

Preparation and thermal studies on tetranitrodibenzo tetraazapentalene (TACOT): A thermally stable high explosive

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Abstract

Thermally stable high explosive, tetranitro-2,3,5,6-dibenzo-1,3a,4,6a-tetraazapentalene (TACOT) was synthesized and characterized during this work. Thermo analytical techniques (TG and DSC) were applied to study the thermal decomposition behaviour of TACOT in comparison with benchmark thermally stable high explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Kinetic parameters such as reaction order, activation energy and pre-exponential factors were computed from the thermal data. The activation energy for TACOT (292 kJ/mol) was found 1.5 times to that of TATB (200 kJ/mol), which can account for its higher thermal stability and can be attributed to pentalene moiety in the former. © 2006 Published by Elsevier B.V.

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1. Introduction

Thermal stability is one of the important characteristics of the energetic materials to ensure safe production, desired shelf life of munitions and low vulnerability to accidental initiations. Specific missions demanding thermal stability led to emergence of special class of high energy materials (HEMs) superior to that of benchmark high explosive 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) (>260 °C). Nitro compounds namely 2,4,6-tripicryl-*s*-triazine (TPT), 2,2',4,4',6,6'-hexanitrostilbene (HNS), 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl (DIPAM) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) having decomposition temperatures in the range of 290–350 °C have received attention for applications in supersonic missiles where high temperatures are encountered in the space environ [1–3]. Tetranitro-2,3,5,6-dibenzo-1,3a,4,6a-tetraazapentalene (TACOT) has emerged as one of the most thermally stable HEMs with decomposition temperature of 410 °C. The crystal density of the compound is 1.82 g/cm³. It can offer velocity of detonation of 7060 m/s and detonation pressure of 203 kbar [4]. Its extraordinary thermal stability and reasonable insensitivity to mechanical stimuli has led to its emergence as

HEM of choice for military applications requiring flexible linear shaped charge (FLSC) and sheet explosives as well as civil applications such as oil-well perforating operations [5–7].

This paper reports the synthesis and characterization of TACOT. Detailed thermal studies were conducted by applying differential scanning calorimetry (DSC) and thermogravimetry (TG) to determine the decomposition pattern in comparison to TATB. A mixture of TACOT with 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) was also subjected to DSC with the aim of achieving optimization of decomposition temperature and energetics.

2. Experimental

2.1. Materials and methods

All the reagents and chemicals of AR grade were used as such in the present study. Fourier transform infrared (FTIR) spectra were recorded on Perkin-Elmer FTIR-1600 spectrophotometer in KBr matrix and ¹H NMR spectra scanned on a 300 MHz with pulsed Fourier transform system in DMSO-*d*₆ (TMS as internal standard). Elemental analysis of the sample was carried out on elemental analyzer of CE instruments make (Model CHNO-1110).

Thermal analysis was undertaken on DSC (sample mass: 2 mg, nitrogen flow rate: 40 ml/min, aluminium pan, hermetic

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mode) of Perkin-Elmer make at heating rates of 5, 10, 15 and 20 °C min⁻¹ as well as simultaneous thermal analyzer (STA) of Mettler Toledo make at 10 °C min⁻¹ in N₂ atmosphere (sample mass: 4 mg, nitrogen flow rate: 40 ml/min, aluminium pan, hermetic mode). Activation energy of the compounds was calculated from DSC results using American Society of Testing and Materials (ASTM) standard method based on Kissinger correlation [8]. Dynamic TG (sample mass: 4 mg, air flow rate: 80 ml/min, aluminium pan) data was analyzed by Coats and Redfern method [9]. The decomposition patterns under the isothermal conditions (sample mass: 4 mg, nitrogen flow rate: 80 ml/min, aluminium pan) were also obtained for TACOT at 370, 375, 380 and 385 °C as well as for TATB at 325, 330, 335 and 340 °C. Activation energy was computed using a Thermal program developed in-house for the prediction of activation energy of energetic systems [10].

The sensitivity to impact stimuli was determined by applying standard Bruceton staircase method using a 2 kg drop weight and the results are reported in terms of height for 50% probability of explosion (*h*_{50%}) [11]. Figure of insensitivity (F of I) was computed by using tetryl (composition exploding; CE), as reference. The friction sensitivity of the compound was determined on a Julius Peter's apparatus until there was no explosion/ignition in five consecutive test samples at that weight [12].

2.2. Synthesis

The compound was synthesized and characterized on the lines of the method reported by Carboni et al. [13] with little modifications. All the starting materials were of >97% purity and solvent used were dried by standard procedure. The first step involved the oxidation of *O*-phenylenediamine by lead oxide/potassium superoxide in benzene/toluene under reflux to obtain 2,2'-diaminio azobenzene (I) which was doubly diazotized and treated with excess sodium azide in the second step to realize 2,2'-diazidoazobenzene (II). The third step involved the cyclization of (II) to dibenzotetraazapentalene (III). Nitration of III with HNO₃ and H₂SO₄ led to the formation of tetranitrodibenzo tetraazapentalene (IV) in 50% yield. The various reactions that are involved in the synthesis are given in Scheme 1. TATB and CL-20 used in the study were synthesized in house and are of required purity.

3. Results and discussion

3.1. Spectral studies

The FTIR spectrum of TACOT exhibited absorption at 1530 and 1325 cm⁻¹ attributable to asymmetric and symmetric stretching of –NO₂ group and at 3100 cm⁻¹ due to aromatic –CH stretching. In ¹H NMR, TACOT gave two signals at 9.98 δ and 9.31 δ which can be assigned to C₁–H and C₇–H protons. The IR and NMR patterns obtained during this work are concurrent with the reported values [13]. The elemental analysis results for TACOT (C: 37.3, N: 28.73, H: 1.01) were close to the theoretical values (C: 37.12, N: 28.86, H: 1.03).

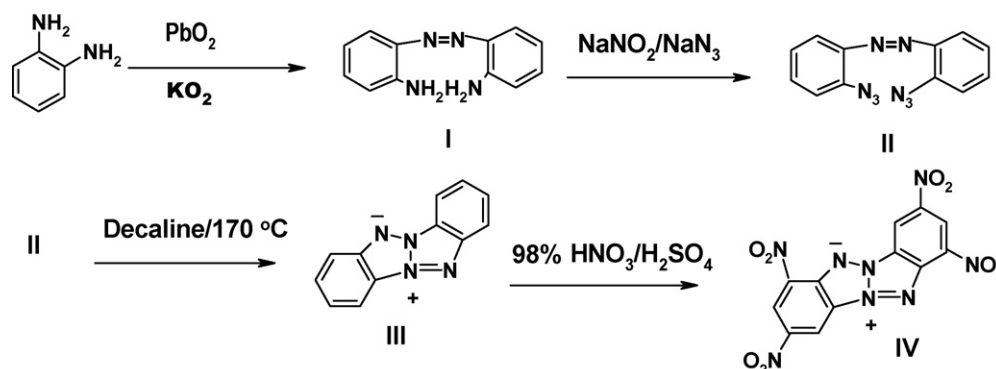
3.2. Sensitivity

The experimentally obtained impact sensitivity of TACOT is 68 cm and it is friction insensitive upto 36 kg. TATB is insensitive to impact (>170 cm) and friction (up to 36 kg). The results revealed that TACOT is completely insensitive to friction stimuli and reasonably insensitive to impact.

3.3. Thermal studies

The DSC of both TACOT and TATB exhibited single stage exothermic decomposition with decomposition maximum (*T*_{max}) at 403 and 376 °C, respectively. The heat evolved during exothermic decomposition of TACOT was 1795–2712 J/g in comparison to that of 832–1409 J/g for TATB at heating rates of 5, 10, 15 and 20 °C. The DSC curves were analyzed by Kissinger method. In this method, ln(β/T_m^2) is plotted against 1/*T*_m (where β is the heating rate, *T*_m is maximum decomposition temperature). From the slope of the curve, activation energy is calculated. The activation energy of TACOT computed from DSC results obtained was 292 kJ/mol whereas that obtained for TATB was 200 kJ/mol (Table 1).

Dynamic TG of TACOT in conjunction with DTG also revealed single stage exothermic decomposition at 403 °C (Fig. 1). Coats and Redfern plot of the dynamic TG data gave straight line with order parameter of zero. The slope of plot ($-E/2.3R$) corresponded to *E*_a of 330 kJ/mol whereas *E*_a obtained for TATB was 221 kJ/mol.



Scheme 1. Synthesis of TACOT.

Table 1
DSC data for TACOT and TATB at different heating rates (Kissinger method)

Compound	Heating rate, β ($^{\circ}\text{C}$)	Decomposition temperature, T_{max} (K)	$\ln(\beta/T_m^2)$	Activation energy, E_a (kJ/mol)	Frequency factor $\ln A$ (min^{-1})
TACOT	5	667.0	-11.3962	292	41.3
	10	676.4	-10.7312		
	15	680.8	-10.3385		
	20	684.4	-10.0613		
TATB	5	639.4	-11.3178	200	26.5
	10	649.8	-10.6508		
	15	659.3	-10.2745		
	20	660.6	-9.9907		

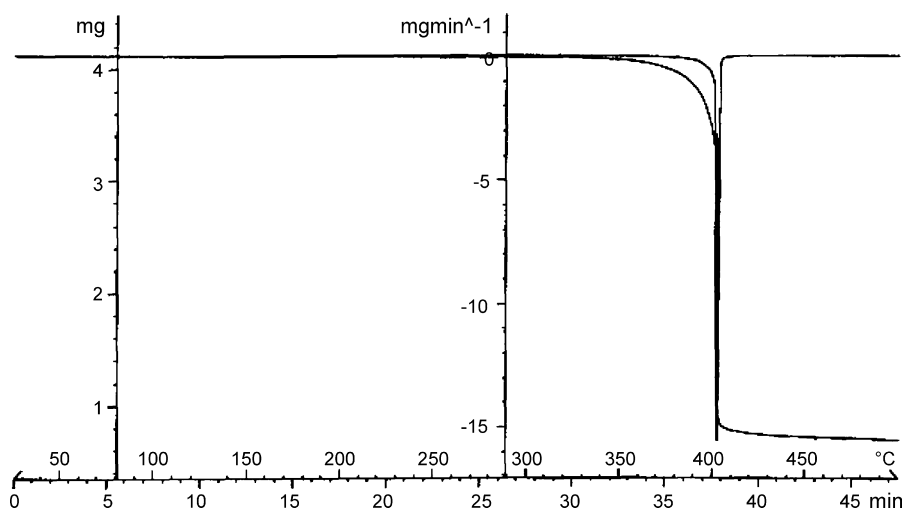


Fig. 1. Dynamic TG of TACOT.

In order to determine mechanistic pathways of decomposition, isothermal TG data was plotted to obtain α versus time (t) graphs for both TACOT (Fig. 2a) and TATB (Fig. 2b). The plot for TACOT exhibited sigmoid nature, whereas that for TATB gave a straight line indicating different mechanistic pathways for thermal decomposition reaction.

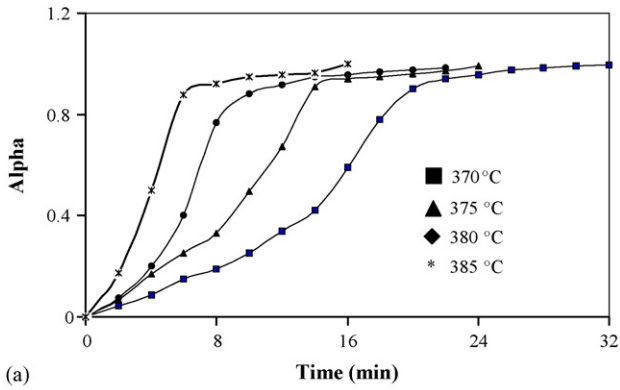
An attempt has been made to determine the best value of n for Avrami–Erofeev equation in case of TACOT. All the experimental α – t curves were converted to reduced-time scales ($t_{\text{red}} = t/t_{0.5}$), where $t_{0.5}$ is the time at each temperature for $\alpha = 0.5$. All these plots (Fig. 3) pass through a single point suggesting that similar decomposition mechanism is operative throughout the temperature range of 370–385 $^{\circ}\text{C}$. Comparison has been made between the experimental curve at 380 $^{\circ}\text{C}$ with the theoretical reduced time curves of Avrami–Erofeev mode and theoretical α values were calculated from the model $\alpha = 1 - \exp(-k_{0.5}t_{\text{red}}^n)$ where $k_{0.5} = \{-\ln(0.5)\}^{1/n}$ considering $n = 2, 3, 4$ [14]. The graph (Fig. 4) confirms that the accelerating period is closer to $n = 2$, whereas deceleratory period fitted best when n lies between 2 and 3. Accordingly, rate coefficients k_{n2} ($0.05 < \alpha < 0.5$) as well as $K_{n2.5}$ ($0.5 < \alpha < 0.95$) were determined at each temperature and apparent E_a and frequency factor ‘A’ were determined by Arrhenius plots (Table 2). For acceleratory period, E_a was found to be 384 kJ/mol, whereas for deceleratory it was 107 kJ/mol.

To determine the order parameter and activation energy for TATB, the graph was drawn between $\alpha^{1/n}$ (where $n = 1, 2, 3$) versus t at different temperatures (325, 330, 335 and 340 $^{\circ}\text{C}$). The order parameter (n) of 2 was computed based on the correlation coefficient value r ($r = 0.9886$). The activation energies computed by Arrhenius equation was found to be 213 kJ/mol (Table 3), which falls in the range of the reported values, scattered between 167 and 251 kJ/mol [15–17].

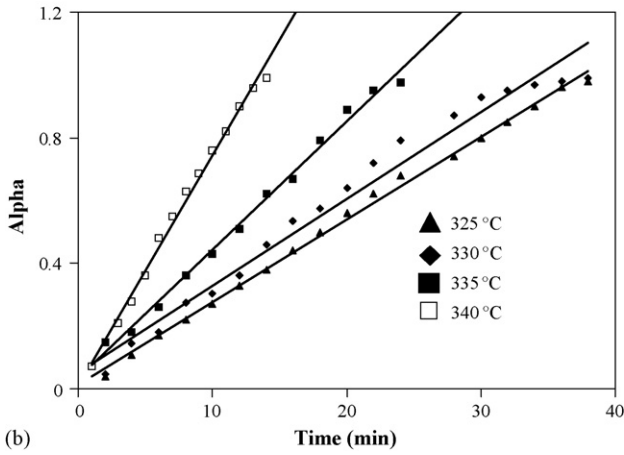
In view of high thermal stability of TACOT, its effect on decomposition pattern of hexanitrohexaazaisowurtzitane (CL-20, decomposition temperature T_{max} : 243 $^{\circ}\text{C}$) [18] was also studied by subjecting their 1:1 mix to DSC. Reference data was also generated on TATB/CL-20 mix (1:1). It was observed that both (TACOT and CL-20) decompose independently and TACOT does not influence the decomposition temperature of

Table 2
Apparent Arrhenius parameters for the thermal decomposition of TACOT (643–658 K)

Parameter	Activation energy (kJ/mol)	$\ln A$ (min^{-1})
Acceleratory period Avrami $n = 2$ ($0.05 < \alpha < 0.5$)	384	68.6
Deceleratory period Avrami $n = 2.5$ ($0.5 < \alpha < 0.95$)	105	22.8



(a)



(b)

Fig. 2. (a) Plot of α vs. time in min for TACOT and (b) plot of α vs. time in min for TATB.

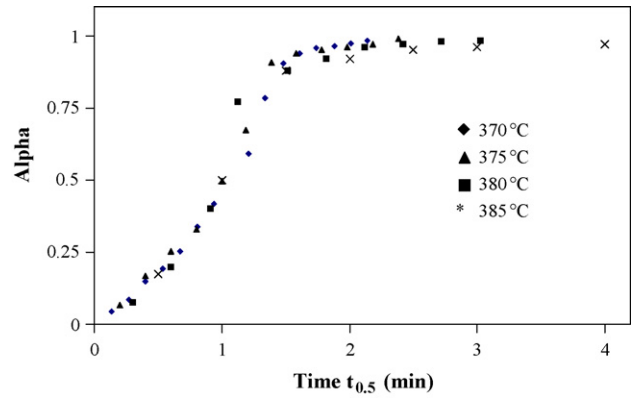


Fig. 3. Graph between α vs. $t_{0.5}$ for TACOT.

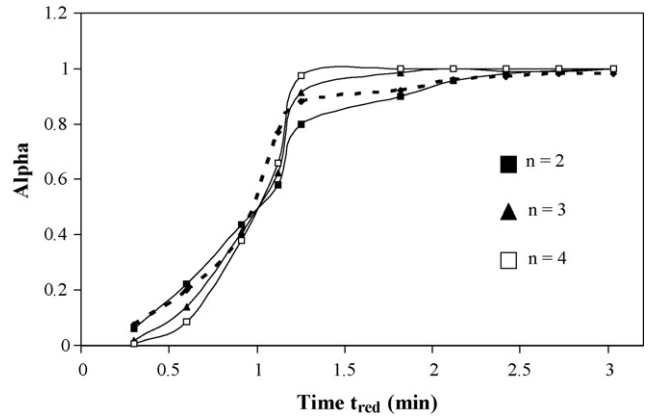


Fig. 4. Experimental (—) and theoretical (---) (Avrami–Erofeev) reduced time curve for TACOT for ‘n’ values at 300 °C.

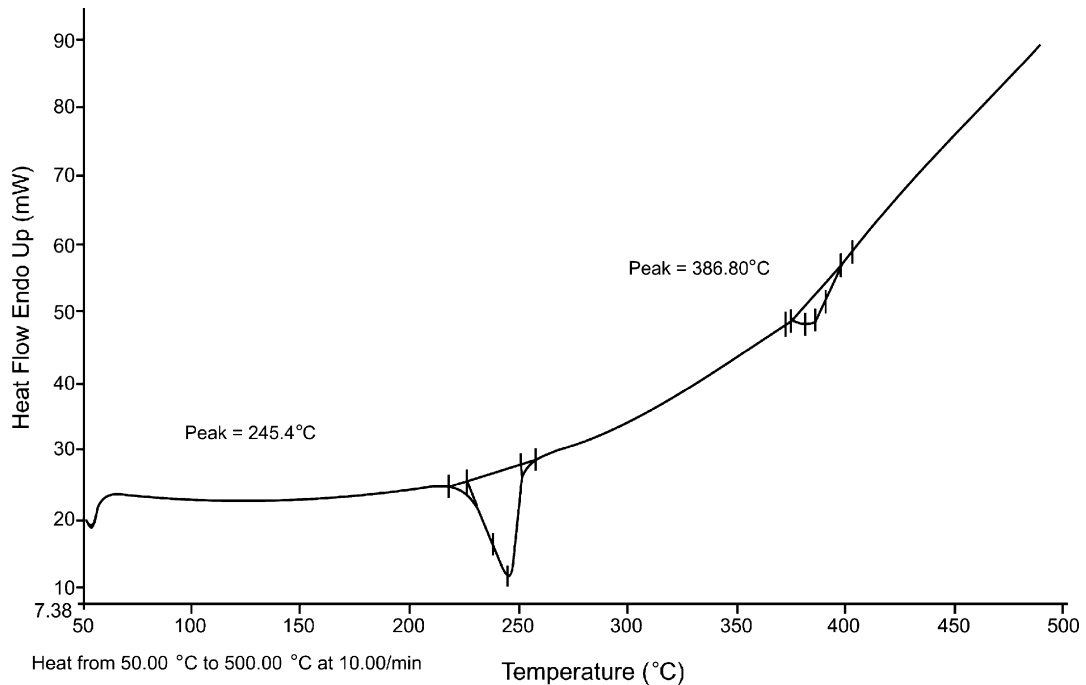


Fig. 5. DSC of TACOT + CL-20 (1:1) mix.

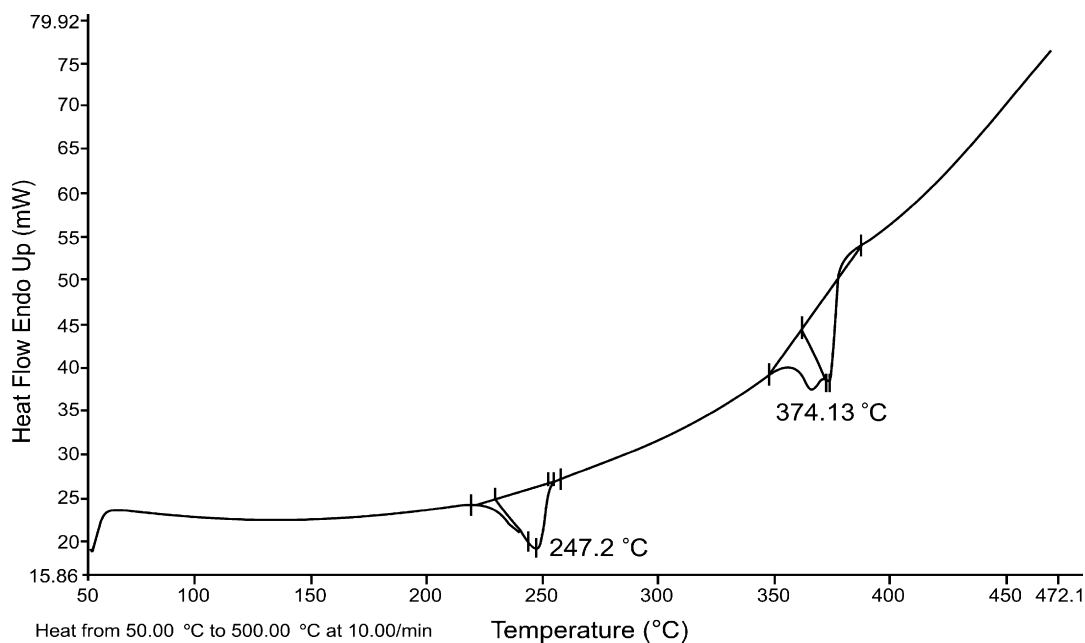


Fig. 6. DSC of TATB + CL-20 (1:1) mix.

CL-20 to a remarkable extent. Similar pattern was observed for TATB. However, a combination of TATB–TACOT (1:1) exhibited single decomposition at 365 °C, which is close to the decomposition temperature of TATB (Figs. 5–7).

The much higher activation energy of decomposition obtained for TACOT than that of TATB accounts for its exceptionally higher thermal stability. This may be due to the basic structural features of TACOT. Its precursor dibenzo-1,3a,4,6a-tetraazapentalene is reported to have planar structure and shows no detectable dipole moment [13,19]. This precursor belongs to tetraaza pentalene class of compounds, which are known to

have high thermal and chemical stability derived out of aromaticity [20]. These tetraazapentalenes can be represented as hybrids of two charge-separated forms. The four nitrogen atoms, contribute six electrons to the π system, and the parent structures may be considered in terms of their relationship with the isoelectronic naphthalene and the carbocyclic analog pentalene dianion. It seems to be an admirable skeletal system on which to base a thermally stable energetic material. It has high melting point (237–238 °C) and decomposes at 238 °C [21]. To investigate further and obtain confirmatory evidences, dibenzo-1,3a,4,6a-tetraazapentalene was subjected to dynamic

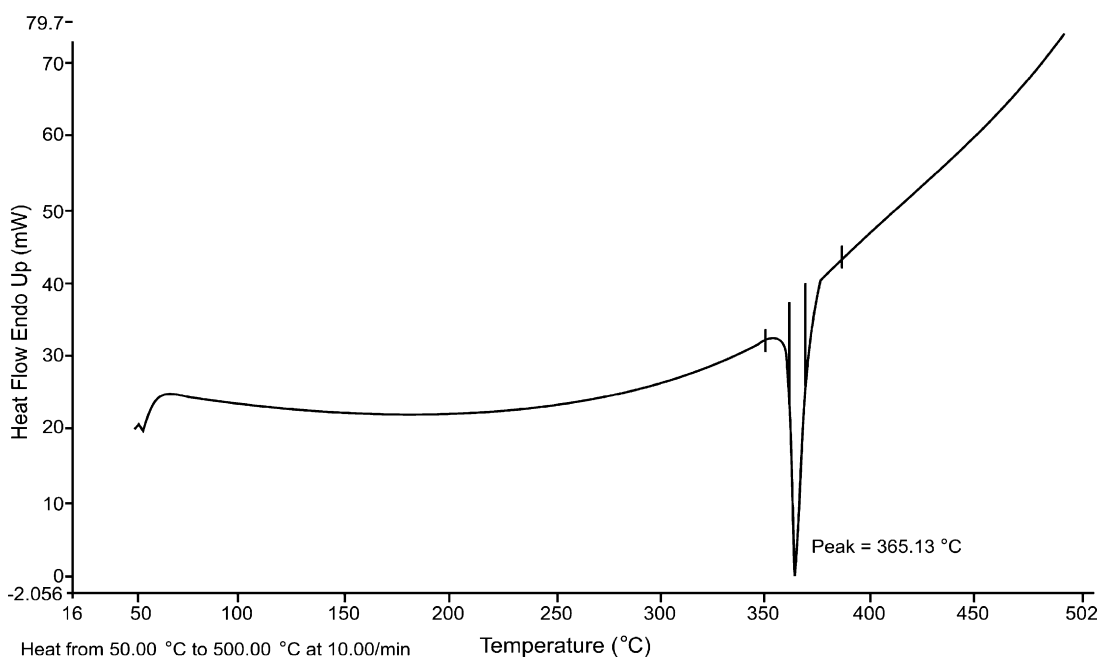


Fig. 7. DSC of TACOT + TATB (1:1) mix.

Table 3
Apparent Arrhenius parameters for the thermal decomposition of TATB (598–613 K)

$f(\alpha) = \alpha^{1/n}$ ($0.05 < \alpha < 0.9$)	Activation energy (kJ/mol)	$\ln A$ (min^{-1})	Correlation coefficient
$n = 1$	215.70	39.2	0.9686
$n = 2$	175.72	31.1	0.8126
$n = 3$	211.31	38.6	0.8828

TG studies. E_a obtained by Coats and Redfern method was found to be 510 kJ/mol.

In case of TATB, solid-state physical structure involving intra and intermolecular interaction appears to play the significant role in conferring stability on it [22]. In the molecule, an amino group interacts with ortho nitro groups on the same benzene ring and with a nitro group on a nearest neighbour TATB molecule to form infinite planar sheets of TATB that are bonded intermolecularly by strong hydrogen bonds [23,24].

4. Conclusions

TACOT was prepared in good yield and characterized by instrumental techniques including spectral methods. The kinetic parameters of TACOT were determined by thermal techniques (DSC and TG). The activation energy of TACOT was found to be 292–330 kJ/mol in comparison to 200–221 kJ/mol for TATB using Dynamic DSC and TG. These results provide evidence in support of superior thermal stability of TACOT, which is reported to emanate from its typical structural features. Isothermal studies reveal that the thermal decomposition of TACOT follows Avrami–Erofeev equation where as that of TATB follows power law.

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