

Thermal properties of TEX decomposition or sublimation

Katarzyna Gańczyk¹ · Angelika Zygmunt¹ · Tomasz Gołofit¹

Received: 29 July 2015 / Accepted: 11 April 2016 / Published online: 28 April 2016
© The Author(s) 2016. This article is published with open access at Springerlink.com

Abstract TEX is a thermostable compound and less sensitive to external stimuli. It sublimates and decomposes at high temperature. The influence of DSC and TG measurement conditions and substance mass on the thermal decomposition of TEX was determined. It was observed that substance mass, pan type and fulfillment degree of pan influence the thermal decomposition and kinetic parameters of TEX decomposition. Sublimation of the sample was the main observed process; thermal decomposition was the secondary process during the heating of TEX in open pans. With increasing substance mass, the participation of thermal decomposition of TEX increased. Uncontrolled thermal decomposition was observed for larger mass of a sample. The sublimation and decomposition processes were confirmed by FT-IR method. Thermal decomposition was the main process observed during heating the sample of TEX in hermetic pans. Sublimation of a sample was marginal. The sublimation effect decreased with increasing the degree of fulfillment pan. The kinetic parameters were determined with the Friedman's isoconversional method. The conversion, mass of sample and the type of pan caused the large changes in the values of kinetic parameters. The apparent activation energy varied from 128 to 355 kJ mol⁻¹ and logA varied from 9.95 to 30.64 in initial step ($\alpha = 0.02$) for different condition of measurements. The low values of apparent activation energy (about

130 kJ mol⁻¹) were associated with sublimation process and the high values (about 340 kJ mol⁻¹) with the decomposition process.

Keywords Thermal decomposition · 4,10-Dinitro-2,5,8,12-tetraoxy-4,10-diazotetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (TEX) · DSC · TG · Kinetic parameters · Sublimation process

Introduction

4,10-Dinitro-2,5,8,12-tetraoxa-4,10-diazotetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (TEX) is caged polynitramine. Its structure (Fig. 1) is similar to that of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (CL-20)—one of the strongest explosive materials. TEX is characterized with high density ($\rho = 1.985 \text{ g cm}^{-3}$) [1].

TEX is the representative of low-sensitive explosive materials class. TEX sensitivity to impact and friction is similar to those of 3-nitro-1,2,4-triazol-5-one (NTO) and 1,1-diamino-2,2-dinitroethene (FOX-7). The friction sensitivity for TEX, NTO and FOX-7 is more than 350 N [2–4]. The impact sensitivity in BAM fall-hammer test for TEX equals 24 J [2] and for FOX-7 25.2–31.8 J [5]. The impact sensitivity in ABL test for TEX (200 μ) equals 33 cm and for NTO (250 μ) 26 cm [1]. TEX sensitivity to the electric spark is lower in comparison with those of FOX-7 and NTO (TEX—13.1 J [2], NTO—8.98 J [3], FOX-7 4.5 J [5]). TEX is widely used in insensitive munition (IM) [6]. Several examples were found in the literature about its use in, e.g., castable high explosive compositions, pressable or extrudable explosives formulations, plastic bonded explosives (PBX) [7–12]. Lin et al. determined the detonation parameters of TEX based on

Electronic supplementary material The online version of this article (doi:10.1007/s10973-016-5476-9) contains supplementary material, which is available to authorized users.

✉ Tomasz Gołofit
tomgol@ch.pw.edu.pl

¹ Department of High-Energetic Materials, Warsaw University of Technology, Noakowskiego 3, Warsaw, Poland

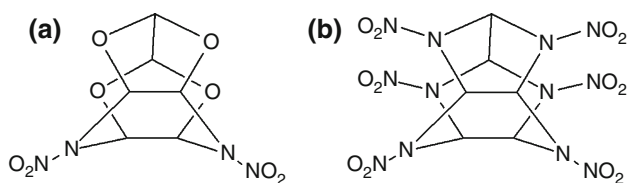


Fig. 1 The structure of TEX (a) and CL-20 (b)

density functional theory (DFT). The detonation parameters of TEX were slightly lower than for CL-20. The parameters for TEX calculated were based on Kamlet–Jacobs equation: detonation velocity $V_{\text{det}} = 9.28 \text{ km s}^{-1}$ ($\rho = 2.01 \text{ g cm}^{-3}$), detonation pressure $p_{\text{CJ}} = 40.72 \text{ GPa}$ and detonation energy $Q_{\text{det}} = 5.65 \text{ kJ g}^{-1}$ [3, 13]. In the work [14], the authors determined experimentally detonation velocity of PBX containing TEX—the detonation velocity equaled $V_{\text{det}} = 7.45 \text{ km s}^{-1}$ ($\rho = 1.87 \text{ g cm}^{-3}$). The detonation velocity and impact sensitivity of PBX containing mixture of TEX and 1,3,5-trinitroperhydro-1,3,5-triazine (hexogen, RDX) were also studied and compared with PBX containing RDX. The addition of 40 % TEX caused a significant decrease in impact sensitivity, and the detonation velocity was at the same level.

TEX is thermostable compound, and its stability is comparable with that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [15]. TEX undergoes decomposition above $260 \text{ }^{\circ}\text{C}$ with heat effect $Q = 1.5 \text{ kJ g}^{-1}$. TEX evolves small amount of gases (0.05 mL of gases after 48 h at $100 \text{ }^{\circ}\text{C}$) in vacuum thermal stability test [1]. The properties of TEX were also studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) [16, 17]. DSC studies were performed on 2–3 mg samples in closed hermetic aluminum pans with the heating rate $\beta = 2 \text{ }^{\circ}\text{C min}^{-1}$. Single exothermic peak corresponding to decomposition at $297 \text{ }^{\circ}\text{C}$ was observable on the DSC curve. TG studies were performed on 5 mg samples in open aluminum pans with the different heating rate ($\beta = 2.5\text{--}20 \text{ }^{\circ}\text{C min}^{-1}$). The results indicated that TEX sublimates at temperature above $240 \text{ }^{\circ}\text{C}$. Single peak at $284 \text{ }^{\circ}\text{C}$ was visible on the DTG curve. The activation energy (E_a) was calculated using model-free isoconversional methods and equals $E_a = 133 \pm 2 \text{ kJ mol}^{-1}$ in the conversion range $0.12 \leq \alpha \leq 0.96$. In works [18, 19], activation energy using Soviet manometric method (SMM) was also notified. The TEX decomposition was analyzed in the temperature range $210\text{--}225 \text{ }^{\circ}\text{C}$. Kinetic parameters equal: $E_a = 196.8 \text{ kJ mol}^{-1}$ and $\log A = 15.4$. Xiao et al. [20] studied the thermal decomposition of TEX using microcalorimeter C-500 type Calvet (SETARAM, France) in 10-mL vessels. The study was done for very low heating rates $\beta = 0.2\text{--}0.6 \text{ }^{\circ}\text{C min}^{-1}$. Single exothermic transition

was visible on the DSC curve. This transition was shifted from 265.7 to $282.2 \text{ }^{\circ}\text{C}$ with the increasing heating rate. Obtained kinetic parameters equal: $E_a = 156.65 \text{ kJ mol}^{-1}$ and $\log A = 11.54$. Kinetic parameters of TEX decomposition described in the literature are divergent. Activation energy varied in the range of $133.0\text{--}196.8 \text{ kJ mol}^{-1}$, $\log A$ $11.5\text{--}15.4$. The difference in obtained values is associated with different measurement conditions.

The influence of measurement conditions on obtained values of kinetic parameters was also observed for another compound [21–25]. Authors of publication [21] observed constant activation energy (isothermal condition) of decomposition process for poly(vinyl chloride) (PVC). The dependence of apparent activation energy on conversion of PVC was obtained for non-isothermal condition [22, 23]. The effect of measurement conditions in higher temperature on processes was also observed for 1,3,3-trinitroazetidine (TNAZ). The authors determined the activation energy of TNAZ decomposition for large sample mass using microcalorimeter [24]. The processes of sublimation and evaporation were observed for this compound for low sample mass using DSC and TG–DTA technics. They also determined the kinetic parameters of these processes [25]. The thermal decomposition study should be performed to minimize the influence of physical processes (polymorphic transitions, melting, sublimation, evaporation) on analyzed decomposition process.

The uncontrolled decomposition of high-energetic materials might run to the thermal explosion [26]. This situation may take place for low conversion degrees [27]. For this reason, it is important to know the kinetic parameters of decomposition reaction for initial decomposition stage.

The aim of work was to study the thermal decomposition process of TEX in different conditions. Kinetic parameters of decomposition reaction and sublimation of TEX were calculated. The influence of measurement condition on the decomposition process was analyzed. Obtained kinetic parameters for initial decomposition stage are important for users for the estimation of TEX use and storage safety.

Experimental

Materials

TEX was synthesized in the Department of High-Energetic Materials of the Warsaw University of Technology [28]. The purity of compound was determined using high-performance liquid chromatography (HPLC) and equals 99.5 %.

Instrumental analysis

DSC analysis was carried out using Thermal Analysis (TA) Instruments Q2000 calorimeter. The measurements were done in hermetic aluminum pans (TA 900786.901, 900779.901) with nitrogen flow rate equal to 50 mL min^{-1} . The thermogravimetric analysis was carried out using TA Instruments SDT Q600 thermogravimeter. The measurements were done in open aluminum pans (TA 901684.901) with the nitrogen rate of 100 mL min^{-1} . DSC and TG analyses were performed using six different heating rates in the range: $\beta = 0.5\text{--}16.0 \text{ }^\circ\text{C min}^{-1}$. The measurements for extreme heating rate were repeated three times in accordance with International Confederation for Thermal Analysis and Calorimetry (ICTAC) [29]. The partial decomposition of TEX was done at the heating rate $\beta = 2 \text{ }^\circ\text{C min}^{-1}$ using TG method.

The Fourier transform infrared spectroscopy (FTIR) analysis was carried out using Thermo Scientific NICOLET 6700 spectrometer. The disk for analysis was prepared by triturating and pressing 1 mg of TEX sample and 200 mg potassium bromide. The spectrum was recorded in the wave number range: $4000\text{--}400 \text{ cm}^{-1}$. The bands were separated using PeakFit program of SeaSolve Software Inc. company.

Kinetic analysis

Kinetic parameters of decomposition reaction were calculated using Thermokinetics 3.1 program of NETZSCH company. Many parallel and sequent reactions take place during TEX decomposition. Obtained kinetic parameters were the resultant of all reactions. For this reason, the calculated activation energy in the next part of this manuscript was called apparent activation energy (${}_aE_a$) [20, 28]. The apparent activation energy and logarithm of pre-exponential factor were calculated using Friedman's isoconversional method according to the ICTAC recommendation [29]. The first-order kinetic model was assumed in order to determine pre-exponential factor.

Results and discussion

Thermogravimetric analysis (TG) of TEX decomposition performed in open pan

TG–DSC measurements were performed in open pans for TEX sample mass of $3.8 \pm 0.2 \text{ mg}$. Typical TG–DSC curve for heating rate $\beta = 16 \text{ }^\circ\text{C min}^{-1}$ is presented in the Fig. 2.

The mass loss of the sample begins at $200 \text{ }^\circ\text{C}$. This is a one-step process. One endothermic process was observed

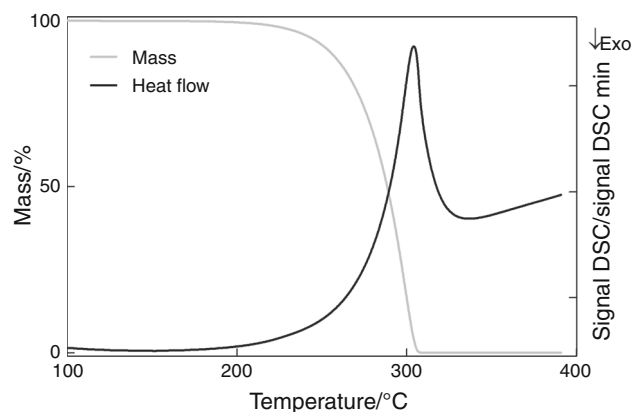


Fig. 2 Typical TG and DSC curves for TEX sample mass of $m = 3.8 \pm 0.2 \text{ mg}$ for heating rate $\beta = 16 \text{ }^\circ\text{C min}^{-1}$

on the DSC curve (the temperature of process was $T_{\text{peak}} = 304.0 \text{ }^\circ\text{C}$, and the enthalpy was $\Delta H = 315 \text{ J g}^{-1}$). This process was associated primarily with the sublimation of sample. The series of TG–DSC measurements with different heating rates were performed for samples of $3.8 \pm 0.2 \text{ mg}$. The mass loss for all samples was associated with endothermic processes. TG curves are presented in Fig. 3.

As expected, with increasing the heating rate, the mass loss process occurred at higher temperature. The termination of mass loss process shifts in temperature from 244 to $306 \text{ }^\circ\text{C}$. Kinetic parameters were determined using TG curves. The dependence of apparent activation energy and logarithm of pre-exponential factor on conversion degree is presented in Fig. 4. The values of apparent activation energy and the logarithm of pre-exponential factor are presented in Table S1 (Supplementary Material).

The apparent activation energy was constant up to $\alpha = 0.6$ and equaled ${}_aE_a = 128 \pm 3 \text{ kJ mol}^{-1}$. For

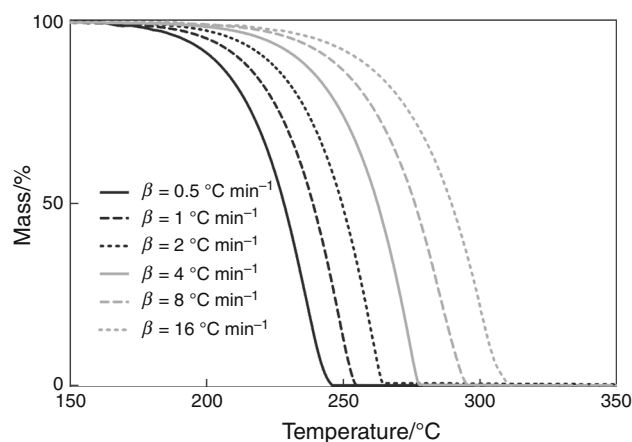


Fig. 3 TG curves for TEX samples of $3.8 \pm 0.2 \text{ mg}$ for different heating rates ($\beta = 0.5, 1, 2, 4, 8, 16 \text{ }^\circ\text{C min}^{-1}$)

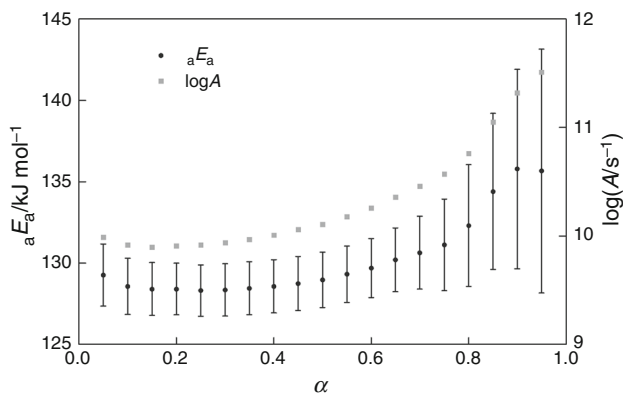


Fig. 4 The dependence of apparent activation energy (${}_aE_a$) and the logarithm of pre-exponential factor ($\log A$) on conversion degree (α) for TEX decomposition reaction for the samples of 3.8 ± 0.2 mg in open pans determined with TG method

conversion degrees higher than $\alpha = 0.6$, the apparent activation energy increased to value ${}_aE_a = 136 \pm 8$ kJ mol $^{-1}$ for $\alpha = 0.95$. The results corresponded well to the published literature where the activation energy equals $E_a = 133 \pm 2$ kJ mol $^{-1}$ [16, 17]. The logarithm of pre-exponential factor increased with increasing conversion degree and ranges from 9.95 for $\alpha = 0.02$ to 11.51 for $\alpha = 0.95$. The characteristics of $\log A$ changed with a pattern similar to the apparent activation energy. In order to examine the influence of sample mass on the mass loss process, TG–DSC measurements for samples of 4, 10 and 20 mg were performed. DSC curves are shown in Fig. 5.

The mass loss (TG–DSC measurement) for sample mass of 4 mg was associated with endothermic process. For the sample of 10 mg, the exothermic process overlapped with the endothermic transition. The decomposition for the

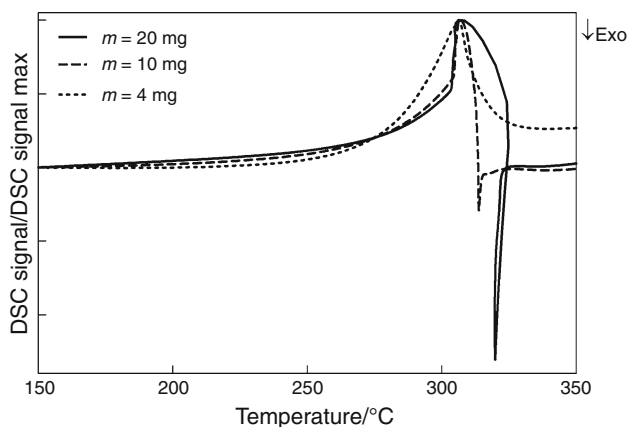


Fig. 5 DSC curves for TEX samples of 3.8 ± 0.2 , 10.2 ± 0.2 and 20 mg. The measurements were performed in open pans in which heating rate equals $\beta = 16$ °C min $^{-1}$

sample of 20 mg was uncontrolled because strong exothermic effect on the graph was visible, which took place in the end of mass loss process. The series of TG–DSC measurements with the different heating rates were performed for samples of 10.2 ± 0.2 mg to determine the influence of sample mass on kinetic parameters. Kinetic parameters were determined using TG curves. The apparent activation energy and the logarithm of pre-exponential factor for different conversion degrees are shown in Fig. 6. The values of apparent activation energy and the logarithm of pre-exponential factor are presented in Table S2 (Supplementary Material).

The apparent activation energy is constant up to $\alpha = 0.55$ and equals ${}_aE_a = 132 \pm 3$ kJ mol $^{-1}$. For conversion degrees higher than $\alpha = 0.55$, the apparent activation energy increases to the value of ${}_aE_a = 186 \pm 20$ kJ mol $^{-1}$ for $\alpha = 0.80$. The apparent activation energy equals ${}_aE_a = 154 \pm 9$ kJ mol $^{-1}$ for conversion degree $\alpha = 0.95$. The characteristics of $\log A$ changed with a pattern similar to the apparent activation energy. $\log A$ equals 10.23 for $\alpha = 0.02$. For $\alpha = 0.81$, the logarithm of pre-exponential factor achieves maximum and is equal to 15.62. In the end of decomposition, $\log A$ (for $\alpha = 0.95$) equals 13.04. The results (from $\alpha = 0.02$ to $\alpha = 0.55$) correspond well to the published literature where the activation energy is $E_a = 133 \pm 2$ kJ mol $^{-1}$ [7, 17]. The kinetic parameters achieved for $\alpha = 0.80$ correspond well to Soviet manometric method (SMM) where $E_a = 196.8$ kJ mol $^{-1}$ and $\log A = 15.4$. The results achieved during TG–DSC measurement performed in open pans indicated that the mass loss was associated with sublimation process. With increasing the mass sample, the mass loss was associated with greater participation of the TEX decomposition process. The apparent activation energy of sublimation process equals about 130 kJ mol $^{-1}$.

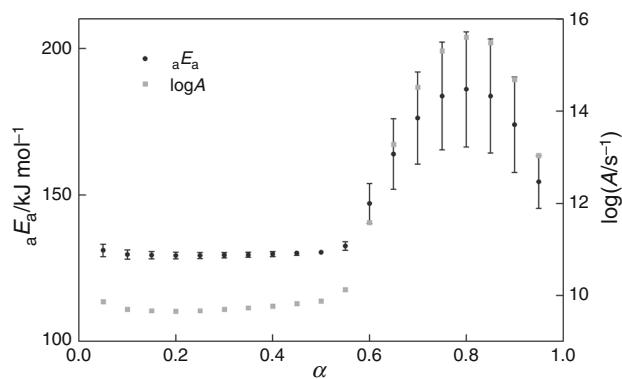


Fig. 6 The dependence of apparent activation energy (${}_aE_a$) and the logarithm of pre-exponential factor ($\log A$) on conversion degree (α) for TEX sample mass of 10.2 ± 0.2 mg achieved in TG measurements

The FTIR analysis of TEX decomposition performed in open pans

The series of TG measurements of TEX were performed with the heating rate $\beta = 2 \text{ }^\circ\text{C min}^{-1}$. The measurements were interrupted in different conversion degrees (from $\alpha = 0.10$ to $\alpha = 0.96$). The comparison of FTIR spectrum obtained for partially decomposed sample and for output sample was made to determine whether the decomposition of TEX in solid phase took place during the sublimation. FTIR spectrum of output TEX in KBr is presented in Fig. 7. FTIR spectra of output TEX and partially decomposed TEX (conversion degree $\alpha = 0.96$) with wave number assigned are presented in Figs. S1 and S2, respectively (Supplementary Material). This spectrum corresponds well to the spectra found in the literature [2, 26]. The absorption bands and the modes of vibration assigned to them are summarized in Table 1.

The comparison of three spectra, output sample of TEX and two sample of partially decomposed TEX (conversion degrees $\alpha = 0.50$ and $\alpha = 0.96$), are presented in Fig. 8. All spectra were normalized relative to the $\nu = 1174 \text{ cm}^{-1}$ band.

The FTIR spectrum of TEX output sample ($\alpha = 0.00$) and that for sample with less mass loss are similar. Ratios of separated peaks heights for the spectrum of TEX samples with higher mass loss are changed. It was very good visible for conversion degree $\alpha = 0.96$. The differences in heights were visible for peaks, e.g., 1596, 1330, 1174, 1116, 1055, 874 cm^{-1} . The ratio of peak height to peak height at $\nu = 1174 \text{ cm}^{-1}$ was determined in order to define the changes in band intensity for different conversion degrees (Fig. 9).

The ratios of selected waves varied small in the conversion degree range of $\alpha = 0.00$ – 0.76 . The changes in selected waves for larger conversion degrees are visible.

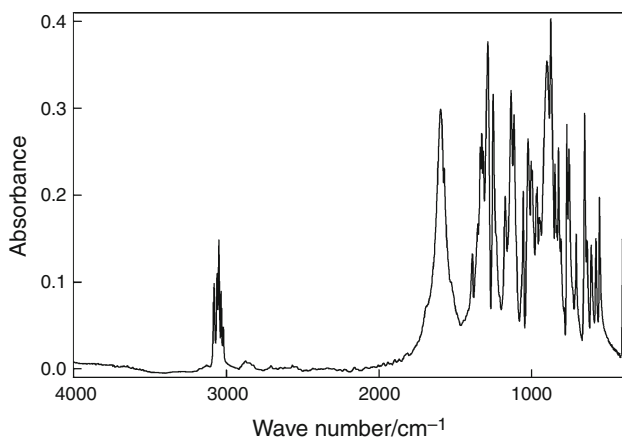


Fig. 7 The FTIR spectrum of TEX in KBr disk

Table 1 The wave number and modes of vibration for TEX sample

Wave number/ cm^{-1}	Modes of vibration
3049	Stretching bond of C–H
1596	Asymmetric stretching bond of N=O in nitro group
1287	Symmetric stretching bond of N=O in nitro group
1252	Stretching bond of C–N
1134	Stretching bond of C–O–C
903	Stretching bond of C–O–C coupled with C–C
874	Skeletal vibrations of C–C coupled with C–O–C

The ratios of waves 873, 903 and 1136 cm^{-1} to 1174 cm^{-1} increased with increasing conversion degree, but for 1100 cm^{-1} , the ratio decreased. FTIR studies have confirmed that for TEX sublimation is the main process and the decomposition in solid phase starts for the conversion degree above $\alpha = 0.76$.

Differential scanning calorimetry (DSC) analysis of TEX decomposition performed in hermetic pans

The series of DSC measurements of TEX thermal decomposition were carried out in hermetic pans with the different heating rates. The measurements were done for the sample mass of $0.095 \pm 0.005 \text{ mg}$. Obtained DSC curves are illustrated in Fig. 10.

TEX decomposition shifts toward higher temperature with the increasing heating rate, which was expected. There were two stages of TEX decomposition for higher heating rates ($\beta = 4$ – $16 \text{ }^\circ\text{C min}^{-1}$). Two stages of decomposition process of caged polynitramines were described in the literature [30, 31]. Kinetic parameters were calculated for TEX decomposition reaction. The dependence of apparent activation energy and the logarithm of pre-exponential factor on the conversion degree is presented in Fig. 11. The values of apparent activation energy and the logarithm of pre-exponential factor are presented in Table S3 (Supplementary Material).

The apparent activation energy at the initial stage ($\alpha = 0.02$) is equal to ${}_aE_a = 328 \pm 19 \text{ kJ mol}^{-1}$ and it decreases with increasing conversion degree to $\alpha = 0.93$ gaining value ${}_aE_a = 36 \pm 25 \text{ kJ mol}^{-1}$. The minimum apparent activation energy corresponds to 0.09 mg of TEX conversion. The apparent activation energy at the terminal stage ($\alpha = 0.95$) is equal to ${}_aE_a = 39 \pm 20 \text{ kJ mol}^{-1}$. The logarithm of pre-exponential factor also decreases with increasing conversion degree, $\log A$ amounted from 28.53 ($\alpha = 0.02$) to 1.80 ($\alpha = 0.95$). The major changes in kinetic parameters indicated that TEX decomposition in hermetic pans was a complex process. The fulfillment of

Fig. 8 The comparison of three FTIR spectra of TEX samples obtained for conversion degrees: $\alpha = 0.00$, 0.50 and 0.96 and for the range of wave number 2000–400 cm^{-1}

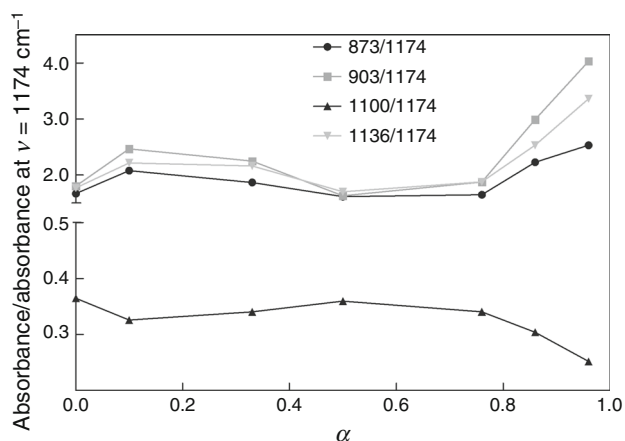
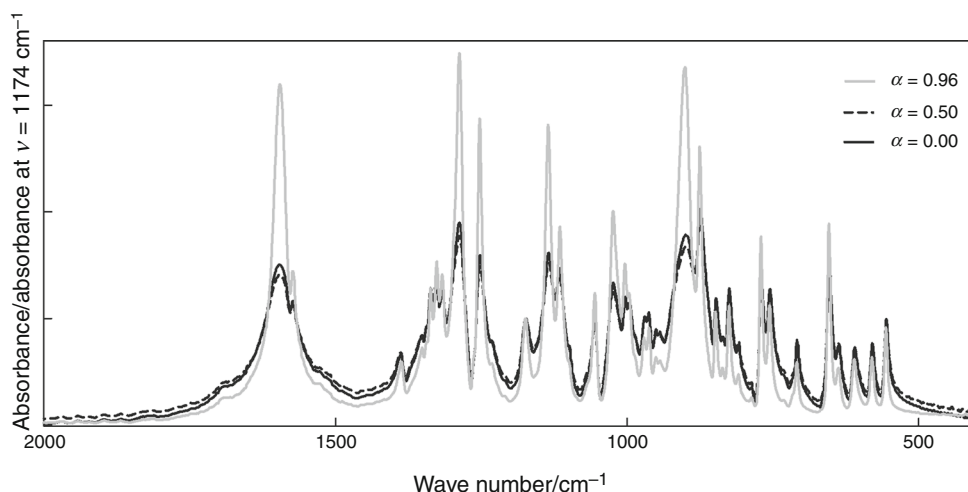


Fig. 9 The ratios of peak heights at 873, 903, 1100 and 1136 cm^{-1} in accordance with 1174 cm^{-1} for TEX sample achieved in partial decomposition with TG method

pan could influence the decomposition process due to the possibility of partial TEX sublimation. For this reason, measurements for higher fulfillment were made for the heating rates of $\beta = 0.5$ and $16 \text{ }^\circ\text{C min}^{-1}$ for the samples of $0.35 \pm 0.05 \text{ mg}$. This was a limit mass for which total decomposition in hermetic pans without pans leakage could be done. In Fig. 12, the comparison of DSC curves of decomposition process for the samples of 0.35 ± 0.05 and $0.095 \pm 0.005 \text{ mg}$ was illustrated.

The large influence of mass on the DSC curves of TEX decomposition reaction is visible on the graph. The shape of peak is changed and also the temperature shift is observable. It was not expected that the larger mass of the sample caused a shift toward higher temperature—about $11 \text{ }^\circ\text{C}$ for the heating rate $\beta = 0.5 \text{ }^\circ\text{C min}^{-1}$ and about $8 \text{ }^\circ\text{C}$ for $\beta = 16 \text{ }^\circ\text{C min}^{-1}$. For sample mass of $0.35 \pm 0.05 \text{ mg}$, new exothermic process at high temperature appeared. The series of DSC measurements of TEX

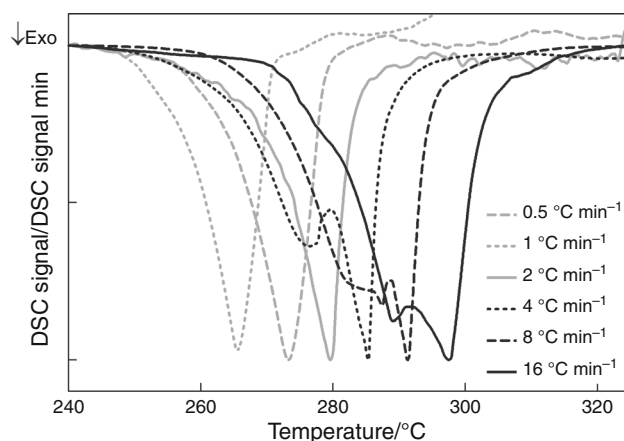


Fig. 10 The DSC curves of TEX decomposition made in hermetic pans for sample mass of $0.095 \pm 0.005 \text{ mg}$ with different heating rates ($\beta = 0.5, 1, 2, 4, 8, 16 \text{ }^\circ\text{C min}^{-1}$)

thermal decomposition were carried out for sample mass of $0.35 \pm 0.05 \text{ mg}$ in hermetic pans for the different heating rates. Obtained DSC curves are illustrated in Fig. 13.

Multistage decomposition of TEX samples is visible on DSC curves. The inflexion is observable at the falling edge of peak for heating rates $\beta = 4\text{--}16 \text{ }^\circ\text{C min}^{-1}$. For all heating rates, exothermic processes at high temperature characterized by a small value of enthalpy are visible. TEX decomposition shifts toward higher temperature with the increasing heating rate, which was expected. The values of shift are different for first and second stages. The first stage shifted toward higher temperature about $5.6 \pm 1.0 \text{ }^\circ\text{C}$ with double increased heating rate, and the second stage about $2.2 \pm 1.0 \text{ }^\circ\text{C}$ with the same change in heating rate. This indicated that the value of activation energy differs significantly for first and second stages of TEX decomposition. Kinetic parameters were calculated for TEX decomposition reaction for the samples of $0.35 \pm 0.05 \text{ mg}$.

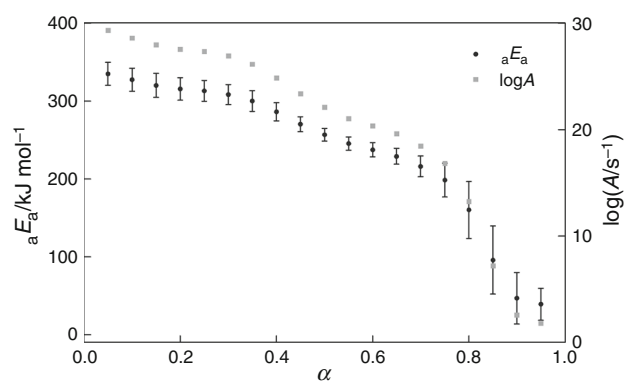


Fig. 11 The dependence of apparent activation energy and the logarithm of pre-exponential factor on the conversion degree for TEX decomposition reaction for sample mass of 0.095 ± 0.005 mg in hermetic pans

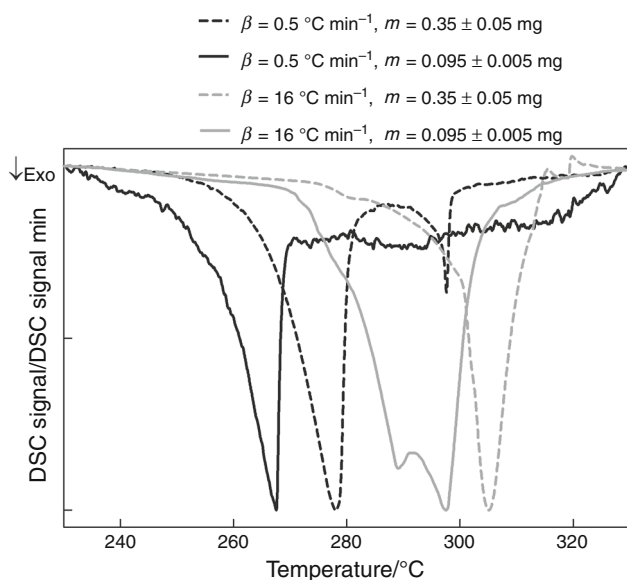


Fig. 12 DSC curves of TEX decomposition for samples of 0.095 ± 0.005 and 0.36 ± 0.05 mg in hermetic pans (heating rates $\beta = 0.5$ and 16 °C min^{-1})

Figure 14 presents the dependence of apparent activation energy and the logarithm of pre-exponential factor on the conversion degree. The values of apparent activation energy and the logarithm of pre-exponential factor are presented in Table S4 (Supplementary Material).

Significant changes in the apparent activation energy with the conversion degree of TEX are visible on the graph. The apparent activation energy at the initial stage of decomposition ($\alpha = 0.02$) is equal to $aE_a = 355 \pm 29$ kJ mol^{-1} . Three extremes of function are observable in the next part of curve: two local minima $aE_a = 290 \pm 6$ kJ mol^{-1} ($\alpha = 0.27$) and $aE_a = 328 \pm 19$ kJ mol^{-1} ($\alpha = 0.78$) and one local maximum $aE_a = 362 \pm 14$ kJ mol^{-1} ($\alpha = 0.42$).

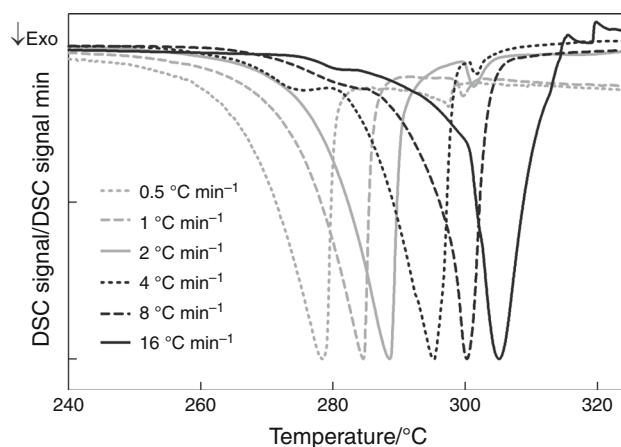


Fig. 13 DSC curves of TEX decomposition made in hermetic pans for sample mass of 0.35 ± 0.05 mg with different heating rates ($\beta = 0.5, 1, 2, 4, 8, 16$ °C min^{-1})

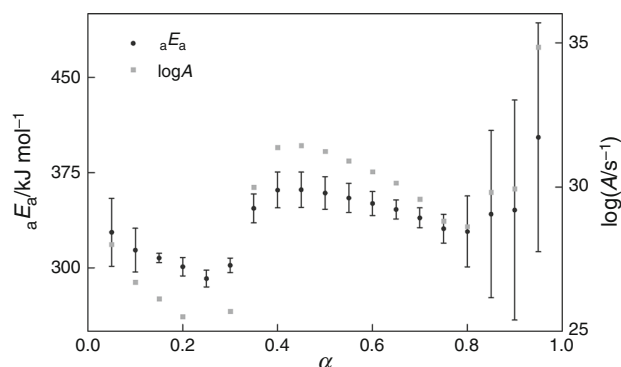


Fig. 14 The dependence of apparent activation energy and the logarithm of pre-exponential factor on the conversion degree of TEX decomposition reaction for the samples of 0.35 ± 0.05 mg in hermetic pans

The apparent activation energy at the end of decomposition ($\alpha = 0.95$) equals $aE_a = 403 \pm 90$ kJ mol^{-1} . LogA at the initial stage of decomposition ($\alpha = 0.02$) equals 30.64 and also significantly changes with the conversion degree of TEX. The pattern of these changes is similar to the changes in the apparent activation energy. The first decrease in the apparent activation energy with local minimum for conversion degree $\alpha = 0.27$ corresponds to 0.09 mg of TEX reacted. It was observed that first decrease in the apparent activation energy in two series of measurement (0.095 ± 0.005 and 0.35 ± 0.05 mg) was for the same amount of TEX reacted. In order to confirm the influence of pans fulfillment on the TEX decomposition process, another series of DSC measurements for the sample mass of 0.195 ± 0.005 mg in hermetic pans for different heating rates were made. Kinetic parameters were calculated for TEX decomposition reaction, which was illustrated in Fig. 15. The values of apparent activation energy and the

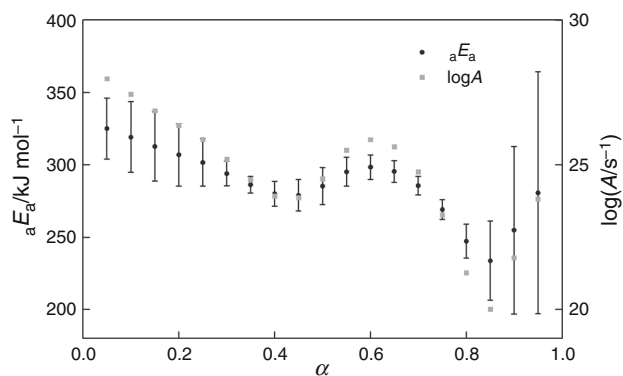


Fig. 15 The dependence of apparent activation energy and the logarithm of pre-exponential factor on the conversion degree for TEX decomposition reaction for the samples of 0.195 ± 0.005 mg in hermetic pans

logarithm of pre-exponential factor are presented in Table S5 (Supplementary Material).

The apparent activation energy at the initial stage of TEX decomposition ($\alpha = 0.02$) is equal to $aE_a = 331 \pm 18$ kJ mol⁻¹, and three extremes of function were observable in the next part of the curve: two local minima $aE_a = 279 \pm 10$ kJ mol⁻¹ ($\alpha = 0.43$) and $aE_a = 234 \pm 28$ kJ mol⁻¹ ($\alpha = 0.78$) and one local maximum $aE_a = 297 \pm 10$ kJ mol⁻¹ ($\alpha = 0.56$). The apparent activation energy at the end of decomposition ($\alpha = 0.95$) equals $aE_a = 334 \pm 111$ kJ mol⁻¹. The logarithm of pre-exponential factor also significantly changes with the conversion degree of TEX. The pattern of these changes is similar to the changes in the apparent activation energy with conversion degree. The first decrease in the apparent activation energy with local minimum for conversion degree $\alpha = 0.43$ corresponds to 0.08 mg TEX reacted and it corresponds well to the measurements for the samples of 0.095 ± 0.005 and 0.35 ± 0.05 mg. The obtained results indicated that the first decrease in the apparent activation energy was connected with the sublimation of the sample. For three series of measurements for the sample mass of 0.095 ± 0.005 , 0.195 ± 0.005 and 0.35 ± 0.05 mg, the initial value of apparent activation energy is equal to, respectively, $aE_a = 328 \pm 19$, 331 ± 18 and 355 ± 29 kJ mol⁻¹ and logarithm of pre-exponential factor equals, respectively, $\log A = 28.53$, 28.55 and 30.64 .

Conclusions

The processes observed during thermal analysis depended on measurement conditions, the sample mass and the pan filling degree. Sublimation of the sample was the main process, whereas the thermal decomposition was the secondary process during the heating of TEX in open pans.

When the sample mass was increased, the participation of thermal decomposition of TEX increased. Thermal decomposition was the main process observed during heating the sample of TEX in hermetic pans. Sublimation of the sample was the marginal process in hermetic pans. This effect decreased with the increase in sample mass. The apparent activation energy for sublimation was about 130 kJ mol⁻¹ and about 340 kJ mol⁻¹ for thermal decomposition.

The studies have shown large influence of measurement conditions on kinetic parameters of TEX decomposition process. The decomposition process of TEX could be measured in hermetic pans with high degree of filling. The low values of apparent activation energy in the literature were associated with overlapping the sublimation process with the decomposition process of TEX. Kinetic parameters determined for the initial decomposition stage of TEX in hermetic pans should be used for the security evaluation of TEX use (because decomposition is the main observed process).

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Braithwaite PC, Edwards WW, Hajik RM, Highsmith TK, Lund GK, Wardle RB. TEX-A promising new insensitive high explosive. *Energy Mater Technol Manuf Process*. 1998;29:62.
- Koch EC. TEX-4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane—review of a promising high density insensitive energetic material. *Propellants Explos Pyrotech*. 2015;40(3):374–87.
- Smith MW, Cliff MD. NTO-based explosive formulations: a technology review. DSTO-TR-0796. 1999;22:16–20.
- Anniyappan M, Talawar MB, Gore GM, Venugopalan S, Gandhe BR. Synthesis, characterization and thermolysis of 1,1-diamino-2,2-dinitroethylene (FOX-7) and its salts. *J Hazard Mater*. 2006;137:812–9.
- Lochert IJ. FOX-7-a new insensitive explosive. DSTO-TR-1238. 2001;86:7–15.
- Sikder AK, Sikder N. A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space applications. *J Hazard Mater*. 2004;112:1–15.
- Doll DW, Rasmussen N. Impact resistant explosive compositions. US Patent 7,744,710 B2, USA. 2010.
- Wallace IA, Braithwaite PC, Neidert JB. Plastisol explosive. US Patent 5,468,313 A, USA. 1995.
- Lund GK, Highsmith TK, Braithwaite PC, Wardle RB. Insensitive high performance explosive compositions. US Patent 5,529,649 A, USA. 1996.
- Doll D, Hanks J, Highsmith T, Lund G, Niles J. Reduced sensitivity melt-cast explosives. US Patent 6,648,998 B2, USA. 2004.

- Lee KE, Braithwaite PC, Nicolich S, Mezger M. Low-sensitivity explosive composition. US Patent 6,881,283 B2, USA. 2005.
- Lee KE. Reformulation of composition C-4 explosive. US Patent 6,887,324 B2, USA. 2005.
- Zhang JY, Du HC, Wang F, Gong XD, Huang YS. DFT studies on a high energy density cage compound 4-Trinitroethyl-2,6,8,10,12-pentanitroheptaazaisowurtzitane. *J Phys Chem A*. 2011;115:6617–21.
- Powała D, Orzechowski A, Maranda A. Małowrażliwe materiały wybuchowe: 4, 10-Dinitro-2, 6, 8, 12-tetraoksa-4, 10-diazatetracyklo [5.5. 0.05, 903, 11] dodekan. *Przemysł Chemiczny*. 2011;90:112–8.
- Lin H, Zhu SG, Zhang L, Peng XH, Chen PY, Li HZ. Theoretical investigation of a novel high density cage compound 4,8,11,14,15-pentanitro-2,6,9,13-tetraoxa-4,8,11,14,15-pentaazaheptacyclo[5.5.1.1.3,11. 15,9] pentadecane. *J Mol Model*. 2013;19:1019–26.
- Pisharath S, Ang HG. Thermal decomposition kinetics of a mixture of energetic polymer and nitramine oxidizer. *Thermochim Acta*. 2007;459:26–33.
- Pisharath S, Ghee AH. Decomposition kinetics of GAP binder in the presence of an energetic component. *New Trends Res Energ Mater Proc Semin*. 2005;8:296–301.
- Zeman S. New aspects of impact reactivity of Polynitro compounds. Part IV. Allocation of Polynitro compounds on the basis of their impact sensitivities. *Propellants Explos Pyrotech*. 2003;28:308–13.
- Zeman S, Yan Q, Vlček M. Recent advances in the study of the initiation of energetic materials rising characteristics of their thermal decomposition. Part I. Cyclic nitramines. *Cent Eur J Energ Mater*. 2014;11:173–89.
- Xiao LB, Zhao FQ, Luo Y, Gao HX, Li N, Meng ZH, et al. Thermal behavior and safety of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane. *J Therm Anal Calorim*. 2015;121: 839–42.
- Kronguaz VV, Lee YP, Bourassa A. Kinetics of thermal degradation of poly(vinyl chloride) thermogravimetry and spectroscopy. *J Therm Anal Calorim*. 2011;106:139–49.
- Jakić M, Vrandečić NS, Erceg M. Kinetic analysis of the non-isothermal degradation of poly(vinyl chloride)/poly(ethylene oxide) blends. *J Therm Anal Calorim*. 2016;123:1513–22.
- Jakić M, Vrandečić NS, Klarić I. Thermal degradation of poly(vinyl chloride)/poly(ethylene oxide) blends: Thermogravimetric analysis. *Polym Degrad Stab*. 2013;98:1738–43.
- Jiaoqiang Z, Rongzu H, Chunhua Z, Guofu F, Quihe L. *Thermochim Acta*. 1997;298:31–5.
- Sučeska M, Rajić M, Matecic-Musanić S, Zeman S, Jalovy Z. Kinetics and heats of sublimation and evaporation of 1,3,3-trinitroazetidine (TNAZ). *J Therm Anal Calorim*. 2003;74: 853–66.
- Semenov NN. *Chemical kinetics and chain reactions*. London: Oxford University Press; 1935.
- Abramov VG, Vaganova NI. Effect of a side reaction with small heat liberation on the critical thermal-explosion condition of the main self-catalyzed reaction. *Fizika Goreniya i Vzryva*. 1978;14:135–41.
- Maksimowski P, Gołofit T. 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo5.5.0.05,903,11]dodecane synthesis. *J Energy Mater*. 2013;74:853–66.
- Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim Acta*. 2011;520:1–19.
- Gołofit T, Zyśk K. Thermal decomposition properties and compatibility of CL-20 with binders HTPB, PBAN, GAP and poly-NIMMO. *J Therm Anal Calorim*. 2015;119:1931–9.
- Yan QL, Zeman S, Elbeih A, Song ZW, Malek J. The effect of crystal structure on the thermal reactivity of CL-20 and its C4 bonded explosives (I): thermodynamic properties and decomposition kinetics. *J Therm Anal Calorim*. 2013;112:823–36.