



Thermal Behavior and Decomposition Kinetics of RDX and RDX/HTPB Composition Using Various Techniques and Methods

Mohamed ABD-ELGHANY, Ahmed ELBEIH,*
Saeed HASSANEIN

Military Technical College, Kobry Elkobbah, Cairo, Egypt

**E-mail: elbeih.czech@gmail.com*

Abstract: In this paper, the thermal behavior and decomposition kinetics of trinitrohexahydrotriazine (RDX) and its polymer bonded explosive (PBX) containing a hydroxyl-terminated polybutadiene (HTPB) based polyurethane binder in the ratio 80% RDX/ 20% HTPB were investigated using various experimental techniques and analytical methods. The HTPB polyurethane matrix contains other additives and was cured using hexamethylene diisocyanate (HMDI). Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), Vacuum Stability Test (VST) and Ignition Delay Techniques were applied both isothermally and non-isothermally. The kinetic parameters were determined using both the isoconversional (model free) and the model-fitting methods. For comparison, Advanced Kinetics and Technology Solution (AKTS) software was also used. It was found that the addition of an HTPB-based polyurethane matrix to pure RDX decreased its decomposition temperature. It was also found that RDX/HTPB has a lower activation energy than pure RDX. The polyurethane matrix had a significant effect on the decomposition mechanism of RDX resulting in different reaction models. It was concluded that the activation energies obtained using the Ozawa, Flynn, and Wall (OFW) and Kissinger-Akahira-Sunose (KAS) methods were very close to the results obtained *via* the AKTS software lying in the range 218.3-220.2 kJ·mol⁻¹. The VST technique yielded kinetic parameters close to those obtained using TG/DTG. On the other hand, the Ignition Delay Technique yielded different and inconsistent kinetic parameters.

Keywords: RDX, RDX/HTPB, thermal decomposition, model fitting, model free

1 Introduction

The traditional cyclic nitramine explosives such as trinitrohexahydrotriazine (RDX) and tetranitrooctahydrodiazocine (HMX) have been widely used in propellants due to their high energy output and availability [1-5]. However, they are sensitive to impact and friction and their flame temperatures are relatively high. Many studies have been performed to overcome these problems without affecting the performance *via* mixing these nitramine explosives with some selected polymeric binders [6-14]. Polymeric binders can also improve the mechanical and chemical properties of explosives. Several polymers have been used in solid propellants during the last decades [15-17]. However, these polymers are mostly inert, and consequently cause significant reduction in performance.

Hydroxyl terminated polybutadiene (HTPB) is one of the most commonly used polymeric binders for both composite solid rocket propellants (CSRPs) and polymer bonded explosives (PBXs). HTPB acts as a matrix that binds together the fuel, oxidizer and other additives in many composite solid rocket propellants (CSRPs). HTPB has a similar role in binding together the explosive powders in many PBXs. It has also many other applications as binder, adhesive, sealant and potting compound. The high loading capability, easy processibility, and excellent physical and mechanical properties make HTPB-based propellants superior to those based on polyester binders [18].

The thermal behavior of energetic materials is a necessary area of research and development from the safety point of view and also for the evaluation of the performance parameters. Due to multi-step reactions in the different phases and zones, analysis of the collected results is highly complex. The problem becomes much more complicated for PBXs, due to the addition of binder and other chemicals to the energetic compound. Even very small amounts of binder may have a significant effect and may control the mechanism of thermal decomposition of PBXs [19-27].

The kinetic parameters of energetic materials can be evaluated and correlated to their performance. Both conventional and isoconversional methods may be used for fitting and for describing the mechanism [28-30]. In this study, the thermal behavior of pure RDX and RDX/HTPB was investigated using Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Vacuum Stability Test (VST), and Ignition Delay Techniques. The kinetic parameters were calculated by isoconversional and model fitting methods. The results of each technique were compared with each other. AKTS software was used to calculate the kinetic parameters. The results of the calculations were then compared with the experimental methods.

2 Experimental

2.1 Material

1,3,5-trinitro-1,3,5-triazine (RDX) was obtained from Heliopolis Company, Egypt. The following chemicals were used in the preparation of binder samples: HTPB (R-45M of ARCO Co.) as prepolymer with hydroxyl content of $0.84 \text{ meq}\cdot\text{g}^{-1}$, hexamethylene diisocyanate (HMDI, of Shandong Yucheng Yiao Technology Co., Ltd. China) as a curing agent with an NCO equivalence value of $11.83 \text{ meq}\cdot\text{g}^{-1}$, tris-1-(2-methyl aziridinyl) phosphine oxide (MAPO, of Hangzhou Yuhao Chemical Technology Co., Ltd. China) as bonding agent and dioctyl adipate (DOA, of Island Pyrochemical Industries, China) as plasticizer.

2.2 Preparation of the polyurethane binder and the PBX samples

Polyurethane binder sample was prepared in a 4 L vertical sigma mixer. The speed of the mixer was varied between 20 rpm and 40 rpm for different durations. The mixing temperature was maintained at $40 \pm 2 \text{ }^\circ\text{C}$. Hot water was circulated through the mixer jacket to maintain this temperature. HTPB, MAPO and DOA were added and mixed for 20 min followed by vacuum mixing for another 20 min to drive out the entrapped air. Then the explosive material (RDX) was added in three portions at $40 \text{ }^\circ\text{C}$ over a period of 30 min. The curing agent, HMDI, was then added at $55 \text{ }^\circ\text{C}$ and the ingredients were mixed for another 30 min. The binder system was then cast and cured at $60 \pm 2 \text{ }^\circ\text{C}$ for seven days under vacuum [31]. The cured HTPB binder system was prepared with an NCO/OH ratio of 0.83. MAPO made up 0.5 wt.% and DOA 20 wt.% of the total weight of the binder sample. The prepared PBX (RDX/HTPB) contained 80 wt.% RDX and 20 wt.% HTPB binder.

2.3 Experimental techniques

As mentioned before, the thermal decomposition kinetics and the heat flow properties of the prepared samples were measured using TGA (Q500 V20.10 Build 36 instrument), DSC (Q2000, 2000-1334 instrument), VST (STABIL, OZM research, Czech Republic; the original apparatus is described in Ref. [32]), and Ignition Delay Technique.

The experimental procedures were as follows:

TG/DTG: 4.52–6.46 mg samples were examined at heating rates of 2, 4, and $8 \text{ K}\cdot\text{min}^{-1}$ using a data collection rate of 40 points K^{-1} and $16 \text{ K}\cdot\text{min}^{-1}$ using a data collection rate of 60 points per K^{-1} in the temperature range $25\text{--}600 \text{ }^\circ\text{C}$ under a dynamic nitrogen flow rate of $30 \text{ mL}\cdot\text{min}^{-1}$.

DSC: samples of approximately 3.2 mg were placed in an aluminum pan

with a pin-hole cover, and heated at a constant heating rate of $5 \text{ K}\cdot\text{min}^{-1}$ under a 0.1 MPa dynamic nitrogen atmosphere from $25 \text{ }^\circ\text{C}$ to $350 \text{ }^\circ\text{C}$.

VST: the thermal decomposition kinetics were obtained isothermally at 140, 145, 150, and $155 \text{ }^\circ\text{C}$; the samples' mass were 20.0 mg and they were kept in completely evacuated sealed test tubes for 7-10 days.

Ignition delay: samples of approximately 0.1 g were placed in test tubes which were inserted into a heating block maintained at temperatures ranging from $250 \text{ }^\circ\text{C}$ to $320 \text{ }^\circ\text{C}$ (10 K steps) to detect the time needed for ignition.

3 Theoretical

3.1 Kinetic analysis

Solid-phase reactions are usually complex and may include several interfering processes. The kinetic analysis of such reactions is interesting. The kinetic parameters, including activation energy (E_a), the pre-exponential factor (A) and the kinetic model ($f(\alpha)$) of each individual process, are needed for complete kinetic description of the overall reaction. A large number of analytical methods are available for the evaluation of the kinetic parameters of distinct solid-phase reactions. However, the number of procedures for the analysis of complex processes is much more limited. Methods for the analysis of distinct processes include isoconversional (model-free) and model-fitting methods. Kinetic parameters can be determined using isoconversional or model-fitting methods either isothermally or nonisothermally [33, 34].

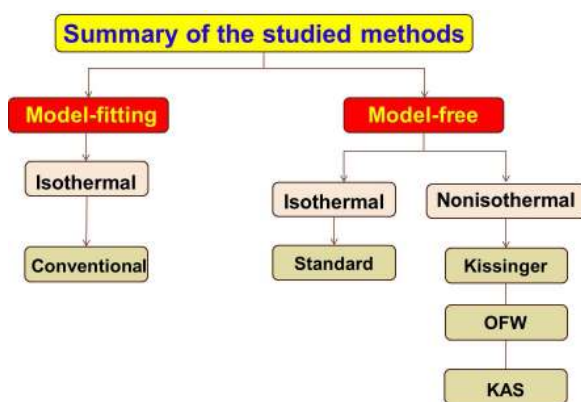


Figure 1. Diagram showing the relationships of the kinetic methods studied.

3.1.1 Model fitting method

The kinetics of thermally stimulated reactions in solids is usually described using the following equation:

$$d\alpha/dt = k(T) \cdot f(\alpha) \quad (1)$$

where α is the extent of conversion, t is time (s), T is absolute temperature (K), $k(T)$ is the temperature dependent rate constant and $f(\alpha)$ is a function called the reaction model. The temperature dependency of the rate constant is assumed to obey the Arrhenius expression:

$$k(T) = A \exp(-E/RT) \quad (2)$$

where A is the pre-exponential (Arrhenius) factor, E is the activation energy (J) and R is the universal gas constant ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). Equation 1 is often used in its integral form, which for isothermal conditions becomes:

$$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha = k(T)t \quad (3)$$

where $g(\alpha)$ is the integrated form of the reaction model. Substituting a particular reaction model into Equation 3 allows the corresponding rate constant to be evaluated from the slope of the plot of $g(\alpha)$ vs. t . The rate constants were evaluated at several temperatures for each reaction model selected, and the Arrhenius parameters were evaluated using the Arrhenius equation in its logarithmic form:

$$\ln k(T) = \ln A - E/RT \quad (4)$$

3.1.2 Isoconversional method

In the isoconversional method, it is assumed that the reaction model in Equation 1 is independent of temperature. Under isothermal conditions, we may combine Equations 3 and 4 to obtain:

$$-\ln t_{\alpha,i} = \ln[A/g(\alpha)] - E_a/RT_i \quad (5)$$

where E_a is evaluated from the slope for the plot of $-\ln t_{\alpha,i}$ vs. T_i^{-1} .

3.2 Calculation of activation energy

The value of the activation energy E_a of the main exothermic decomposition reaction of PBXs can be easily evaluated by applying Kissinger's method

(see Equation 6) [35, 36]:

$$-\frac{E_a}{R} = \frac{d \ln(\beta/T_p^2)}{d(1/T_p)} \quad (6)$$

where β is the heating rate ($\text{K}\cdot\text{s}^{-1}$) and T_p is the peak temperature of the DTG or DSC curve at that rate. The activation energy is calculated from the slope of the straight line obtained by plotting $\ln(\beta/T_p^2)$ against $1/T_p$. According to the recommendations of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) and the Kinetics Committee [35], a rough temperature integral approximation may result in inaccurate values of E_a . The following more accurate equation that has been frequently called the Kissinger-Akahira-Sunose (KAS) equation [37] gives, according to Starink [38], a more accurate estimate of E_a :

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{const} - 1.0008 \frac{E_a}{RT_{\alpha}} \quad (7)$$

Ozawa, Flynn and Wall independently developed the following isoconversional calculation method (OFW) for nonisothermal data through taking the logarithm of the nonisothermal rate law to give the following equation [39]:

$$\log g(\alpha) = \log \frac{AE_a}{\beta R} + \log \int_{\frac{E_a}{RT}}^{\infty} \frac{e^{-\frac{E_a}{RT}}}{\left(\frac{E_a}{RT}\right)^2} d \frac{E_a}{RT} \quad (8)$$

By substituting Doyle's approximation [40-42]:

$$\log \int_{\frac{E_a}{RT}}^{\infty} \frac{e^{-\frac{E_a}{RT}}}{\left(\frac{E_a}{RT}\right)^2} d \frac{E_a}{RT} \approx -2.315 - 0.4567 \frac{E_a}{RT} \quad (9)$$

The OFW equation is therefore,

$$\log \beta = \log \frac{AE_a}{g(\alpha)R} - 2.315 - 0.457 \frac{E_a}{RT} \quad (10)$$

Compared to the OFW method, the modified KAS method yields a significant

improvement in the accuracy of the E_a values. Note that the purpose of theoretical kinetic analysis is the interpretation of the experimentally determined kinetic triplets. It has been stated that each of the components of a kinetic triplet is associated with some fundamental theoretical concept, where E_a is associated with the energy barrier and A with the frequency of vibrations of the activated complex [43], and $f(\alpha)$ or $g(\alpha)$ with the reaction mechanism [20, 44].

4 Results and Discussion

4.1 TG/DTG studies

TG/DTG curves of RDX and RDX/HTPB at four heating rates 2, 4, 8, and 16 $\text{K}\cdot\text{min}^{-1}$ were recorded (see Figure 2). Figure 2 shows that the thermal decomposition of RDX/HTPB is faster than that of pure RDX. The peak DTG temperature was lower for RDX/HTPB than for RDX. To make a quantitative comparison, the characteristic parameters of these TG/DTG curves are summarized in Table 1.

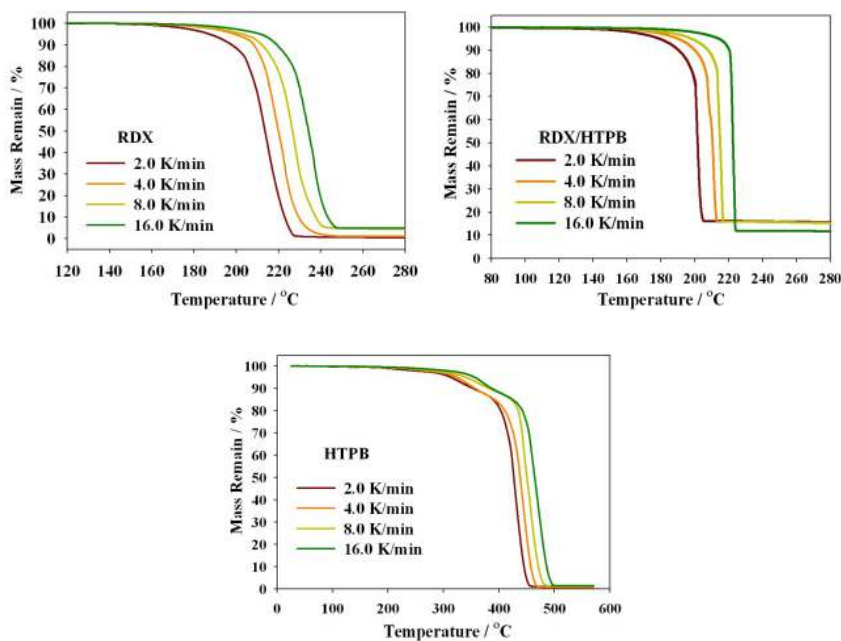


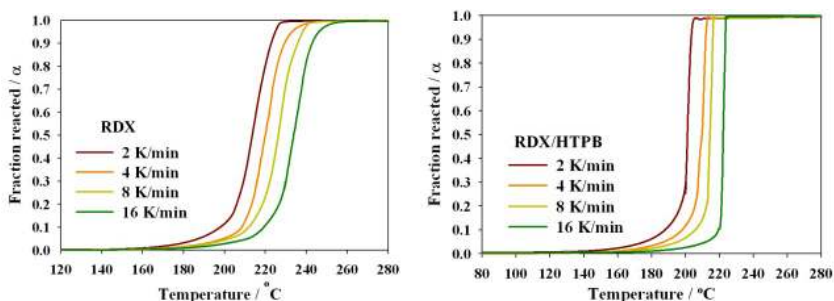
Figure 2. TG curves of RDX, RDX/HTPB and HTPB binder system for heating rates of 2, 4, 8 and 16.0 $\text{K}\cdot\text{min}^{-1}$.

Table 1. The kinetic parameters from non-isothermal TG/DTG data for RDX and HTPB/RDX

Material	β [$^{\circ}\text{C}\cdot\text{min}^{-1}$]	TG curves			DTG peaks	
		T_{ot} [$^{\circ}\text{C}$]	T_i [$^{\circ}\text{C}$]	Mass loss [%]	T_p [$^{\circ}\text{C}$]	T_{oe} [$^{\circ}\text{C}$]
RDX	2.0	172.48	202.23	98.06	214.74	233.34
	4.0	173.16	207.3	99.00	216.77	240.77
	8.0	176.20	211.36	99.07	227.25	248.21
	16.0	185.67	220.15	98.83	230.80	252.61
RDX/HTPB	2.0	155.24	194.46	98.47	200.21	221.8
	4.0	158.62	201.56	99.17	205.34	231.98
	8.0	162.34	208.32	99.21	217.45	238.74
	16.0	177.55	217.11	99.19	221.60	247.20

Notes: T_{ot} : decomposition onset temperature; T_{oe} : onset temperature of the end decomposition; T_i : the initial temperature for thermal decomposition; T_p : the peak temperature of mass loss rate; Mass loss: from initial temperature to the end temperature of DTG peak.

According to Table 1, it is obvious that the decomposition of PBX took place at a lower temperature than pure RDX. The difference in decomposition temperature is clearly visible for low heating rates but was less pronounced at high heating rates. The corresponding α - T curves were obtained from mass remaining vs. temperature data (see Figure 3). The early decomposition of RDX/HTPB may be due to the effect of exothermic decomposition of HTPB and the attraction of gaseous products from the early thermal decomposition of RDX in the polymer matrix both of which could lead to secondary reactions in the gas phase. It is also clear from Figure 2 that the HTPB binder system has a two stage decomposition. The onset decomposition temperature for first stage decomposition as seen from the TG curve was found to be higher than 270 $^{\circ}\text{C}$ at the different heating rates studied [34].

**Figure 3.** The α - T curves of RDX and RDX/HTPB for heating rates of 2, 4, 8 and 16.0 $\text{K}\cdot\text{min}^{-1}$.

Therefore, it is also possible that during the decomposition of HTPB, the evolved species interact chemically with the RDX decomposition products. Thus the mechanism of decomposition of HTPB/RDX may differ from that of the pure RDX.

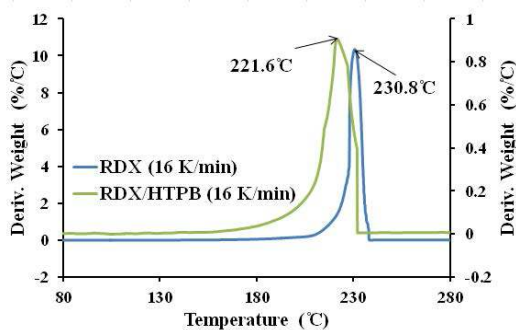


Figure 4. DTG curves for RDX and RDX/HTPB for $16.0 \text{ K} \cdot \text{min}^{-1}$ heating rate.

DTG curves for pure RDX and those for the HTPB/RDX samples are given in Figure 4. These show the effect of the non-energetic binder on the thermal decomposition behavior of the pure energetic materials. The binder decreases the decomposition temperature of the pure RDX and also decreases the activation energy of the overall reaction.

4.1.1 Kinetic parameters obtained by the Kissinger method

The activation energy E_a obtained by the conventional Kissinger method is usually comparable to the activation energy at half conversion obtained by the isoconversional method [45]. The kinetics of the thermal decomposition of HTPB-bonded PBX at different temperatures was studied by the non-isothermal TG (the mass loss was recorded with respect to temperature). The kinetic parameters were calculated according to the conventional Kissinger method.

For the four heating rates $2, 4, 8,$ and $16 \text{ K} \cdot \text{min}^{-1}$, $\ln(\beta/T^2)$ was plotted vs. $1/T$ as shown in Figure 5 to determine the activation energy from its slope according to the Kissinger equation. The main disadvantages of this method is that it is unable to demonstrate the steps of the reaction or give individual activation energies for each conversion fraction (α). The overall activation energy of RDX for the whole reaction was found to be $211.7 \text{ kJ} \cdot \text{mol}^{-1}$ as compared to $167.4 \text{ kJ} \cdot \text{mol}^{-1}$ for RDX/HTPB. This may indicate the earlier decomposition of RDX/HTPB relative to the pure RDX.

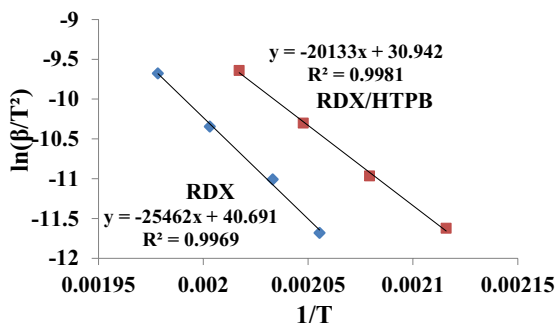


Figure 4. Relationship between $\ln(\beta/T^2)$ and $1/T$ to determine the activation energy of RDX and RDX/HTPB by the Kissinger method.

4.1.2 Kinetic parameters obtained by the Ozawa, Flynn, and Wall (OFW) method

Ozawa, Flynn and Wall independently developed an isoconversional calculation method for nonisothermal data. A plot of $\log\beta$ versus $1/T$ for each α yields E_a from the slope for that α regardless of the model employed. Figure 6 presents the effect of HTPB binder system on the activation energy of decomposition of pure RDX. The heat evolved from the exothermic initial decomposition of RDX supported by the initial decomposition of HTPB binder system may result in a secondary reaction and consequently decrease the total activation energy leading to early decomposition in the overall process. The activation energy for pure RDX using the non-isothermal OFW method was found to be $218.3 \text{ kJ}\cdot\text{mol}^{-1}$ and $157.8 \text{ kJ}\cdot\text{mol}^{-1}$ for the RDX/HTPB. This result is once again an indication of the effect of the binder system on the decomposition mechanism of the RDX.

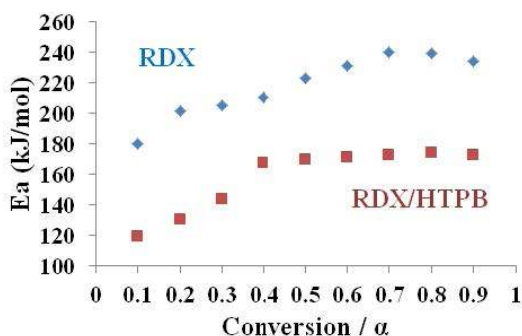


Figure 6. Activation energy E_a for every conversion step using isoconversional OFW method.

4.1.3 Kissinger-Akahira-Sunose (KAS) method

The modified Kissinger-Akahira-Sunose (KAS) isoconversional method was used to investigate the dependence of the activation energy on the degree of conversion. The activation energies for conversion rates of 0.1-0.9 are presented in Figure 7. The activation energies for conversion rates from 10% up to 90% were determined. However, the mean values were calculated only for the (0.3-0.7) α interval as it is commonly suggested there is increased inaccuracy outside this range due to the DTG peak tails [22-24]. According to the investigations on the thermal decomposition kinetics of RDX-based PBXs, the activation energy of PBXs with non-energetic binders is lower than that of the pure explosive filler. The activation energy for pure RDX using the modified KAS method was found to be **220.2** $\text{kJ}\cdot\text{mol}^{-1}$ and **158.7** $\text{kJ}\cdot\text{mol}^{-1}$ for the RDX/HTPB. These values are very close to the values obtained by the OFW method, but slightly further away from those obtained using the conventional Kissinger method. In the case of the conventional Kissinger method, the mean value was calculated for all the intervals and the decrease in the accuracy of estimation for the kinetic values couldn't be estimated for a selected interval.

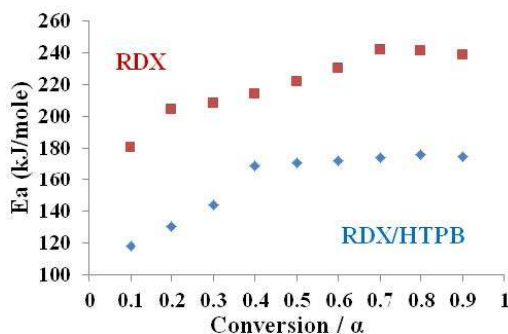


Figure 7. Activation energy E_a for every conversion step using isoconversional modified KAS method.

Table 2. Comparison of the values of activation energy using TG/DTG techniques and three different calculation methods

Calculation Method	Activation Energy, E_a [$\text{kJ}\cdot\text{mol}^{-1}$]	
	RDX	RDX/HTPB
Kissinger	211.7	167.4
OFW ($\alpha = 0.3-0.7$)	218.3	157.8
KAS ($\alpha = 0.3-0.7$)	220.2	158.7

4.2 DSC studies

TG/DTG results were supplemented by DSC studies which were performed at a heating rate of $5 \text{ K}\cdot\text{min}^{-1}$. The prepared samples were encapsulated in an aluminum pan and measurements were performed under similar conditions for both pure RDX and RDX/HTPB. The curves that were obtained are shown in Figure 8. The curves show an endothermic peak followed by an exothermic one for both RDX and RDX/HTPB. For the pure RDX, the initial sharp endothermic peak at 205°C is due to melting of the RDX. According to Szala *et al.* [46], the melting point of RDX is in the temperature range $203\text{--}206^\circ\text{C}$. A similar peak was also found at 198°C for RDX/HTPB, which confirms that both RDX and RDX/HTPB decompose in the liquid state. The RDX exothermic peak is well formed, showing signs of kinetically controlled decomposition processes. However, for the RDX/HTPB mixture, the sharp exothermic peak corresponding to rapid heat evolution is due to a fast combustion process.

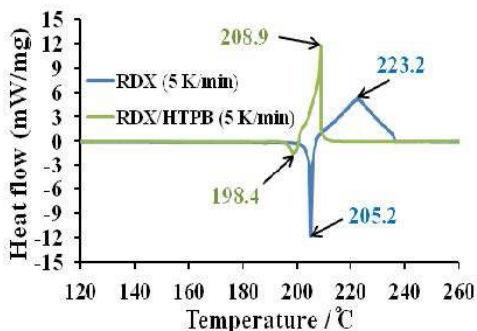


Figure 8. DSC curves for RDX and RDX/HTPB for a $5.0 \text{ K}\cdot\text{min}^{-1}$ heating rate.

4.3 Vacuum Stability Test (VST) studies

The Vacuum Stability Test (VST) is widely used to assess the stability and compatibility of many chemicals. The modernized STABIL 16-Ex apparatus [47] is manufactured by OZM Research. Their original apparatus is described in Ref. [33]. The temperatures for the isothermal measurements were chosen to be $140, 145, 150,$ and 155°C . Three 20 mg mass samples of pure RDX and RDX/HTPB were studied at each temperature. The pressures of the gases that were produced from the decomposition of the samples were continuously measured during the whole reaction.

The conversion fraction at any time (α_t) is given by:

$$\alpha_t = \frac{P_t - P_0}{P_{max} - P_0} \quad (11)$$

where P_{max} is the maximum pressure at the end of reaction, P_t is the pressure at any time, and P_0 is the initial pressure.

The conversion fraction (α) was plotted versus time (t) using Equation 11 (see Figure 9). It is clear that the conversion increased exponentially and the decomposition rate increased rapidly with raising the temperature. It is obvious from Figure 9 that the decomposition rate and conversion fraction of the RDX-based PBX both occur faster than for pure RDX especially at high temperatures (150 °C and 155 °C). The conversion was complete after nearly 33 h in the case of RDX/HTPB. However conversion took around 83 h in the case of pure RDX. Consequently it is clear that the binder increases the rate of thermal decomposition of pure RDX.

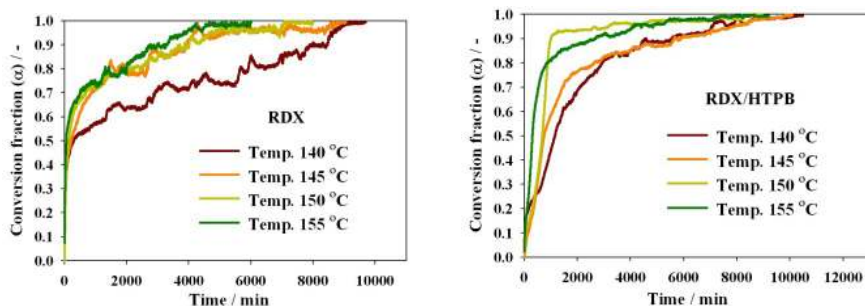


Figure 9. Conversion fractions (α) vs. time for pure RDX and RDX/HTPB.

4.3.1 Conventional isothermal model-fitting method

Fourteen of the conversional isothermal models given in Table 3 were selected for fitting to the conversion fraction obtained from the STABIL data. The model giving the best statistical fit was chosen as the model of choice from which the activation energy, E_a , and pre-exponential factor, A , were calculated. This process involves two fits: the *first* to determine the rate constant (k) of the model that best fits the data, the *second* to determine specific kinetic parameters such as the activation energy and pre-exponential factor using the Arrhenius equation [48].

Table 3. Various mechanisms-based kinetic models generally used to describe thermal decomposition of solids [48]

Model	$f(\alpha)$	$g(\alpha)$
Power law (P2)	$2 \alpha^{(1/2)}$	$\alpha^{(1/2)}$
Power law (P3)	$3 \alpha^{(2/3)}$	$\alpha^{(1/3)}$
Power law (P4)	$4 \alpha^{(3/4)}$	$\alpha^{(1/4)}$
Avarami-Erofe'ev (A2)	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Avarami-Erofe'ev (A3)	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Avarami-Erofe'ev (A4)	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
Contracting volume (R3)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
1-D diffusion (D1)	$1/2\alpha$	α^2
2-D diffusion (D2)	$[- \ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
3-D diffusion-Jander eqn. (D3)	$3(1-\alpha)^{2/3}/2(1-(1-\alpha)^{1/3})$	$[1-(1-\alpha)^{1/3}]^2$
First-order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$
Second-order (F2)	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third-order (F3)	$(1-\alpha)^3$	$0.5((1-\alpha)^{-2}-1)$

By plotting $g(\alpha)$ vs. time for each temperature according to Equation 3, it was found that the best model that fits the data for pure RDX was the contracting volume (R3) model, while the 3-D diffusion-Jander equation (D3) was the best model for RDX/HTPB. It means that the binder system has an obvious effect on changing the decomposition reaction mechanism of pure RDX. By obtaining the values of the rate constant k at different temperatures from the straight line slopes of plots of Equation 3, the activation energies, E_a , and pre-exponential factors, A , were determined using the Arrhenius equation in its logarithmic form (see Equation 4).

The activation energies, E_a , were **205.4** kJ·mol⁻¹ and **160.6** kJ·mol⁻¹ for pure RDX and RDX/HTPB, respectively. These values are in the same range of the calculated values obtained by using the TG/DTG technique applying non-isothermal isoconversional methods. It means that the vacuum stability test is a good technique for determining the activation energy of explosives. On the other side the value of $\log(A)$ was **21.2** s⁻¹ for pure RDX and **16** s⁻¹ for RDX/HTPB.

4.3.2 Standard isothermal isoconversional method

By plotting $-\ln(t)$ versus $1/T$ according to Equation 5 for each α , the activation energies at each α were obtained and these are presented in Figure 10.

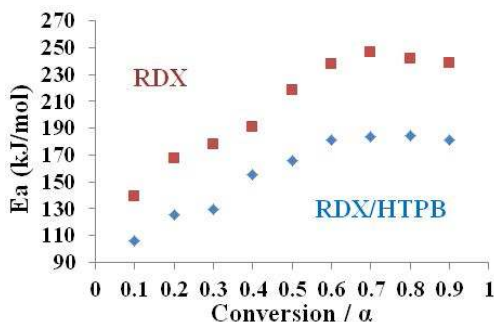


Figure 10. Activation energy, E_a , at each conversion step using standard isothermal isoconversional method.

The activation energy was found to be $206.5 \text{ kJ}\cdot\text{mol}^{-1}$ for pure RDX and $157.1 \text{ kJ}\cdot\text{mol}^{-1}$ for RDX/HTPB. A comparison of the results of both the isoconversional and model fitting methods showed that there is an insignificant difference between the results. The activation energy obtained by the isoconversional method is very close to that obtained by model fitting in case of the vacuum stability test device.

4.4 Ignition delay (t_{id}) studies

Calculations of t_{id} at various temperatures for RDX and RDX/HTPB were performed. The results are shown in Table 4. The values were fitted according to the following equation [49]:

$$t_{id} = A \exp \frac{E_a}{RT} \quad (12)$$

where E_a is the activation energy, R is the universal gas constant, T is the temperature, and A is the pre-exponential factor. A plot of $\ln(t_{id})$ versus $1/T$ (see Figure 11) was used to determine the activation energy from the slope.

Table 4. Ignition delay time (t_{id}) and activation energy (E_a) for RDX and its PBX

Sample	t_{id} [s] at temperatures [°C]								E_a [kJ·mol ⁻¹]	r
	250	260	270	280	290	300	310	320		
RDX	32	20	12	9	6	5	3	2	95.7	0.9943
RDX/HTPB	20	11	8	5	4	3	2	--	89.9	0.994

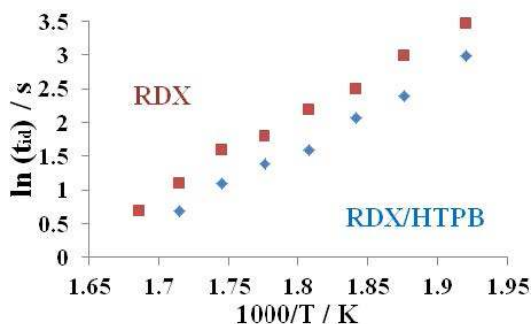


Figure 11. $\ln(t_{id})$ vs. $1/T$ for RDX and RDX/HTPB.

The values of t_{id} for RDX at various temperatures were higher than those for the RDX/HTPB (see Table 5). The difference is clear at lower temperatures, the difference slowly disappearing at high temperatures. The value of E_a for pure RDX is higher than that of RDX/HTPB. It is clear that the values obtained for activation energies for both RDX and RDX/HTPB were not consistent with those obtained by the other techniques. This might be due to the inaccuracy of the device used, the simplicity of the equation used or the dependence on human observation. For these reasons, the ignition delay method can only be used for qualitative evaluation of the thermal stability of the tested samples.

4.5 Advanced Kinetics and Technology Solution (AKTS) software

AKTS is a global solution for kinetic analysis and determination of the thermal stability of materials. A thermo-kinetics software package is used to facilitate kinetic analysis of DSC, DTA, and TGA data in the study of the thermal behaviour of materials for the purpose of research, development and quality assurance. The software provides a means to infer additional characteristics and thermal properties of examined substances based on conventional thermo-analytical measurements. The procedure begins with the determination of the kinetic parameters for a given substance. These parameters are then used to predict reaction progress for various temperature ranges. Using the AKTS Thermo-kinetics Software, the rate and the progress of the reactions can be predicted for a variety of temperature profiles such as: isothermal, non-isothermal, stepwise, modulated temperature or periodic temperature variations, rapid temperature increase (temperature shock) and real atmospheric temperature profiles (up to 7000 climates) [50].

The activation energies, E_a , for RDX and RDX/HTPB were calculated using the AKTS Thermo-kinetics software using the American Society for Testing and

Materials (ASTM E698) method. The results were very close to those obtained using the OFW and KAS methods and the TG/DTG technique. The activation energy for pure RDX was **219.1** kJ·mol⁻¹ and **158.2** kJ·mol⁻¹ for RDX/HTPB (see Figure 12).

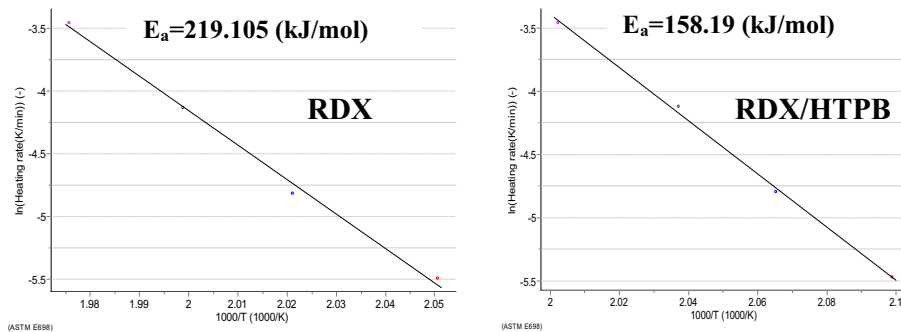


Figure 12. Activation energy (E_a) for RDX and RDX/HTPB using the AKTS software and the ASTM E698 method.

Table 5. Activation energy (E_a) for RDX and RDX/HTPB obtained using various techniques and methods

Samples	Activation Energy, E_a [kJ·mol ⁻¹]						
	TG/DTG		VST		Ignition delay	AKTS software	
	Kissinger	$\alpha = 0.3-0.7$ OFW	KAS	model fitting	Isocon- versional	Arrhenius eqn.	ASTM E698
RDX	211.7	218.3	220.2	205.4	206.5	95.7	219.1
RDX/ HTPB	167.4	157.8	158.7	160.6	157.1	89.9	158.2

From Table 5, it is clear that the activation energy for decomposition of RDX/HTPB is lower than that of pure RDX which indicates the effect of the polymeric matrix on decreasing the initiation energy barrier of RDX. This may be attributed to the effect of the polar plasticizer (DOA) incorporated in the polyurethane matrix which acts as a solvent for RDX [13]. It has been shown by Maksimov [51] that some RDX solvents are able to accelerate its decomposition. It has also been shown that these additives interfere with intermolecular interactions in RDX crystals by removing the stabilization effect of the crystal lattice [52].

The range of values of the activation energy, E_a , obtained using the OFW, KAS, and ASTM E698 methods was 218-220 kJ·mol⁻¹ for pure RDX and

157-159 $\text{kJ}\cdot\text{mol}^{-1}$ for RDX/HTPB. The narrowness of these ranges (about a 1% difference) proves the compatibility of these methods with each other. It was reported in Ref. [53] that the activation energy of RDX is $197.1 \text{ kJ}\cdot\text{mol}^{-1}$. Singh *et al.* [54] stated that the mean activation energy of pure RDX is nearly $200 \text{ kJ}\cdot\text{mol}^{-1}$ and that of RDX bonded by 15 wt.% HTPB is $143 \text{ kJ}\cdot\text{mol}^{-1}$. They also stated that the decomposition mechanism of RDX is not simple and so cannot be described by a global value of activation energy. By comparing the results for RDX presented in references [53, 55] ($197.1 \text{ kJ}\cdot\text{mol}^{-1}$ and $200 \text{ kJ}\cdot\text{mol}^{-1}$, respectively) with results of non-isothermal TGA measurements presented in this paper, it can be seen that the maximum difference between the activation energy obtained using various methods is around 10%. Our results obtained isothermally by VST are higher than those in studies published by other researchers by about 3% in case of pure RDX and by about 10% for its PBX. The main reasons for the minor difference between our results and the references might be the different sources for the RDX, the purity of the RDX, the effect of the particle size used and differences in the composition of the polymeric binders. Singh *et al.* [54] used the polymeric matrix contained IPDI as a curing agent while we used HMDI and DOA as plasticizer. Our results prove the efficacy of using VST as a technique to determine the decomposition kinetics isothermally.

5 Conclusions

The thermal behavior and decomposition kinetics of RDX and RDX/HTPB (RDX 80% HTPB-based binder 20%) composition were investigated by nonisothermal TG/DTG, isothermal VST and ignition delay techniques. The TG/DTG technique along with all the calculation methods employed resulted in kinetic parameters that were sufficiently close to those found in the published literature. The activation energies obtained by AKTS software using the ASTM E698 method were very close to those obtained by the OFW and KAS methods lying in the ranges $218\text{-}220 \text{ kJ}\cdot\text{mol}^{-1}$ for pure RDX and $157\text{-}159 \text{ kJ}\cdot\text{mol}^{-1}$ for RDX/HTPB. Thermolysis of RDX/HTPB occurs at a lower temperature and at a faster rate compared with pure RDX. Results of DSC measurements confirm the negative effect of the polymeric matrix in decreasing the exothermic peak temperature of the pure RDX. The VST technique displayed kinetic parameters in the same range as those found in the literature and those obtained from the TG/DTG technique for both RDX and RDX/HTPB. The ignition delay technique employed was less accurate for obtaining kinetic parameters than the TGA and VST techniques. So it should only be used for qualitative stability assessments.

References

- [1] Kubota N., *Propellants and explosives: Thermochemical Aspects of Combustion*, John Wiley & Sons, **2002**; ISBN 3527302107.
- [2] Agrawal J., *High Energy Materials: Propellants, Explosives and Pyrotechnics*, John Wiley & Sons, **2010**; ISBN 3527326103.
- [3] Talawar M., Sivabalan R., Mukundan T., Muthurajan H., Sikder A.K., Gandhe B.R., Rao A.S., Environmentally Compatible Next Generation Green Energetic Materials (GEMs), *J. Hazard. Mater.*, **2009**, *161*, 589-607.
- [4] Badgujar D., Talawar M., Asthana S., Mahulikar P., Advances in Science and Technology of Modern Energetic Materials: an Overview, *J. Hazard. Mater.*, **2008**, *151*, 289-305.
- [5] An C., Li F., Song X., Wang Y., Guo X., Surface Coating of RDX with a Composite of TNT and an Energetic-Polymer and its Safety Investigation, *Propellants Explos. Pyrotech.*, **2009**, *34*, 400-405.
- [6] Elbeih A., Pachman J., Trzcinski W., Zeman S., Akstein Z., Selesovsky J., Study of Plastic Explosives Based on Attractive Cyclic Nitramines, Part I. Detonation Characteristics of Explosives with PIB Binder, *Propellants Explos. Pyrotech.*, **2011**, *36*(5), 433.
- [7] Elbeih A., Pachman J., Zeman S., Vavra P., Trzcinski W., Akstein Z., Detonation Characteristics of Plastic Explosives Based on Attractive Nitramines with Polyisobutylene and Poly(methyl methacrylate) Binders, *J. Energ. Mater.*, **2011**, *30*(4), 358.
- [8] Elbeih A., Pachman J., Zeman S., Akstein Z., Replacement of PETN by BicycloHMX in Semtex 10, *Problems of Mechatronics*, **2010**, *2*(2), 7.
- [9] Elbeih A., Pachman J., Zeman S., Trzciński W.A., Akstein Z., Advanced Plastic Explosive Based on BCHMX Compared with Composition C4 and Semtex 10, *New Trends Res. Energ. Mater., Proc. Semin.*, 14th, Pardubice, Czech Republic, **2011**, 119.
- [10] Elbeih A., Zeman S., Jungova M., Vavra P., Attractive Nitramines and Related PBXs, *Propellants Explos. Pyrotech.*, **2013**, *38*(3), 379.
- [11] Elbeih A., Zeman S., Jungova M., Akstein Z., Effect of Different Polymeric Matrices on Sensitivity and Performance of Interesting Cyclic Nitramines, *Cent. Eur. J. Energ. Mater.*, **2012**, *9*(2), 17.
- [12] Elbeih A., Zeman S., Jungova M., Vavra P., Akstein Z., Effect of Different Polymeric Matrices on Some Properties of Plastic Bonded Explosives, *Propellants Explos. Pyrotech.*, **2012**, *37*(6), 676.
- [13] Elbeih A., Zeman S., Pachman J., Effect of Polar Plasticizers on the Characteristics of Selected Cyclic Nitramines, *Cent. Eur. J. Energ. Mater.*, **2013**, *10*(3), 339.
- [14] Elbeih A., Zeman S., Jungová M., Akstein Y., Vávra P., Detonation Characteristics and Penetration Performance of Plastic Explosives, in: *Proc. 2011 Int. Autumn Seminar on Propellants, Explosives and Pyrotechnics*, (Li S., Niu P., Eds.), Nanjing, Sept. 20-23, 2011, *Theory and Practice of Energetic Materials*, Vol. IX, Sci. Press,

- Beijing, **2011**, pp. 508-513.
- [15] Mulage K., Patkar R., Deuskar V., Studies on a Novel Thermoplastic Polyurethane as a Binder for Extruded Composite Propellants, *Cent. Eur. J. Energ. Mater.*, **2007**, *4*, 233-245.
- [16] Celina M., Minier L., Assink R., Development and Application of Tools to Characterize the Oxidative Degradation of AP/HTPB/Al Propellants in a Propellant Reliability Study, *Thermochim. Acta*, **2002**, *384*, 343.
- [17] Chen F., Duo Y., Luo S., Luo Y., Tan H., Novel Segmented Thermoplastic Polyurethanes Elastomers Based on Tetrahydrofuran Ethylene Oxide Copolyethers as High Energetic Propellant Binders, *Propellants Explos. Pyrotech.*, **2003**, *28*, 7-11.
- [18] Adnan H., *Investigation of the Service Life of Binders Used in Rocket Propellants and High Explosives*, Msc Thesis, Military Technical College, Cairo, **1999**.
- [19] Yan Q.-L., Zeman S., Selesovsky J., Svoboda R., Elbeih A., Thermal Behaviour and Decomposition Kinetics of Formex-bonded Explosives Containing Different Cyclic Nitramines, *J. Therm. Anal. Calorim.*, **2013**, *111*, 1419.
- [20] Yan Q.-L., Zeman S., Svoboda R., Elbeih A., Thermodynamic Properties, Decomposition Kinetics and Reaction Models of BCHMX and its Formex Bonded Explosive, *Thermochim. Acta*, **2012**, *547*, 150.
- [21] Yan Q.-L., Zeman S., Elbeih A., Recent Advances in Thermal Analysis and Stability Evaluation of Insensitive Plastic Bonded Explosives (PBXs), *Thermochim. Acta*, **2012**, *537*, 1-12.
- [22] Yan Q.-L., Zeman S., Zhao F., Elbeih A., Non-isothermal Analysis of C4 Bonded Explosives Containing Different Cyclic Nitramines, *Thermochim. Acta*, **2013**, *556*, 6.
- [23] Yan Q.-L., Zeman S., Elbeih A., Thermal Behavior and Decomposition Kinetics of Viton A Bonded Explosives Containing Attractive Cyclic Nitramines, *Thermochim. Acta*, **2013**, *562*, 56.
- [24] Yan Q.-L., Zeman S., Zang T., Elbeih A., Non-isothermal Decomposition Behaviour of Fluorel Bonded Explosives Containing Attractive Cyclic Nitramines, *Thermochim. Acta*, **2013**, *574*, 10.
- [25] Yan Q.-L., Zeman S., Elbeih A., Zbynek A., The Influence of the Semtex Matrix on the Thermal Behaviour and Decomposition Kinetics of Cyclic Nitramines, *Cent. Eur. J. Energ. Mater.*, **2013**, *10*(4), 509.
- [26] Zeman S., Elbeih A., Yan Q.-L., Note on the Use of the Vacuum Stability Test in the Study of Initiation Reactivity of Attractive Cyclic Nitramines in Formex P1, *J. Therm. Anal. Calorim.*, **2013**, *111*, 1503.
- [27] Zeman S., Elbeih A., Yan Q.-L., Notes on the Use of the Vacuum Stability Test in the Study of Initiation Reactivity of Attractive Cyclic Nitramines in the C4 Matrix, *J. Therm. Anal. Calorim.*, **2013**, *112*, 1433-1437.
- [28] Vyazovkin S., Wight C., Model-free and Model-fitting Approaches to Kinetic Analysis of Isothermal and Nonisothermal Data, *Thermochim. Acta*, **1999**, *340*, 53-68.

- [29] Singh G., Felix S., Soni P., Studies on Energetic Compounds Part 28: Thermolysis of HMX and its Plastic Bonded Explosives Containing Estane, *Thermochim. Acta*, **2003**, 399, 153-165.
- [30] Singh G., Felix S., Soni P., Studies on Energetic Compounds: Part 31. Thermolysis and Kinetics of RDX and Some of its Plastic Bonded Explosives, *Thermochim. Acta*, **2005**, 426, 131-139.
- [31] Manu S., Varghese T., Mathew S., Ninan K., Studies on Structure Property Correlation of Cross-linked Glycidyl Azide Polymer, *J. Appl. Polymer Sci.*, **2009**, 114, 3360-3368.
- [32] Zeman S., Gazda Š., Štolcová A., Dimun A., Dependence on Temperature of the Results of the Vacuum Stability Test for Explosives, *Thermochim. Acta*, **1994**, 247, 447-454.
- [33] Khawam A., Flanagan D., Basics and Applications of Solid-state Kinetics: A Pharmaceutical Perspective, *J. Pharm. Sciences*, **2006**, 95, 472-498.
- [34] Abd-Elghany M., Elbeih A., Hassanein S., Study of Decomposition Kinetics of Binder System Based on HTPB Using Different Techniques and Methods, *New Trends Res. Energ. Mater. Proc. Semin.*, 18th, Czech Republic, **2015**, 101.
- [35] Vyazovkin S., Burnham A., Criado J., Pérez-Maqueda L., Popescu C., Sbirrazzuoli N., ICTAC Kinetics Committee Recommendations for Performing Kinetic Computations on Thermal Analysis Data, *Thermochim. Acta*, **2011**, 520, 1-19.
- [36] Kissinger H., Reaction Kinetics in Differential Thermal Analysis, *Anal. Chem.*, **1957**, 29, 1702-1706.
- [37] Akahira T., Sunose T., Method of Determining Activation Deterioration Constant of Electrical Insulating Materials, *Res. Report Chiba Inst. Technol. (Sci. Technol.)*, **1971**, 16, 22-31.
- [38] Starink M., The Determination of Activation Energy From Linear Heating Rate Experiments: a Comparison of the Accuracy of Isoconversion Methods, *Thermochim. Acta*, **2003**, 404, 163-176.
- [39] Vyazovkin S., Dollimore D., Linear and Nonlinear Procedures in Isoconversional Computations of the Activation Energy of Nonisothermal Reactions in Solids, *J. Chem. Inf. Comput. Sci.*, **1996**, 36, 42-45.
- [40] Doyle C., Kinetic Analysis of Thermogravimetric Data, *J. Appl. Polym. Sci.*, **1961**, 5, 285-292.
- [41] Doyle C., Estimating Isothermal Life from Thermogravimetric Data, *J. Appl. Polym. Sci.*, **1962**, 6, 639-642.
- [42] Doyle C., *Series Approximations to the Equation of Thermogravimetric Data*, **1965**.
- [43] Brown M., *Introduction to Thermal Analysis: Techniques and Applications*, Kluwer Academic Publishers, **2001**, 181-214; ISBN 978-1-4020-0472-9.
- [44] Yan Q.-L., Zeman S., Svoboda R., Elbeih A., Málek J., The Effect of Crystal Structure on the Thermal Initiation of CL-20 and its C4 Bonded Explosives (II): Models for Overlapped Reactions and Thermal Stability, *J. Therm. Anal. Calorim.*, **2012**.

- [45] Vyazovkin S., Sbirrazzuoli N., Isoconversional Kinetic Analysis of Thermally Stimulated Processes in Polymers, *Macromol. Rapid Commun.*, **2006**, *27*, 1515-1532.
- [46] Szala M., Sałaciński T., 2,4,6-Trinitrotoluene as a Source of Modern Explosives. Review (in Polish), *High-Energetic Materials*, **2015**, *7*, 125-143.
- [47] Krupka M., Devices and Equipment for Testing of Energetic Materials, *New Trends Res. Energ. Mater., Proc. Semin.*, 4th, Pardubice, Czech Republic, **2001**.
- [48] Khawam A., Flanagan D., Complementary Use of Model-free and Modelistic Methods in the Analysis of Solid-state Kinetics, *J. Phys. Chem.*, **2005**, *109*, 10073-10080.
- [49] Zinn J., Rogers R., Thermal Initiation of Explosives1, *J. Phys. Chem.*, **1962**, *66*, 2646-2653.
- [50] AKTS; <http://www.akts.com/akts-thermokinetics-tga-dsc-dta-tma-ftir-ms/download-tga-dsc-dta-tma-ms-ftir-akts-thermokinetics-software.html>, **2012**.
- [51] Maksimov Yu.Ya., Thermal Decomposition of Hexogen and Octogen, *Tr. Mosk. Khim.-Teknol. Inst. im. Mendeleeva*, **1967**, *53*, 73-84.
- [52] Manelis G., Nazin G., Prokudin V., Dependence of Thermal Stability of Energetic Compounds on Physicochemical Properties of Crystals, in: *Successes in Special Chemistry and Chemical Technology*, (Sinditskii V., Serushkin V., Shepelov G., Eds.), Khim.-Teknol. Univ. Mendeleeva, Moscow, **2010**, 191.
- [53] Dobratz B., Crawford P., *LLNL Explosives Handbook – Properties of Chemical Explosives and Explosive Simulants*, **1985**, 6-90.
- [54] Singh G., Prem Felix S., Pandey D., Agrawal J., Sikder A., Studies on Energetic Materials, Part 39: Thermal Analysis of a Plastic Bonded Explosives Containing RDX and HTPB, *J. Therm. Anal. Calorim.*, **2005**, *79*, 631.