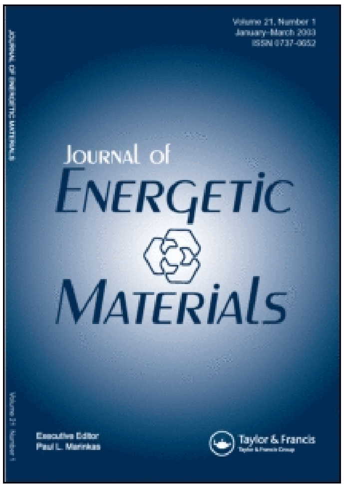

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Studies on energetic compounds part 7 thermolysis of ring substituted arylammonium salts of 3-nitro-1,2,4-triazole-5-one (NTO)

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To cite this Article Singh, G. , Kapoor, I. P. S. , Mannan, S. M. and Tiwari, S. K.(1998) 'Studies on energetic compounds part 7 thermolysis of ring substituted arylammonium salts of 3-nitro-1,2,4-triazole-5-one (NTO)', Journal of Energetic Materials, 16: 2, 101 — 118

To link to this Article: DOI: 10.1080/07370659808217507

URL: http://dx.doi.org/10.1080/07370659808217507

STUDIES ON ENERGETIC COMPOUNDS

PART 7 THERMOLYSIS OF RING SUBSTITUTED ARYLAMMONIUM SALTS OF 3-NITRO-1,2,4-TRIAZOLE-5-ONE(NTO)

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ABSTRACT

Thermolysis of fifteen ring-substituted arylammonium salts of NTO (RSA NTOates, C-NO_2 explosive) have been studied by dynamic and isothermal TG; DTA and explosion delay measurements. Kinetics of their thermolysis was evaluatedusing TG and explosion delay data. Some of the RSA NTOates have been found to liberate amine by N-H bond heterolysis prior to explosion whereas in other cases, amine part is not liberated. However formation of NO_2 seems plausible to cause explosion. The oxidation-reduction reactions near the surface of thermolysing materials (RSA NTOates) may be responsible for the decomposition of these salts prior to explosion.

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Journal of Energetic Materials Vol. 16, 101-118 (1998)
Published in 1998 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

As a part of our ongoing programme to understand the mechanism of thermolysis of energetic materials,[1-11] we have synthesised and characterised the ring-substituted arylammonium salts of NTO (RSA NTOates) reported in our earlier paper[12]. The thermolysis of these salts is not yet reported in literature. However, some workers have investigated ammonium[13] and aliphatic amine salts[14] of NTO. In the present communication, we have carried out the thermolysis of RSA NTOates using TG, DTA and explosion delay measurements and plausible pathways for their decomposition have also been proposed.

EXPERIMENTAL

1. TG studies on NTO and RSA NTOates:

(i) Dynamic TG:

Dynamic TG studies were undertaken on indegeneously fabricated TG apparatus[15]. The sample (30 mg, 100-200 mesh) was taken in a platinum crucible and TG data were undertaken in static air at heating rate of 5°C/min. The percent decomposed (α) values are plotted against temperature, °C (Figure 1) and the sdt (starting decomposition temperature) and fdt (final decomposition temperature) are presented in Table 1.

(ii) Isothermal TG:

Isothermal TG studies on compound Nos. 2,3,4,5,7,12,13 and 15 (weight 30 mg., 100-200 mesh) were taken in static air. The accuracy of the furnace was ± 1°C. The percent decomposed (α) values have been plotted against time (minute). The activation energy for decomposition (E_d) values were obtained using Avrami-Erofeev (n=2) equation (1)[16-18], (Table 2).

$$-\left[\ln(1-\alpha)\right]^{1/2} = kt \qquad \ldots.(1)$$

2. DTA studies on NTO and RSA NTOates:

DTA studies on compound Nos. 1,3,4,5,9,11 and 16 were carried out in static air at HEMRL, Pune using 5.0 mg (100-200 mesh) of the samples at a heating rate of 10°C/min and thermograms are given in Figure 2.

3. Explosion delay measurements on NTO and RSA NTOates :

The explosion delay (D_E) measurements were undertaken by the tube furnace (TF) technique as described in our earlier publications[1-4]. The sample (weight = 20 mg, 100-200 mesh) was taken in ignition tube (5 cm length and 0.4 cm diameter) and the time interval between the insertion of the tube into the TF and the moment of an audible explosion, noted with the help of a stop watch with accuracy of 0.1 second, gave the value of D_E. The ignition tube loaded with the sample, clamped in a bent wire, was inserted manually into the TF upto a fix depth (8 cm) just above the probe of the temperature indicator cum controller (Century, CT 808T). The time taken for insertion of the ignition tube was also kept constant throughout the measurements. The accuracy of TF was ±1°C. Each reading was repeated three times, and mean D_E values are reported in Table 3. The explosion temperature (ET) for these samples were taken at D_E of 15 seconds and data are given in Table 3. D_E data were found to fit in the following equation (2)[19-21].

$$1/D_E = Ae^{E^*/RT} \qquad \ldots.(2)$$

where E^* is the activation energy for explosion and T is the absolute temperature. Typical plots are shown in Figure 3.

RESULTS AND DISCUSSION

TG results reported in Figure 1 and Table 1 clearly show that two types of decomposition mechanisms are involved for the thermolysis of RSA NTOates. Compound Nos. 2-5,7,12,13 and 15 (Figure 1A) seems to decompose in two steps, firstly amine part is given off leaving NTO which then thermolyze to liberate gaseous products. Liberation of amines does not seem to involve during thermolysis of rest of the compounds (Figure 1B). They are giving sigmoidal curves and the whole molecule seems to decompose to gaseous products. Two types of DTA thermograms (Figure 2) are also obtained for these compounds. The liberation of amines is quite evident in case of compound Nos. 3 & 5 as the temperature and shape of exothermic peaks (very sharp) are quite comparable with that of NTO. On the other hand, compound Nos. 9,11 and 16 gave smaller and medium exotherms at lower temperatures as compared to NTO. Moreover, these are not superimposable with NTO peak.

The decomposition pathways (a and b) shown in Scheme I are based on the TG results described above. It seems that RSA NTOates (I) decomposes in solid phase, via proton transfer (N-H bond heterolysis) to form corresponding amine and NTO molecules. It is reported[22,23] that the basicity of the anion (3-Nitro-1,2,4-triazole-5-onate) increases with the rise in temperature till it reaches the basic strength of the arylamine. At this temperature, the anion base removes the proton from arylammonium ion to generate corresponding arylamine and NTO molecules. However, the N-H bond heterolysis occurs through an activated complex (Scheme I, step 1). Proton transfer seems to occur in case of compound Nos. 2-5, 7, 12, 13 and 15 (Figure 1A). Further, the arylamine is given off as vapours at higher temperatures (Figure 1A, Part a ⟶ b). The α values, experimental and theoretical, represented in Table 1 also support the evolution of amines. Such type of proton transfer has also been reported by many workers[1,2,5,6,24-29] for various ammonium salts. Part b ⟶ c of the curve (Figure 1A) represents the stability of the NTO in the temperature range (~175-275°C). The NTO decomposition seems to involve the formation of NO_2 as reported[30,31] earlier, NO_2 may rapidly reacts with the heterocyclic backbone (Figure 1A, Part c ⟶ d) to cause explosion liberating secondary oxidation and reduction products of carbon and nitrogen (step 3, Scheme I). Compound Nos. 6,8,9,10,11,14 and 16 seems to decompose via NO_2 formation followed by oxidation - reduction reactions (Scheme I, route 2a and b) to cause explosion. It is very clear from the Table 1 that among the series A NTOate and salts having substituents $2\text{-}CH_3$, $3\text{-}CH_3$, $4\text{-}CH_3$, 3-Cl, $4\text{-}NO_2$, $2\text{-}OCH_3$ and $2\text{-}OC_2H_5$ have lower sdt (< 100°C) whereas $4\text{-}CO_2HA$ NTOate showed the highest value of sdt (138°C) and fdt (372°C).

The kinetics of the thermal decomposition of RSA NTOates ($R=H$, $2-CH_3$, $3-CH_3$, $4-CH_3$, 3-Cl, $2-OCH_3$, $3-OCH_3$ and $2-OC_2H_5$) was evaluated using Avrami-Erofeev ($n=2$) equation and their rate constant and activation energy for thermal decomposition (E_d) are presented in Table 2. Thus, it is inferred that the rate controlling process, in the thermal decomposition of RSA NTOates, is two-dimensional random nucleation followed by the growth of nuclei.

Although all the RSA NTOates are found to be quite stable at room temperature, but they explode when subjected to higher temperatures (> 450°C). Therefore it was deemed to be of interest to undertake explosion delay measurements. All the RSA NTOates gave higher values D_E and ET as compared to NTO. It is observed that the E^* values are nearly half of the E_d values. It is reported that kinetic parameters vary with experimental conditions[32,33]

Summarising the data it can be concluded that thermolysis of some of the RSA NTOates involve evolution of amines prior to explosion. The other type of RSA NTOates explode without liberation of amine.

ACKNOWLEDGEMENTS

Thanks are due to DST, New Delhi for financial assistance . The Director, HEMRL, Pune is also thanked for DTA studies and Head, Chemistry Department, Gorakhpur University, for laboratory facilities.

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Table 1

Decomposition parameters for NTO and RSA NTOates

Compound No.	IUPAC Name	Acronym	Decomposition of NTO and RSA NTOates		α from Dynamic TG	
			sdt^{*} (°C)	$fdt^{\#}$ (°C)	Theoretical	Observed
1.	3-Nitro-1,2,4-triazole-5-one	NTO	132	447	-	-
2.	Anilinium 3-nitro-1,2,4-triazole-5-onate	A NTOate	93	345	41.7	42.6
3.	2-Methylanilinium 3-nitro-1,2,4-triazole-5-onate	2-CH_3A NTOate	96	270	45.1	53.3
4.	3-Methylanilinium 3-nitro-1,2,4-triazole-5-onate	3-CH_3A NTOate	99	327	45.1	45.3
5.	4-Methylanilinium 3-nitro-1,2,4-triazole-5-onate	4-CH_3A NTOate	92	260	45.1	48.0
6.	2-Chloroanilinium 3-nitro-1,2,4-triazole-5-onate	2-ClA NTOate	114	363	42.3	5.3
7.	3-Chloroanilinium 3-nitro-1,2,4-triazole-5-onate	3-ClA NTOate	78	261	42.3	42.6
8.	2-Nitroanilinium 3-nitro-1,2,4-triazole-5-onate	2-NO_2A NTOate	135	258	51.5	22.6

(Continued)

Table 1 (Continued)

9.	3-Nitroanilinium 3-nitro-1,2,4-triazole-5-onate	3-NO_2A NTOate	137	300	51.5	41.3
10.	4-Nitroanilinium 3-nitro-1,2,4-triazole-5-onate	4-NO_2A NTOate	70	342	51.5	5.3
11.	4-Carboxylanilinium 3-nitro-1,2,4-triazole-5-onate	4-CO_2HA NTOate	138	372	51.4	4.0
12.	2-Methoxyanilinium 3-nitro-1,2,4-triazole-5-onate	2-OCH_3A NTOate	75	267	48.6	56.0
13.	3-Methoxyanilinium 3-nitro-1,2,4-triazole-5-onate	3-OCH_3A NTOate	126	243	48.6	45.3
14.	4-Methoxyanilinium 3-nitro-1,2,4-triazole-5-onate	4-OCH_3A NTOate	110	340	48.6	6.6
15.	2-Ethoxyanilinium 3-nitro-1,2,4-triazole-5-onate	2-OC_2H_5A NTOate	95	270	51.3	48.0
16.	4-Ethoxyanilinium 3-nitro-1,2,4-triazole-5-onate	4-OC_2H_5A NTOate	160	303	51.3	4.0

* starting decomposition temperature; # final decomposition temperature

TABLE - 2

Kinetic Parameters for NTO and RSA NTOates from Isothermal TG

Compound No.	$K(10^{-3})/Min.$ (Temp. °K)				Ed (K.Cal/Mole)
2.	40.0	75.0	150.0	-	13.07
	(413)	(433)	(443)		
3.	21.1	33.3	83.3	95.0	9.15
	(383)	(393)	(413)	(428)	
4.	8.6	17.3	38.8	106.0	18.30
	(398)	(408)	(428)	(438)	
5.	13.0	25.3	70.0	160.0	11.44
	(438)	(455)	(463)	(483)	
7.	125.0	141.0	186.0	225.0	12.99
	(473)	(483)	(498)	(513)	
12.	40.9	62.0	83.3	114.0	11.74
	(398)	(408)	(418)	(433)	
13.	24.0	46.0	70.0	90.0	13.31
	(433)	(448)	(463)	(483)	
15.	21.2	29.0	52.9	72.2	12.81
	(408)	(418)	(433)	(453)	

TABLE - 3

Explosion Delay (D_E), Explosion Temperature (ET) and Activation Energy for Explosion (E^*) of NTO and RSA NTOates

Compound No.	D_E at					ET, °C for D_E of 15 Seconds	E^* (K.Cal/Mole)
	475°C	500°C	525°C	550°C	575°C		
1.	14.7±0.1	13.8±0.5	10.5±0.7	8.5±0.1	7.8±0.1	481	7.56
2.	22.9±0.6	21.3±0.2	17.4±0.2	13.1±0.3	11.8±0.1	537	6.86
3.	29.0±0.2	26.5±0.9	15.4±0.5	14.5±0.5	13.3±0.5	544	17.43
4.	16.8±0.4	15.5±0.2	12.2±0.4	11.5±0.2	10.3±0.6	497	6.21
5.	19.9±0.4	18.7±0.3	11.4±0.5	10.4±0.2	8.9±0.1	504	9.63
6.	18.8±0.3	17.3±0.1	11.2±0.2	9.8±0.1	9.3±0.1	525	8.69
7.	21.7±0.4	20.3±0.2	13.5±0.3	11.4±0.2	10.2±0.1	519	10.11
8.	22.9±0.5	21.0±0.4	11.4±0.3	9.7±0.3	9.1±0.0	512	13.72
9.	16.8±0.3	15.3±0.2	11.3±0.5	10.3±0.8	7.5±0.3	495	8.32
10.	19.9±0.4	18.3±0.0	11.7±1.4	10.1±0.0	9.2±0.2	527	10.16
11.	22.6±0.9	17.0±0.0	14.3±0.2	11.0±0.4	8.2±0.5	516	12.20
12.	16.5±0.3	11.8±0.2	11.0±0.2	10.4±0.4	8.8±0.1	475	5.63
13.	14.7±0.2	12.6±0.3	11.2±0.2	9.8±0.4	8.0±0.1	477	6.71
14.	17.6±0.3	15.7±0.4	9.7±0.3	8.3±0.1	7.7±0.3	497	12.12
15.	18.9±0.2	17.7±0.1	13.4±0.5	11.2±0.2	10.6±0.3	512	7.24
16.	16.3±0.3	14.9±0.1	10.5±0.3	9.5±0.1	8.1±0.3	491	8.64

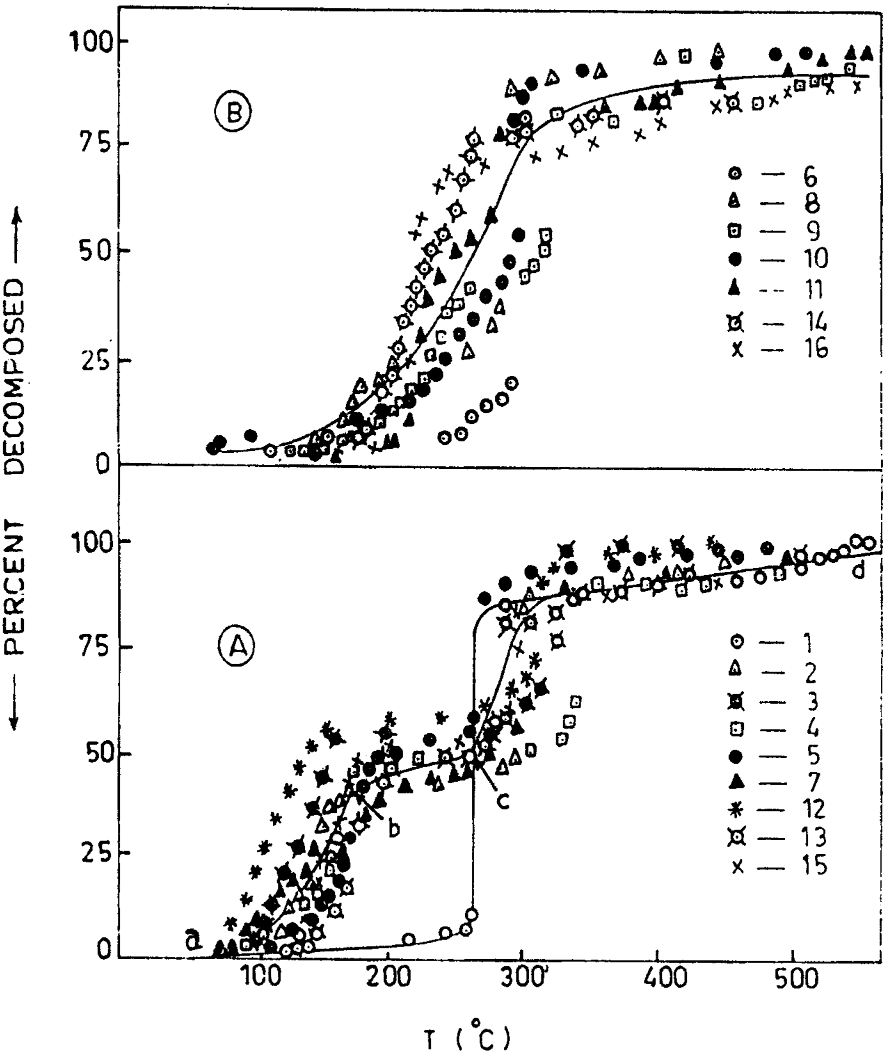


Figure 1 : TG Thermograms of NTO and RSA NTOates.

(A) : 1=NTO; 2=H; 3=2-CH_3; 4=4-CH_3; 5=4-CH_3; 7=3-Cl; 12=2-OCH_3; 13=3-OCH_3; 15=OC_2H_5

(B) : 6=2-Cl; 8=2-NO_2; 9=3-NO_2; 10=4-NO_2; 11=4-CO_2H; 14=4-OCH_3; 16=4-OC_2H_5.

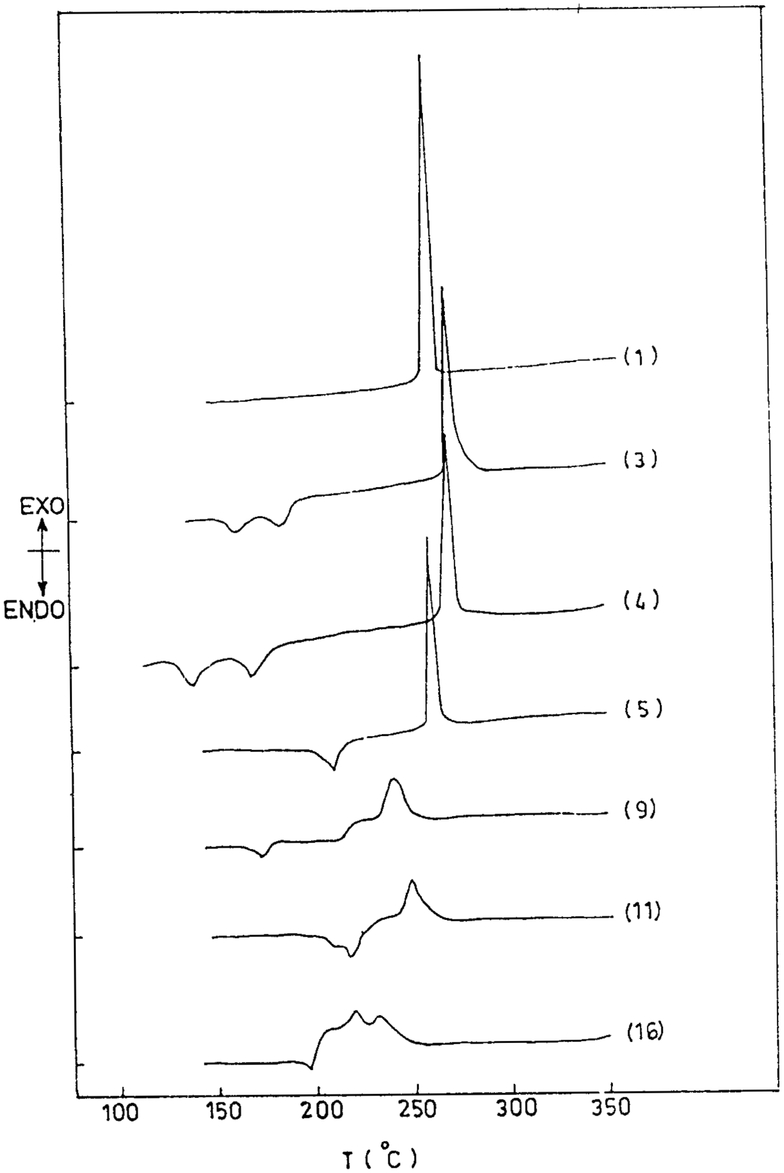


Figure 2 :

DTA Traces of NTO and RSA NTOates.

1=NTO; 3=2-CH_3; 4=CH_3; 5=4-CH_3; 9=3-NO_2; 11=4-CO_2H; 16=4-OC_2H_5.

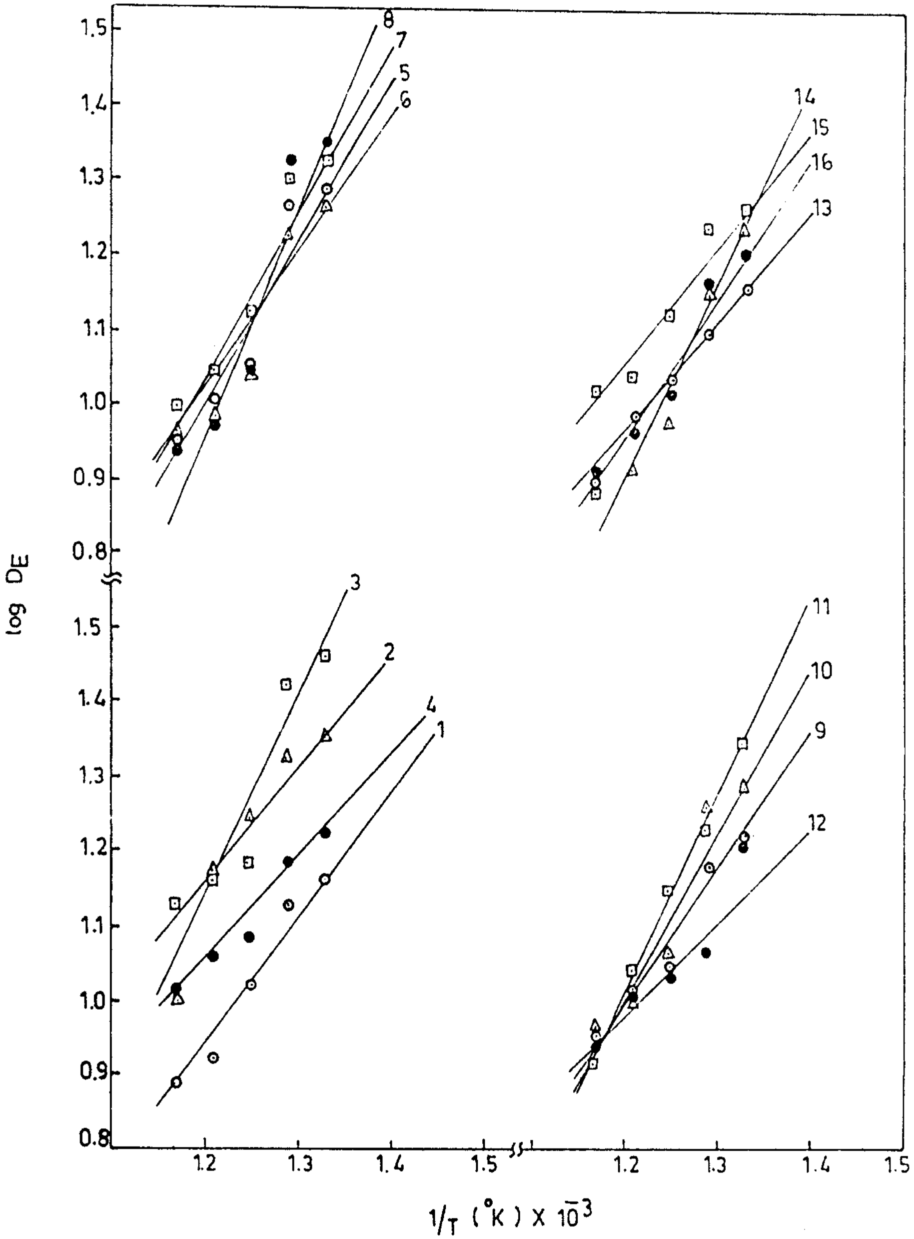
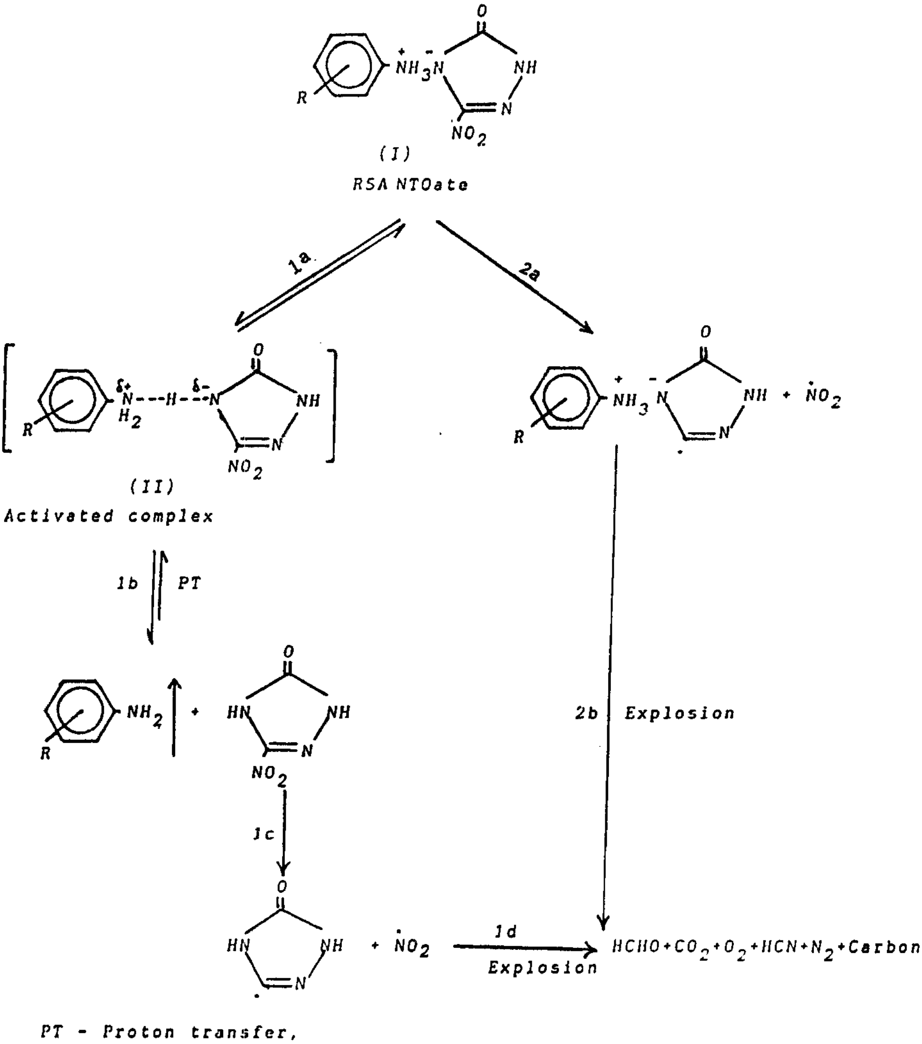


Figure 3 :

Plots of Log D_E Vs 1/T (°K) for NTO and RSA NTOates.



Scheme I - Schematic representation of thermolysis of RSA NTOates