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THE PREDICTION OF THERMAL STABILITY OF SELF-REACTIVE CHEMICALS
From milligrams to tons

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An advanced study on the thermal behaviour of double base (boost and sustain propellant) rocket motor used in a ground to air missile has been carried out by differential scanning calorimetry (DSC). The presence of two propellants as well as the different experimental conditions (open *vs*. closed crucibles) influence the relative thermal stability of the energetic materials. Several methods have been presented for predictions of the reaction progress of exothermic reactions under adiabatic conditions. However, because decomposition reactions usually have a multi-step nature, 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 is usually the main source of serious errors for the determination of the time to maximum rate under adiabatic conditions (TMR_{ad}). It is hazardous to develop safety predictive models that are based on simplified kinetics determined by thermoanalytical methods. Applications of finite element analysis (FEA) and accurate kinetic description allow determination of the effect of scale, geometry, heat transfer, thermal conductivity and ambient temperature on the heat accumulation conditions. Due to limited thermal conductivity, a progressive temperature increase in the sample can easily take place resulting in a thermal explosion. Use of both, kinetics and FEA [1], enables the determination of the reaction progress and temperature profiles in storage containers. The reaction progress and temperature can be determined quantitatively at every point in time and in space. This information is essential for the design of containers of self-reactive chemicals, cooling systems and the measures to be taken in the event of a cooling failure.

Keywords: *adiabatic conditions, kinetics, safety, thermal ageing, thermal hazards, time to maximum rate, TMR_{ad}*

Introduction

In the early nineties of the last century several rocket motors of a ground to air missile started burning after a fire in a rock cavern. Due to this heavy accident the Swiss General Staff were interested to understand the time of ignition for stored rocket motors after a fire in a storage facility. One example of a rocket motor is shown in Fig. 1. The motor contains two propellants: Boost propellant and sustain propellant (glycerol nitrate, cellulose nitrate, stabilizers and other components).

Generally, all energetic materials liberate heat during decomposition. Processing, design, quality control, and operational applications all require an evaluation of thermal hazards and an ability to predict the safety limits and the course of the decomposition process in extended temperature ranges [1–5]. The present paper is designed to answer the following issues:

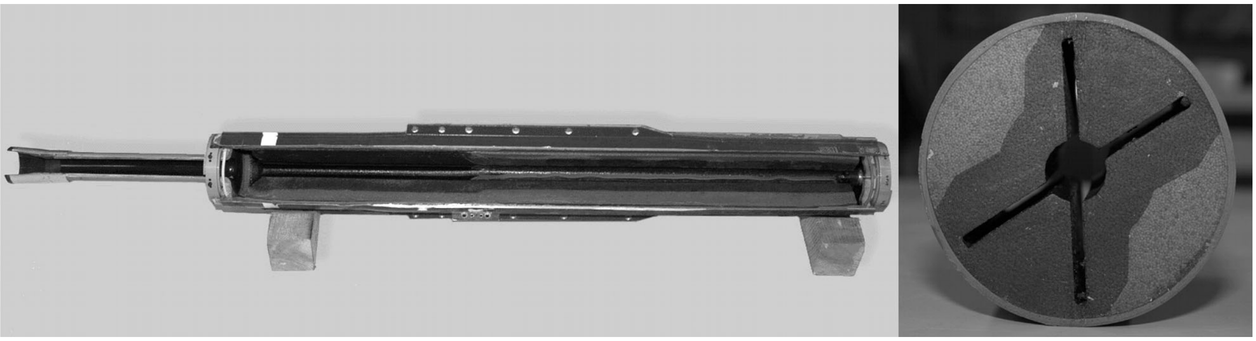

Fig. 1 Left – rocket motor for a ground to air missile; right – rocket propellant. Boost propellant (dark), sustain propellant (hell)

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- What is the reaction progress of the propellants under any temperature profile?
- Does a thermal hazard exist?
- At what temperature does the thermal hazard begin?
- What is the time to maximum rate under adiabatic conditions (TMR_{ad}) at any temperature?
- What is the temperature of maximum self-heating?
- How much influence does isolation/heat transfer have on the heat accumulation conditions?
- What are the critical storage container sizes or transport temperatures?
- What influence do the surrounding temperature profiles have on the reaction progress and on the heat accumulation conditions?

Experimental and analysis process

Collection of experimental data and baseline determination

The analysis process requires determination of the kinetic characteristics of the reaction. The kinetic parameters can be extracted in principle from experimental data gathered by any of the following dynamic thermoanalytical methods: DSC (differential scanning calorimetry), DTA (differential thermal analysis), TG (thermogravimetry) or EGA (evolved gas analysis TG-MS or TG-FTIR). The application of the thermoanalytical techniques is widely recognized for the characterization of the degradation of solids [6].

The correct kinetic analysis of a decomposition reaction has at least three major stages: (1) collection of experimental data; (2) computation of kinetic parameters, and (3) prediction of the reaction progress for required temperature profiles applying determined kinetic parameters. Kinetic evaluation of the reactions should be carried out with thermoanalytical data obtained at several heating rates (non-isothermal) or temperatures (isothermal) to ensure reliable results. Kinetic methods that use single heating rate experimental results should be avoided because they tend to produce highly ambiguous kinetic descriptions [7, 8]. At least three heating rates or temperatures are recommended. Applying the results obtained by thermoanalytical techniques (DSC), the kinetic analysis presented in this paper enables accurate prediction of the reaction progress of materials in a broad temperature range that may be difficult to explore for time, sensitivity or safety reasons. The presented study focuses on the evaluation of the experimental results obtained by DSC under isobaric (open crucibles) and isochoric (closed crucibles) conditions. For these measurements a Mettler differential scanning calorimeter (DSC) type DSC 821^{e} was used. The thermal behaviour of both propellants was examined at different heating rates ranging from 0.25 to 10 K min^{-1}. Figure 2 shows the DSC heat flow curve and the baseline subtracted heat flow curve of the sustain propellant at 0.25 K min^{-1} under isochoric conditions (closed crucibles). Generally, the application of straight-line form for the baseline is incorrect. The tangential area-proportional baseline is the most widely applied because of its correction possibilities [9]. 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. 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 [1].

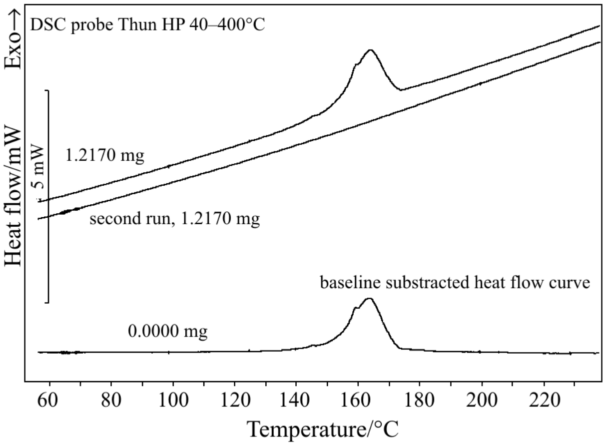

Fig. 2 DSC heat flow curve and the baseline subtracted heat flow curve of the sustain propellant at 0.25 K min^{-1} under isochoric conditions (closed crucibles)

Determination of the kinetic characteristics

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 'multi-curve' methods over the past few years, as discussed in the International ICTAC kinetics project [7, 10–12]. 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 [7, 8, 10–13]. This data set usually contains:

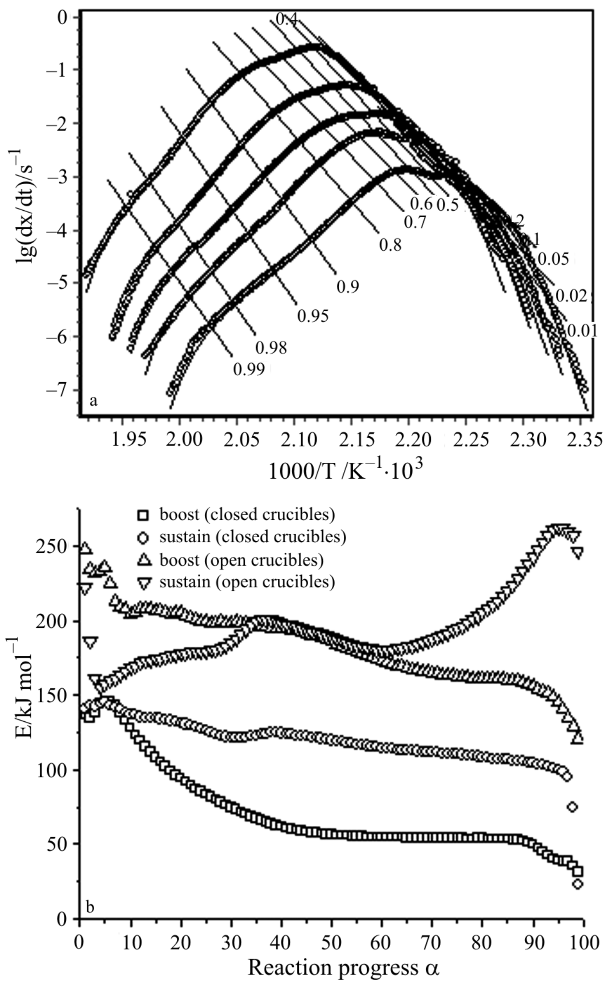

Fig. 3 a – Friedman analysis of decomposition of the sustain propellant under isobaric conditions (open crucibles); b – activation energy as a function of the reaction progress for decomposition of the boost and sustain propellant under isochoric (DSC closed crucibles) and isobaric conditions (DSC open crucibles)

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

Commonly applied are the following isoconversional methods known as: Friedman [14] and Ozawa–Flynn–Wall [15, 16]. A detailed analysis of the various isoconversional methods (i.e. the isoconversional differential and integral methods) for the determination of the activation energy has been reported in the literature by Budrugeac [17]. The convergence of the activation energy values obtained by means of a differential method (Friedman) 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. Friedman analysis, based on the Arrhenius equation, applies the logarithm of the conversion rate dα/dt as a function of the reciprocal temperature at different degrees of the conversion. As $f(\alpha)$ is constant at each conversion degree α_i, the method is so-called ‘isoconversional’ and the dependence of the logarithm of the reaction rate over $1/T$ is linear with the slope of $m=E/R$ as presented in Fig. 3a. 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 situation the reaction rate can be described only by complex equations, where the activation energy term is no more constant but is dependent on the reaction progress α ($E\neq$const. but $E=E(\alpha)$) (Fig. 3b) [14–16].

As far as isoconversional integral methods are concerned, these techniques are based on the equation:

$$g(\alpha)=\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_{\alpha=0}}^{T}\exp\left(-\frac{E}{RT}\right)dT \qquad (1)$$

where $g(\alpha)$ is the integral conversion function and $f(\alpha)$ the function dependent on the reaction model. The isoconversional integral methods with the integration over low ranges of the degree of conversion and, respectively temperature, are based on the equation:

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

which is derived by supposing that in the range of the variation of the conversion degree $\Delta\alpha$, the activation energy E can be assumed constant. Obviously, the use of such an approach leads to a plot of E *vs*. the degree of conversion α. However, the activation energy as a function of the conversion progress looks like a stair function in which the low ranges of $\Delta\alpha$ where E keeps a constant value 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, we obtain:

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

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

Since the number of stairs (where the activation energy E is assumed constant in the isoconversional integral methods) depends directly on the range of chosen $\Delta\alpha$, an unlimited number of stairs can be reached by making $\Delta\alpha$ infinitesimal for calculating the dependence of the activation energy $E(\alpha)$ at each conversion degree α. For $\Delta\alpha\to 0$, we have $T_{\xi}\to T$ and

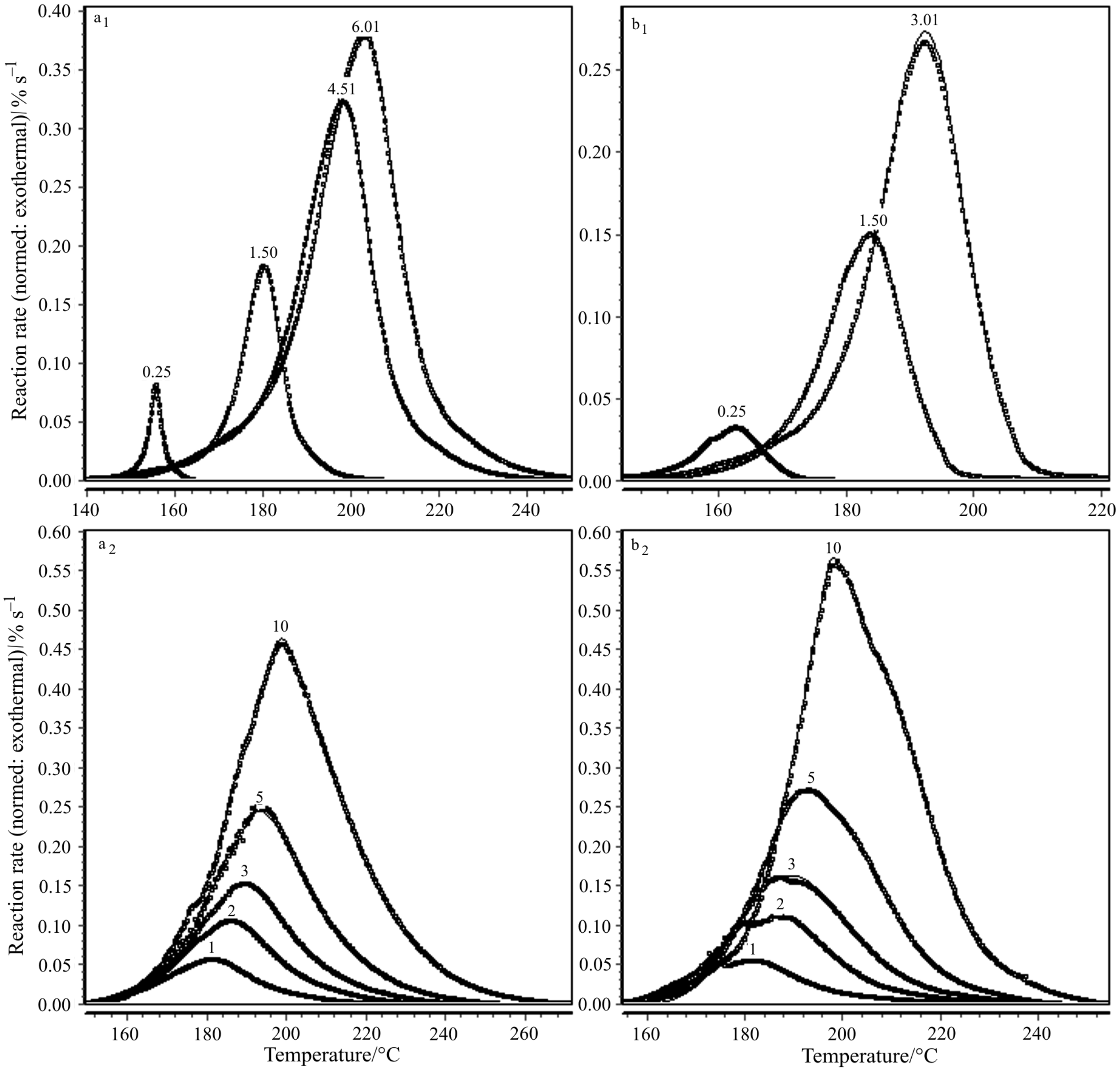

Fig. 4 Advanced kinetic description of normalized non-isothermal DSC-signals as a function of the temperature for the decomposition of double base rocket motor propellants. Experimental data are represented as symbols, solid lines represent the calculated signals. The values of the heating rate in K min^{-1} are marked on the curves; closed crucibles (isochoric conditions): a_1 – boost propellant, b_1 – sustain propellant, open crucibles (isobaric conditions): a_2 – boost propellant, b_2 – sustain propellant

$f(\alpha_\xi)\rightarrow f(\alpha)$. A consequence is that the previous equation turns back into its differential form:

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

that grounds the isoconversional differential methods, which corresponds to the Friedman approach that is applied in the present study. More generally, the conversion rate expression can be adapted to an arbitrary variation of temperature (as well as to isothermal conditions) by replacing $\beta(\mathrm{d}\alpha/\mathrm{d}T)$ with $\mathrm{d}\alpha/\mathrm{d}t$. Friedman analysis applies the logarithm of the Arrhenius equation. The function dependent on the reaction model $f(\alpha)$ becomes a constant at each conversion degree $\alpha_{i,j}$ ('isoconversional method') and the dependence of the logarithm of the reaction rate over $1/T$ is linear with the slope of E_i/R (with i – index of conversion, j – index of heating rate). The activation energy as a function of the reaction progress for decomposition of the examined samples can thus be calculated by applying the following equation:

$$\ln\left.\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right|_{\alpha_i}=\ln[A_i f(\alpha_{i,j})]-\frac{E_i}{RT_{i,j}} \tag{5}$$

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

The linear dependence of the logarithm of the reaction rate over $1/T$ with the slope of E/R for the different conversion degrees α_i becomes $E(\alpha)$ by making $\Delta\alpha$ infinitesimal. It is displayed in the range of 1 up to 99% in Fig. 3a with the experimental data. As illustrated in Fig. 3b, the various decompositions do not follow a single mechanism because the resulting activation energy is not constant but a function of the reaction progress for the decomposition of the considered samples. It shows that the decomposition of the examined propellants follows complex reactions which cannot be described in terms of a single pair of Arrhenius parameters and the commonly used set of reaction models.

Figure 4 presents the normalized non-isothermal DSC-signals as a function of the temperature or time for the decomposition of the double base rocket motor (boost- and sustain propellants). Experimental data are represented as symbols. Solid lines represent the calculated signals. The comparison between experimental and calculated reaction extents indicates that the applied numerical technique enables accurate prediction of the reaction course under any experimentally chosen temperature mode.

Kinetics and milligram scale – thermal stability predictions

Verification of numerical computations and confidence interval for the prediction of the reaction progress

Verification of numerical computations can be readily achieved by graphical comparison of the calculated reaction progress or rate with subsequently obtained experimental data. Figure 5a presents the comparison of experimental and calculated DSC signals for the stepwise temperature program and isothermal conditions. In this program, heating with a rate of 3 K min^{-1} was followed by an isothermal run at 160°C. Accurate prediction of the thermal stability is achieved. In this case, the predicted reaction rate has been calculated for a temperature of 160°C, laying inside the observed temperature window used for the determination of the kinetic parameters under non-isothermal conditions (from 140 for the beginning to 250°C at the end of the reaction, Fig. $4a_1$). In fact such a prediction of the propellant behaviour refers to an interpolation of the detected reaction rate from other experimental temperature profiles (non-isothermal conditions) but still in a temperature range where the thermal event occurs. However, for many applications it is relevant to examine how accurate is the prediction of the reaction rate for isothermal temperatures lying below the onset temperature observed under non-isothermal conditions. Therefore let us determine if the model used for the revelation of potentially hazardous behaviour of substances at elevated temperatures is still valid for the prediction of the reaction rate at prolonged times exposures at lower temperatures such as 110 and 100°C for the double base propellant (Fig. 5b). At lower temperature the thermal event will occur over a much longer period of time with some confidence interval which has to be determined for the predictions (lower limit, mean value, upper limit).

During the determination of correct course of the baseline for all differential signal types, like DTA and/or DSC measurements and the calculation of the kinetic parameters for a decomposition reaction, the predictions give the ‘central tendency’, for which the chance of the good reproducibility on subsequent measurements is maximal. A Gaussian distribution is expected around this ‘best value’. The illustration of these remarks for the investigation of the rocket propellant (isochoric conditions) is presented in Fig. 5b. The predicted and experimental rates of the self-accelerating reactions are shown when the rocket propellant is held isothermally at 110 and 100°C. This system is strongly autocatalytic, the rate of the initiation is low, leading to a long induction time under isothermal conditions. The reaction remains undetected for a relatively long period of time because the product catalysing the self-acceleration is formed slowly and/or the reaction begins when the stabilizers have been used up. When the reaction accelerates the rate increases so rapidly that it may lead to a runaway. For the rocket propellant, the mean value of the prediction for reaching the reaction progress of 65% (which corresponds to the maximum rate under isothermal conditions at T=110°C) is 47 h. The lower and upper limits of the confidence intervals are 38 and 58 h, respectively. These values indicate that there is a 95% probability that the mean time required for reaching 65% reaction progress is greater than 38 and lower than 58 h. Similar measurements were done for 100°C showing again the long induction time under isothermal conditions. Extrapolation at lower temperature than the beginning of the reaction under non-isothermal conditions is therefore possible for in-depth awareness of the propellant thermal behaviour under varied eventualities. As a safety measure the confidence interval of the reaction progress is required to determine the range of validity of the prediction. In that way very significant time/expertise savings can be achieved compared to real time analysis which can extend over prolonged periods, even years.

Cyclic temperature changes and prediction of the reaction progress under temperature mode corresponding to real atmospheric temperature changes

The kinetic parameters calculated from the non-isothermal experiments enable prediction of the reaction progress for any temperature mode: isothermal, non-isothermal, stepwise and therefore intermediate intervals in the heating rate, expressed, e.g. in oscillatory temperature modes. The prediction of the reaction progress in oscillatory temperature mode (widely applied in temperature-modulated calorimetry) is given below.

Figure 6a shows the reaction extents α of the decomposition of boost propellant in isothermal (50°C) and oscillatory (50±40°C, 24 h period) temperature modes (isochoric conditions, closed crucibles). The arithmetic mean temperature (50°C) of the oscillatory temperature mode is the same as in the isothermal experiment. However, the presence of the temperature amplitudes greatly influences the reaction progress. The

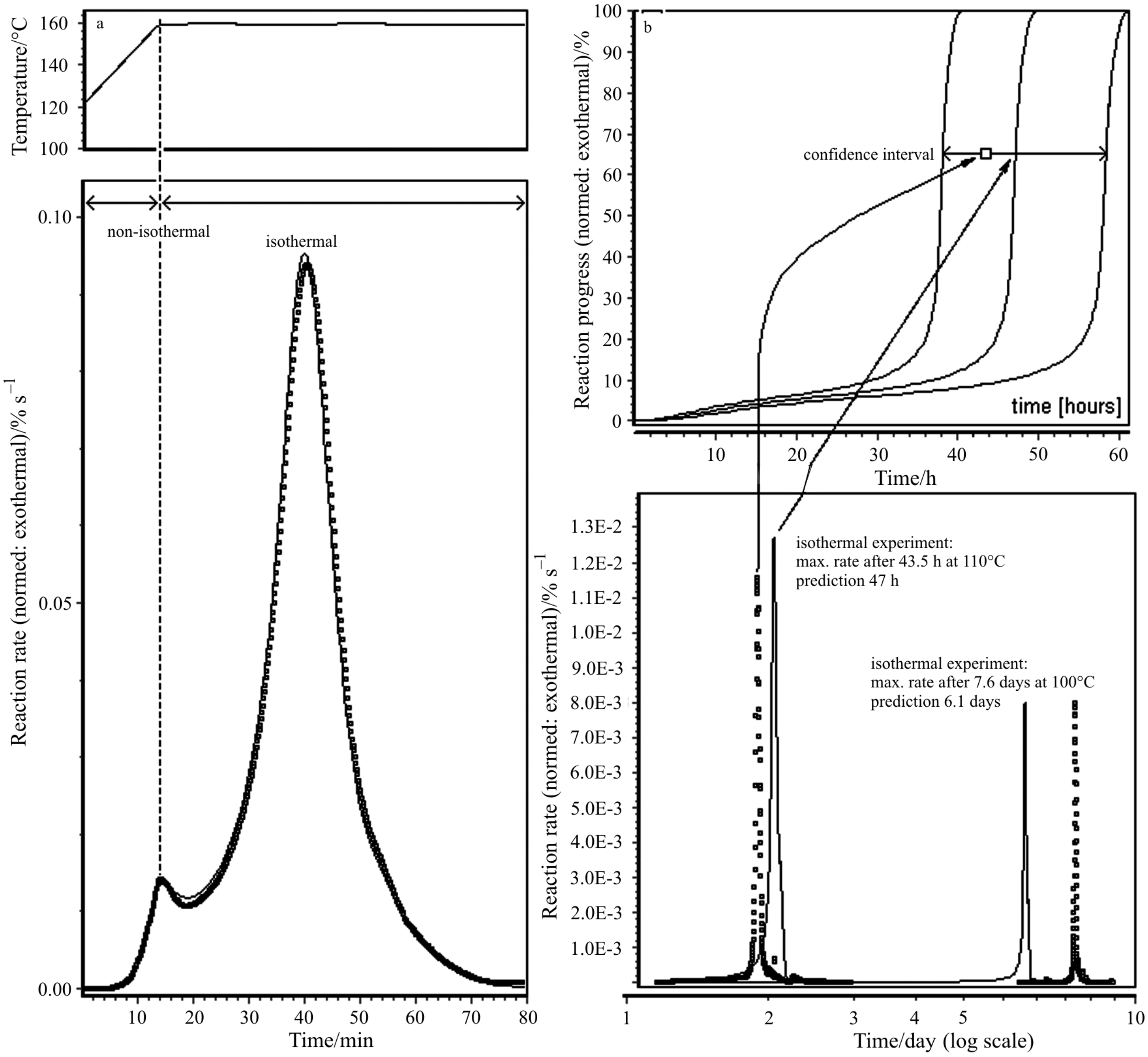

Fig. 5 a – Experimental data for the boost propellant decomposition (stepwise temperature program: heating rate of 3 K min^{-1} followed by an isothermal run at 160°C, closed crucibles i.e. isochoric conditions) are presented together with the reaction rate predictions. Experimental data are represented as symbols, solid lines represent the calculated relationships of dα/dt over t. Accurate prediction of the thermal stability is achieved; b – predicted (solid line) and experimental reaction rates (points) of the rocket propellant under isothermal conditions (110 and 100°C). The reaction is strongly autocatalytic because the initiation rate of the reaction is low leading to a long induction time under isothermal conditions. The figure at the top illustrates the reaction extent (DSC, normalized signals) of the rocket propellant with the confidence interval (95% probability) as a function of time under isothermal conditions (T=110°C, closed crucibles/isochoric conditions)

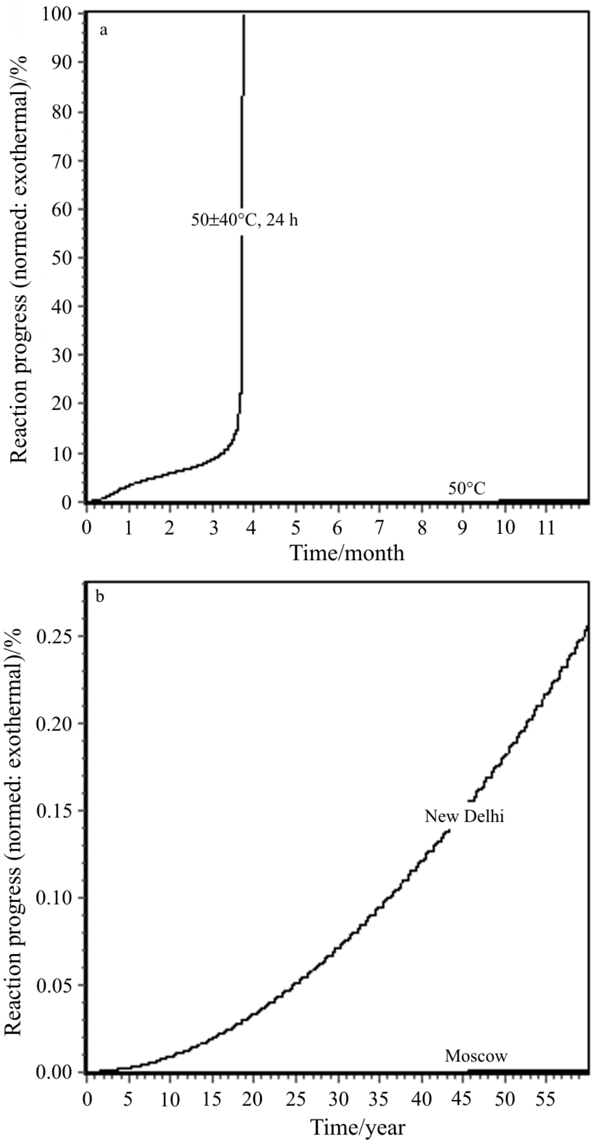

Fig. 6 a – Reaction extents α of the decomposition of boost propellant in isothermal (50°C) and oscillatory (50±40°C, 24 h period) temperature modes (isochoric conditions, closed crucibles); b – predictions of the extent of boost propellant decomposition for the New Delhi and Moscow temperature profiles under isochoric conditions (closed crucibles). The substance exposed to daily temperature changes decomposes only slightly in New Delhi (about 0.25% after 60 years). In Moscow the reaction will progress even much less in this period of time

prediction of the decomposition of the boost propellant under isochoric conditions at 50 with ±40°C amplitude and 24 h period indicates that after 3.5 months the sample is fully decomposed. For the same mean temperature (50°C) under isothermal conditions, the boost propellant will decompose only slightly after 12 months (<1%).

One of the main reasons for investigating the kinetics of thermal decompositions is the need to determine the thermal stability of substances, i.e. the temperature range over which a substance does not decompose at an appreciable rate. The correct prediction of the reaction progress of unstable materials such as some pyrotechnics, propellants, food, drugs, polymers, etc. under ambient conditions requires accurate knowledge of both:

- the kinetic parameters
- the exact temperature profile for a given climate

As an example one may predict the extent of the decomposition of the boost propellant in New Delhi and Moscow. The temperature profile used for the calculations is the average of all daily minimal and maximal temperatures recorded for each day of the year between the years 1961 and 1990. These temperature fluctuations will be applied in the calculations of the thermal properties with cyclic temperature changes over the years. The calculation of the kinetic parameter *E* (activation energy) as a function of the reaction progress (Fig. 3b) enables calculation of the thermal stability of the propellant expressed in Fig. 6b as a function of time. The boost propellant under isochoric conditions exposed to daily temperature changes in these two places decomposes only slightly over this period. These results show that within 60 years, the reaction reaches about 0.25% in New Delhi. In Moscow, the reaction will progress even much less in this period of time.

Kinetics and scale up – thermal stability and safety analysis

Adiabatic conditions: calculation of time of maximum rate under adiabatic conditions (TMR_{ad}) from non-isothermal DSC measurements

The precise prediction of the reaction progress in adiabatic conditions is necessary for the safety analysis of many technological processes. Calculations of an adiabatic temperature-time curve for the reaction progress can also be used to determine the decrease of 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 material can easily take place, resulting in an explosion.

Several methods have been presented for predicting the reaction progress of exothermic reactions under heat accumulation conditions [18–22]. However, because decomposition reactions usually have a multistep nature, the accurate determination of the kinetic characteristics strongly influences the ability to correctly describe the progress of the reaction. The use of simplified kinetic models for the assessment of runaway reactions can, on the one hand, lead to economic drawbacks, since they result in exaggerated safety margins. On the other hand, it can cause dangerous situations when the heat accumulation is underestimated. For adiabatic self-heating reactions, incorrect kinetic description of the process is usually the main source of prediction errors.

To be able to assess the probability of occurrence of a decomposition reaction, it is necessary to replace simple rules by sound methods based on reaction kinetics. The concept of time to explosion or TMR$_{ad}$ (time to maximum rate under adiabatic conditions) is of great utility for that purpose [23]. A commonly used approach for the determination of the TMR$_{ad}$ applies the following formula with the arbitrarily chosen zero-order reaction [24]:

$$\mathrm{TMR}_{\mathrm{ad}} = c_{\mathrm{p}} R T_0^2 \, / \, (q_0 E_{\mathrm{a}})$$

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 gives unfortunately 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. 3b, the activation energy is strongly dependent on the reaction progress for the considered compounds. In addition, it can be observed that 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. 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 decomposition of the boost propellant is a highly exothermal process. Using the reaction heat (ΔH_r) and the heat capacity (c_p), one can calculate the reaction progress due to self-heating for different values of ΔT_{ad} (with $\Delta T_{ad}=\Delta H_r/c_p$). In Fig. 7a, the simulated T-time relationships with a starting temperature of 100°C are presented for $\Delta T_{ad}=2651\pm233$°C (boost propellant, isochoric conditions). Figure 7b presents the starting temperature and corresponding adiabatic induction time TMR$_{ad}$ relationship. The confidence interval was determined for 95% probability. The inset

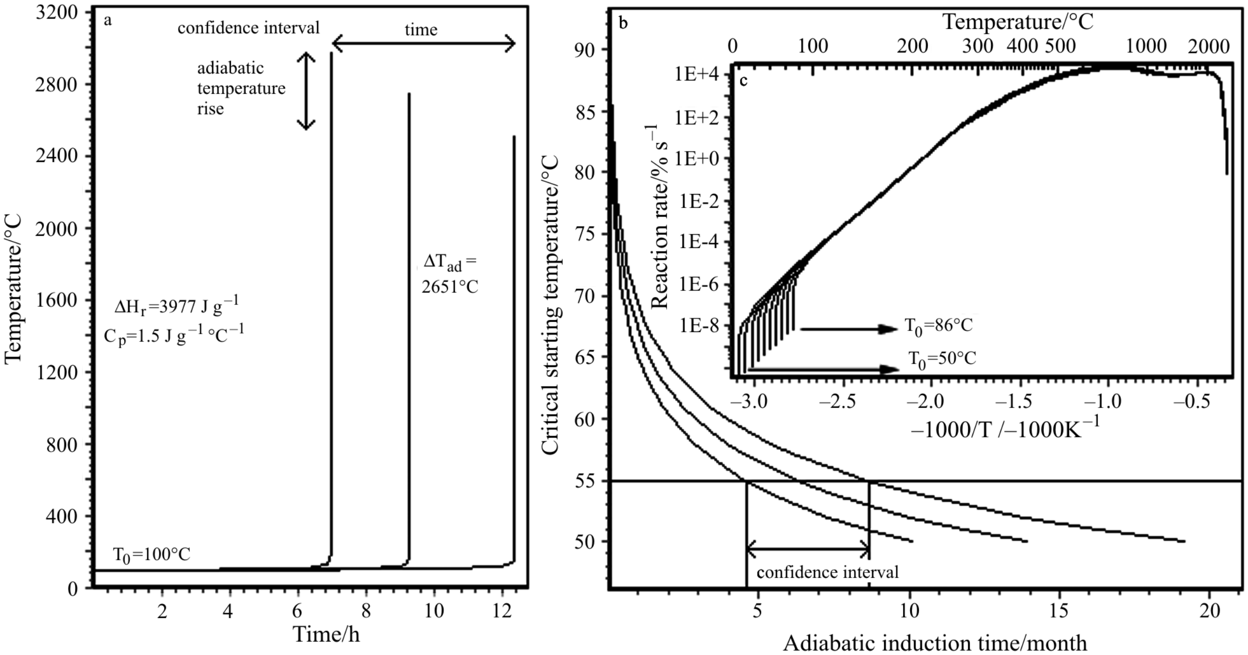

Fig. 7 a – Adiabatic runaway curves for the boost propellant (isochoric conditions) showing the confidence interval for the prediction (T_{begin}=100°C and $\Delta T_{ad}=\Delta H_r/c_p=2651\pm233$°C). The confidence interval was determined for 95% probability; ΔH_r=3977 J g^{-1}, c_p=1.5 J g^{-1} °C^{-1}. b – starting temperature and corresponding adiabatic induction time TMR$_{ad}$ relationship of the boost propellant under isochoric conditions. The choice of the starting temperatures strongly influences the adiabatic induction time (confidence interval: 95% probability) and c – heat rate curves *vs*. temperature for the boost propellant under isochoric conditions

Table 1 Starting temperatures for $\mathrm{TMR_{ad}}$ of 8 h and 10 days for the boost and sustain propellants under isochoric and isobaric heat accumulation conditions

		c_p/ J g^{-1} °C^{-1}	ΔH_r/ J g^{-1}	$\Delta T_{ad}=\Delta H_r/c_p$/ °C	Starting T for $\mathrm{TMR_{ad}}$=8 h/°C	Sarting T for $\mathrm{TMR_{ad}}$=10 days/°C
Closed crucibles/	boost propellant (A)	1.5	3977	2651	101	75
isochoric conditions	sustain propellant (B)	1.5	2994	1996	109	82
Open crucibles/	boost propellant (C)	1.5	1400	933	127	110
isobaric conditions	sustain propellant (D)	1.5	979	653	131	113

(Fig. 7c) presents the heat rate curves of the boost propellant under isochoric conditions for the different starting temperatures.

The adiabatic induction time is defined as the time which is needed for self-heating from the start temperature to the time to maximum rate under adiabatic conditions ($\mathrm{TMR_{ad}}$). 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). It can be observed that the reaction is more exothermal (higher ΔT_{ad}) and less stable (lower starting temperatures for the same $\mathrm{TMR_{ad}}$) for the boost propellant than for the sustain propellant. The same observation is also valid for the isochoric conditions (closed crucibles) compared to the isobaric conditions (open crucibles).

Non-adiabatic conditions: application of finite element analysis (FEA) for the determination of heat balances

The second field of application for numerical simulation techniques in process safety is the solution of partial differential equations as they are encountered in the heat conduction problems. Applications of finite element analysis (FEA) and appropriate decomposition kinetics enable the determination of the effect of scale and geometry of the container as well as the heat transfer, thermal conductivity and ambient temperature on the heat accumulation conditions. This analysis enables the optimal choice of critical design parameters of the containers such as critical radius, insulation and safe storage or transportation conditions (i.e. determination of the best storage container size, insulation and/or optimal transport temperatures). Using the generalized heat balance over one layer element in the confinement wall, we can relate the heat transfer in each layer. Thermal energy can be transferred into a bounded region by conduction, convection, or radiation. For some systems, the mathematical problem can be reduced to the conduction of heat, to which the discussion will be largely confined, but the other modes of heat transfer may occur at the boundaries. The scheme of the grid-point distribution applied for calculating the temperature profile in each layer is presented in Fig. 8. The function of the heat balance can be singular at the interface of the different layers and at the beginning of the heat transfer process (times around 0). Therefore the grid-point distribution must be chosen with variable step lengths. The generation of adaptive meshes allows achievement of a desired resolution in localized regions and decreases by orders of magnitude the calculation time. Grid points are added in regions of high gradients to generate a denser mesh in that region, and subtracted from regions where the solution is decaying or flattening out. FEA and kinetics enables calculations of the temperature gradients using finite element methods and considering the heat transfer progress in the multi-layers [1]. It can be assumed that the heat transfer obeys Fourier's law (rate of heat transfer is proportional to the temperature gradient). The equations were developed using coordinates (x, y and t) where the whole surface of the volume will be derived from the different pre-defined geometries.

The heat balance can be expressed by the following equations:

$$\frac{\mathrm{d}T}{\mathrm{d}t}=\frac{\lambda}{c_v\rho}\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}\right)$$

or for cylindrical coordinates

$$\frac{\mathrm{d}T}{\mathrm{d}t}=\frac{\lambda}{c_v\rho}\left(\frac{\partial^2 T}{\partial r^2}+\frac{J}{r}\frac{\partial T}{\partial r}\right)$$

where J is a geometry factor which is dependent on the type of recipient: J=0 for the infinite plate, J=1 for the infinite cylinder and J=2 for the sphere. The above equation has been extended by the consideration of heat produced by the decomposition reaction Q_r which rate is derived from the kinetics of the reaction. The heat balance equation can be now solved from r=0 (centre of cylinder) to r=R (surface of the cylinder) with AKTS-Thermal Safety Software [1]. The temperature profiles have to be considered for all layers. In each layer the initial temperatures at t=0 have to be introduced. At the centre and if a layer is perfectly isolated on its left or right side, the boundary condition (Fig. 8) is derived from the symmetrical properties of the temperature profile at the wall surface. The other boundary conditions (II, Fig. 8) are

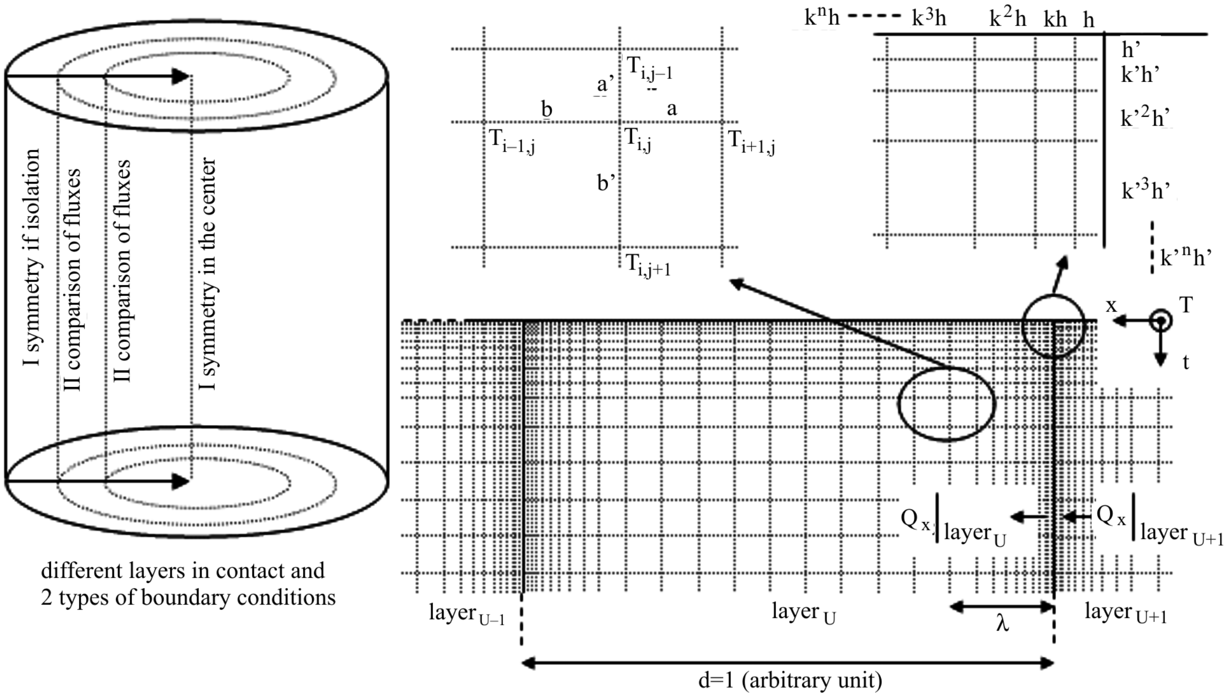

Fig. 8 Scheme of the multilayer confinement. The simulation of the whole multilayer confinement reduces to the analysis of a single layer and can then be extended from layer to layer. The grid-point distribution is chosen with variable step lengths in the heat transfer direction as well as in the time direction

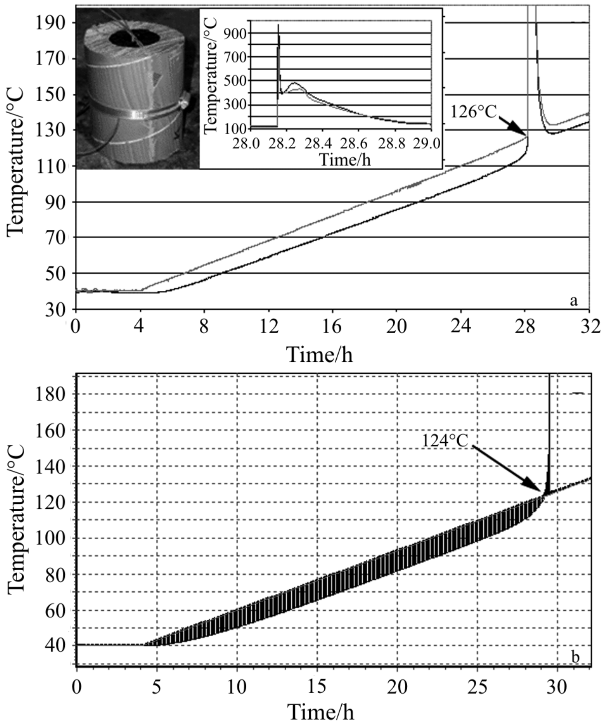

Fig. 9 Slow cook-off experiments of the a – rocket motor and b – simulation. The predicted temperature of ignition was 124°C. It is in good agreement with the slow cook-off experiments (126°C)

derived from comparison of the heat transfers at the interface between the different layers. We have for two layers in contact:

- boundary (I): symmetry axis $(\partial T/\partial x)\big|_U=0$ (if perfect isolation)
- boundary (II): interface:

$$Q_x\Big|_{\text{layer}_U}=Q_x\Big|_{\text{layer}_{U+1}}\Leftrightarrow\lambda_{\text{layer}_U}\frac{\partial T}{\partial x}\Big|_U=\lambda_{\text{layer}_{U+1}}\frac{\partial T}{\partial x}\Big|_{U+1}$$

Consideration of the decomposition kinetics and application of the boundary conditions enable the calculation of the heat transfer, the temperature distribution and the reaction progress in a larger amount of material as encountered in the cook-off experiments. The slow cook-off simulation and experiments of the rocket motor are presented in Fig. 9. The ignition temperature of the slow cook-off was 126°C (Fig. 9a). The simulation of the cook-off behaviour and the predicted ignition temperature of 124°C (Fig. 9b) are in good agreement with the experiments. In the simulation the following parameters were used: $T_{\text{rocket initial}}$=40°C during 4 h followed by a heating rate of 3.3 K h^{-1}; rocket motor diameter=125 mm, thickness of the boost propellant layer=31.5 mm, thickness of the sustain propellant layer=31 mm; thermal diffusivity of boost and sustain propellant $\lambda/(\rho C_p)$=0.02 $cm^2\ s^{-1}$. Knowledge of the decomposition kinetics, thermal diffusivity and specific heat combined with FEA can be used to determine the ignition temperature very precisely. More generally, applications of FEA and accurate kinetic description enable the determination of the effect of scale, geometry, heat transfer (isolation), thermal conductivity and ambient temperature on the heat accumulation conditions. In fact, the assumption that it is safe to handle an energetic material at any temperature below the first appearance of an exothermic signal on the DSC curve can be false and even dangerous. The highest safe temperature for handling any energetic material depends on several factors such as its size, shape, and prior thermal history. Therefore, safe storage or transport conditions with tailored safety margins can be defined using numerical simulation.

Conclusions

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. For these calculations the results obtained by thermoanalytical techniques recording the heat generation (DSC) were used. In general, the same approach can be applied to other thermoanalytical signals such as the change of the mass (TG), the rate of evolution of the gaseous products (TG-MS, TG-FTIR) as well as the change of the pressure under isochoric conditions (isoperibolic calorimetry). Employing advanced mathematical modeling and kinetics, it is possible to calculate the progress of decomposition reactions under temperature conditions different from those at which the experiments were carried out. In general, accurate kinetics enables calculation of the reaction progress in extended temperature ranges and under temperature conditions for which the experimental collection of the data is difficult. These difficulties are prevalent at low temperatures (requiring very long investigation times), as well as under specific temperature fluctuations.

Thermal safety simulation of self-reactive chemicals depends on the properties of the energetic substance (decomposition kinetics, heat conductivity, specific heat, loading density), properties of the container (e.g. size, geometry, the rate of the heat transfer to the environment) and surrounding temperature. FEA and advanced kinetic description enable determination of the effect of scale, geometry, heat transfer, thermal conductivity and ambient temperature on the heat accumulation conditions. Influence of complex thermal environment such as stepwise temperature profile of cook-off experiments can be used for verification of the numerical computations. It is then possible to cover in detail several different situations, problem definitions and results interpretation for thermal stability and safety analysis. In general, the heat accumulation conditions can be calculated for any surrounding temperature profile 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). This analysis can then be applied for the determination of the critical design parameters such as critical radius of a cylinder or sphere, the thickness of the insulation, influence of the surrounding temperature for safe storage or transport conditions. In fact, numerical simulations can be used to replace experiments in situations, which are not directly accessible to the experiment for timing reasons. The examples of such modeling analysis can be helpful for guiding screening and development activities of candidate energetic materials. If modeling proceeds in parallel with experimental studies, then it should result in lower costs in the development phase of a project.

The proposed method has several advantages:

- it is convenient: adiabatic devices of the required complexity are not available in every safety laboratory; DSC devices are however more widely available
- it is versatile: with one set of measurements different adiabatic and non-adiabatic situations can be calculated. The method can be used to predict the rate of the reaction progress dα/dt and temperature rise dT/dt for any temperature. If the pressure rise is measured, the rate of the pressure rise dP/dt can be determined for any temperature as well
- it is secure and economical: the calculation of adiabatic reaction progress and/or explosion conditions requires only a small amount of material

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