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KINETICS OF INITIAL THERMAL DECOMPOSITION AND DETONATION PARAMETERS-STUDIES ON RDX:TNT SYSTEM

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The initial low temperature thermal decomposition of various compositions in the binary system—1,3,5 trinitro-1,3,5 triazacyclohexane (RDX) and 2,4,6 trinitro toluene (TNT) has been studied using thermogravimetry, high temperature infrared spectroscopy and photomicroscopy. A linear correlation has been observed between the activation energies for the initial stage of thermal decomposition and velocity of detonation in this system.

Kinetic data pertaining to the initial stage of thermal decomposition of some energetic materials has lately been found to have a correlation with their detonation parameters [1]. The correlation has been established for groups of compounds having structural similarities. Detonation so far has been considered as a thermohydrodynamic phenomenon and the detonation characteristics i.e., detonation velocity, detonation pressure and energy can be specified empirically or obtained by calculation on the basis of hydrodynamic theory. The detonation theory does not take into account the chemical nature of the material but is restricted to the heat of explosion, initial density and equation of state of the detonation products. However, a simple empirical linear relationship between detonation velocity at theoretical maximum density and factor F which solely depends upon chemical composition and structure is also postulated [2].

The correlation between detonation velocity and activation energy of the initial thermal decomposition has been established for single compounds in polynitro compounds [1]. An attempt has been made in the present study to extend the theory to a binary system of RDX : TNT.

Experimental

The RDX and TNT used in the system were of Indian Ordnance Factory origin corresponding to specification IND/ME/722 and IND/ME/451 for RDX and TNT, respectively. RDX : TNT mixtures $(100-X):X$, where X varies in multiples

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of 10 up to 60, were investigated. The mixtures were prepared by adding desensitized RDX to molten TNT at about 90–95°. The mixtures were then cooled to room temperature. The samples used for investigation were small granules of about 150 μm diameter. The homogeneity of the composition was confirmed by analysing the samples by HPLC (DuPont model No. 8800 with refractive index detector) using Zorbax CN column and methanol : water (70 : 30) as mobile phase.

A simultaneous thermo analyser STA 409, Netzsch was used to study the initial thermal decomposition upto about 40% of the initial mass. To avoid self-heating only about 10 mg of sample was taken wrapped in aluminium foil to prevent volatilisation of TNT. For isothermal studies, the sample in platinum–iridium thermocups was introduced into the furnace, of silicon carbide heating element, and the temperature was raised to the desired level at 10 deg/min. The temperature range investigated was 180 to 202°.

A Perkin–Elmer 683 ratio recording spectrophotometer was used to record the IR spectra of RDX–TNT mixtures in KBr matrix. A heating rate of 10 deg/min was used to reach the temperature range of the thermal decomposition with the desired temperature quickly stabilised. Infrared spectra were recorded as a function of time at each temperature. In IR studies, the bands of the decomposition products of RDX and TNT did not interfere with their characteristic bands i.e. 1090–1110 cm^{-1} for TNT and 1010–1040 cm^{-1} for RDX selected for analysis [3]. Loss of absorbance for bands characteristic of RDX and TNT was measured at specific time intervals to determine the rate of thermal decomposition as a function of time.

A Leitz–Orthoplan Pol polarising microscope with hot stage was used under dynamic heating conditions to characterise different phases.

Results and discussion

Simultaneous DTA–TG profiles obtained for various RDX : TNT mixtures are reproduced in Fig. 1. DTA–TG profiles show systematic variation with the change in composition. Thermal decomposition sets in at 175, 178, 179, 188, 192 and 198° for RDX : TNT compositions with 40–90% RDX, respectively. These decomposition temperatures are much below the decomposition temperature of 204°, for RDX alone and above 250° for TNT alone. This clearly shows that RDX : TNT mixtures behave differently from RDX and TNT alone and RDX decomposition and TNT decomposition mutually influence and accelerate each other resulting in a much faster thermal decomposition in the mixed state than in single pure states.

Figure 2 gives the variation with time of infrared intensity of the characteristic bands of RDX and TNT for a typical composition during the thermal

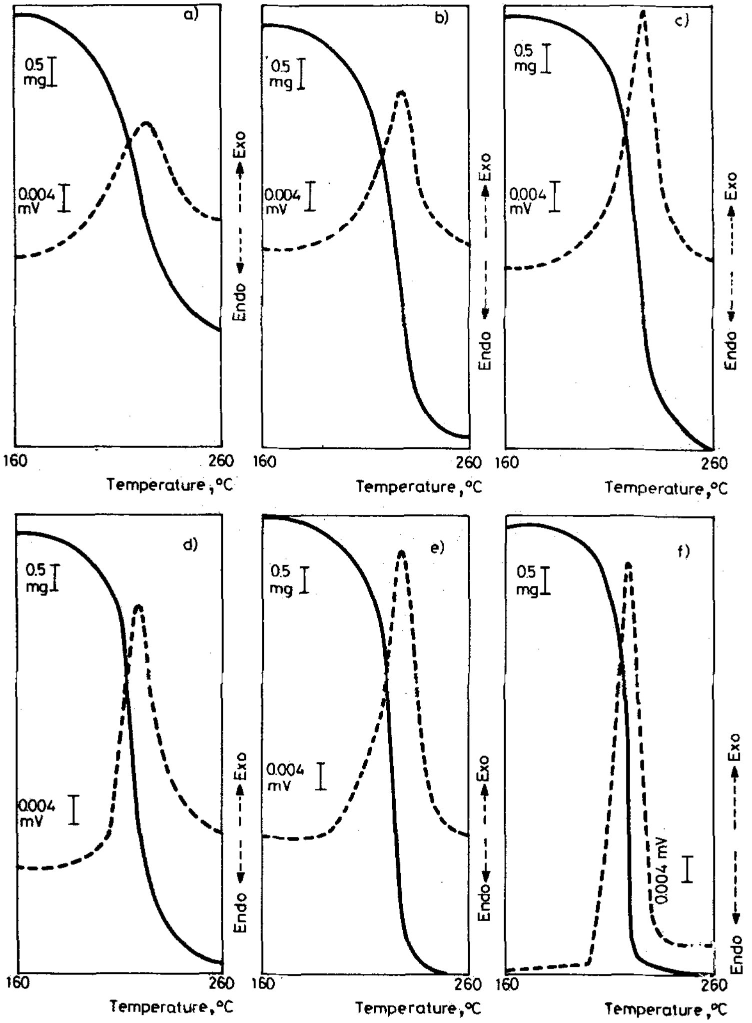

Fig. 1 TG and DTA curves of RDX : TNT compositions. a – 40 : 60, b – 50 : 50, c – 60 : 40, d – 70 : 30, e – 80 : 20, f – 90 : 10; wt. 10 mg, heating rate 5 deg/min

decomposition. It is evident from the spectral data that in the initial stage the decrease in infrared band intensity of RDX is faster than that of the TNT band which shows preferential accelerated thermal decomposition of RDX to TNT.

Hot stage microscopy shows formation of a completely molten phase at 180° and above for RDX : TNT mixtures up to a ratio of 70 : 30, but two distinct phases even up to 202° for mixtures above 70 : 30 Figs 3, 4.

The overall kinetics of thermal decomposition has been obtained from

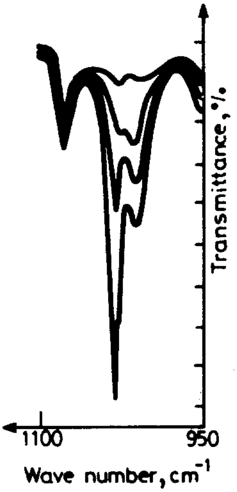

Fig. 2 Infrared spectra of RDX : TNT, 40 : 60 at 190 °C at 20 min interval

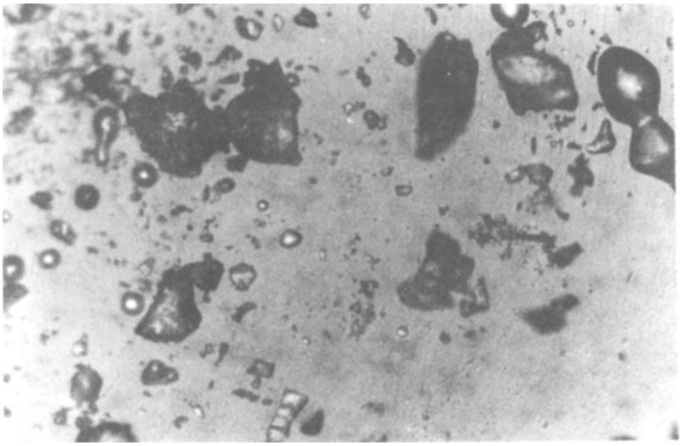

Fig. 3 Photomicrograph of RDX : TNT 70 : 30 at 180 °C

isothermal TG. Plots of fraction decomposed (α) *vs.* time (t) for various RDX : TNT compositions are sigmoidal in nature, in the temperature range investigated. Representative $\alpha - t$ curves obtained are given in Figs 5 and 6. Plots of $\ln\left(\frac{1}{1-\alpha}\right)$ produced straight lines with a correlation coefficient of 0.99 to 1.00, which is characteristic of a first order reaction, for the RDX : TNT compositions in the range 40 : 60 to 70 : 30. A representative plot is given in Fig. 7. However, $\alpha - t$ for

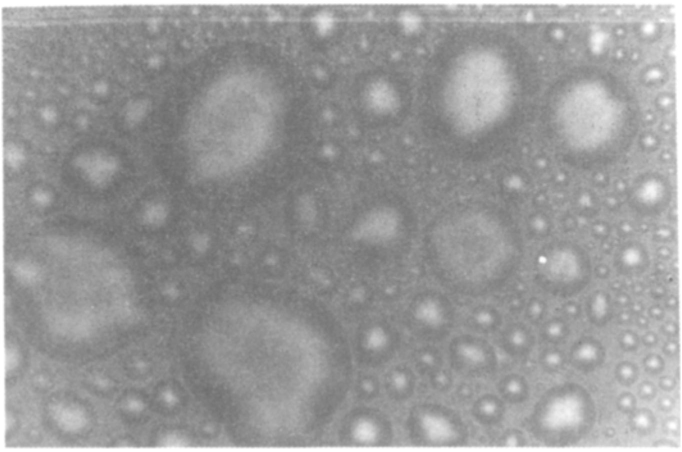

Fig. 4 Photomicrograph of RDX : TNT 90 : 10 at 180 °C

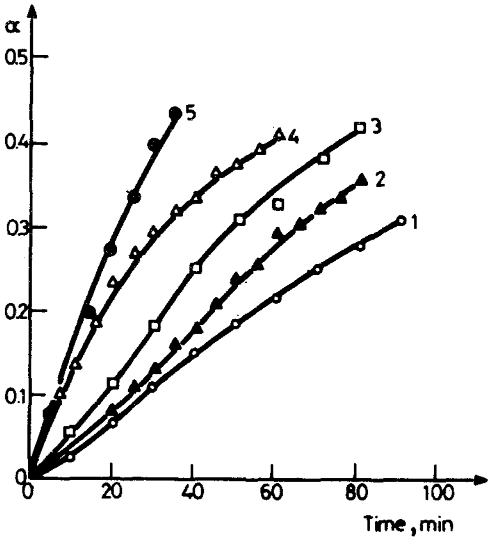

Fig. 5 Plot of α *vs.* time for RDX : TNT, 50 : 50 at 1: 180 °C, 2: 185 °C, 3: 190 °C, 4: 198 °C, 5: 202 °C

RDX : TNT compositions with RDX more than 70% obeyed Mampel's equation (Fig. 8) for $n=2$ with a correlation coefficient of 0.99 to 1.00,

$$1-(1-\alpha)^{1/n} = k\cdot t$$

where

k: rate constant,

n: number of dimension in which the reaction interface advances.

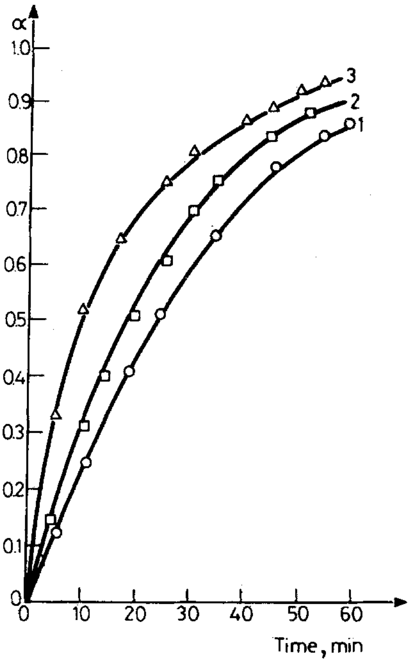

Fig. 6 Plot of RDX band intensity α *vs.* time for RDX : TNT, 40 : 60 at 1; 180 °C; 2: 190 °C; 3: 198 °C

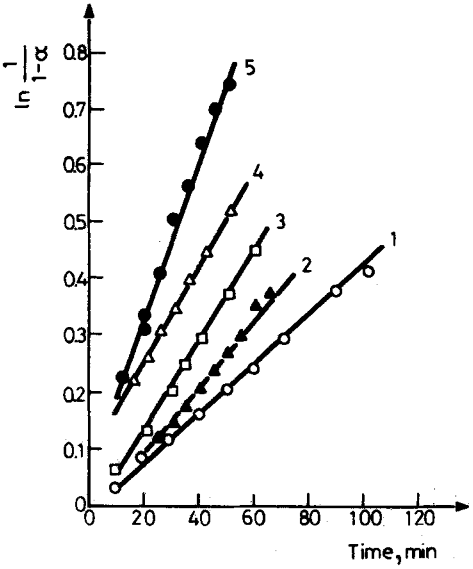

Fig. 7 Plot of $\ln\frac{1}{(1-\alpha)}$ *vs.* time for RDX : TNT, 50 : 50 at 1: 180 °C, 2: 185 °C, 3: 190 °C, 4: 198 °C, 5: 202 °C

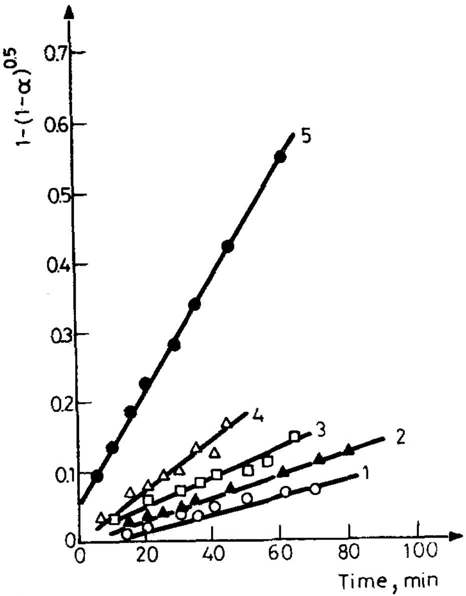

Fig. 8 Plot of $1-(1-\alpha)^{\frac{1}{2}}$ *vs.* time for RDX : TNT, 80 : 20 at 1: 180 °C, 2: 185 °C, 3: 190 °C, 4: 198 °C, 5: 202 °C

This change in obedience to the rate equation from first order to Mampel's when the composition changes to above 70% RDX may be due to the change from homogeneous to heterogeneous phase as observed in photomicroscopy.

It can be shown that the activation energy of the low temperature thermal decomposition in polynitro compounds is related to the detonation velocity by the expression (1)

$$\log \frac{E}{T_D} = b + a \cdot D^2 \qquad (1)$$

where

E: activation energy
T_D: decomposition temperature
a, b: constants
D: detonation velocity

The energy of activation obtained for the thermal decomposition was plotted against detonation velocity obtained both theoretically and experimentally for various compositions in the RDX : TNT system (Fig. 9). A linear correlation was obtained with correlation coefficients of 0.9938 and 0.9912, respectively between energy of activation and velocity of detonation, which confirms the validity of the above correlation for RDX : TNT composition in the range investigated.

The kinetics of thermolysis was also calculated from the TG–DTA data using the appropriate function for $f(\alpha)$ obtained from the isothermal studies in the non isothermal kinetic expression [4].

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)}\right] = \ln\left[\frac{A}{b}\right] - \frac{E}{RT}$$

where b = constant rate of heating. "E" values thus obtained though of higher order than those obtained from the isothermal method obeyed nevertheless the expression [1], as the relevant plot was found to be linear.

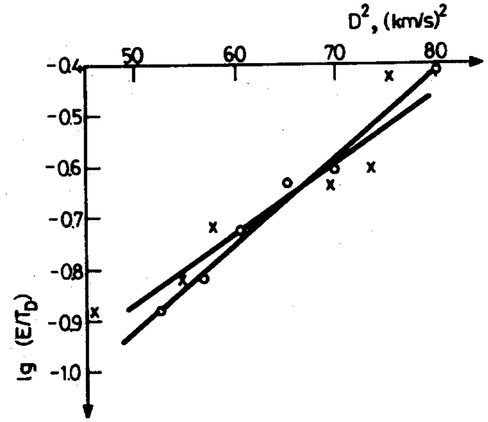

Fig. 9 Plot of $\log\left(\frac{E}{T_D}\right)$ *vs.* D^2. —— × —— using experimental values of D, —— ⊙ —— using theoretical values of D

The acceleration of thermal decomposition of RDX in TNT solution has been attributed to the role of liquid phase [3]. But this acceleration has been observed in the solid phase too, when RDX is no longer only in solution for compositions having more than 70% RDX, where a heterogeneous phase is observed. Therefore this accelerated thermal decomposition of RDX in TNT and vice versa, in RDX : TNT mixtures can not solely be attributed to phase effect but mainly to an induced effects of one thermal decomposition on the other and this constitutes an important instance of induced reaction in polynitro compounds. An induced reaction normally involves participation of a transient reactive intermediate, like free radicals generated in situ. This induced reaction observed in RDX : TNT systems thus underlines the dominant role of free radicals like NO_2 in the thermal decomposition of polynitro compounds which many studies tend to indicate. Both N–N as well as C–N bond ruptures expected to be the first reaction step in thermal decomposition [6], leads initially to the formation of NO_2 and other parent free radicals, thus emphasizing the role of the initial bond breaking in the detonation process.

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Zusammenfassung — Mittels Thermogravimetrie, Hochtemperatur-IR-Spektroskopie und Fotomikroskopie wurde die einleitende thermische Zersetzung bei niedriger Temperatur von verschiedenen Gemischen des binären Systems von 1,3,5-Trinitro-1,3,5-triazazyklohexan (RDX) und 2,4,6-Trinitrotoluol (TNT) untersucht. Zwischen der Aktivierungsenergie des Anfangsschrittes der thermischen Zersetzung und der Detonationsgeschwindigkeit in diesem System konnte einer lineare Korrelation nachgewiesen werden.

Резюме — Методом ТГ, высокотемпературной ИК спектроскопии и фотомикроскопии изучено начальное низкотемпературное разложение двойной системы 1,3,5-тринитро-1,3,5-триазациклогексан и 2,4,6-тринитротолуол с различным соотношением компонент. Наблюдалась линейная корреляция между энергиями активации начальной стадии термического разложения и скоростью детонации такой системы.