

XRD, spectroscopic and thermal analysis studies on *trans*-1,4,5,8-tetranitrosotetraazadecalin (TNSTAD)

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(Received 20 August 1992; accepted 15 September 1992)

Abstract

The thermal decomposition of *trans*-1,4,5,8-tetranitrosotetraazadecalin (TNSTAD), a polycyclic polynitrosamine, has been studied with regard to the kinetics, mechanism, morphology and the gaseous products thereof, using thermogravimetry (TG), differential thermal analysis (DTA), IR spectroscopy, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and hot-stage microscopy. The crystal structure parameters obtained from the XRD pattern are $a = 10.785 \pm 0.005 \text{ \AA}$, $b = 10.785 \pm 0.005 \text{ \AA}$, $c = 18.525 \pm 0.004 \text{ \AA}$; c/a ratio = 1.718.

The crystal belongs to the tetragonal system. IR spectra of TNSTAD have also been recorded and the bands assigned.

The kinetics of thermolysis has been followed by both isothermal TG and IR. The best linearity (with a correlation coefficient of 0.996) was obtained for the Jander's equation for the range 0–53% in isothermal TG. The activation energy was found to be $195.38 \text{ kJ mol}^{-1}$ and $\log(A \text{ in s}^{-1})$ was 18.21. The effect of a series of additives (incorporated to the extent of 5%) on the initial thermolysis of TNSTAD has also been studied. Evolved gas analysis by IR showed that HCHO, NO₂, NO and N₂O are produced in larger amounts than CO₂ and HCN. The cleavage of the N–N bond appears to be the primary step in the thermolysis of TNSTAD.

INTRODUCTION

Nitrosamines have many structural and chemical features in common with nitramines. However, in contrast to studies on the kinetics and mechanism of the thermal decomposition of nitramines, nitrosamines have received little attention. They have been implicated as products of the thermal decomposition of nitramines either by product analysis [1, 2] or by inference [3–5]. We found only a few papers [6–11] published on the thermal decomposition of nitrosamines in the condensed phase. A study of nitramines in which the nitramine functionality is replaced by a nitrosamine will advance the cause of understanding the complex reaction pathways of nitramine decomposition, which is not yet fully understood. The present

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work therefore deals with the characterisation and thermal decomposition studies of *trans*-1,4,5,8-tetranitrosotetraazadecalin (TNSTAD), a polycyclic nitrosamine.

EXPERIMENTAL

TNSTAD was prepared in gram batches in the laboratory by previously reported methods [10, 11]. The reagents used were of either AnalaR or pro analysi grade. TG–DTA and isothermal TG were carried out on a Netzsch STA 409 thermal analyser. DTA with additives was carried out on an instrument fabricated in this laboratory. About 10 mg of the sample in a platinum cup was used for each run, with calcined alumina as the reference material. IR spectra were recorded on a Perkin-Elmer model 683 in the range of 4000–200 cm^{-1} in KBr matrix. For kinetics by IR, the experimental technique developed by Bent and Crawford [12] and Hisatsune et al. [13, 14], was used with some modifications. They found that when the KBr disc containing the sample was heated it lost its transparency but regained it on repressing. This repressing method was used for trapping the gases/decomposition products in the present study.

The kinetics was followed by the loose mix method. In this method the sample and matrix were thoroughly mixed and the desired isothermal temperature was achieved with programmed heating and control, using the same thermal cycle for a set of experiments. 200 mg of the mixture was withdrawn from the isothermal bath at regular intervals, sprinkled, cooled, smothered in the die, pelletised and scanned at normal temperature. In this way the kinetics determined were devoid of the problems encountered by earlier workers.

A special gas cell with a furnace was designed for identifying the gases evolved in the thermal decomposition. The heating of the furnace was programmed through a Stanton Redcroft temperature programmer and controller using a Cr–Al thermocouple. 10 mg of the sample was placed in the sample tube and connected to the IR gas cell. The IR gas cell was sealed with freshly prepared KBr pellet. A similar gas cell sealed with KBr discs was used as the reference. The IR spectra of gaseous molecules obtained on heating was assigned by comparing with reported spectra [15].

XRD patterns were recorded on a Philips diffractometer model 1390 using nickel filtered $\text{Cu K}\alpha_1$ radiation. DSC experiments were carried out on Perkin-Elmer DSC-7 and hot-stage microscopy with a Leitz polarising microscope.

RESULTS

The results of the IR studies on TNSTAD are summarised in Fig. 1 and Table 1. XRD studies of the sample by powder diffraction show that the sample belongs to the tetragonal crystal system with a c/a axial ratio of 1.718 (Fig. 2 and Table 2).

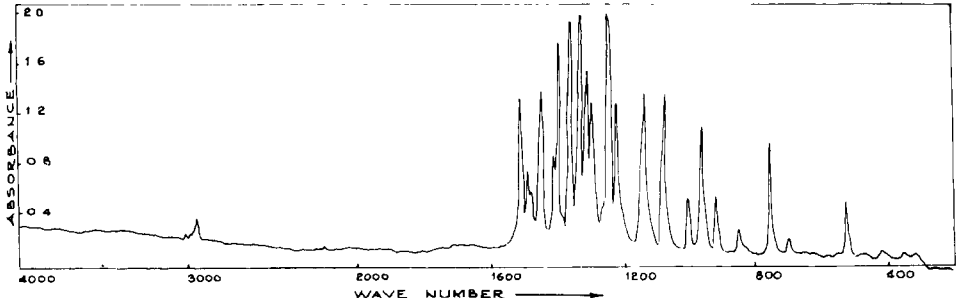


Fig. 1. IR Spectra of TNSTAD.

TABLE 1
IR spectral assignments of TNSTAD

Wavenumber (cm ⁻¹)		Assignments
3080 w	3000 w	CH ₂
2940 w		
1480 s		N–N=O
1465 m	1450 w	δ CH ₂
1440	1410 s	Scissoring
1380 s	1370 s	CH ₂ wagging/twisting
1330 s	1310 s	
1280 s	1270 s	N–N=O
1220 s	1190 s	
1110 s	1055 s	Ring
975 m	935 s	CH ₂ rocking
900 m		
830 m	740 s	Ring
680 m		δ N–N=O

Key: m = medium; s = sharp; sh = shoulder; w = weak; vs = very strong.

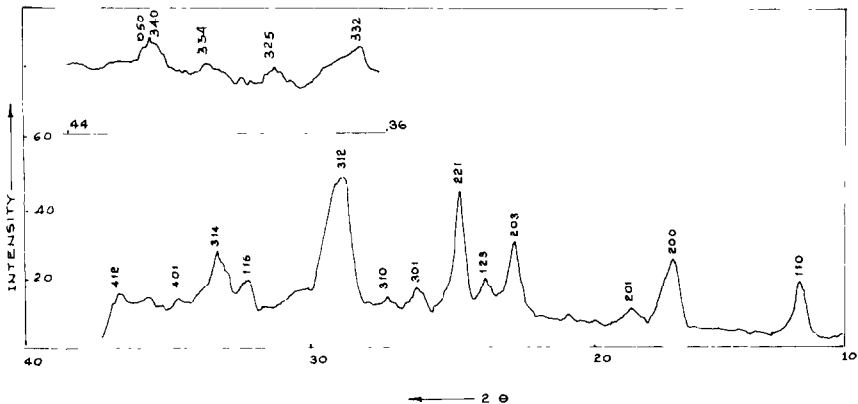


Fig. 2. XRD Pattern of TNSTAD.

TABLE 2

Intensities, d values and refined crystal data of TNSTAD calculated from the Bragg angle ^a

Line No.	Bragg angle θ (deg)	Intensity (%)	d_{hkl} (Å)	$\text{Sin}^2 \theta$		d_{hkl}
				Exptl.	Calcd.	
1	5.800	47	7.629	0.0102	0.0102	110
2	8.100	59	5.493	0.0199	0.0204	200
3	8.800	18	5.040	0.0234	0.0222	201
4	10.875	71	4.087	0.0356	0.0360	203
5	11.400	18	3.901	0.0307	0.0414	123
6	11.875	100	3.747	0.0423	0.0426	221
7	12.600	21	3.534	0.0476	0.0477	301
8	13.125	12	3.395	0.0516	0.0511	310
9	13.900	100	3.209	0.0577	0.0580	312
10	15.600	29	2.867	0.0726	0.0728	116
11	16.200	41	2.764	0.0778	0.0788	314
12	16.800	12	2.668	0.0835	0.0835	401
13	17.850	12	2.514	0.0939	0.0938	412
14	18.300	18	2.455	0.0986	0.0982	332
15	19.350	12	2.326	0.1098	0.1097	325
16	20.200	18	2.232	0.1192	0.1197	334
17	20.900	18	2.161	0.1273	0.1278	050/340

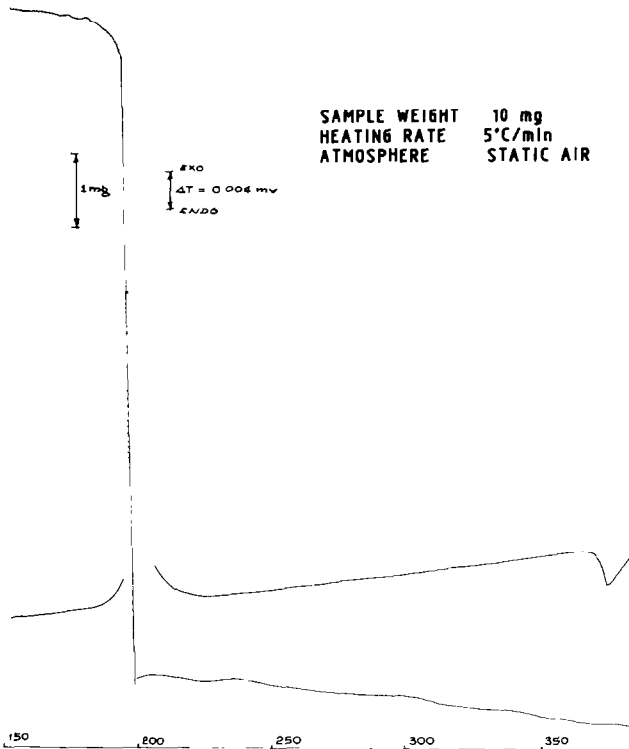
^a $a = 10.785 \text{ \AA}$; $b = 10.785 \text{ \AA}$; $c = 18.525 \text{ \AA}$; c/a axial ratio = 1.718.

Fig. 3. TG-DTA of TNSTAD.

Figure 3 gives the simultaneous TG–DTA results of TNSTAD recorded in a static air atmosphere at a heating rate of $5^{\circ}\text{C min}^{-1}$. The TG curve yielded a sharp change in weight of about 90% in the temperature range 192–208°C. Thereafter a further loss in weight of about 8% was observed in the temperature range 208–406°C.

The DTA in static air atmosphere (Fig. 3) showed a pronounced exothermic change in the temperature range 192–221°C with a peak maximum at 210°C. Thereafter no change in the DTA was noticed until 364°C. A sharp endotherm was thereafter noticed in the temperature range 364–391°C.

EFFECT OF ADDITIVES

The DTA of TNSTAD was recorded to study the effect of metal oxides/additives (incorporated to the extent of 5%) on the thermolysis. From the DTA traces the initial temperature of decomposition T_i , the temperature of peak maximum T_m and the final temperature of decomposition T_f were evaluated. These values, arranged in the order of increasing temperature of peak maximum, are given in the Table 3.

TABLE 3

The effect of additives on the initial thermolysis of TNSTAD

Sr No.	Additives	Temperature of decomposition ($^{\circ}\text{C}$)		
		T_i	T_m	T_f
1	Monobasic copper stearate	161	194	206
2	Copper chromite	182	200	204
3	Beryllium oxide	198	204	223
4	Lead monoxide	203	208	214
5	Zirconium dioxide	201	209	229
6	TNSTAD	192	210	221
7	Nickel oxide	204	211	223
8	Cupric oxide	196	212	221
9	Thorium oxide	204	212	229
10	Cuprous oxide	205	212	223
11	Magnesium oxide	206	212	220
12	Ferric oxide	207	213	220
13	Cobaltic oxide	211	213	231
14	Lanthanum oxide	208	214	220
15	Hydroquinone	209	214	224
16	Titanium dioxide	209	216	221
17	Cerium oxide	211	217	229
18	Monobasic lead stearate	205	219	228

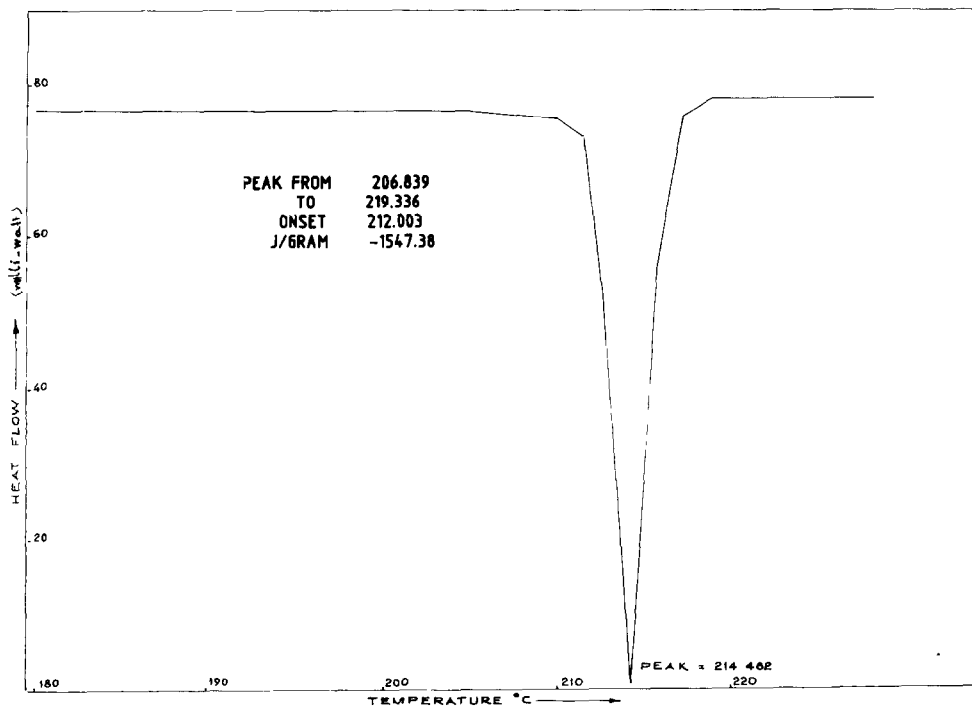
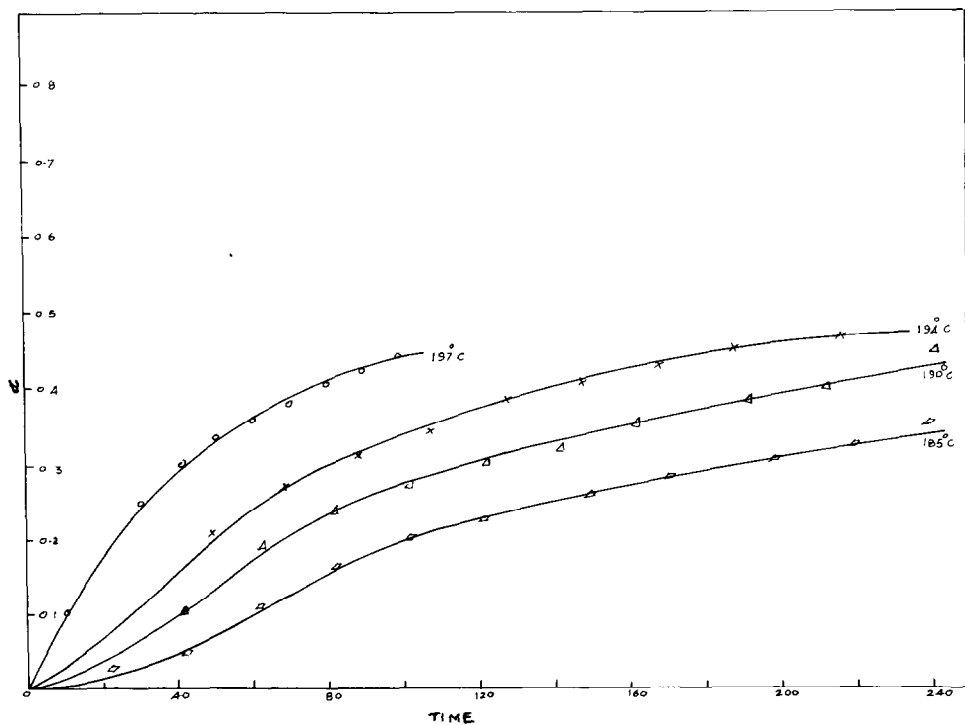


Fig. 4. DSC Trace of TNSTAD.

Fig. 5. Plot of α vs. t for the thermal decomposition of TNSTAD (TG).

It can be seen from Table 3 that monobasic copper stearate, copper chromite, beryllium oxide, lead monoxide and zirconium dioxide brought down the temperature of the peak maximum, thereby indicating that they accelerated the initial thermolysis; the others decelerated the initial thermolysis of TNSTAD. All the initial thermolysis reactions took place in the solid state.

DSC STUDIES

The DSC curve (Fig. 4) shows a sharp dominant exothermic change, covered by an energy change of 1547.38 J g^{-1} in the temperature range $207\text{--}219^\circ\text{C}$, with a peak maximum at 214°C .

KINETICS BY ISOTHERMAL TG

The kinetics [16] of the isothermal decomposition of TNSTAD at various temperatures in the temperature range $185\text{--}197^\circ\text{C}$ under static air atmosphere was studied. From these results the fraction decomposed α at

TABLE 4

Correlation coefficient R obtained for various $F(\alpha)$ by isothermal TG

No.	$F(\alpha)$	Isothermal temperature ($^\circ\text{C}$)			
		185	190	194	197
1	α	0.9701	0.9545	0.9329	0.9080
2	α^2	0.9943	0.9945	0.9888	0.9857
3	$\alpha^{1/2}$	0.9414	0.9105	0.8789	0.8386
4	$\alpha^{1/3}$	0.9292	0.8919	0.8566	0.8121
5	$\alpha^{1/4}$	0.9226	0.8818	0.8448	0.7984
6	$1 - (1 - \alpha)^{1/2}$	0.9762	0.9656	0.9492	0.9291
7	$1 - (1 - \alpha)^{1/3}$	0.9780	0.9689	0.9542	0.9356
8	$[-\ln(1 - \alpha)]$	0.9814	0.9749	0.9633	0.9477
9	$[-\ln(1 - \alpha)]^{3/2}$	0.9656	0.9508	0.9326	0.9052
10	$[-\ln(1 - \alpha)]^{1/2}$	0.9552	0.9348	0.9128	0.8792
11	$[-\ln(1 - \alpha)]^{1/3}$	0.9430	0.9162	0.8901	0.8504
12	$[-\ln(1 - \alpha)]^{1/4}$	0.9363	0.9059	0.8776	0.8351
13	$(1 - \alpha)[\ln(1 - \alpha)] + \alpha$	0.9946	0.9961	0.9937	0.9919
14	$[1 - (2/3)\alpha] - (1 - \alpha)^{2/3}$	0.9945	0.9964	0.9950	0.9936
15	$[1 - (1 - \alpha)^{1/3}]^2$	0.9942	0.9966	0.9971	0.9960
16	$\ln [\alpha/(1 - \alpha)]$	0.9246	0.8900	0.8611	0.8145
17	$[1/(1 - \alpha)] - 1$	0.9891	0.9884	0.9842	0.9763
18	$\ln \alpha$	0.9009	0.8490	0.8061	0.7562

given time t was evaluated. For evaluating the rate constants the curve of α vs. t (Fig. 5) was analysed, using various kinetic expressions listed in Table 4 and a computer program. The best linearity with a correlation coefficient of 0.996 was obtained for Jander's equation $[1 - (1 - \alpha)^{1/3}]^2$ for the range of 0–53% α . Close correlation was observed with the diffusion controlled equation and also with the two-dimensional diffusion controlled equation (Table 4).

The rate constants were obtained from the slope of the plots of the above equation and were substituted in the Arrhenius equation. The activation energy calculated from the slope of this plot was 195.38 kJ mol⁻¹ and log(A in s⁻¹) was 18.21.

KINETICS BY IR SPECTROSCOPY

In IR the variation in the intensity of the nitroso band at 1480 cm⁻¹ was used to monitor the decomposition by the loose mix method.

The curve of α vs. t thus obtained (Fig. 6) was analysed using various rate equations to evaluate the rate constants. Close correlation was observed with the one-dimensional diffusion controlled equation α , α^2 , the two-dimensional diffusion controlled equation $(1 - \alpha)[\ln(1 - \alpha)] + \alpha$ and the

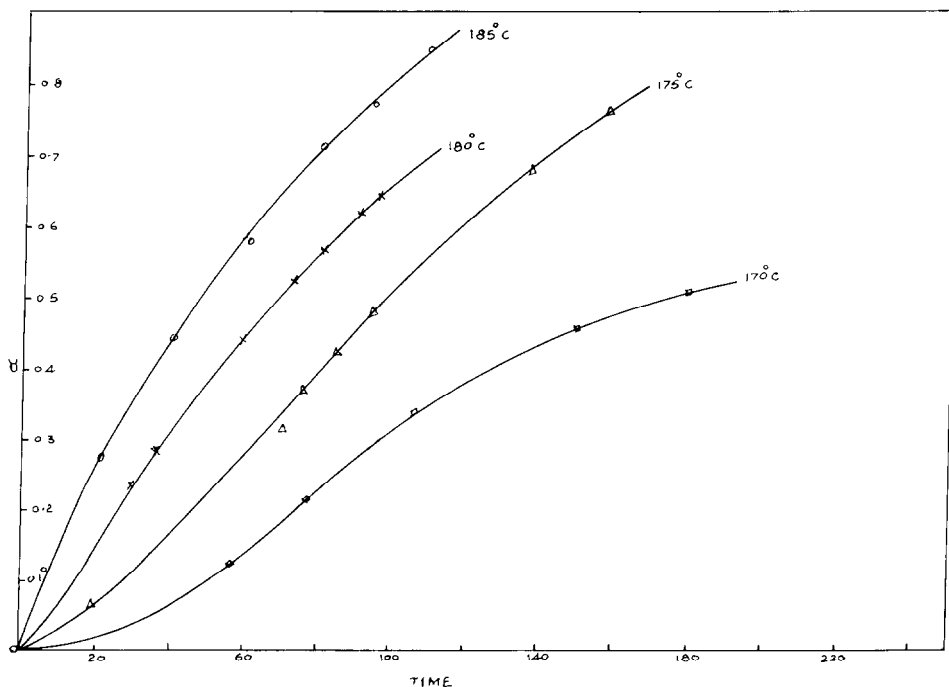


Fig. 6. Plot of α vs. t for the thermal decomposition of TNSTAD (IR).

TABLE 5

Correlation coefficient R obtained for various $F(\alpha)$ by IR

No.	$F(\alpha)$	Isothermal temperature (°C)			
		170	175	180	185
1	α	0.9483	0.9776	0.9983	0.9880
2	α^2	0.9954	0.9781	0.9873	0.9963
3	$\alpha^{1/2}$	0.8895	0.9678	0.9944	0.9687
4	$\alpha^{1/3}$	0.8644	0.9630	0.9917	0.9599
5	$\alpha^{1/4}$	0.8509	0.9604	0.9900	0.9551
6	$1 - (1 - \alpha)^{1/2}$	0.9748	0.9793	0.9970	0.9978
7	$1 - (1 - \alpha)^{1/3}$	0.9812	0.9784	0.9955	0.9984
8	$[-\ln(1 - \alpha)]$	0.9899	0.9744	0.9908	0.9955
9	$[-\ln(1 - \alpha)]^{3/2}$	0.9686	0.9781	0.9975	0.9985
10	$[-\ln(1 - \alpha)]^{1/2}$	0.9502	0.9776	0.9987	0.9963
11	$[-\ln(1 - \alpha)]^{1/3}$	0.9264	0.9757	0.9985	0.9914
12	$[-\ln(1 - \alpha)]^{1/4}$	0.9125	0.9741	0.9979	0.9880
13	$(1 - \alpha)[\ln(1 - \alpha)] + \alpha$	0.9944	0.9696	0.9769	0.9890
14	$[1 - (2/3)\alpha] - (1 - \alpha)^{2/3}$	0.9919	0.9649	0.9720	0.9840
15	$[1 - (1 - \alpha)^{1/3}]^2$	0.9838	0.9541	0.9612	0.9715
16	$\ln[\alpha/(1 - \alpha)]$	0.9071	0.9742	0.9982	0.9910
17	$[1/(1 - \alpha)] - 1$	0.9819	0.9460	0.9643	0.9576
18	$\ln \alpha$	0.8071	0.9514	0.9843	0.9390

diffusion controlled Ginstling and Brounstein equation $[1 - (2/3)\alpha] - (1 - \alpha)^{2/3}$ (Table 5). The latter equation, however, gave the best linear Arrhenius plot and hence was used for the evaluation of the rate parameters. The activation energy was found to be $150.21 \text{ kJ mol}^{-1}$ and $\log(A \text{ in s}^{-1})$ was 14.31. There is thus a difference in the rate parameters arrived at by TG and IR. This may be due to the fact that the TG data pertains to global kinetics whereas the data by IR is specific to the nitroso group.

EVOLVED GAS ANALYSIS BY IR

Gaseous species evolved when 10 mg of the sample was decomposed at controlled heating rate of $10^\circ\text{C min}^{-1}$ were identified using IR spectroscopy. Around 200°C the decomposition was spontaneous, liberating various gaseous products, which are given in Table 6, along with the spectra (Fig. 7). From the intensities of the IR bands it was found that formaldehyde, nitrous oxide, nitrogen dioxide and nitric oxide are produced in larger amounts than carbon dioxide and hydrogen cyanide.

MICROSCOPIC STUDIES

At room temperature the crystals are needle shaped and transparent. As the temperature is increased the transparency continues to decrease. At

TABLE 6
Gaseous thermolysis products of TNSTAD (IR spectra)

Gaseous species	Wavenumber (cm ⁻¹)	
	Reported	Observed
Nitrogen dioxide	1730 st	1740
	1625 st	1630
		1610
	1258 st	1260
	754 st	760
Formaldehyde	2900 st	2900
	1760 st	1760
	1702 m	1710
Nitrous oxide	2565 st	2560
	2220 st	2220
	1309 st	1310
	1250 st	1240
Hydrogen cyanide	3246 m	3280
	1379 st	1360
	720 st	720
Nitric oxide	1840 m	1810
	1760 m	1790
Carbon dioxide	2340 st	2340
	720 m	720
	666 st	660

Key: m = medium; st = strong.

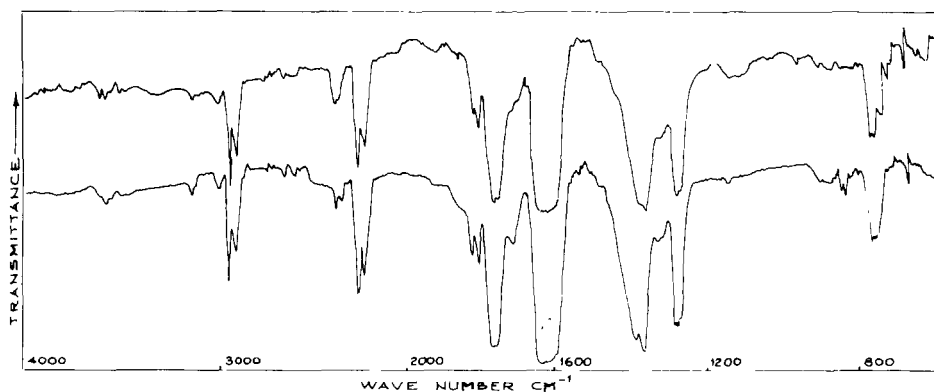


Fig. 7. Gaseous decomposition products of TNSTAD (IR spectra).

190°C random movements were noticed. At 230°C evolution of brown gases sets in and finally a black carbonaceous residue is left behind.

DISCUSSION

The TG–DTA results (Fig. 3) indicate that the thermal decomposition of TNSTAD proceeds in two stages. During the thermal decomposition studies of TNSTAD by IR it was found that although the intensities of the bands due to nitroso and other groups decreased with time, new bands developed and increased in intensity in the KBr pellet and in the loose mix.

In the loose mix method new bands at 3420, 1670, 1630, 1530 and 1380 cm^{-1} were noticed. The bands at 3420, 1630 and 1530 cm^{-1} are best ascribable to a trans amide group formed during the course of the reaction; the band at 1670 cm^{-1} to the C=N group.

In the usual pellet method, in addition to the above bands, new bands at 2340 and 2220 cm^{-1} were observed (Fig. 8). The bands at 2340 and 2220 cm^{-1} can be ascribed to species like CO_2 (2340 cm^{-1}) and N_2O (2220 cm^{-1}), which are trapped in the matrix. The band at 1380 cm^{-1} may arise from the nitrate ion formed by the physisorbed oxygen reacting with the large quantity of NO formed, producing the NO_2 radical, which subsequently reacts with the KBr matrix (Fig. 8). Oyumi and Brill [17] have

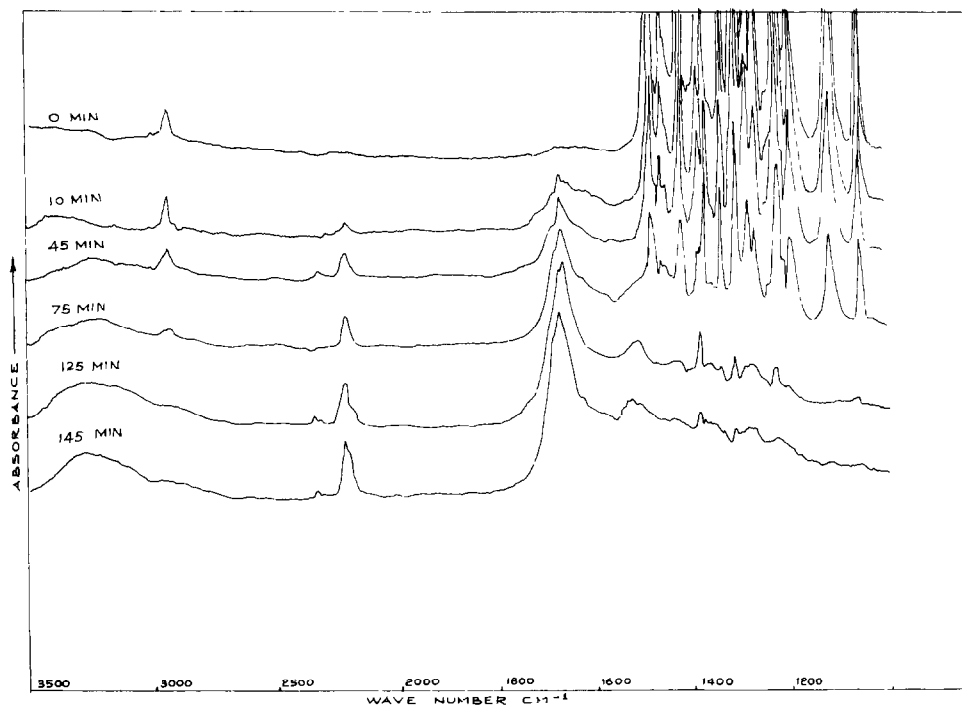


Fig. 8. IR Spectra of TNSTAD at 185°C in KBr pellet.

suggested such a mechanism to account for the large quantities of NO_2 produced by the thermal decomposition of 1,3,5-trinitroso-1,3,5-triazacyclohexane (TRDX). The band at 1380 cm^{-1} may also arise from the nitrate intermediate formed by the combination of the NO_2 with the other ring fragments.

A weak band at 1730 cm^{-1} assignable to $-\text{N}-\text{CH}_2\text{CHO}-$ was noticed in the loose mix method at the end of isothermal studies, most probably arising from further degradation of the residue.

In the IR experiment at 185°C the reaction lasted for about 155 min when the sample was pelletised, compared to 100 min in the loose KBr mix. The latter results suggest that consolidation prevents the escape of decomposition products from the matrix and this in turn decelerates the decomposition. This is consistent with the observation of bands due to CO_2 (2340 cm^{-1}) and N_2O (2220 cm^{-1}) in the pellet method, because these bands were not observed in the loose mix method.

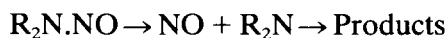
In evolved gas analysis (Fig. 7), nitrous oxide, nitrogen dioxide, formaldehyde and nitric oxide are the dominant gaseous decomposition products detected. Oyumi and Brill [17], however, have reported formaldehyde as a significant product only at elevated pressures. The IR spectra also showed smaller quantities of carbon dioxide and hydrogen cyanide.

Thermolysis studies of various N–NO compounds indicate [6–9, 17–21] that N–N bond fission is the most important initial step in the thermal decomposition of nitrosamines. The energy of dissociation of the N–NO bond in nitrosamines is strongly dependent on the nature of the substituent [6] in the molecule $\text{R}-\text{N}(\text{NO})\text{R}$. Pepekin et al. [8] are of the opinion that the energy of the N–N bond in nitrosamines may vary in the range $168.0\text{--}231.0\text{ kJ mol}^{-1}$, depending upon the electronegativity of the amino nitrogen atom linking the nitroso group. They also observed that when $\text{R} = \text{alkyl}$, the strength of the N–NO bond exceeds 210 kJ mol^{-1} . However, if $\text{R} = \text{nitroalkyl}$, the energy of the bond decreases to 168 kJ mol^{-1} . Golavnova et al. [9] observed that the N–N bond dissociation energy in nitrosopiperidine is $172.2\text{--}176.4\text{ kJ mol}^{-1}$, compared to the value of 231 kJ mol^{-1} observed for aliphatic N-nitrosamines.

Lure et al. [21] studied the thermal decomposition of TRDX in the melt phase and concluded from the rate expressions that autocatalysis is an important stage in the thermal decomposition of TRDX. They proposed that formation of radical and C-nitroso intermediates are important in the initial thermolysis of this compound. FT-IR studies of the gaseous species evolved initially showed that nitric oxide is the most prominent gaseous decomposition product. Based on the observations with TRDX, Oyumi and Brill [17] proposed that N–N bond homolysis is the most important initial step in the thermal decomposition of nitrosamines. They also observed that nitrous oxide is a dominant product at all heating rates they used, which implied that C–N bond cleavage becomes competitive at later stages of the

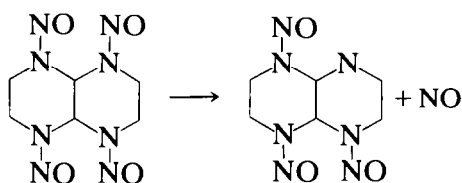
thermal decomposition. Oyumi and Brill report that at higher pressures the predominant pathway is C–N bond homolysis, not N–N bond homolysis.

The molar N–NO bond enthalpies for heterocyclic *N*-nitrosamines are significantly lower than those for O–N or C–C bonds, and the cleavage of the N–NO bond occurs for virtually all nitrosamines [22] on heating. This may be represented as

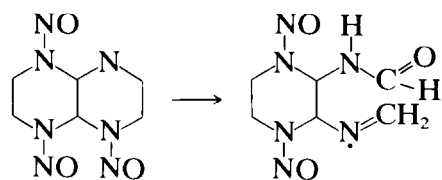


These reactions thus form the basis of the degradative decomposition of *N*-nitrosamines. The primary step in the decomposition of TNSTAD is thus the cleavage of the N–N bond.

Strong IR evidence for the formation of groups like N=CH and NHCHO can be rationalised by postulating a reaction mechanism for TNSTAD as below, involving the cleavage of the C–C bond after the cleavage of the N–N bond.



In the next stage, C–N bond fission could occur, giving rise to products like CH₂O and N₂O. The intensity of the N₂O band is strong, so it would appear that as time elapses there is a competition between the N–N, C–C and C–N bond dissociations.



KINETICS OF INITIAL THERMOLYSIS AND VELOCITY OF DETONATION

Zeman et al. [23–27] have proposed that the mechanism of the primary process of thermal decomposition occurring in polynitro compounds is identical to the primary chemical process in the detonation of polynitrosamines, nitramines, nitroarenes, nitric esters and tetrazoles, and that there exists a relation between the kinetic data of the low temperature

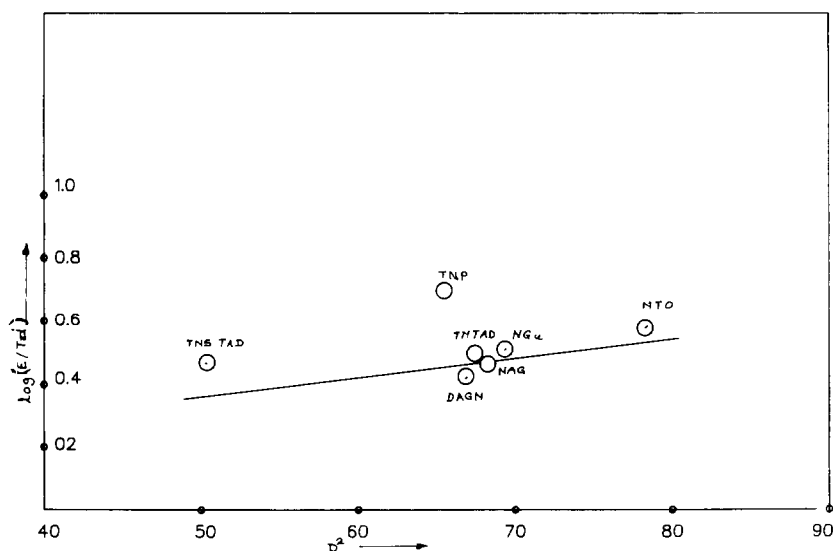


Fig. 9. Plot of $\log[(E \text{ in kJ mol}^{-1})/(T_d \text{ in K})]$ vs. detonation velocity.

thermolysis and the detonation parameters. Avachat [22], Naidu [28] and Kurian and co-workers [29] have reported that the correlation proposed by Zeman was found to be fairly valid for hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX), and hexahydro-1,3,5-trinitroso-s-triazine (TRDX [22]), diaminoguanidine nitrate (DAGN), nitroaminoguanidine nitrate [NAG], nitroguanidine (NGu [28]) and binary RDX–TNT systems [29], from the linearity of the plot of $\log(E/T_d)$ against D^2 using the isothermal kinetic data instead of the dynamic data (E = activation energy of the decomposition; T_d = initial decomposition temperature; $P = C-J$ pressure; ρ = crystal density).

The term P/ρ is directly proportional to D^2 , where D = velocity of detonation. Good correlation was observed between rate parameters for the initial thermolysis of TNSTAD as obtained by IR and its detonation parameters (Fig. 9).

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