Journal of Thermal Analysis, Vol. 45 (1995) 501-509

STUDIES ON KINETICS AND MECHANISM OF INITIAL THERMAL DECOMPOSITION OF NITROCELLULOSE

Isothermal and non-isothermal techniques

*P. S. Makashir, R. R. Mahajan and J. P. Agrawal**

Explosives Research and Development Laboratory, Sutarwadi, Pune – 411 008, India

(Received January 16, 1994; in revised form September 7, 1994)

Abstract

The thermal decomposition of nitrocellulose (*NC*) 12.1% N, has been studied with regard to kinetics, mechanism, morphology and the gaseous products thereof, using thermogravimetry (TG), differential thermal analysis (DTA), IR spectroscopy, differential scanning calorimetry (DSC) and hot stage microscopy.

The kinetics of the initial stage of thermolysis of *NC* in condensed state has been investigated by isothermal high temperature infrared spectroscopy (IR). The decomposition of *NC* in KBr matrix in the temperature range of 142–151°C shows rapid decrease in $O-NO_2$ band intensity, suggesting that the decomposition of NC occurs by the rupture of $O-NO_2$ bond. The energy of activation for this process has been determined with the help of Avrami-Erofe'ev equation ($n=1$) and is ≈188.35 $kJ\cdot mol^{-1}$. Further, the IR spectra of the decomposition products in the initial stage of thermal decomposition of *NC*, indicates the presence of mainly NO_2 gas and aldehyde.

Keywords: DSC, DTA-TG, IR, kinetics, nitrocellulose

Introduction

Thermal decomposition data constitutes an essential component in the study of explosive properties of polynitro compounds. Nitrocellulose (*NC*) is widely used as a chief ingredient in the production of smokeless powder, blasting gelatine, dynamite, single-base, double-base and triple-base propellants.

The gun and rocket propellants based on *NC* and nitroglycerine (*NC*) deteriorate on storage due to liberation of nitrogen peroxide and nitric oxide. These oxides react with moisture to give nitric acid (HNO_3) which causes further degradation of *NC* and *NG*. This process of breakdown of NC and NG continues

---

* To whom correspondence should be addressed.

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

and is termed as 'auto-catalytic'. The breakdown of *NC*, leads to deterioration of ballistic and mechanical properties as well as chemical stability of propellants.

The study of effect of heat on *NC* is likely to provide a clue for degradation of *NC* [1–4]. The decomposition of *NC* proceeds [1, 3] through the intermediate formation of aldehyde, alcohol, NO_2 gas. Beard *et al.* [5] studied the surface changes of thermally aged *NC* and suggested formation of amines, oximes and urethanes as products of secondary reactions of NO_2 with the *NC* residue. Jutier and coworkers [4] carried out the non-isothermal decomposition study of *NC* films using Fourier transform infrared (FTIR) spectroscopy. They pointed out that the basic carbon skeleton of *NC* does not change drastically during the decomposition. The decomposition has been found to be autocatalytic [1, 4].

Since the products of initial thermal decomposition also decompose simultaneously with *NC*, the kinetic parameters determined by mass loss studied are likely to give an average value for all the decomposition reactions. A precise study of the kinetics of initial thermal decomposition of *NC* is possible by following the change in the chemical bond involved in the decomposition process. The high temperature IR spectroscopic technique has been used in the present study to determine the structural rearrangement and mechanism of the initial thermal decomposition of *NC* in conjunction with hot stage microscopy and product analysis by IR. The kinetics of the initial isothermal decomposition has also been followed by the same technique.

Experimental

Materials

NC, nitrogen content 12.1–12.3%, was obtained from the Ordnance Factory, Bhandara. It was dried under vacuum. The spectroscopic grade potassium bromide (KBr) was used as a matrix material for IR spectroscopic studies.

Thermal analysis

Thermal analysis was carried out using a simultaneous thermal analyser, STA 409, (Netzsch, West Germany). The Pt-10% Ir thermocups (cylindrical in shape) with Pt–Pt 10% Rh thermocouples forming an integral junction with the thermocup were used and the reference material was calcined alumina. The sample used for thermal analysis was 5.0 mg and heating rate was 10 deg·min^{-1}.

High temperature IR spectroscopic technique

A specially designed cylindrical brass furnace with a temperature programmer was used for high temperature studies [6]. It has an arrangement for holding KBr pellet of 1.6 cm in diameter. The KBr pellet is connected by means of a chromel/alumel thermocouple to the Stanton Redcroft's universal temperature programmer for temperature sensing, measurement and control. The accuracy of temperature measurement was ±1°C of the set temperature. The spectra of the sample in KBr matrix were recorded in the frequency range 4000 to 200 cm^{-1}, at the desired elevated temperature at regular time intervals, using medium speed of scanning. It was verified that the peak intensity of the band at 1285 cm^{-1} (corresponding to $-NO_2$ symmetric stretching vibration of $O-NO_2$ bond) varies linearly with the mass of the sample showing applicability of Beer's law in the concentration range of 0.1 to 0.75% *NC* in KBr matrix.

Kinetics

The kinetics of thermal decomposition [6] was followed by Perkin-Elmer. IR spectrophotometer, model 683, with double beam ratio recording system, which generally require no correction for sample temperature.

The kinetics of decomposition of *NC* was followed by the intensity of absorption of $O-NO_2$ band at 1285 cm^{-1}. For calculating fraction of *NC* decomposed (α), the peak intensity after attaining the desired temperature, was taken as initial concentration. The α was then plotted as a function of time and at the desired temperature, kinetics was deduced using standard expressions [7–10] for various exponential 'n' values and also first order equation.

Gas analysis by IR

A specially designed experimental set up and IR gas cell with KBr windows were used to study the gaseous decomposition products of the thermal decomposition of *NC*.

Hot stage microscopy

Leitz orthoplan polarising microscope with hot stage was used under dynamic heating conditions to characterise the morphological sequence of decomposition. The photomicrographs were taken at different temperatures and magnification of 100. The temperature was programmed through the Universal Temperature Programmer of Stanton Redcroft.

Differential scanning calorimetry

DSC experiment was carried out on Perkin-Elmer DSC-7. The sample used for DSC was 0.8 mg and heating rate was 10 $deg \cdot min^{-1}$.

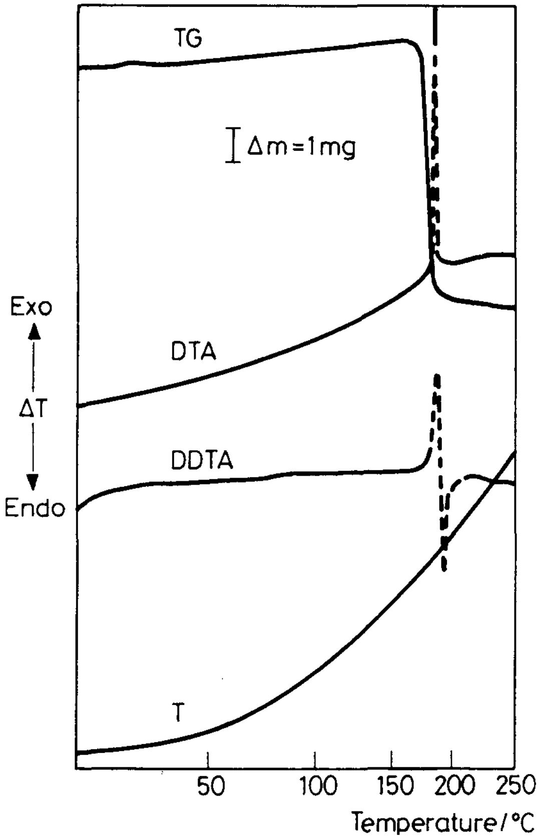

Fig. 1 Thermal analysis curve of nitrocellulose (TG-25 mg, DTA-0.1 mv, DDTA-0.5 mv, Atmosphere: static air)

Results and discussion

Figure 1 shows DTA, DDTA and TG curves for *NC*. Thermogravimetric curve of NC does not show any change in weight up to 167°C. From 168 to 188.5°C, there is a very steep loss in weight amounting to about 99% of the original weight. DTA curve shows sharp exothermic change with peak maximum at 187.2°C.

The DSC curve (Fig. 2) shows a sharp dominant exothermic change, with simultaneous release of 2591.02 J/g energy in the temperature range 181.5–248°C, with peak maxima at 206.88°C.

The microphotographs recorded at different time intervals during heating are shown in Fig. 3 (A–F). It is seen that *NC* shows thread like transparent structure at room temperature (26°C). The transparency gradually decreases with an increase in temperature and at about 160–170°C brown gas evolution starts. The

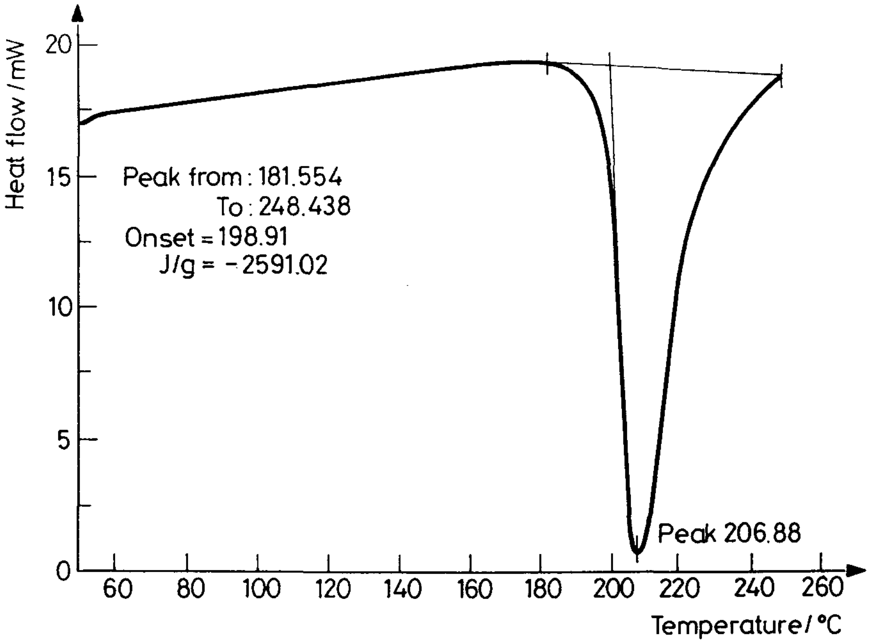

Fig. 2 DSC trace of nitrocellulose. (Atmosphere: nitrogen)

rapid movement of fibrous structure of *NC* is observed during 180–185°C followed by disappearance of fibrous structure. The profuse evolution of brown gas is also observed with increased intensity of brown gas at localised points. Some of the localised points are transformed into holes through which gaseous products bubbled out and finally giving a dark brownish black residue.

Standard IR spectra of *NC* in KBr matrix (Fig. 4) shows absorption bands at 1655, 1285, 830–840, 750 and 680 $\mathrm{cm^{-1}}$ which are due to $O–NO_2$ bond and 1060–1080 $\mathrm{cm^{-1}}$ due to C–O stretching in C–O–C' bridge [4]. Figure 4 represents the variation of band intensity for different groups with time at 151°C, during decomposition of NC. The bond energy data of different linkages in *NC* shows that the $O–NO_2$ is the weakest linkage and as a result, the $O–NO_2$ band intensity shows a loss at faster rate than other bands. This indicates that the decomposition starts at the $O–NO_2$ bond first followed by further decomposition.

The gaseous products evolved in the initial stage of the thermal decomposition of *NC*, shows IR absorption band of medium intensity at 1621 $\mathrm{cm^{-1}}$ due to NO_2. The analysis of the solid residue left after the initial stage of decomposition of *NC*, by IR shows mainly the presence of aldehyde. The formation of NO_2 and aldehyde indicates that the initial thermal decomposition occurs at the $O–NO_2$ bond and is supported by high temperature IR study.

For kinetic studies, at the desired temperature, the fraction of *NC* decomposed (α) in time t, was calculated from the loss in peak intensity of the band

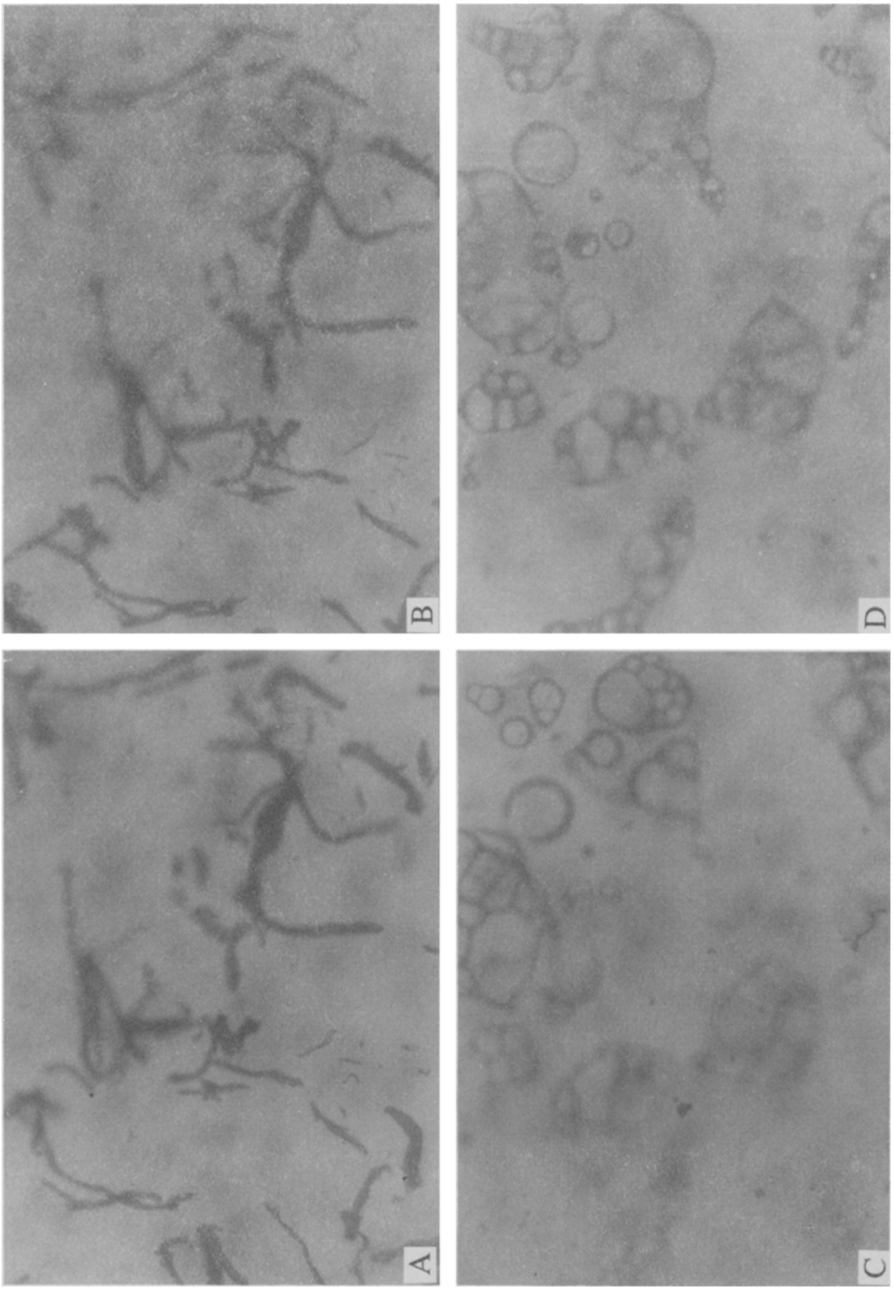

Fig. 3 Photomicrographs of nitrocellulose at room temperature (A), 165°C (B), 185°C (C) and 340°C (D)

corresponding to O–NO_2 linkage. The α–t curves of *NC* by high temperature IR spectroscopy, in the range of 142 to 151°C are shown in Fig. 5. The α–t curves are sigmoidal in nature. The reaction has an induction period followed by an acceleratory region and then a deceleratory one. The induction period is considerably brought down at higher temperatures. The decomposition of *NC* is best described by Avrami-Erofe'ev equation, $n=1$.

$$[-\ln(1-\alpha)]^{1/n} = k(t-t_o) \tag{1}$$

where

n exponent and is $= \beta+\lambda$
β number of steps involved in nucleus formation
λ number of dimensions in which nuclei grow
α fraction decomposed
k rate constant
t time
t_o initial time.

The plot of $[-\log(1-\alpha)]$ *vs.* time, $(t-t_o)$, is a straight line, from the slope of which k was calculated. The activation energy was determined from the Arrhenius plot and the value is 188.3 $kJ\cdot mol^{-1}$.

The IR spectroscopic studies under isothermal conditions show an additional band at 1840 cm^{-1} at the time of decomposition of *NC* and appears to be due to NO. This is, however, somewhat at lower frequency than the usual NO frequency which is reported at 1880 cm^{-1} and is likely to diffuse out of matrix similar to CO. This also confirms the formation of NO_2, in the first stage of decomposition of *NC*, which reacts with MX (matrix) giving NOX (X=Br).

$$2NO_2+MX \rightarrow MNO_3+NOX \tag{2}$$

This is in accordance with the findings of Bent *et al.* [11]. Further, disappearance of this additional band at 1840 cm^{-1} on continued heating is due to the dissociation of NOX in the following manner

$$2NOX \rightleftarrows X_2+2NO \tag{3}$$

The rate of reverse reaction is likely to decline, in the KBr matrix, as NO diffuses out of matrix. It is, therefore expected that the NOX will exhibit metastability as observed. The additional peak at 2320–40 cm^{-1} during isothermal decomposition is likely due to CO_2 suggesting the formation of CO_2 during decomposition of *NC*, after the formation of NO. The additional peaks at 1725–50 cm^{-1} and 1150–1170 cm^{-1} are due to CO and CH_2 respectively in IR spectra of *NC* residue obtained after the initial stage of decomposition and

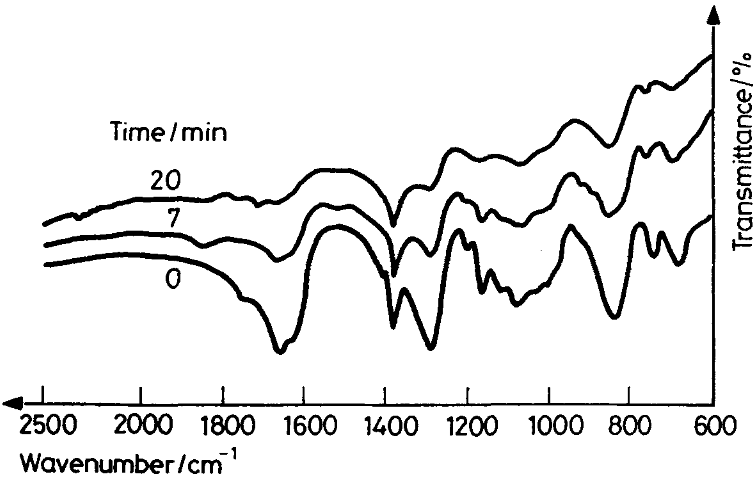

Fig. 4 IR Spectra of nitrocellulose at 151°C as a function of time (min)

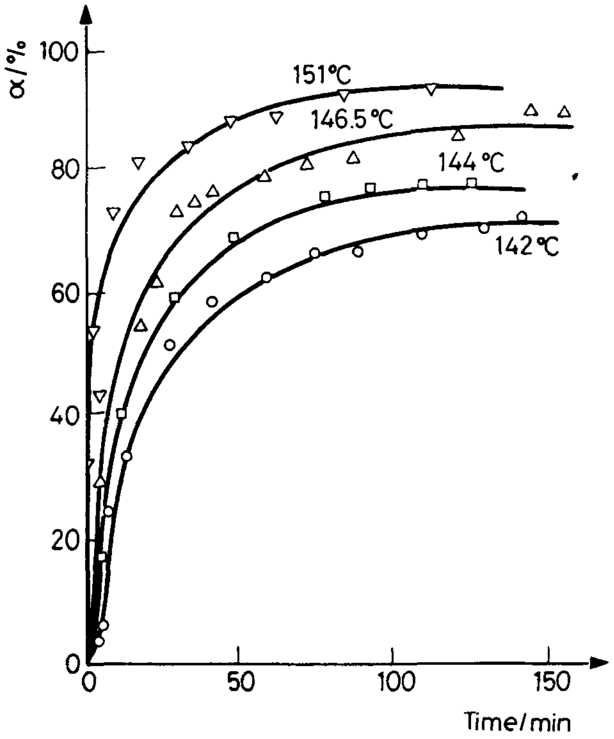

Fig. 5 α–*t* plot for the thermal decomposition of nitrocellulose

shows the presence of formaldehyde structural grouping [12]. The presence of aldehyde, NO_2 and CO_2 is also supported by the work of Saunders and co-workers [1].

The data of high temperature IR spectroscopic studies, product analysis and hot stage microscopic analysis clearly shows that the primary step in the decomposition of *NC* is the cleavage of O–N bond, leading to the formation of RCH_2O free radical [1, 13].

$$\underset{(NC)}{RCH_2ONO_2} \rightarrow RCH_2O^{\cdot} + NO_2 \tag{4}$$

This free radical is converted into intermediate decomposition product such as HCHO (formaldehyde), which may further react with NO_2 formed during decomposition, leading to the formation of CO_2.

References

1 C. W. Saunders and L. T. Taylor, J. Energetic Materials, 8 (1990) 149.
2 J. Isler and D. Kayser, 6th Symposium on Chemical problems connected with the stability of explosives. Kungalv, June 13–17, Sundbyberg, Sweden 1982, Part I., p. 217.
3 J. K. Chen and T. B. Brill, Combust. Flame, 85 (1991) 479.
4 J. J. Jutier, Y. Harrison, S. Premont and R. Prud'homme, J. Appl. Polym. Sci., 33 (1987) 1359.
5 B. C. Beard and J. Sharma, JANNAF Propellant Characterisation Subcommittee Meeting, CPIA Pub. # 470, (1987) 259.
6 K. Raha, P. S. Makashir and E. M. Kurian, J. Thermal Anal., 35 (1989) 1173.
7 E. G. Prout and F. C. Tompkins, Trans. Farad. Soc., 40 (1944) 488.
8 M. Avrami, J. Chem. Phys., 7 (1939) 1103.
9 M. Avrami, J. Chem. Phys., 8 (1940) 212.
10 M. Avrami, J. Chem. Phys., 9 (1941) 177.
11 H. A. Bent and B. Crawford, Jr., J. Am. Chem. Soc., 79 (1957) 1793.
12 K. O. Hartman and R. C. Musso, (1972) West States Sect., Combust. Inst. (Pap.), WSCI 72–30, 29 pp. (Eng.) and Chem. Abstr., 78 (1973) 113507 z.
13 L. Druet and M. Asselin, J. Energetic Materials, 6 (1988) 27.

Zusammenfassung — *Im Hinblick auf Kinetik, Mechanismus, Morphologie und den gasförmigen Produkten wurde mittels Thermogravimetrie und Differential-Thermoanalyse, IR-Spektroskopie, Differential-Scanningkalorimetrie und dem Heiztischmikroskop die thermische Zersetzung von Nitrozellulose (NC) mit 12.1 % N untersucht.*

Die Kinetik des einleitenden Schrittes der Thermolyse von NC im kondensierten Aggregatzustand wurde mittels isothermer Hochtemperatur-Infrarotspektroskopie (IR) untersucht. Die Zersetzung von NC in einer KBr-Matrix im Temperaturbereich 142–151°C zeigt ein schnelles Abnehmen der $O–NO_2$ Bandenintensität, was darauf hindeutet, daß die Zersetzung von NC durch die Spaltung der $O–NO_2$ Bindung erfolgt. Die Aktivierungsenergie für diesen Vorgang wurde mittels der Gleichung von Avrami-Erofe'ev ($n=1$) ermittelt und beträgt ca. 188.35 kJ/mol. Weiterhin zeigen die IR-Spektren der Zersetzungsprodukte im einleitenden Schritt der thermischen Zersetzung von NC die Gegenwart von hauptsächlich NO_2-Gas und Aldehyd.