Thermochimica Acta, 166 (1990) 241–249
Elsevier Science Publishers B.V., Amsterdam

THERMOLYSIS OF NITROARENES: 2,2′,4,4′,6,6′-HEXANITROSTILBENE *

L.M. MINIER and J.C. OXLEY **

Department of Chemistry, New Mexico Institute of Mining and Technology, Socorro, NM 87801 (U.S.A.)

(Received 16 February 1990)

ABSTRACT

Combined analysis techniques, including DSC, manometry and Fourier-transform IR spectrometry, have been used to determine kinetic parameters and to gain insight into the mechanism of liquid-phase thermolysis for HNS (2,2′,4,4′,6,6′-hexanitrostilbene) between 320 °C and 375 °C. Complete pyrolysis did not occur in this temperature range. Thermolysis products were CO_2, CO, N_2 and a polymeric residue. The resulting stoichiometry for the overall reaction at completion was

$$C_{14}H_6N_6O_{12} \rightarrow 3.3CO_2 + 0.4CO + 1.5N_2 + H_2O + C_{9.9}H_{4.2}N_3O_{4.1}$$

The calculated activation energies and frequency factors were as follows: 29.8 kcal mol^{-1} (125 kJ mol^{-1}) and $10^{8.8}$ s^{-1} from DSC data; and 29.4 kcal mol^{-1} (123 kJ mol^{-1}) and $10^{8.3}$ s^{-1} from manometric data. Real-time IR studies revealed the presence of CO_2, CO, HONO and NO_2.

INTRODUCTION

HNS, 2,2′,4,4′,6,6′-hexanitrostilbene, is a thermally stable secondary explosive (Fig. 1). The thermal stability of HNS (melting point 318 °C) permits its use at high temperatures where a conventional explosive, such as RDX, would not survive. Therefore, many applications for HNS have been found in the aerospace industry and in the military [1]. With the widespread use of HNS, concern arises regarding its thermal stability at lower-than-detonation temperatures. Are the handling and storage conditions for HNS safe? Will HNS still perform as expected after storage? Concerns such as these can be addressed by acquiring information on the thermal decomposition reactions and kinetics of HNS at low temperatures.

---

* Presented at the 18th Annual NATAS Conference, San Diego, CA, U.S.A., 24–27 September 1989.

** Author to whom correspondence should be addressed.

0040-6031/90/$03.50

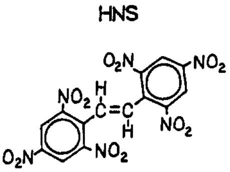

Fig. 1. Structure of *E*-2,2′,4,4′,6,6′-hexanitrostilbene (HNS).

Isothermal thermolyses were performed on liquid HNS from 320 °C to 375 °C to obtain information on the decomposition kinetics. In this temperature range, crystal-lattice effects were eliminated from the reactions; in addition, the reaction rates were readily measurable. However, the thermal decomposition appeared to be complex, making the reaction scheme difficult to elucidate.

EXPERIMENTAL

HNS, melting at 318 °C, was used as received from EG&G Applied Technologies. HNS samples were prepared and thermolyzed by the following procedure. A 1.0–1.7 mg quantity of HNS was sealed in a glass capillary melting-point tube under ambient atmosphere. The prepared tube was then completely immersed in an isothermal molten metal bath for the desired period of time. The amount of gas produced was measured by breaking the sealed tube in a mercury manometer, which had previously been calibrated under atmospheric conditions. The ratio of product gases contained in the sealed tubes was determined using a Varian 3600 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and PORPAK-Q column. Identification and quantification of the gas were established from retention times and standard curves.

Rate constants were obtained by two methods, manometric and differential scanning calorimetry (DSC). The manometric method measured the gas produced vs. time. An average of 15 runs were performed at each temperature. The DSC technique was similar to that described by Rogers [2,3]. The Perkin–Elmer DSC-4 was equipped with a TADS computer system. The sample was sealed in an aluminum DSC sample pan. The aluminum lid was pin-pricked to allow constant pressure throughout the analysis and to eliminate vapor-phase reactions. Rate constants (Table 1) were obtained by analysis of the decaying exothermic portion of the thermograms.

A Perkin–Elmer 1700 Fourier-transform IR (FTIR) spectrometer was used to monitor isothermal evolution of gases in situ at 340 °C and 360 °C in a customized IR cell. Approximately 1.5 mg HNS were placed in a capillary tube. The unsealed tube was placed in a side arm of the IR cell. The cell was then sealed to create a closed system. An aluminum cylinder,

TABLE 1

Average rate data by DSC and manometric methods

Method	Temperature (°C)	k (s^{-1})
Manometric	320	2.5E−03
	330	3.2E−03
	340	5.0E−03
	360	1.2E−02
DSC	355	4.0E−02
	360	5.1E−02
	365	5.2E−02
	370	6.2E−02
	375	8.6E−02

bored so that the IR cell arm would slide into it snugly, was used as a heating block. The cylinder was wrapped with heating tape and brought to and maintained at the desired temperature by a platinum thermocouple. Once at temperature, the aluminum cylinder was slid over the side arm containing the sample. Spectra were taken at measured time intervals, the shortest interval being 1 min. Using a resolution of 4 cm^{-1}, the spectrometer scanned at 20 scans min^{-1}. Two scans were taken per interval.

RESULTS AND DISCUSSION

The products from complete thermolysis of HNS of the temperature range 320–360 °C were a gas and a lustrous, black residue. The residue deposited itself in thin, brittle sheets on the inside of the capillary tube. Analysis of the residue proved difficult, as it was insoluble in protic, aprotic, polar, and nonpolar solvents. The insolubility of the residue suggested that it was polymeric in nature, most likely being derived from radical reactions. An IR spectrum of a KBr pellet of the residue is shown in Fig. 2, along with one of unreacted HNS. The spectrum of the residue is not as clear as that of the starting material, but the only notable differences in the residue are the disappearance of the CH stretch at 3101 cm^{-1} and the appearance of a nitrate or nitrite absorption at 1384 cm^{-1}.

To characterize the residue further, carbon/hydrogen/nitrogen analysis was performed on residue obtained from completely decomposed samples. Reaction was defined to be complete when gas was no longer produced with increased thermolysis time. The elemental analysis showed the residue to be 51.15% carbon, 1.85% hydrogen and 18.10% nitrogen [4]. The mole ratio of C : H : N for the residue was 3.3 : 1.4 : 1.0. On the basis of the oxygen balance of HNS, complete pyrolysis of HNS could follow the equation

$$C_{14}H_6N_6O_{12} \rightarrow 4CO_2 + CO + 3N_2 + 3H_2O + 9C(s) \qquad (1)$$

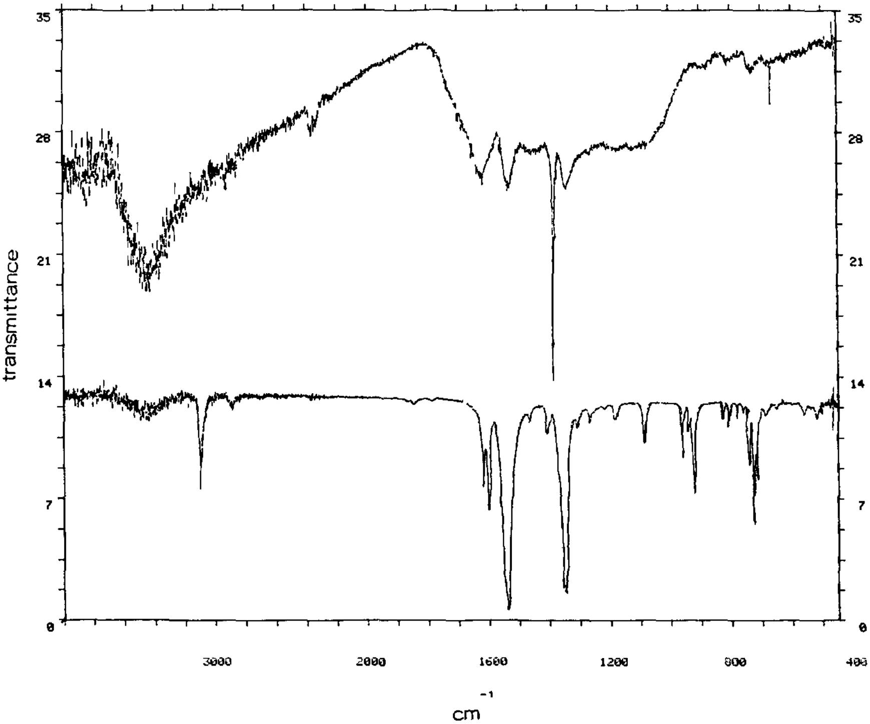

Fig. 2. IR spectra of KBr pellets of: (a) HNS (bottom), 3429 (H_2O), 3101, 1618, 1601, 1540, 1347, 1085, 958, 922, 809, 740, 724, 715 cm^{-1}; and (b) HNS thermolysis residue (top), 3429 (H_2O), 2350 (CO_2), 1617, 1530, 1384, 1340 cm^{-1}.

The nitrogen content of the residue implied that complete combustion of HNS did not occur within the range 320–360 °C. The product gas was comprised of CO_2, CO and N_2. From the manometric study, the maximum amount of gas produced was 5.2 mol per mol HNS (Fig. 3). The gas had a $CO_2:CO:N_2$ molar ratio of 3.3 : 0.4 : 1.5. From the gas data and residue

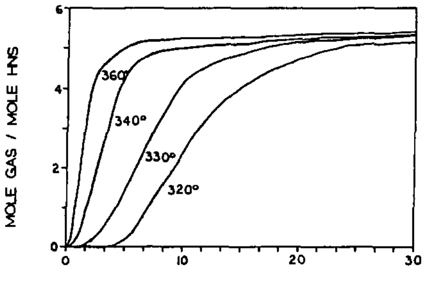

Fig. 3. Mol of gas formed per mol of HNS decomposed, as calculated from manometric data.

TABLE 2

Summary of kinetic parameters

Phase	E_a		log Z	Temperature range	Method	Reference
	(kcal m^{-1})	(kJ m^{-1})		(°C)		
Solution	45.1	189	13.7	260–300	DTA	5
Solid	43.9	184	12.0	260–300	Manometry	6
Liquid	30.3	127	9.2	317–355	DSC	7
Liquid	29.9	125	8.3	320–360	Manometry	[a]
Liquid	29.2	123	8.8	355–375	DSC	[b]

[a] Values from present study by least-square fit; $R^2 = 0.983$.

[b] Values from present study by least-square fit; $R^2 = 0.997$.

analysis, the following stoichiometric equation was found:

$$C_{14}H_6N_6O_{12} \rightarrow 3.3CO_2 + 0.4CO + 1.5N_2 + H_2O + C_{9.9}H_{4.2}N_3O_{4.1} \qquad (2)$$

The activation energies E_a and frequency factors Z from this study and others reported in the literature are presented in Table 2. The E_a and log Z values for the liquid-phase studies were in good agreement. The activation energies and log Z values reported for the solid-phase decomposition and decomposition in solution were higher than those for liquid-phase decomposition. The higher values may reflect different mechanisms, since those studies were conducted below the melting point of HNS [8].

It was reassuring that the DSC and gas methodologies gave similar kinetic parameters. The DSC method measured heat evolved during the reaction at atmospheric pressure where the rate of heat evolution was assumed to equal the rate of reaction. The DSC rate data were taken from the latter portion of the reaction curve (> 45% reacted), where the reaction followed first-order kinetics [9]. The manometric method measured the rate of gas produced and assumed it to be proportional to the rate of reaction. The manometric data followed first-order kinetics after a small induction period. The induction period decreased in length with increasing temperature; this was attributed to initial melting of HNS. Both methodologies gave similar activation energies, but the rate constants determined from the DSC measurements were four times greater.

A concern with the manometric method was that pressure build-up during the thermolysis within the sealed capillaries (~ 15 atm maximum) might affect the reaction. The pressure effect was examined by thermolyzing HNS in a 200 μL glass bulb at atmospheric pressure. The bulb, connected to a 1.0 ml calibrated pipette by rubber tubing, was placed in a 340 °C metal bath. As gas evolved, an oil bubble inside the pipette was displaced. Assuming the rate of gas evolution to be proportional to the reaction rate, the resulting total moles of gas produced per mole of HNS (5.2 mol) and the overall rate (4.0×10^{-3} s^{-1}) were comparable to the 340 °C manometric data. The slight pressure build-up in the tubes had negligible effect on the reaction rate.

The possibility of catalysis of the DSC decompositions by the aluminum sample pan was examined. HNS, mixed with aluminum pieces cut from DSC pans, was thermolyzed in a glass capillary tube at 340 ° C. The amount of gas produced was measured and compared to the amount of gas produced when aluminum was absent. It was found that the rates were enhanced by a factor of 2.5, indicating a slight catalytic effect of aluminum on HNS thermolysis.

What can be inferred about the initial mechanism from these kinetic parameters? Care must be taken when making mechanistic interpretations from activation parameters which are not derived from one authentic rate constant [10]. The activation energies and log Z values are representative of the overall complex thermal reaction, not of an individual reaction. A negative apparent activation entropy $\Delta S^\star$ was obtained from the apparent log Z

$$Z = (2.085 \times 10^{10}\ \mathrm{s}^{-1})(T_\mathrm{M}) \exp(\Delta S^\star/R) \tag{3}$$

where T_M is the average temperature of the overall temperature range used. A negative $\Delta S^\star$ suggests an ordered transition state in the rate-limiting step, but too much emphasis should not be placed on this result, since the rate constants used to obtain the $\Delta S^\star$ value were apparent rate constants.

The activation energies for liquid-phase HNS thermolyses were similar to the values reported for 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) liquid-phase thermolyses [11]. The initial stage of thermolysis for TNT and DNT was proposed to be hydrogen abstraction by the *ortho*-nitro group from the alpha carbon. Thermodynamically, the loss of a C–H bond is countered by the formation of the O–H bond, resulting in a lower activation energy than expected, making the transfer of a hydrogen feasible [12]. This mode of decomposition for HNS has been suggested previously on the basis of the similarity in structure of HNS and TNT [13]. The low activation energies found in the present study support a mechanism of this type.

Because it was difficult to analyze the non-gaseous product of HNS thermolysis, it is extremely difficult to suggest a decomposition mechanism for HNS with much confidence. Therefore, a study to examine liquid-phase thermolysis of *o*-nitrotoluene, DNT and TNT, a little-studied area, was pursued independently. Using the findings of this study, speculation is possible as to plausible initial mechanisms for liquid-phase thermolysis of HNS (Fig. 4a) [14]. The intermediate is probably cyclic in nature, the reaction being intramolecular. However, intermolecular hydrogen abstraction is also viable (Fig. 4b). A study using electron paramagnetic resonance spectrometry during thermolysis of neat TNT has suggested that the hydrogen donor is a second molecule of TNT [15]. However, for HNS, an intramolecular reaction may be favored, as a result of steric constraints in the HNS molecule.

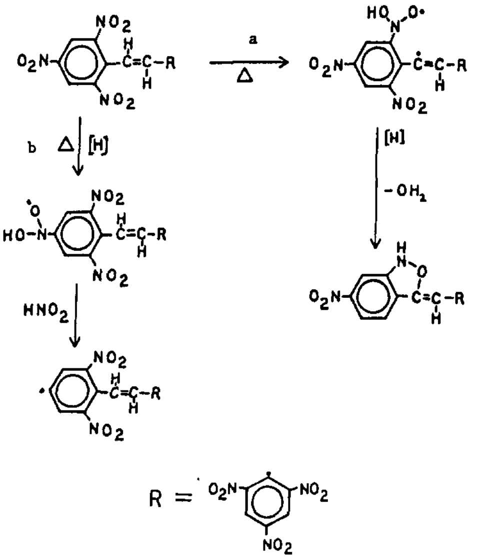

Fig. 4. (a) Feasible intramolecular reaction for HNS. (b) Feasible intermolecular reaction for HNS.

Homolysis of C–NO_2 may occur to some extent in HNS decomposition, although this reaction has not been observed in the liquid-phase decomposition of simple nitroarenes at 340 °C [14]. Detection by FTIR of HONO and other IR active gases evolved during thermolysis provided clues to possible reaction pathways (Fig. 5). It should be noted that any IR inactive gases

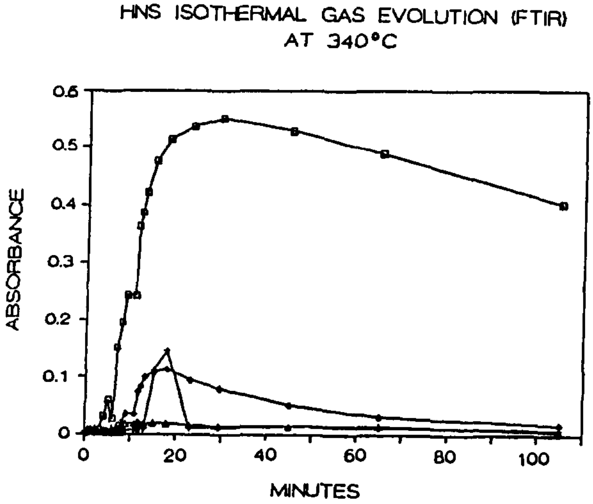

Fig. 5. FTIR detection of gases produced during HNS thermolysis: □, CO_2 (2360 cm^{-1}); +, CO (2181 cm^{-1}); ◇, NO_2 (1790 cm^{-1}); △, HONO (1387 cm^{-1}).

(N_2, O_2, H_2) present would not be detected. The observed wavelength monitored for each gas was taken from the literature [16,17].

Figure 5 provides insights regarding product gas composition vs. time, but it does not represent concentration–time profiles for the gases, since the extinction coefficient of each gas is different. The most notable feature of Fig. 5 is the detection of HONO and NO_2. The HONO probably arose from C–NO_2H scission from the intermediate, shown in Figs. 4a and 4b, but once NO_2 and water are available, HONO can result from their equilibrium. Homolysis of C–NO_2 may have been the source of the NO_2, but its late appearance suggests that it arose from later reactions.

CONCLUSIONS

In liquid-phase thermolyses (320–360 ° C), neat HNS did not undergo complete pyrolysis. The resulting gaseous products and heterogeneous polymeric residue indicated that the reaction was complex. The kinetic parameters from this study and similar works from the literature represent the overall thermal decomposition mechanism. Although reaction mechanisms were difficult to deduce, the overall stoichiometry for liquid-phase thermolysis of HNS from 320 to 360 ° C was established, plausible mechanisms for decomposition were suggested, and kinetic parameters for the thermolysis were determined. A study of the decomposition of simple nitroarenes was initiated to provide some elucidation of the mechanisms operative in HNS liquid-phase thermolyses. The results supported HNS initially undergoing an intramolecular hydrogen abstraction reaction, although an intermolecular hydrogen abstraction process may also occur. Steric factors would most likely govern the extent of each reaction. Intramolecular hydrogen abstraction of the vinylic hydrogen by the *ortho*-nitro group, leading to the breakage of a C–H bond and the formation of an O–H bond via ring closure, do fit the apparent kinetic parameters found. Real-time FTIR analysis revealed the presence of HONO and NO_2 during thermolysis.

REFERENCES

1 E.E. Kilmer, J. Spacecraft, 5(10) (1968) 1216.
2 R.N. Rogers, Thermochim. Acta, 3 (1972) 437.
3 R.N. Rogers, Anal. Chem., 44 (1972) 1336.
4 CHN analyses performed by Gailbraith Laboratories, Inc., Knoxville, TN, U.S.A.
5 Yu.Ya. Maksimov and E.N. Kogut, Tr. Mosk. Khim.-Tekhnol. Inst. im. D.I. Mendeleeva, 104 (1979) 30.
6 Yu.Ya. Maksimov and E.N. Kogut, Khim. Khim. Tekhnol., 20 (1977) 349.
7 R.N. Rogers, Thermochim. Acta, 11 (1975) 131.
8 S. Zeman, Thermochim. Acta, 78 (1984) 181.

9 R.N. Rogers and L.C. Smith, Thermochim. Acta, 1 (1970) 1.
10 J.H. Espenson, Chemical Kinetics and Reaction Mechanisms, McGraw-Hill, New York, 1981.
11 S. Zeman, Thermochim. Acta, 49 (1981) 219.
12 W.A. Pryor, Introduction to Free Radical Chemistry, Prentice Hall, New York, 1966, p. 52.
13 J.M. Rosen and J.C. Dacons, Explosivstoffe, 11 (1968) 250.
14 L.M. Minier, J.C. Oxley and K.R. Brower, manuscript in preparation.
15 T.M. McKinney, L.F. Warren, I.B. Goldberg and J.T. Swanson, J. Phys. Chem., 90 (1986) 1008.
16 Y. Oyumi and T.B. Brill, Combust. Flame, 62 (1985) 213.
17 C.D. Craver (Ed.), Gases and Vapours: A Special Collection of Infrared Spectra, Coblentz Society, Kirkwood, MO (U.S.A.), 1980.