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°C).

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°C, 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 NO/ 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°C followed by an exothermic peak at 209°C. 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