 71

ambient air temperature measured under standard conditions, whereas storage and transit temperature represents the air temperature measured inside temporary unventilated field shelter e.g. in railway boxcar which is exposed to direct solar radiation. Table 2 contains the values of these temperatures for the climatic category A1. The time dependences of the diurnal minimal and maximal meteorological and storage/transit temperatures are presented in Fig. 4. Applying the advanced kinetic software it is possible to calculate the reaction progress for all propellants using the kinetic parameters determined from HFC data and taking into account the dependence of the real temperature changes depicted in Figs 4a and b. The results of the simulations for the diurnal storage/transit and meteorological temperature profiles are shown in Figs 5a and b, respectively.

Presented results indicate the very significant dependence of the thermal stability of the investigated propellants on the storage conditions even in the same climatic category. Note, that for the same propellant e.g. EI-MC1, the 1.6% decomposition progress, occurring after 12 years when the sample is submitted to the diurnal meteorological temperature changes, significantly decreases to ca. 500 days when the propellant is stored under storage/transit temperature conditions. This important issue could be traced only due to the high precision of the HFC data and the application of the software which enables to consider the very complicated temperature profiles. By implementing the climatic variations into advanced kinetic description gathered from the HFC data it was possible to uncover the differences of the reaction progress for the same propellants in the same climatic category.

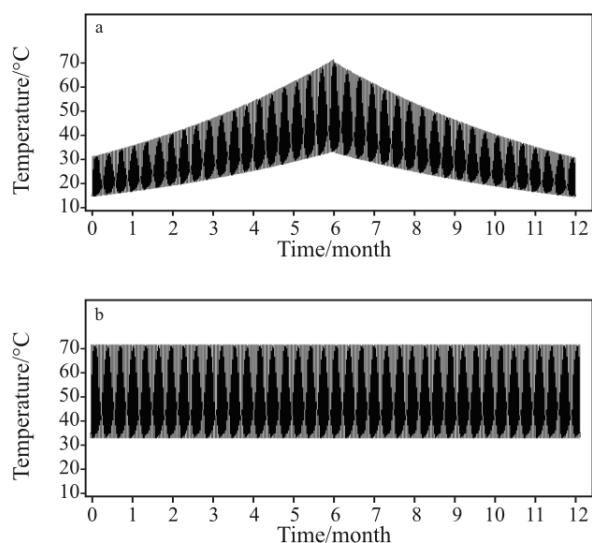


Fig. 4 a – Minimal and maximal diurnal meteorological and b – storage/transit temperatures recorded during one year in the climatic category A1

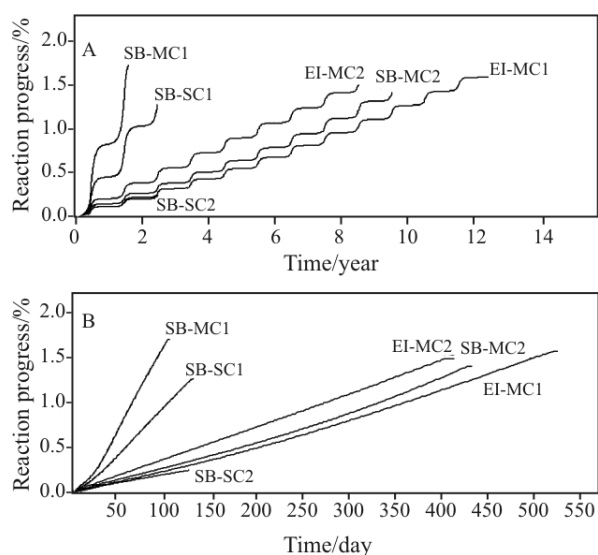


Fig. 5 Predictions of the reaction progress for the propellants due to the temperature variations represented by the a – meteorological temperature and b – diurnal storage/transit profiles

Comparison of the simulation of the reaction progress based on DSC and HFC data

As previously mentioned, the very important issue for the correct prediction of the shelf-life is the correct determination of the reaction progress, especially at very beginning of the reaction. This is not an easy task in DSC measurements due to the possibility of introducing significant errors by the improper construction of the baseline. This problem is well illustrated by the results presented in Fig. 6 showing

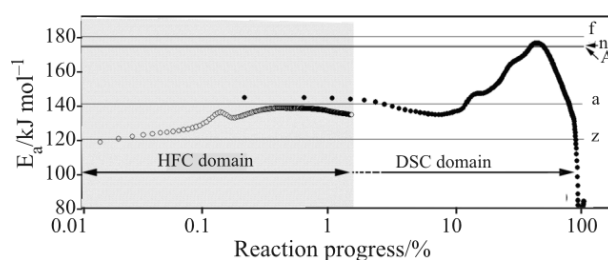


Fig. 6 Comparison of the activation energy for the decomposition of SB-MC2 gathered by the isoconversional method from HFC and DSC data. The horizontal lines represent the values of E calculated from DSC data assuming certain reaction models valid in the full range of the decomposition. In the n -th order model n has value of 0.91. z – zero-th order, f – first order, n – n -th order, a – autocatalytic, A – ASTM E698

the difference of the values of the activation energy E calculated by the isoconversional method from the DSC and HFC data.

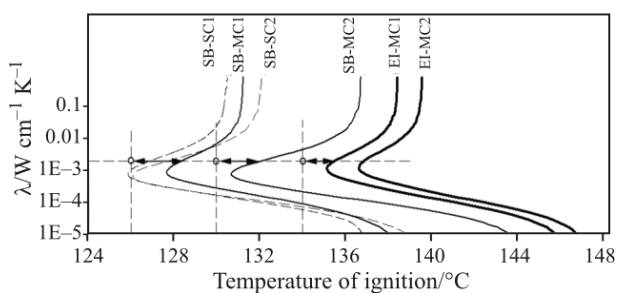
The comparison of the predictions based on the kinetic parameters obtained from DSC (filled circles) with HFC experimental data (open circles) for the propellant SB-MC2 at very low reaction progress (α between 0.002 and 0.016) indicates similar, but not exactly the same, dependence of the activation energy on the reaction progress. The improvement of this fit requires the elaboration of the computational technique enabling the link between the experimental data obtained by means of both techniques for the low decomposition progress α between 0 and 0.05. Such studies are currently under progress.

Calculation of TMR_{ad} , SADT and time to ignition during slow cook-off

Additionally to the prediction of the reaction progress at any temperature profile in mg-scale also the simulations of the thermal properties in kg-scale (slow cook-off experiment) and in ton-scale: self-accelerating decomposition temperature (SADT) and time to maximum rate under adiabatic conditions (TMR_{ad}) have been carried out for all six propellants. Such simulations of reactions triggering require the kinetic parameters describing the broader range of the reaction progress. For the simulation of slow-cook-off the following parameters were used: $T_{initial}=40^{\circ}\text{C}$ during 6 h followed by a heating rate of 3.3 K h^{-1} ; the thickness of the recipient layer=4 mm, material of the container: steel with the density $\rho=8.03\text{ g cm}^{-3}$, specific heat $C_p=0.503\text{ J g}^{-1}\text{ K}^{-1}$, thermal conductivity $0.163\text{ W cm}^{-1}\text{ K}^{-1}$, radius of the energetic layer=23 mm, propellant: density $\rho=1.63\text{ g cm}^{-3}$, specific heat $C_p=1.5\text{ J g}^{-1}\text{ K}^{-1}$, thermal conductivity $0.002\text{ W cm}^{-1}\text{ K}^{-1}$. Figure 7 shows the simulation

Table 3 The properties of the six analyzed propellants with their values of temperature of slow-cook ignition, SADT and TMR_{ad} 24 h

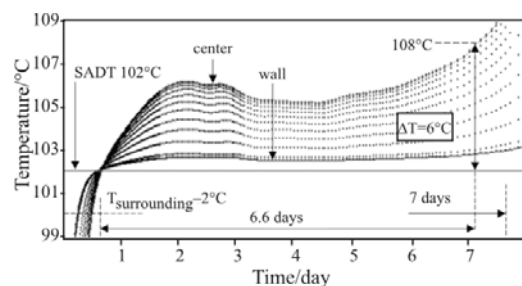
	SB-SC1	SB-SC2	SB-MC1	SB-MC2	EI-MC1	EI-MC2
Thermal conductivity $\lambda/W\text{ cm}^{-1}\text{ K}^{-1}$	0.002	0.002	0.002	0.002	0.002	0.002
Density $\rho/g\text{ cm}^{-3}$	1.63	1.63	1.63	1.63	1.63	1.63
Specific heat $C_p/J\text{ g}^{-1}\text{ K}^{-1}$	1.5	1.5	1.5	1.5	1.5	1.5
Heat release ΔH measured by DSC/ $J\text{ g}^{-1}$	4010	4137	3450	3947	3870	3937
T-slow cook ignition experimental/ $^{\circ}\text{C}$	N.A.	N.A.	126	130	N.A.	134
T-slow cook ignition calculated/ $^{\circ}\text{C}$	126.7	127.5	128.2	131.8	136.7	135.3
SADT/ $^{\circ}\text{C}$	102	102	91	102	106	109
T-TMR _{ad} 24 h/ $^{\circ}\text{C}$	97.5	99.5	98.5	102	109	112

**Fig. 7** Simulation results of the temperature of slow cook-off ignition (thermal conductivity vs. explosion temperature) for the six examined propellants. Experimentally found values for the propellants SB-MC1, SB-MC2, EI-MC1 amounted to 126, 130 and 134°C

results in the form of the dependence thermal conductivity vs. explosion temperature. The experimental parameters and results of the simulation and the experimental results of the slow cook-off investigation are presented in Table 3.

The results presented in Fig. 7 indicate that the change of the thermal conductivity in the range 1e-3 till 1e-2 W cm⁻¹ K⁻¹, which reflects the values characteristic for the propellants, varies the cook-off ignition temperatures of ca. 1–2°C only. For the assumed simulation value of the thermal conductivity of 0.002 W cm⁻¹ K⁻¹ the difference between simulated and experimental values are in the range of 2 K (see the data presented in Table 3 and depicted in Fig. 7).

The differences between the predicted and measured cook-off temperatures are mostly due to the arbitrarily chosen values of the thermal conductivity and too simplified geometry of the container applied for the simulation (infinite cylinder instead of a drum shape).

**Fig. 8** Simulation of the SADT for the propellant SB-MC2. Based on the first definition of the SADT [15], we obtain a value of 102°C. This temperature is the lowest environment temperature at which the overheat in the middle of the specific packaging exceeds 6°C (ΔT_6) after a lapse of the period of seven days (168 h) or less. This period is measured from the time when the packaging centre temperature reaches 2°C below the surrounding temperature. This overheat of 6°C occurs after about 6.6 days. The upper curve represents the temperature of the packaging center, the bottom curve – the temperature of the packaging wall

The kinetic parameters obtained by means of the DSC data enabled determination of the SADT for the six energetic materials. The SADT is an important parameter that characterizes thermal hazard under transport conditions of self-reactive substances. The SADT has been introduced into the international practice by the regulations of the United Nations presented in ‘Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria’ (TDG) [13]. The Globally Harmonized System (GHS) [14] has inherited the SADT as a classification criterion for self-reactive substances. According to the recommendations on TDG, the definition of the SADT is ‘the lowest environment temperature at which overheat in the middle of the specific commercial packaging exceeds 6°C (ΔT_6) after a lapse of the

period of seven days (168 h) or less. This period is measured from the time when the packaging center temperature reaches 2°C below the surrounding temperature.'

The method for evaluating SADT by using advanced kinetics-based simulation approach has been reported elsewhere [15].

Figure 8 presents the results for the propellant SB-MC2. At surrounding temperature of 102°C (SADT temperature) the overheat in the center of the sample (upper curve) reaches 6°C after 6.6 days i.e. according the SADT definition at time shorter than 7 days. In the simulation, the following parameters were used: thickness of the recipient layer=4 mm, a radius of the energetic layer=64.5 mm. The SADT values for all propellants are reported in Table 3. The found values are in accordance with other studies based on a 155 mm artillery charge applied in Swiss army reporting a SADT of 100°C [15].

The DSC data can also be used for the simulation of the properties of the substance under adiabatic conditions i.e. for the processes occurring without heat exchange with surroundings. During simulations of the thermal behavior not only the kinetic parameters of the process but also the heat balance in the system have to be considered because the heat accumulated in the sample can significantly influence the rate of the process. The heat accumulation is the result of the difference between the production of heat and the dissipation of heat depending on the system parameters in the reaction's environment. When the dissipation ability of the system does not exactly compensate the produced heat, it results in a variation of temperature that can lead to explosion.

The results of the calculations of time of maximum rate under adiabatic conditions (TMR_{ad}) based on the kinetic parameters obtained from non-isothermal DSC measurements are shown in Fig. 9.

The amount of the heat produced in the reaction was measured from the DSC traces by calculating the average of the heats of reaction measured at different heating rates. The standard deviation is calculated using the following formula:

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (\Delta H_i - \overline{\Delta H})^2}{n-1}}$$

where $\overline{\Delta H}$ is the mean value of the heat release obtained from the various DSC traces, ΔH_i is the heat release of each DSC trace and n is the number of applied heating rates. For the SB-MC2 propellant a mean value of heat release amounts to $\Delta H=3947 \text{ J g}^{-1}$ with a standard deviation σ of $\pm 273.9 \text{ J g}^{-1}$ (0.25 K min^{-1} : $\Delta H=4377 \text{ J g}^{-1}$, 0.5 K min^{-1} :

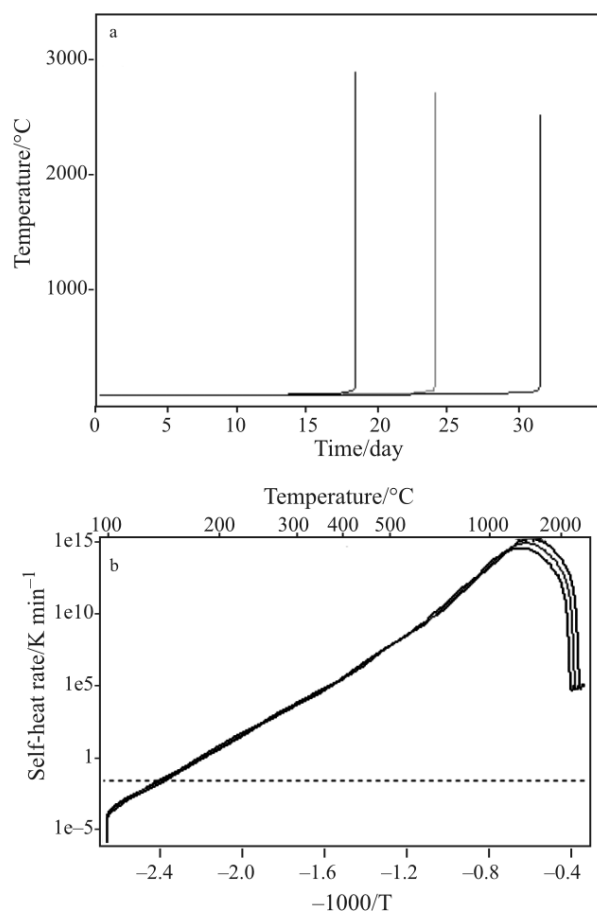


Fig. 9 Adiabatic runaway curves: a – simulation of the temperature change vs. time under adiabatic conditions calculated for the following parameters: TMR_{ad}=24 h (and 95% confidence intervals), $T_{\text{begin}}=102^\circ\text{C}$, $\Delta H=3947\pm 273.9 \text{ J g}^{-1}$, $C_p=1.5 \text{ J g}^{-1} \text{ K}^{-1}$, $\Delta T_{\text{ad}}=2631\pm 182.6^\circ\text{C}$. b – self-heat rate curves for the same simulation parameters (and 95% confidence intervals)

$\Delta H=4045 \text{ J g}^{-1}$, 1 K min^{-1} : $\Delta H=3737 \text{ J g}^{-1}$, 2 K min^{-1} : $\Delta H=3861 \text{ J g}^{-1}$ and 4 K min^{-1} : $\Delta H=3714 \text{ J g}^{-1}$).

Commonly accepted as the safety limit on the industrial scale, the critical temperatures corresponding to a time to maximum rate under adiabatic conditions of 24 h (TMR_{ad}=24 h) for the six propellants have been reported in Table 3. The detailed description of the method of the determination of the TMR_{ad} based on the advanced kinetics-based simulation approach has been reported elsewhere [16]. In addition to the values of the SADT and temperature of ignition of slow cook-off experiments, the value of TMR_{ad} is also a good indicator of the thermal reactivity of energetic materials.

Conclusions

The DSC and HFC data collected with few heating rates and at constant temperatures were applied for the determination of the kinetic parameters of the reaction using differential isoconversional method of Friedman. The evaluation of the kinetics of the propellants decomposition by both methods clearly indicated the significant change of the kinetic parameters E and A during the decomposition course. The thermal behaviour was investigated for significantly different masses of the propellants: (i) In mg-scale the prediction of the thermal stability of the propellants requires the exact determination of the reaction progress at the early beginning of the decomposition process in the range of the reaction progress α between 0 and ca. 0.05 of the total decomposition. This can be achieved by the application of the HFC signals which do not require the subtraction of the baseline being the main source of the errors in the correct evaluation of the α - T relationship. The very good fit of the experimental results with the simulated data indicated the accurate kinetic description of the process and allowed the prediction of the reaction progress (or reaction rates) of propellants under any temperature profile and even under climatic categories according to some specific climatic zones of the STANAG 2895 [12]. (ii) In kg- or ton-scale the prediction of the thermal behaviour of the propellants was performed for semi-adiabatic (simulation of slow cook-off and determination of SADT) and adiabatic conditions (determination of the TMR_{ad}). Under these conditions the kinetic based approach was combined with the heat balance in the system. The comparison of the experimental and simulated data indicates that the applied software can be successfully used for the up-scaling of the results obtained by means of DSC and HFC.

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