

STUDIES ON THE THERMAL DECOMPOSITION OF N-2,4,6 TETRANITRO-N-METHYL ANILINE

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The kinetics of the initial stage of thermal decomposition of N-2,4,6 tetranitro-N-methyl aniline (tetryl) in condensed state has been investigated by high temperature infrared spectroscopy (IR) in conjunction with pyrolysis gas analysis and thermogravimetry (TG). The decomposition in KBr matrix in the temperature range of 131 to 145 °C shows rapid decrease in the N-NO₂ band intensity as compared to the C-NO₂ band. Decomposition products in the initial stage show mainly NO₂ gas and picric acid. The studies show that the initial stage of decomposition of tetryl occurs by the rupture of the N-NO₂ bond and the energy of activation for this process is 177 kJ/mol.

Thermal decomposition data constitute an essential component in the study of explosive properties of polynitro compound N-2,4,6 tetranitro-N-methyl aniline (tetryl) is a widely used high explosive and its decomposition proceeds [1-4] through intermediate formation of picric acid, 2,4,6 trinitro anisol and N-methyl 2,4,6 trinitro aniline. All these decomposition products retain the trinitro benzene ring and, being thermally unstable, decompose simultaneously with tetryl. The decomposition has been found to be autocatalytic [1, 2]. Since the products of initial thermal decomposition decompose simultaneously with tetryl, the kinetic parameters determined by mass loss studies will give an average value for all the decomposition reactions. A precise study of the kinetics of the initial thermal decomposition of tetryl is possible by following the change in the chemical bond involved in the decomposition process. The bond energy of N-NO₂ [5] is around 168 kJ/mol and is the weakest linkage in tetryl [4].

High temperature IR spectroscopy has been used in the present studies to determine the structural rearrangement and mechanism of the initial thermal decomposition of tetryl in conjunction with product analysis by IR and high performance liquid chromatography (HPLC). The kinetics of the initial thermal decomposition has been followed by high temperature IR spectroscopy and compared with the value determined by the TG method.

Experimental

Tetryl was purchased from Indian Ordnance Factory and purified by repeated recrystallisation from acetone (m.p. 129.5°).

Thermal analysis was carried out with a simultaneous thermal analyser, Netzsch STA 409. The kinetics of decomposition was followed by isothermal mass change determination using about 10 mg of sample in the temperature range 150 to 175°, in static air atmosphere. The stability of the temperature was within ± 1 deg. The sample in platinum-iridium thermocup was heated to the desired temperature using programmed heating so that thermal cycle was kept practically the same for different isothermal temperatures.

The kinetics of thermal decomposition was followed by a ratio recording IR Spectrophotometer, Perkin-Elmer 683. The heated cell for high temperature studies was fabricated in the laboratory and temperature programming was done using a Stanton Redcroft's universal temperature programmer having chromel/alumel thermocouple. The temperature remained constant during the trace and was within ± 1 deg 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 1275 cm^{-1} (corresponding to $-\text{NO}_2$ symmetric stretching vibration of the N- NO_2 bond) varied linearly with the amount of sample showing obedience to Beer's law in the concentration range of 0.1 to 0.75% tetryl in KBr matrix.

A specially designed experimental setup and IR gas cell with KBr windows were used to study the gaseous phase composition during the thermal decomposition of tetryl.

A DuPont HPLC 8800 with refractive index detector was used for identification of the decomposition products of tetryl. The column used for the detection was Zorbax- C_8 and mobile phase, methanol/water 70:30 mixture.

Results and discussion

Figure 1 shows DTA, TG curves for the tetryl (5.5 mg and heating rate 10 deg/min). The reaction is a three stage process. It shows melting at 129.5° followed by an exothermic peak at 209°. But it has been found in isothermal mass change determination that tetryl decomposes at an appreciable rate at lower temperatures. The overall decomposition of tetryl is a very complex process because

of various products formed in the decomposition. Pyrolysis gas chromatography (GC) of tetryl shows about 16 products which are yet to be identified completely.

The gaseous products evolved in the thermal decomposition of tetryl at 195° show IR absorption bands of medium intensity due to NO_2 (1621 cm^{-1}) and CO_2 (2330 cm^{-1}) in the initial stage (Fig. 2).

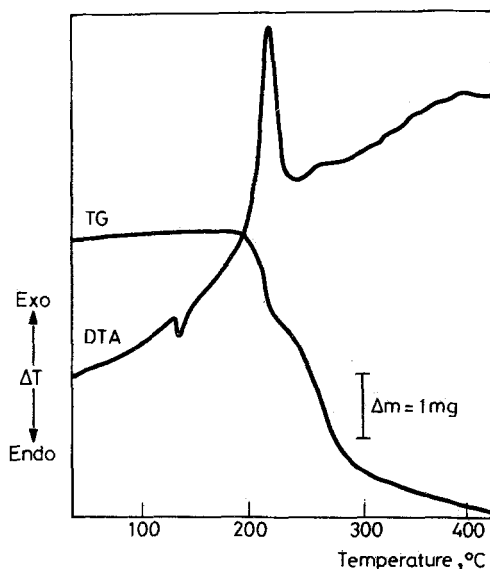


Fig. 1 DTA and TG curves of N-2,4,6 tetranitro-N-methyl aniline (tetryl)

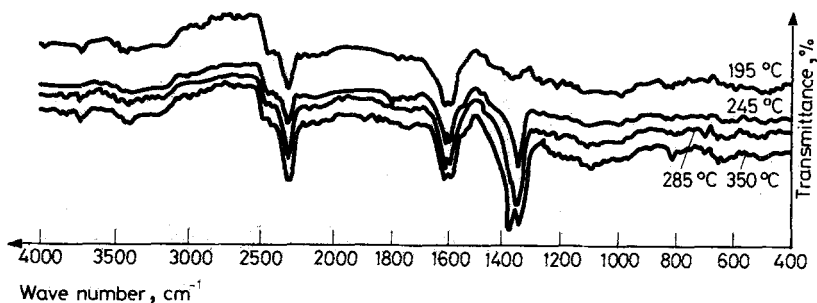


Fig. 2 IR spectra of the gaseous decomposition products of tetryl

Analysis of the solid residue left after the initial stage of decomposition by IR and HPLC shows that it contains mainly picric acid (Fig. 3) where the trinitro benzene ring is retained. Formation of NO_2 and picric acid indicates that the initial thermal decomposition occurs at the $\text{N}-\text{NO}_2$ bond.

Standard IR spectra of tetryl in KBr matrix show absorption bands at 1275 cm^{-1} , 1349 cm^{-1} and 1610 cm^{-1} due to N-NO_2 , C-NO_2 and the aromatic ring respectively [6] (Fig. 4). It is observed that the intensities of bands do not show any variation till 120° , whereafter the band intensities decrease due to decomposition of the explosive compound. Figure 4 presents the variation of band intensity for different groups with time, at 131° due to decomposition. The intensity

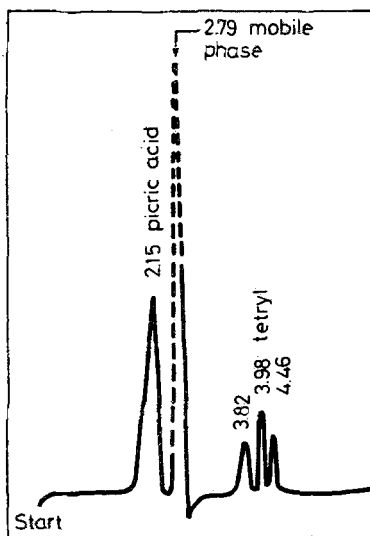


Fig. 3 High performance liquid chromatography of solid decomposition products of tetryl at 160°C . Flow rate: 1 ml/min , mobile phase $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ 70:30

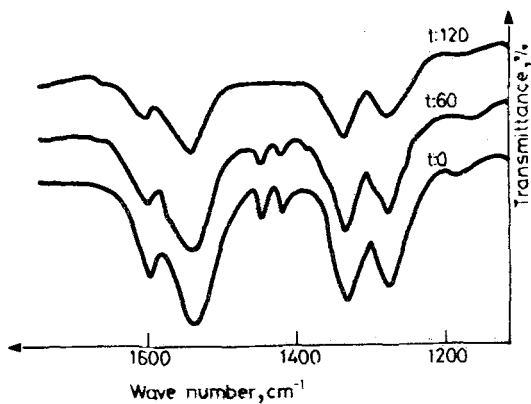


Fig. 4 IR spectra of tetryl at 131°C as a function of time (min)

of the band does not vary uniformly with time, as is to be normally expected. The N-NO₂ band intensity shows a loss at faster rate than the C-NO₂ band. This indicates that the initial attack occurs at the N-NO₂ bond and the products subsequently decompose by C-NO₂ and ring bond fission steps.

The kinetics of decomposition of tetryl was followed by the intensity of absorption of N-NO₂ band at 1275 cm⁻¹. For calculating the fraction of tetryl decomposed (α) the peak intensity after attaining the desired temperature was taken as initial concentration. α was plotted as a function of time. These $\alpha-t$ curves for the initial stage of decomposition reaction in the range of 131 to 145° by high temperature IR spectroscopy are presented in Fig. 5. $\alpha-t$ curves obtained by

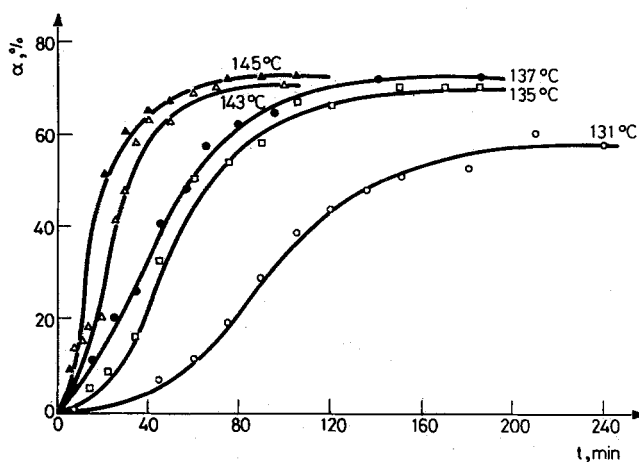


Fig. 5 $\alpha-t$ plot for the initial stage of thermal decomposition of tetryl by IR

isothermal mass change determination are presented in Fig. 6. In both cases the $\alpha-t$ curves are sigmoidal in nature. The decomposition is found to be autocatalytic. The decomposition of tetryl is best described by Avrami-Erofe'ev equation, for 1st order decay:

$$-\ln(1-\alpha) = k \cdot t$$

where k is the velocity coefficient of reaction and t is the time.

Plot of $-\log(1-\alpha)$ against time gave a straight line, from the slope of which k was evaluated. The activation energy was determined from the Arrhenius plot, and the values are 177 kJ mol⁻¹ by IR method and 144 kJ mol⁻¹ by TG method. The values of $\log A$ (sec⁻¹) were 18.84 and 12.96, respectively. The lower value of activation energy as determined by isothermal mass change determination is probably due to simultaneous decomposition of the products of initial decomposition, taking place along with the cleavage of N-NO₂ bond.

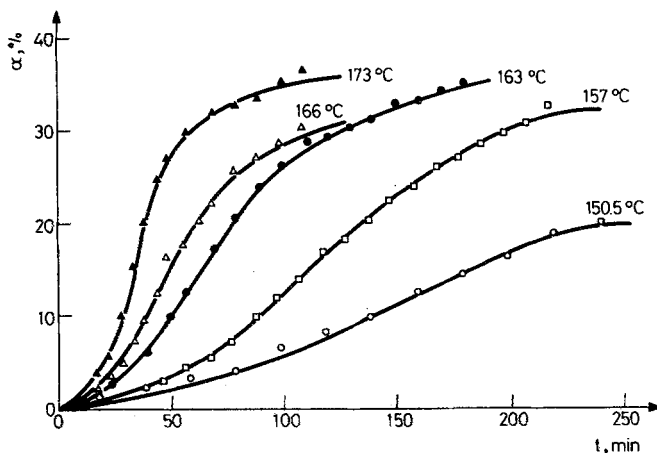


Fig. 6 $\alpha-t$ plot for the initial stage of thermal decomposition of tetryl by TG

Thus, high temperature IR spectroscopic studies and product analysis by IR and HPLC show that the primary step in the decomposition of tetryl is the cleavage of the N-NO₂ bond, possibly by formation of NO₂ [7] as observed in case of other polynitro aromatic compounds [8]. The activation energy of this reaction as determined by IR spectroscopy agrees with the bond energy of N-NO₂.

References

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Zusammenfassung — Mittels Hochtemperatur-IR-Spektroskopie wurde in Verbindung mit Pyrolyse-gasanalyse und Thermogravimetrie (TG) die Kinetik des einleitenden Schrittes der thermischen Zersetzung von N-2,4,6-Tetranitro-N-Methylanilin (Tetryl) im kondensierten Zustand untersucht. Die Zersetzung in einer KBr-Matrix im Temperaturbereich von 131–145 °C äußert sich in einem schnellen Abnehmen der Intensität der N-NO₂ Bande bezogen auf die der C-NO₂ Bande. Zersetzungsprodukte des einleitenden Schrittes sind hauptsächlich NO₂ Gas und Pikrinsäure. Die Untersuchungen zeigten, daß der einleitende Schritt der Zersetzung von Tetryl die Spaltung der N-NO₂ Bindung ist. Die Aktivierungsenergie für diesen Prozess beträgt 177 kJ/mol.

Резюме — Кинетика начальной стадии термического разложения твердого N-2,4,6-тетранитро-N-метиланилина (тетрил) была изучена с помощью высокотемпературной ИК спектроскопии, связанной с пиролизным газовым анализатором и термогравиметрией. Разложение в матрице из бромистого калия в температурном интервале 131–145 °C показало быстрое уменьшение интенсивности полосы N–NO₂ по сравнению с интенсивностью полосы C–NO₂. Основными продуктами разложения на начальной стадии были газообразная двуокись азота и пикриновая кислота. Проведенные исследования показали, что начальная стадия разложения тетрила происходит с разрывом связи N–NO₂, энергия активации которого составляла 177 кДж/моль.