

SPECTROSCOPIC AND THERMAL STUDIES ON THE DECOMPOSITION OF 1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE (TATB)

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Abstract

The kinetics of the thermal decomposition of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in condensed state has been investigated by high temperature infrared spectroscopy (IR) and thermogravimetry (TG) in conjunction with pyrolysis gas analysis, differential thermal analysis (DTA) and hot stage microscopy. The decomposition proceeds in two main stages under isothermal conditions and the initial stage involving about 24% loss in weight obeys Avrami-Erofe'ev equation ($n=1$), and is governed by an activation energy (E) of $150.58 \text{ kJ}\cdot\text{mol}^{-1}$ and $\log(A \text{ in s}^{-1})$ 12.06. The second stage corresponding to 24 to 90% loss in weight gave best fit for Avrami-Erofe'ev equation, $n=2$, with $E=239.56 \text{ kJ}\cdot\text{mol}^{-1}$ and $\log(A \text{ in s}^{-1})$ 19.88 by isothermal TG. The effect of additives, on the initial thermolysis of TATB has also been studied. Evolved gas analysis by IR showed that NH_3 , CO_2 , NO_2 , HCN and H_2O are produced in the initial stage of decomposition. The decomposition in KBr matrix in the temperature range 272 to 311.5°C shows relative preferential loss in the $-\text{NH}_2$ to $-\text{NO}_2$ band intensity which indicates that the rupture of $\text{C}-\text{NH}_2$ bond, weakened also by the interaction of the NH_2 with the neighbouring NO_2 group, appears to be the primary step in the thermolysis of TATB.

Keywords: IR, kinetics, TG-DTG-DTA, 1,3,5-triamino-2,4,6-trinitrobenzene

Introduction

Thermal decomposition data constitutes an essential component in the study of explosive properties of polynitro compounds. 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) possesses excellent thermal stability for space application. The mode of thermal decomposition, both alone and in the presence of additives has added significance to its practical application. The study of thermal process provides a clue for the degradation of TATB [1-5]. Decomposition products [1] observed are CO_2 , C_2H_2 , NO , CHNO and HCN in flow experiments in an inert atmosphere and CO_2 , N_2 , CO , NH_3 and H_2O in static experiments. Two possible reaction schemes for the decomposition of TATB have been proposed in which intramolecular and intermolecular elimination of water and subsequent decomposition are involved. Mass spectroscopic [2] studies

suggest that primary decomposition is ring cleavage leading to free radicals. ESR spectroscopic studies [6] confirm the formation of free radicals in the thermal decomposition of TATB. It has been concluded from infrared matrix isolation spectra [7] and pressure-time response of the product gases and mass spectra that intramolecular water abstraction cannot be an important mechanism since little water is released.

A precise study of the kinetics of thermal decomposition is possible by following the change in chemical bond involved in the decomposition process. High temperature IR spectroscopy [8, 9] has been used in the present study to determine the structural rearrangement and mechanism of the initial thermal decomposition of TATB in conjunction with pyrolysis gas analysis and hot stage microscopy. The kinetics of thermolysis, stagewise, has been followed both by isothermal TG and IR.

Experimental

TATB was synthesised in the laboratory and purified by repeated recrystallisation from nitrobenzene. Elemental analysis was carried out using Perkin-Elmer 240 C. TG-DTA and isothermal TG were carried out on Netzsch STA 409 EP thermal analysers. The kinetics of decomposition was followed by isothermal mass change determination using about 10 mg of sample in the temperature range 273 to 296°C, in static air atmosphere. The stability of the temperature was within $\pm 1^\circ\text{C}$. In isothermal TG the sample in platinum-iridium cup was heated to the desired temperature using programmed heating of 10 deg-min⁻¹. Smooth gradual transformation from dynamic to the desired isothermal temperature with no overshooting ensured temperature equilibrium and uniformity without disturbing the equilibrium of the microbalance.

For kinetics by IR [9, 10], a ratio recording IR spectrophotometer, Perkin-Elmer 683 was used. The high temperature IR cell was fabricated in the laboratory [9] and temperature programming was done using a Stanton Redcroft universal temperature programmer having chromel-alumel thermocouple. The temperature remained constant during the experiment within $\pm 1^\circ\text{C}$ of the set temperature.

Spectroscopic grade KBr was used as the matrix material. Spectra of the sample in KBr matrix were recorded in the frequency range 4000 to 200 cm⁻¹ at the desired temperature at regular time intervals using medium speed of scanning.

It was verified that the peak intensity of the band at 1220 cm⁻¹ corresponding to -NO₂ symmetric stretching vibration of C-NO₂ bond, varied linearly with the amount of sample in the concentration range of 0.1 to 0.75% TATB in KBr matrix.

A specially designed experimental set up and IR gas cell made of pyrex glass with KBr windows were used to study the gaseous phase composition during the thermal decomposition of TATB.

A Leitz-Orthoplan polarising microscope with hot stage attachment was used under dynamic heating conditions to observe the morphological sequence of the decomposition.

Results

Simultaneous TG–DTG–DTA of TATB were recorded at different heating rates and the one obtained $7 \text{ deg}\cdot\text{min}^{-1}$ is given in Fig. 1 which is in agreement with the reported ones [5]. The exothermic decomposition sets in above 320°C . TG–DTG curves show that TATB decomposes mainly in two stages in the temperature range 320 to 370°C followed by a very gradual loss in weight above 370°C . It may be pointed out that melting point of TATB is reported to be 330°C [5, 11]. Differential scanning calorimetry [5] also showed two exothermic peaks with peak maxima at 356 and 362.5°C , revealing a two stage decomposition in this range.

Kinetics by isothermal TG

The kinetics [12] of the thermal decomposition of TATB in the temperature range 273 – 296°C , under static air atmosphere was studied using isothermal TG. An isothermal TG curve shows two clearcut stages of decomposition. The first stage involved a loss in weight of about 24%. The loss in weight of TATB at definite time intervals was measured from the respective isothermal TG curve. From these data the fraction decomposed, α , with respect to the original weight of the same, in time, t , was calculated. For the second stage, α was calculated with respect to the weight of the sample remaining after the first stage. For

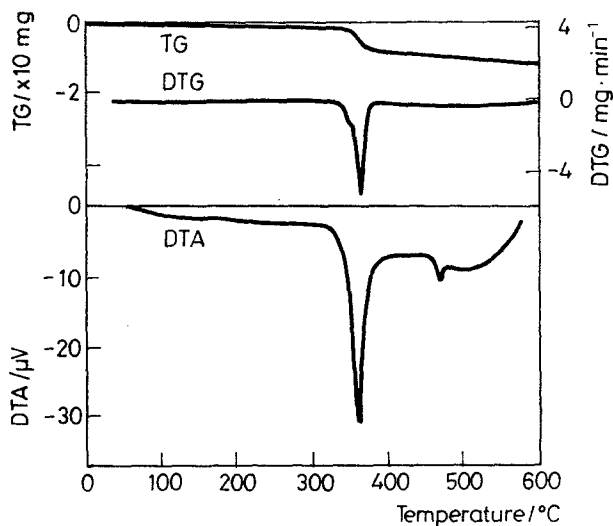


Fig. 1 TG–DTG–DTA curve of TATB. Sample mass: 11 mg; Atmosphere: static air

evaluating the rate constant the α vs. t curve was analysed, using various kinetic expressions and a computer programme [13]. First stage of decomposition, upto 24%, shows best linearity with a correlation coefficient of 0.9915, for Avrami-Erofe'ev equation [14–16], $n=1$.

For the second stage of decomposition i.e. above 24% best linearity with a correlation coefficient of 0.9944 was obtained for Avrami-Erofe'ev equation [14–16], $n=2$. The rate constants obtained from the slope of the plots of the above equation were substituted in the Arrhenius equation. The activation energies and 'A' values calculated from the slope of this plot are $150.58 \text{ kJ}\cdot\text{mol}^{-1}$ and $\log(A \text{ in s}^{-1})$ 12.06 for the first stage and $239.56 \text{ kJ}\cdot\text{mol}^{-1}$ and $\log(A \text{ s}^{-1})$ 19.88 for second stage of decomposition.

Maksimov *et al.* [17] obtained a value of $174.9 \text{ kJ}\cdot\text{mol}^{-1}$ for the activation energy with $\log A=11.6$ for the thermolysis of TATB by Soviet manometric method, which is nearer to the value we got for the first stage decomposition in the present study. Rogers [18] has reported an activation energy of $250.6 \text{ kJ}\cdot\text{mol}^{-1}$ with $\log A=19.5$ by isothermal differential scanning calorimetric method and this is interestingly close to the value we got for the second stage decomposition.

Kinetics by IR spectroscopy

IR spectra of TATB in KBr matrix at room temperature and at desired elevated temperatures at regular intervals were recorded. Band intensities did not show any variation till the temperature of decomposition was attained whereafter the band intensities decreased. Figure 2 presents the variation of band intensity for different groups with time at 294°C , with progressive decomposition. The intensity of the bands were not found to vary uniformly with time, as is to be expected normally. Instead $-\text{NH}_2$ and $-\text{NO}_2$ band intensities showed preferential losses.

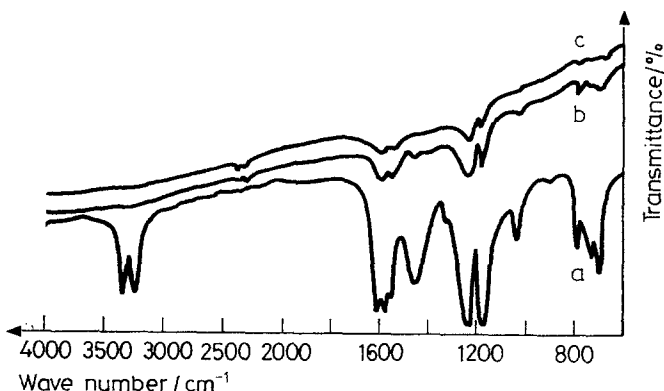


Fig. 2 IR spectra of TATB; a) at 25°C ; b) at 294°C after 13 min; c) at 294°C after 45 min

In IR the variation in intensity of $-\text{NO}_2$ symmetric stretching vibration at 1220 cm^{-1} was used to monitor the decomposition by KBr pellet method. For calculating the fraction of TATB decomposed the peak intensity after attaining the selected isothermal temperature was taken as initial concentration. α vs. t , thus obtained (Fig. 3) was analysed using various rate equations and a computer programme to evaluate the rate constants. Correlation coefficient was evaluated for eighteen equations listed in reference [13] and eight equations where close correlation has been obtained are given in Table 1, along with the corresponding activation energy and $\log A$ values. Out of it, rate parameters based on Avrami-Erofe'ev equation [14–16], (Eq. (5), Table 1), $n=2$, has been selected based on better correlation. The activation energy was found to be $203.07\text{ kJ}\cdot\text{mol}^{-1}$ and $\log(A\text{ in s}^{-1})$ 16.98 which are closer to those obtained by iso TG for the second stage. The difference may be attributed to the fact that the IR kinetics is specific to the nitro group whereas the TG data corresponds to global kinetics.

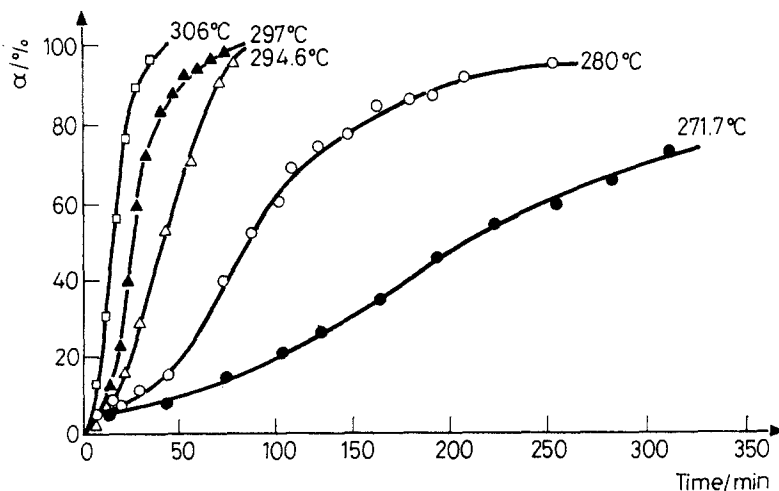


Fig. 3 α - t plot for the thermal decomposition of TATB by isothermal IR

Effect of additives

Effect of additives on the kinetics of thermal decomposition of TATB, has been studied using IR spectroscopy. IR spectra of pure TATB and TATB mixed with 10% additives in KBr matrix, were recorded at 280°C , at regular intervals. The variation in intensity of $-\text{NO}_2$ symmetric stretching vibration at 1220 cm^{-1} was used to monitor the decomposition. α - t plots of pure TATB and those of TATB mixed with 10% carbamate, calcium carbonate and magnesium oxide at 280°C are given in Fig. 4. It is evident from the Fig. 4, that there is an accelerating effect by carbamate and magnesium oxide on the decomposition of TATB.

Table I Correlation coefficient 'R' obtained for various, $F(\alpha)$ and rate parameters by isothermal IR

No.	$F(\alpha)$	'R' Isothermal temperature/°C				E / kJ·mole ⁻¹	logA/ s ⁻¹	
		271.7	280	297	294.6			306
1.	α	0.99108	0.94560	0.96979	0.99668	0.99241	195.86	16.16
2.	$1-(1-\alpha)^{1/2}$	0.98390	0.98366	0.98344	0.98522	0.99154	207.62	17.12
3.	$1-(1-\alpha)^{1/3}$	0.97914	0.98972	0.98091	0.97116	0.98360	212.35	17.45
4.	$[-\ln(1-\alpha)]^{3/2}$	0.99098	0.99024	0.98855	0.97826	0.98871	209.69	17.69
5.	$[-\ln(1-\alpha)]^{1/2}$	0.99512	0.97926	0.99286	0.99258	0.99756	203.07	16.98
6.	$[-\ln(1-\alpha)]^{1/3}$	0.99201	0.95873	0.98845	0.99558	0.99920	196.51	16.23
7.	$[-\ln(1-\alpha)]^{1/4}$	0.98748	0.94479	0.98242	0.99218	0.99702	193.24	15.82
8.	$\ln(\alpha/1-\alpha)$	0.98195	0.95158	0.98881	0.98958	0.99893	194.30	16.74

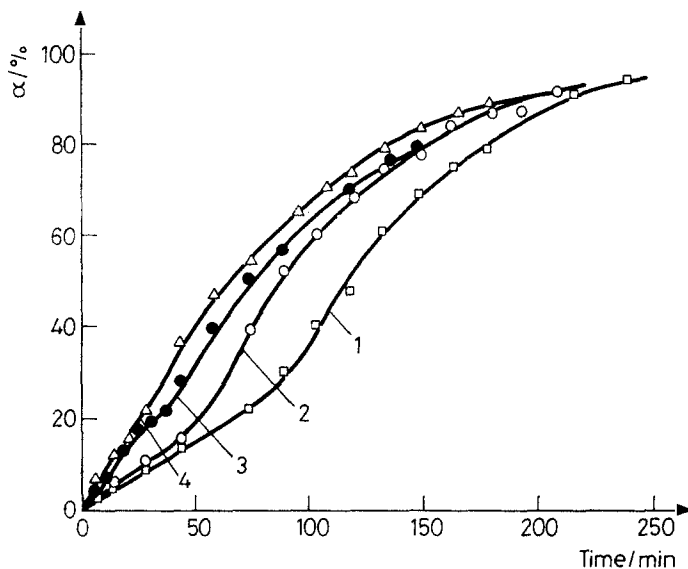


Fig. 4 Effect of additives on the thermal decomposition of TATB at 280°C by IR. 1) TATB with calcium carbonate; 2) TATB; 3) TATB with carbamate; 4) TATB with magnesium oxide

Evolved gas analysis by IR

Gaseous species evolved when 10 mg of the sample was decomposed at controlled heating rate of $5 \text{ deg}\cdot\text{min}^{-1}$ were identified using IR spectroscopy. Around 300°C , profuse gas evolution sets in and increases with temperature. Between $300\text{--}330^\circ\text{C}$, IR absorption bands of medium intensity due to ammonia (3340 cm^{-1}), NO_2 (1625 cm^{-1}), CO_2 (2330 cm^{-1}), H_2O (1595 cm^{-1}) and HCN (710 cm^{-1}) are noticed [19].

Microscopic studies

Microscopic studies on the thermal decomposition of TATB under dynamic temperature conditions (Fig. 5) reveals that TATB crystals gradually loose their transparency, from outer surface to inner surface layer by layer. It does not show any clearcut melting. Above 310°C , rapid crystal movements were observed and evolution of gas sets in and increases in intensity at localised points and finally a black charred residue is left behind.

Discussion

The structure of TATB [1] contains unusual features. X-ray diffraction pattern of crystalline TATB reveals that C–C bond orders are approximately 1.2 and the amine C–N and N–O bond orders are nearly 1.5. Molecule is nearly

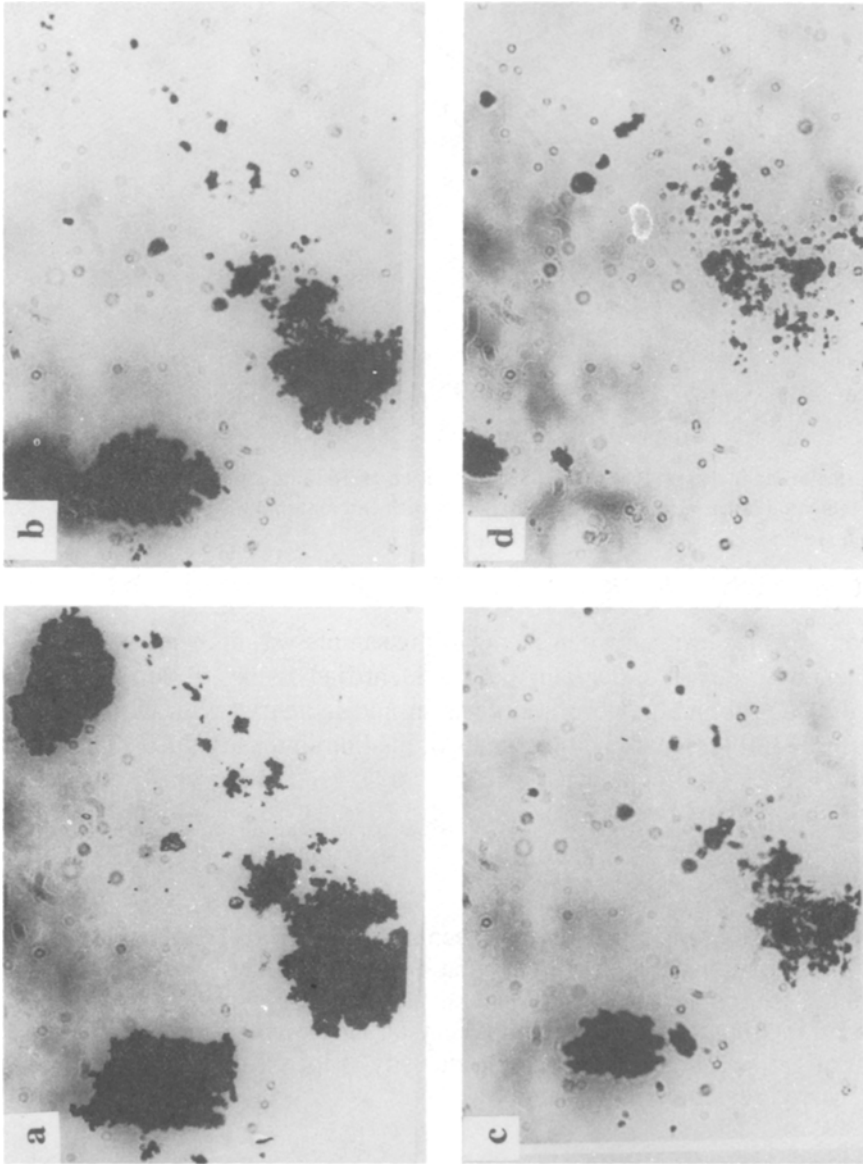


Fig. 5 Photomicrographs of TATB ($\times 300$) at a) room temperature; b) 320°C ; c) 340°C and d) 360°C

planar and have extensive system of hydrogen bonds [20] and intermolecular interactions as shown in Exhibit-1 contributing to its exceptional thermal stability.

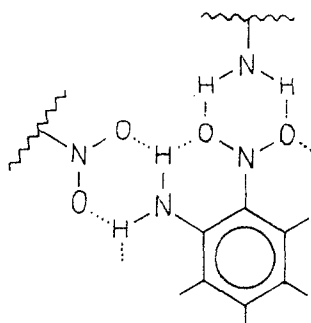


Exhibit-1

Thermal analysis [21, 5] data indicate that the thermal decomposition of TATB is complex [22], having a series of consecutive and concurrent reactions starting with an endothermic step followed by exothermic stages. The reaction is autocatalytic too.

During the isothermal decomposition studies by IR, it is found that drop in relative intensity with time of -NH_2 stretching vibration band is faster than that of bands corresponding to -NO_2 symmetric stretching vibration and the latter faster than that of ring stretch. Also new band at $2320\text{--}40\text{ cm}^{-1}$ developed which increased in intensity as decomposition progressed. This band disappears at high temperatures.

Figure 6 shows that under dynamic heating conditions also, band intensity decreased in the order of -NH_2 asymmetric stretching (3320 cm^{-1}) $>$ NO_2 symmetric stretching (1220 cm^{-1}) and ring stretching vibration (1440 cm^{-1}) as was noticed under isothermal conditions. Also additional band was observed at $2320\text{--}40\text{ cm}^{-1}$.

The interaction between neighbouring NH_2 and NO_2 groups in TATB (Exhibit-1) which has been clearly brought out by the crystal structural studies [1, 20] though contributes to higher thermal stability of the molecule as a whole, leads to relative weakening of the C-NH_2 bond and hence its ease of cleavage [22].

The reported formation of substituted benzofurazan [22, 23] in the decomposition of TATB is also in agreement with the existence of such an interaction. Therefore the rupture of the C-NH_2 bond, as indicated by the preferential loss of IR band intensity of this group, constitutes the primary step in the thermal decomposition of TATB. This is consistent with the fact that triaminotrinitro benzene, which is a highly insensitive explosive, has a larger C-NO_2 bond dissociated energy; for the $\text{NH}_2\text{CH=CHNO}_2$ molecular species possess an amino group on the β -carbon connected to the nitro group through the unsaturated C=C double bond [24]. This is followed by the C-NO_2 and then the ring cleav-

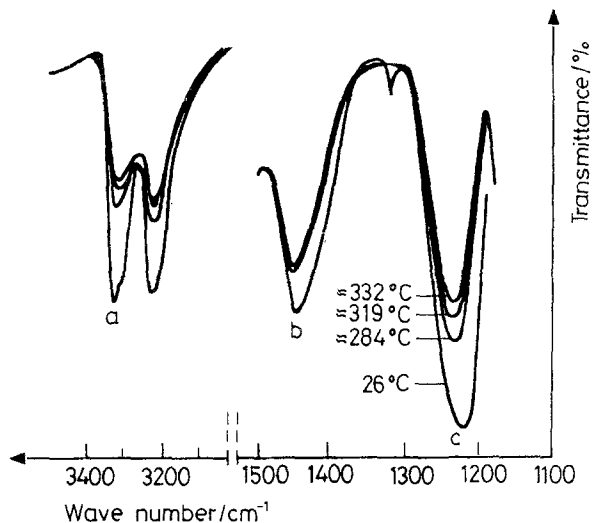


Fig. 6 Variation of intensity of selected IR bands of TATB with temperature under dynamic heating. a) 3320 cm^{-1} ($-\text{NH}_2$ asymmetric stretching); b) 1440 cm^{-1} (ring stretching); c) 1220 cm^{-1} ($-\text{NO}_2$ symmetric stretching)

ages as evidenced by IR spectral data leading to the formation of radicals. The observation of additional IR band at $2320\text{--}40\text{ cm}^{-1}$, attributable to molecular species having $\text{C}=\text{N}$, $\text{C}=\text{C}$, $\text{N}=\text{O}$ bonds in conjugation during the thermal decomposition of TATB also supports this mechanism. Therefore, the ring cleavage though constitutes an essential step in the decomposition, it appears, is not the primary step. The initial deamination [22] reaction is expected to generate NH_2 free radical insitu which abstracts hydrogen atom to form NH_3 . Mass spectroscopic study of the decomposition of TATB [25] has also assumed the formation of NH_2 radical [26].

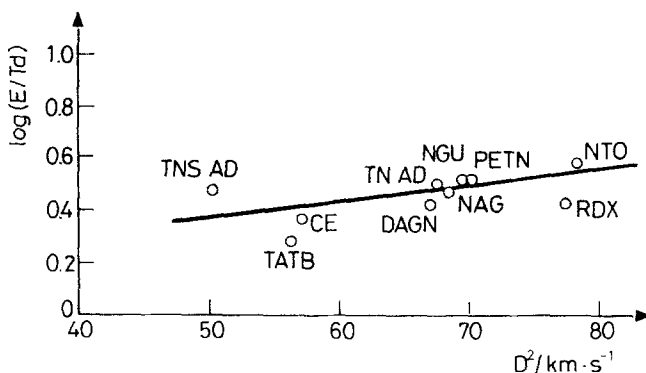


Fig. 7 Plot of $\lg\{(E\text{ in kJ}\cdot\text{mol}^{-1})/T_d\text{ in K}\}$ vs. detonation velocity

Nitroanilines, in general, produce free radicals upon heating. TATB [6] produces free radicals on exposure to ultraviolet light. Mass spectroscopic [2] results do indicate the formation of radical having C=N or C=C bonds, which further decompose to give free radicals, giving rise to radical chain mechanism, which in turn can explain the autocatalysis observed in the thermal decomposition of TATB. The formation of polymeric residue in the decomposition also supports free radical chain mechanism as observed in the case of other polynitro aromatic compounds.

Kinetics of initial thermolysis and velocity of detonation

Correlation observed between the rate parameters for the initial thermal decomposition and the detonation parameters [27] in certain group of compounds as observed by Zeman [21, 28–31] and others [13] have been found to be valid in the case of TATB too as is to be concluded from the linearity of plots of this relation as given in Fig. 7 for N-2,4,6 tetranitro-N-methylaniline (tetryl), *trans*-1,4,5,8-tetranitrosotetraazadecalin (TNSAD), *trans*-1,4,5,8-tetranitrotetra aza decalin (TNAD), diaminoguanidine nitrate (DAGN), nitroaminoguanidine (NAG), nitroguanidine (NGu), pentaerythritol tetranitrate (PETN), 3-nitro-1,2,4-triazole-5-one (NTO) and hexahydro-1,3,5-trinitro 1,3,5-triazine (RDX) [13].

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