



Applicability of Non-isothermal DSC and Ozawa Method for Studying Kinetics of Double Base Propellant Decomposition

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Abstract: In order to determine Arrhenius kinetic constants various experimental techniques and testing conditions have been used. Also, various kinetic approaches and data treatment procedures have been applied, resulting sometimes in considerable disagreement in the values of the kinetic parameters reported in literature.

Kinetics of decomposition of DB propellants from non-isothermal DSC experiments using unhermetically closed sample pans, and effect of nitroglycerine (NG) evaporation on the kinetic results and kinetics of NG evaporation has been studied by isothermal thermogravimetry.

It has been shown by experiments and numerical simulation that at slower heating rates and smaller sample mass NG may completely evaporate before DSC peak maximum, resulting in a higher values of the activation energy (173 kJ/mol). At faster heating rates and larger sample masses certain amount of NG still exists in the propellant at the peak maximum temperature, resulting in lower values of the activation energy (142 kJ/mol). The discontinuity point on the Ozawa plot is connected with the presence of NG in the propellant at DSC peak maximum temperature. This implies that the activation energy obtained using small samples and slow heating rates (173 kJ/mol) corresponds to the activation energy of decomposition of nitrocellulose from DB propellant.

Keywords: double base propellant, kinetics, Ozawa method, nitroglycerine, evaporation

Introduction

There are many reasons why the mechanism and kinetics of thermal decomposition of energetic materials are so important for explosive community. From a practical point of view, the most important are that the rate of thermal decomposition affects the quality of an energetic material and its shelf life, as well as its thermal hazard potential [1].

In order to predict accurately the shelf-life and thermal hazard potential of an explosive material, a true decomposition mechanism and true kinetic constants should be known [2-9]. To determine Arrhenius kinetic constants, various experimental techniques and testing conditions, as well as various kinetic approaches and data treatment procedures have been applied, resulting in considerable disagreement in the values of the kinetic parameters reported in literature [10].

Non-isothermal isoconversional methods described by Ozawa, and Flynn and Wall are very often used to study kinetics of energetic materials [11-13]. The methods are based on the principle according to which the reaction rate at a constant conversion is only a function of temperature [3, 14].

The Ozawa equation [11-13] can be derived by the integration of the basic kinetic equation for the special case of non-isothermal experiments in which samples are heated at a constant heating rate: $\beta = dT/dt$. If a series of experiments are conducted at different heating rates, and if T_m is DSC peak maximum temperature, then plot of $\ln(\beta) - 1/T_m$ will give a straight line the slope of which is:

$$\log(\beta) \cong -0.4567 \frac{E}{R} \cdot \frac{1}{T_m}, \quad (1)$$

where E is the activation energy.

However, the Ozawa method is used sometimes uncritically, i.e. not taking into account certain limitations of the method and possible dependence of experimental data on testing conditions applied. Another serious problem with the use of isoconversional methods is that variation of Arrhenius constants with the extent of reaction poses difficulties in the interpretation of the kinetic data [3, 15-17].

From the theory of non-isothermal isoconversional method reported in literature [11-13, 19-20], follows that in order to apply the non-isothermal DSC measurements and the Ozawa method the certain preconditions should be fulfilled:

- the extent of reaction at the peak maximum is constant and independent on

- the heating rate,
- the temperature dependence of the reaction rate constant obeys the Arrhenius equation,
 - in order to calculate the pre-exponential factor, the reaction model should be known.

The Achilles heel of the Ozawa and Flynn and Wall methods is excess self-heating [1, 14, 19-21], i.e. the tendency of energetic materials to increase the rate of heating of the sample to a greater degree than that of the programmed rate. Although the reaction kinetics and enthalpy of reaction are obviously the root cause of heating, for an energetic materials the degree of self-heating is also influenced by the heating rate and sample size. The main consequences of self-heating are:

- the actual heating rate of sample is greater than the programmed heating rate, and
- the peak maximum temperature for some programmed heating rate does not have the same value as the temperature obtained with no self-heating.

The measurable effect of self-heating during the exothermal decomposition is substantial deviation of the $T = f(t)$ curve from linearity (Figure 1). While a sufficiently small sample will give an essentially straight line with no evidence of self-heating, a large sample will show pronounced deviation (i.e. peak) on $T = f(t)$. Larger sample size will give the greater self-heating and the greater deviation of the actual sample heating rate from the programmed heating rate. Finally, self-heating will result in a lower value of the calculated activation energy [1, 17, 22].

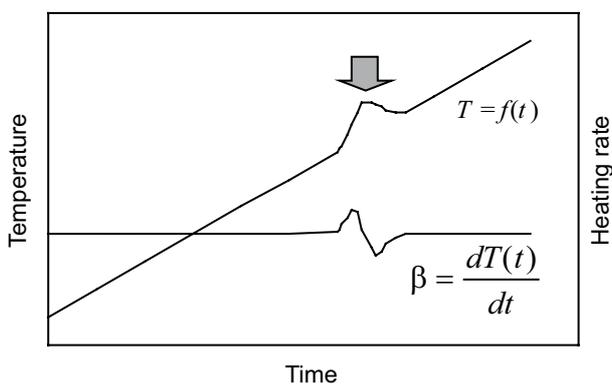


Figure 1. Effect of self-heating on actual heating rate and temperature (maximum difference between actual and programmed heating rate is assigned as degree of self heating, $\Delta\beta = \beta_{\max} - \beta_{\text{prog}}$).

In practice, it is common to use the non-isothermal isoconversional DSC method applying a constant sample size method. The consequence of using a constant sample size for all heating rates may be considerable self-heating at faster heating rates, and consequently an incorrect value of the activation energy calculated.

In our previous papers [19, 20, 23] we have reported that testing conditions (sample mass, heating rate, type of sample pan, etc.) and data treatment method may considerably affect the kinetic results determined by the Ozawa non-isothermal isoconversional method.

An unusual behaviour which manifests in the existence of a discontinuity and slope change of Ozawa plot was observed in the case of double base (DB) propellants, but such behaviour was not observed in the case of single base propellants. We explained such behaviour by the sample self-heating effect at faster heating rates and larger samples. However, some of our recent studies [24] on nitroglycerine (NG) evaporation kinetics threw new light to that conclusion and motivated us for additional studies and more detailed explanation of the reasons for the discontinuity appearance.

It should be mentioned that there is not too much information in available literature on evaporation of NG from DB propellant. A. Tompa [25] has studied evaporation kinetics of NG from DB propellant applying isothermal thermogravimetry. He has found that the rate of evaporation depends on the sample shape and size, surrounding atmosphere, etc. For example, he has found that the evaporation rate increases with the sample's surface area - the larger surface area of the sample, the more NG there is on the surface, and consequently it will evaporate at a faster rate. He reported that the activation energies of NG evaporation range between 58 and 75 kJ/mol and pre-exponential factor between $4.1 \cdot 10^3$ and $2.7 \cdot 10^6$ 1/s, depending on experimental conditions.

Experiment

Kinetics of decomposition was studied using DB propellant containing ~40% of NG. The samples weighing 0.5-2.5 mg were cut from the strip-like propellant grains. In order to reduce the influence of sample shape on testing results, the thickness of all samples was maintained constant (0.15 mm).

Non-isothermal DSC experiments were conducted using the *TA instruments DSC 2910* apparatus that is based on the heat flux type of the cell. The measurements were done using aluminium sample pans with perforated aluminium cover, and under nitrogen purging with 100 ml/min.

The evaporation of NG was studied using a DB rocket propellant containing 27% of NG. Isothermal TGA experiments were conducted using thin plate samples weighing around 4.0 mg and having a thickness of 0.2-0.4 mm. The experiments were conducted using *TA Instruments* SDT, Model 2960. The samples were tested in open aluminium sample pans under nitrogen atmosphere with a flow rate of 50 ml/min and in the temperature range 50-90 °C.

Results and Discussion

Ozawa kinetics

According to the common practice in many studies, the non-isothermal DSC measurements are carried out at different heating rates using samples having the same mass. Mass of samples is in the range from 0.5 mg to 2.5 mg, while the heating rates ranges from 0.2 °C/min to 30 °C/min. Typical DSC curves of tested DB propellants at different heating rates are given in Figure 2, and data necessary for the calculation of kinetic data are summarized in Table 1.

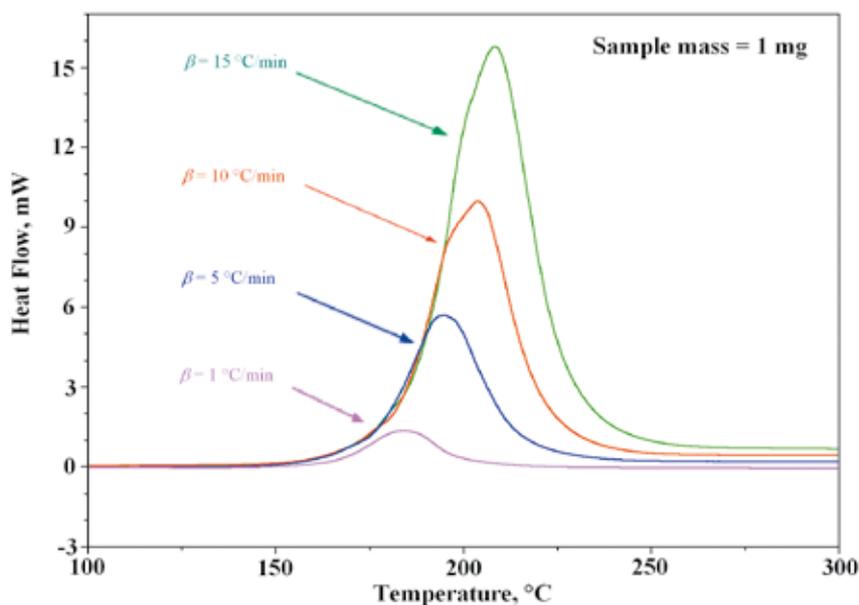


Figure 2. Non-isothermal DSC curves of DB propellant obtained at several different heating rates.

The consequence of using various heating rates and constant sample masses is apparent from Figure 2 faster heating rates yield higher peak temperatures, while the peak height increases proportionally with the heating rate.

As an illustration, the Ozawa plots, i.e. the $\log(\beta)$ vs. $1/T_m$ curve for 1 mg sample is given in Figure 3, along with corresponding degree of the sample self-heating.

It is clear from Figure 3 that there is a point at which the Ozawa plot abruptly changes both its position and slope – below and above this point the slopes are different, giving different values of the activation energy. Also, one may note that the point of discontinuity coincides with the appearance of the sample self-heating increase.

Table 1. Summarized experimental data obtained from non-isothermal DSC measurements

| Sample mass, mg | $\beta_{\text{programmed}}$, °C/min | Parameters derived from non-isothermal DSC measurements | | | | |
|-----------------|--------------------------------------|---|------------|----------------|-------------------------------|--------------------------------|
| | | T_m , °C | h_m , mW | α_m , % | β_{max} , °C/min | β_{prog} , °C/min |
| 0.5 ±0.02 | 0.2 | 165.63 | 0.20 | 48.92 | 0.2 | 0.20 |
| | 0.5 | 178.22 | 0.32 | 46.67 | 0.50 | 0.50 |
| | 1 | 185.25 | 0.70 | 55.35 | 1.00 | 1.00 |
| | 2 | 192.11 | 1.10 | 55.59 | 2.00 | 2.00 |
| | 3 | 195.80 | 1.53 | 57.48 | 3.00 | 3.00 |
| | 5 | 197.37 | 2.70 | 50.56 | 5.05 | 5.00 |
| | 7 | 199.96 | 3.65 | 50.01 | 7.09 | 7.00 |
| | 10 | 203.96 | 4.71 | 48.74 | 10.15 | 10.00 |
| | 15 | 210.09 | 6.25 | 49.08 | 15.39 | 15.00 |
| | 20 | 210.08 | 8.35 | 45.08 | 20.67 | 20.00 |
| | 25 | 214.75 | 11.73 | 52.42 | 25.87 | 25.00 |
| | 30 | 216.54 | 10.76 | 49.65 | 31.24 | 30.00 |
| 1.0 ±0.02 | 0.2 | 169.95 | 0.30 | 47.03 | 0.20 | 0.19 |
| | 0.5 | 178.57 | 0.66 | 50.48 | 0.50 | 0.50 |
| | 1 | 184.90 | 1.37 | 52.71 | 1.00 | 1.00 |
| | 2 | 189.27 | 2.28 | 55.05 | 2.02 | 1.98 |
| | 3 | 189.44 | 3.52 | 45.47 | 3.04 | 2.95 |
| | 5 | 194.94 | 5.54 | 46.28 | 5.08 | 4.90 |
| | 7 | 197.86 | 7.01 | 44.54 | 7.17 | 6.85 |
| | 10 | 202.03 | 9.65 | 46.78 | 10.33 | 9.66 |
| | 15 | 208.13 | 14.90 | 50.60 | 15.81 | 14.27 |
| | 20 | 212.22 | 19.24 | 53.55 | 21.08 | 18.75 |
| | 25 | 214.89 | 25.07 | 51.33 | 26.53 | 23.04 |
| | 30 | 217.59 | 26.85 | 52.26 | 32.15 | 27.48 |

| | | | | | | |
|-----------|-----|--------|-------|-------|-------|-------|
| 1.5 ±0.02 | 0.2 | 170.17 | 0.49 | - | 0.20 | 0.20 |
| | 0.5 | 179.25 | 0.93 | 57.14 | 0.50 | 0.50 |
| | 1 | 183.48 | 1.73 | 55.07 | 1.00 | 0.99 |
| | 3 | 188.89 | 5.34 | 46.49 | 3.05 | 2.95 |
| | 5 | 194.83 | 8.53 | 49.80 | 5.15 | 4.86 |
| | 7 | 198.69 | 11.73 | 49.43 | 7.24 | 6.72 |
| | 10 | 201.99 | 12.93 | 45.40 | 10.41 | 9.56 |
| | 15 | 208.19 | 21.23 | 51.15 | 15.94 | 13.81 |
| | 20 | 212.06 | 29.43 | 52.27 | 21.70 | 17.92 |
| | 25 | 215.11 | 34.74 | 55.90 | 27.40 | 22.00 |
| 2.0 ±0.04 | 0.2 | 170.30 | 0.57 | - | 0.20 | 0.20 |
| | 0.5 | 178.52 | 1.24 | 56.89 | 0.50 | 0.50 |
| | 1 | 181.08 | 2.43 | 51.04 | 1.00 | 0.99 |
| | 3 | 190.35 | 7.68 | 51.65 | 3.08 | 2.90 |
| | 5 | 193.88 | 11.41 | 47.58 | 5.19 | 4.81 |
| | 7 | 198.34 | 15.19 | 48.55 | 7.43 | 6.60 |
| | 10 | 202.89 | 22.94 | 51.18 | 10.67 | 9.21 |
| | 15 | 208.13 | 30.28 | 53.08 | 16.38 | 13.22 |
| | 20 | 211.38 | 38.01 | 51.38 | 22.30 | 17.26 |
| | 25 | 214.62 | 48.72 | 52.93 | 29.02 | 20.41 |
| 2.5±0.05 | 0.2 | 169.22 | 0.70 | 45.92 | 0.20 | 0.20 |
| | 0.5 | 174.68 | 1.60 | 50.13 | 0.50 | 0.50 |
| | 1 | 180.21 | 4.01 | 50.10 | 1.01 | 0.98 |
| | 3 | 190.12 | 10.06 | 51.15 | 3.10 | 2.87 |
| | 5 | 195.13 | 15.58 | 50.40 | 5.22 | 4.76 |
| | 7 | 198.84 | 20.67 | 51.25 | 7.44 | 6.51 |
| | 10 | 202.83 | 26.87 | 50.42 | 10.84 | 9.04 |
| | 15 | 208.20 | 38.80 | 52.43 | 16.86 | 12.73 |
| | 20 | 211.93 | 51.79 | 50.77 | 23.36 | 16.28 |
| | 25 | 214.20 | 58.66 | 49.39 | 30.22 | 18.64 |

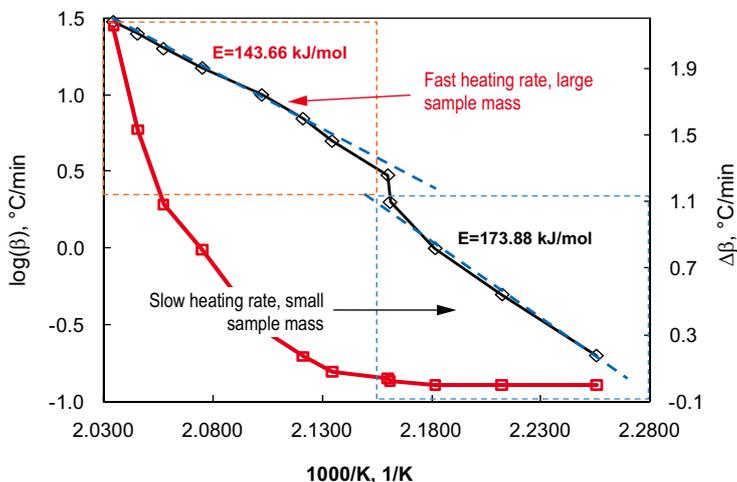


Figure 3. Ozawa plot and degree of self-heating curves (sample mass is 1 mg).

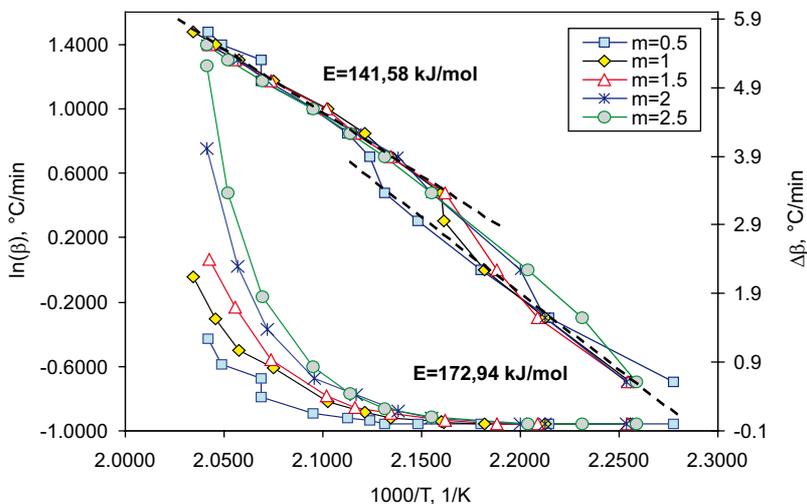


Figure 4. Ozawa plots and degree of self-heating curves for DB propellant samples having different mass.

From Figure 4 showing the Ozawa plots for five samples having different masses it is visible that the discontinuity point changes with the sample mass – for larger samples the point of discontinuity shifts to lower temperature and slower heating rates (Figure 5).

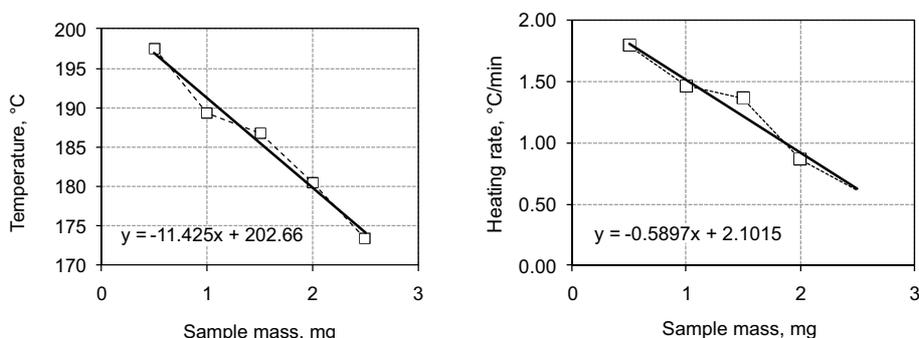


Figure 5. Change of discontinuity point with sample mass and heating rate.

It follows from Figure 4 that all data points at which self-heating exists lie on the same straight line the slope of which yields an average value of the activation energy of 141.58 kJ/mol. Similarly, all data points at which self-heating was avoided lie on the other straight line the slope of which yields an average value of the activation energy of 172.94 kJ/mol. These data clearly show that the calculated value of the activation energy of the studied DB propellant in these two regions differs for about 20%.

On the other hand, these data show that in order to avoid the sample self-heating (which is one of the preconditions to apply the Ozawa method), slow heating rates and small sample have to be used – e.g. if the sample mass is 2.5 mg, the heating rates must be slower than 0.6 °C/min.

Evaporation of nitroglycerine from DB propellant

It is common practice to conduct DSC experiments using unhermetically closed sample pans (e.g. sample pans with a small hole punctured in the pan cover). Under such experimental conditions gaseous decomposition products (as well as evaporation products) can freely get out the pan – particularly if the heating rate is slow or the sample mass small enough.

In the case of a DB propellant two parallel processes will take place under such experimental conditions: NG evaporation and decomposition of nitrocellulose (NC) and NG. The rates of these processes, as well as progresses of the reactions are different and result will be a continuous change of composition of the DB propellant, i.e. change of NC/NG ratio. For example, at slow heating rates the evaporation of NG (which begins at lower temperatures), will be considerable since the time to reach DSC peak maximum will be longer – the consequence is that a considerable amount of NG will evaporate before DSC peak maximum temperature. If heating rate is slow enough, NG can completely

evaporate before DSC peak maximum temperature is attained. On the contrary, at faster heating rates there is not enough time for the evaporation of considerable amount of NG, and consequently only small portion of NG will evaporate before DSC peak maximum temperature is reached.

We have shown in paper [26] that thermal method can clearly distinguish between single base and double base propellants (Figure 6), as well as that isothermal and non-isothermal thermogravimetry can be used to study NG evaporation.

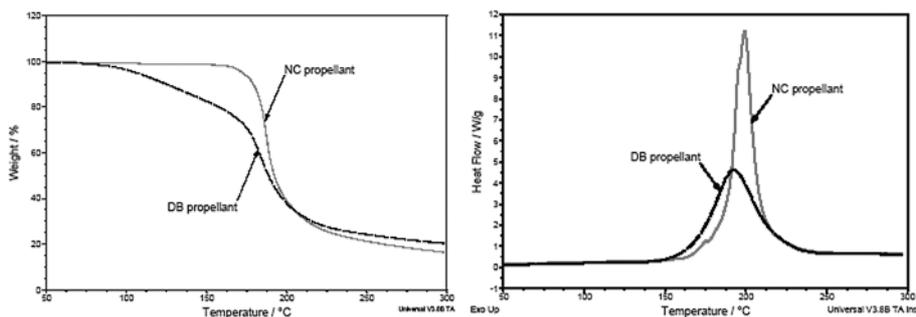


Figure 6. Non-isothermal TGA and DSC curves of NC and DB propellants (experimental conditions: heating rate 2 °C/min, sample mass 2 mg).

It is visible from Figure 6 that in the case of NC propellant a measurable mass loss occurs above 150 °C, while in the case of DB propellant a measurable mass loss is observed above 70 °C. At the same time it is clear from non-isothermal DSC experiments that there are no measurable exothermal processes for both NC and DB propellants below 140 °C at a given testing conditions. This confirms that at lower temperatures (below 150 °C) the mass loss is due to NG evaporation, i.e. that NG evaporation is a dominant process.

Kinetics of evaporation of NG is studied by isothermal thermogravimetry at temperatures below 90 °C. Isothermal weight-time curves obtained in this way are shown in Figure 7, along with the rate of conversion *vs.* conversion data derived.

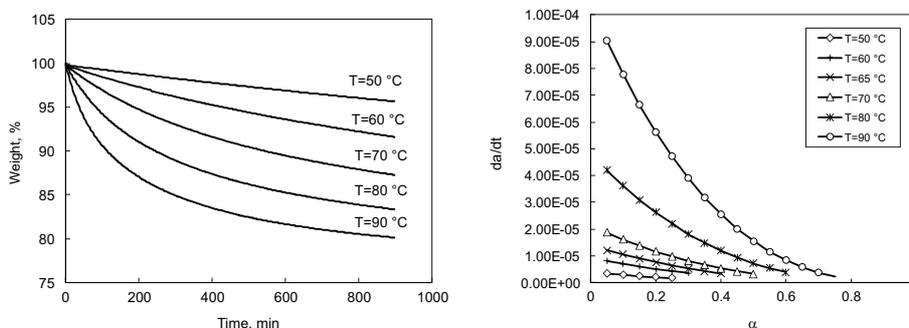


Figure 7. Isothermal weight loss vs. time and rate of conversion vs. conversion data for tested DB propellant.

It was shown by non-linear regression analysis of $(d\alpha / dt) - \alpha$ data [24] that the evaporation process could be best described by the n-th order kinetic model (where $n = 2.75$):

$$\frac{d\alpha}{dt} = k_{vap} \cdot (1 - \alpha)^{2.75}, \quad (2)$$

where k_{vap} is the evaporation rate constant.

The evaporation rate constants were calculated for each temperature, and then the activation energy (E_{vap}) was calculated from the Arrhenius plot of $\ln(k_{vap})$ vs. $1/T$. The obtained values of the kinetic parameters are: $E_{vap} = 81.9$ kJ/mol and $A_{vap} = 5.6 \cdot 10^7$ 1/s.

Experimental verification and simulation of DSC and TGA measurements

Based on the facts mentioned previously we have assumed that the discontinuity of the Ozawa plot is connected with the presence of NG in DB propellant at DSC peak maximum temperature. In other words, we have assumed that at sufficiently slow heating rates NG can completely evaporate before DSC peak maximum temperature. In this case DSC peak maximum is connected completely with NC decomposition, and consequently kinetic parameters correspond to thermal decomposition of NC. At faster heating rates some amount of NG still exists in DB propellants at DSC peak maximum temperature, and consequently DSC peak maximum corresponds to decomposition of both NG and NC.

To test this hypothesis the following experiments were done. Firstly, DSC

experiment was run using ~ 2 mg sample and a very slow heating rate (0.2 °C/min), Figure 8. The run was stopped at 150 °C – which is about 20 °C before DSC peak maximum temperature (at 0.2 °C/min heating rate DSC peak maximum temperature is about 169 °C), and then the amount of remaining NG in the sample was determined using method described in [26].

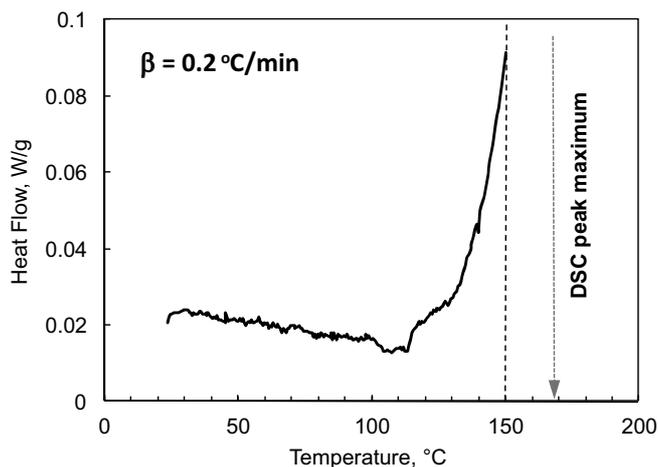


Figure 8. DSC curve of DB propellant obtained at 0.2 °C/min heating rate (run was terminated at 150 °C).

By weighing the sample before and after DSC experiment, it was found that the sample mass loss was 24.8 %. Since the original content of NG in the sample was 26.7 %, this means that the amount of remaining NG was 1.9 % (neglecting any contributions of decomposition of NC and NG). Isothermal TGA experiment at 110 °C has shown that mass loss (i.e. amount of remaining NG) was 1.03 %, which is in good agreement with the previous result.

The experiment confirms that in this case the amount of NG at DSC peak maximum temperature can be neglected and that the peak maximum corresponds to decomposition of NC only. This is in very good agreement with the experimental results obtained for NC propellant [20] for which it was found out for the same heating rate of 0.2 °C/min that DSC peak maximum temperature is around 169 °C – the same as in the case of DB propellant.

Applying a simplified model based on the evaporation of NG and decomposition of NC, we have carried out numerical simulation in order to analyze behaviour (e.g. rates of NG evaporation and NC decomposition, conversions of NG and NC and change of DB propellant composition) at various heating rates. Basically, the model includes calculation of conversions of NG,

NC, and DB propellant as functions of time or temperature by the integration of the general kinetic equation:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha), \quad (3)$$

where $k = A \exp(-E / RT)$ is temperature dependent rate constant and $f(\alpha)$ is kinetic model.

The integration of the above equation gives conversion at time t , $\alpha(t)$. We applied numerical integration by the following formula:

$$\alpha_t = \alpha_{t-1} + [k \cdot f(\alpha_{t-1})] \cdot \Delta t, \quad (4)$$

where α_t and α_{t-1} are conversions at current and previous steps, and Δt is time step.

The following kinetic data were used in the simulation:

- evaporation of nitroglycerine (NG):

$$\frac{d\alpha}{dt} = 5.6 \cdot 10^7 \cdot e^{(-81900/RT)} \cdot (1-\alpha)^{2.75}, \quad \Delta H_{vap} = 365.2 \text{ J/g} \quad (5)$$

- decomposition of NC is described by the following two-step autocatalytic model [27]:

$$\frac{d\alpha}{dt} = 2.1 \cdot 10^{13} \cdot e^{(-125000/RT)} \cdot [\alpha^{1.8} \cdot (1-\alpha)^{14.5}] + 1.2 \cdot 10^{18} \cdot e^{(-176000/RT)} \cdot [\alpha^{0.65} \cdot (1-\alpha)^{1.8}],$$

$$\Delta H_{rxn} = -2700 \text{ J/g}. \quad (6)$$

The heat flow (Φ) is calculated by the formula:

$$\Phi = \frac{d(\Delta H_{vap} + \Delta H_{rxn})}{dt}. \quad (7)$$

The calculated mass loss-temperature data for DB propellant containing 40% NG and 60% NC at two different heating rates are given in Figure 9. It follows

from the calculation that at 150 °C the amount of remaining NG at 0.2 °C/min heating rate is about 10% of its initial mass, while at 10 °C/min heating rate the amount of remaining NG at the same temperature is 70% of its initial mass. At the same time the amount of NC at 150 °C is almost unchanged since its decomposition starts at higher temperatures. The amount of NG at DSC peak maximum temperature is around 5% and 25% of initial mass at 0.2 and 10 °C/min heating rates respectively.

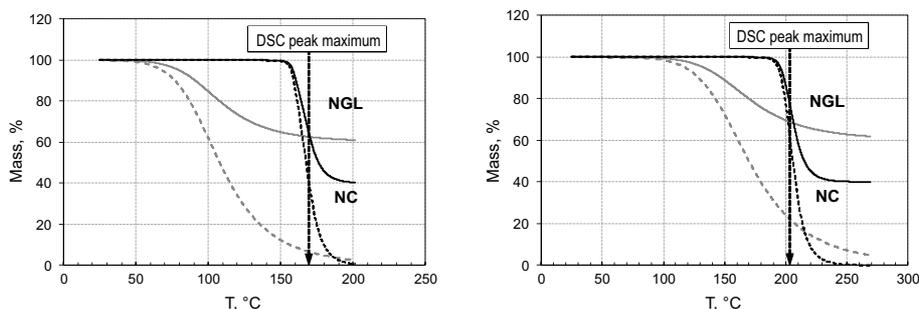


Figure 9. Calculated mass loss – temperature data for NG and NC at 0.2 and 10 °C/min heating rates (solid lines – in respect to DB propellant, dashed line – in respect to individual initial weights of NG and NC)

The results of calculations are close to the experimental – the experimentally determined amount of NG at 150 °C at 0.2 °C/min heating rate was around 3.8% its initial mass. The reason for a slightly higher value obtained by the calculation lies in the fact that our simplified model does not take into account decomposition of NG, and it is also due to the considerable influence of the sample mass and geometry on NG evaporation kinetics.

Non-isothermal DSC runs at two different heating rates are also simulated by the same model. The results are given in Figures 10 and 11.

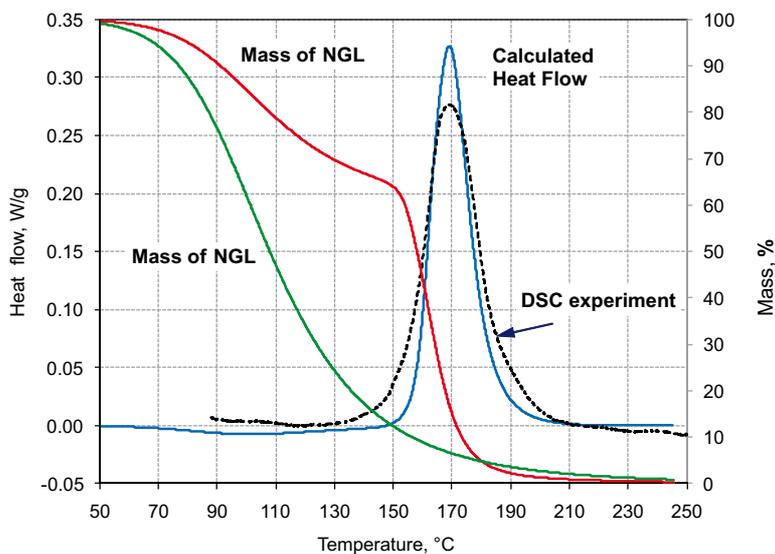


Figure 10. Comparison of calculated and experimental heat flow, along with NG and DB mass loss at 0.2 °C/min heating rate.

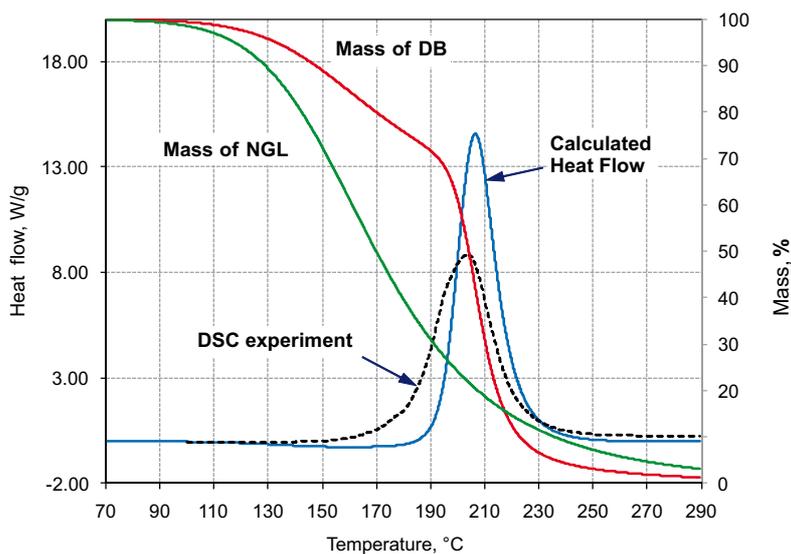


Figure 11. Comparison of calculated and experimental heat flow, along with NG and DB mass loss at 10 °C/min heating rate.

The results of simulation are in reasonable agreement with experimentally obtained DSC curves – particularly when it approaches to DSC peak maximum temperature. The deviation between calculated and experimental heat flow curves is higher at the beginning of the exothermal process, probably due to the fact that the model does not take into account decomposition of NG. The deviation is higher at a higher heating rate since at the same temperature the amount of NG is higher.

In spite of the imperfection of the model, it clearly shows that at different heating rates the amount of NG at the peak maximum temperature is different, and that at slower heating rates NG can almost completely evaporate from DB propellants before DSC peak maximum temperature is reached. As a result, the Ozawa method in the case of DB propellant will give different values of the activation energy at slower and at faster heating rates.

Conclusion

Due to its simplicity and relative quickness, the non-isothermal isoconversional kinetic Ozawa method is very often used by the explosive community. The results presented in this paper, as well as the results of our previous studies, show that the Ozawa method should be used with extreme care. The study shows that when unhermetically closed sample pans are used to study kinetics of decomposition of DB propellants, the Ozawa method will give unreliable results due to the following reasons.

Two parallel processes take place in DB propellants during DSC experiments – the evaporation of NG and the decomposition of NG and NC. The rates of these processes are different and dependent on experimental conditions. As a result, DB propellant composition changes continuously during the heating. At a sufficiently slow heating rate NG can completely evaporate before DSC peak maximum temperature is reached. In such a case DSC peak maximum temperature corresponds to decomposition of NC, and consequently the activation energy (which equals 173 kJ/mol) corresponds to decomposition of NC. This has been confirmed by comparing DSC peak maximum temperature for NC propellant and DB propellants and by simulation. At higher heating rates the amount of evaporated NG at DSC peak maximum temperature is lower, but the sample self-heating increases causing a temperature gradient within the sample and consequently inaccurate values of activation energy.

A pronounced discontinuity of the Ozawa plot is observed at tested samples weighing between 0.5 and 2.5 mg. The discontinuity point changes with the

sample mass – for larger samples it shifts to lower temperatures and slower heating rates. This point is connected with the amount, i.e. presence, of NG in DB propellant – below the discontinuity point (at slower heating rates) there is no NG at the peak maximum temperature, while above this point (at higher heating rates) considerable amount of NG is still present in DB propellant.

The discontinuity point roughly coincides with the point of appearance of measurable sample self-heating – below this point the self-heating is negligible since heating rates are very slow, but above this point the self-heating increases with heating rates as a consequence of fast exothermic decomposition of NC and remaining NG. Since the effect of self-heating is the occurrence of thermal gradient within the sample, it is obvious that it will influence the kinetic results. The values of the activation energies calculated from the slopes of Ozawa plots below and above discontinuity point differ for about 20%.

It is usually recommended to use small samples and a slow heating rate in order to avoid occurrence of sample self-heating. However, in the case of DB propellant it is not applicable since it causes another problem – intensive evaporation of NG and unreliable kinetic results derived by the Ozawa method.

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