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THERMAL STABILITIES OF HEXANITROAZOBENZENE (HNAB) AND HEXANITROBIPHENYL (HNB)

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Thermal Stabilities of Hexanitroazobenzene (HNAB) and Hexanitrobiphenyl (HNB)

by

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ABSTRACT: Rates of thermal decompositions for 2,2',4,4',6,6'-hexanitroazobenzene (HNAB) and 2,2',4,4',6,6'-hexanitrobiphenyl (HNB) were measured in the temperature range 215°C to 280°C by analysis for undecomposed explosive. HNAB decomposed 1.3%/hour at 230°C, about 18 times faster than HNB. At 280°C HNAB decomposed 60%/hour, 4 times faster than HNB. Supercooled liquids of both HNAB and HNB decomposed faster than the solids measured at the same temperature; however, the relative increase in liquid decomposition was much greater for HNB. Isolation and identification of several products from these decompositions indicate the presence of free radicals. Evidence for the formation of picryl radicals during HNAB decomposition is presented.

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The rate of decomposition at elevated temperatures of the thermally stable explosive compounds synthesized at this laboratrory is a critical measure of their utility. The reaction mechanism by which they decompose can serve as a guide to the synthesis of more stable explosives. Thin layer chromatography has been used to measure the relative thermal stabilities of two compounds, 2,2',4,4',6,6'-hexanitroazobenzene and 2,2',4,4',6,6'-hexanitrobiphenyl. These studies indicate clearly the complex nature of the slow thermal decompositions of explosives and give insight as to the mechanisms by which these processes occur. The thin layer chromatographic technique, although somewhat imprecise for quantitative estimation, provides the best method for investigating the degradation of minute quantities of these compounds.

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ALBERT LIGHTBODY
By direction

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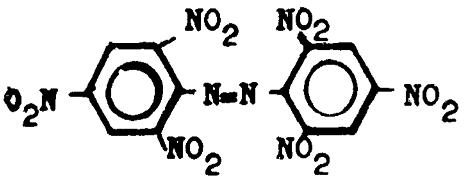
INTRODUCTION

The ability of a particular explosive to withstand high temperatures for long periods of time and to maintain its original integrity is by definition a measure of its thermal stability. This is valid regardless of the physical state of the compound, i.e., solid or liquid. The stability of a particular explosive or series of explosives may depend in widely varying degrees on a number of variables among which are, (a) chemical reactivity, for example oxidizable groups in the molecule which may react inter- or intramolecularly (1), (b) strong crystal lattice forces within and between molecules (2), (c) bond strengths between different kinds of atoms for different classes of explosives, as for example the N-N linkage in HNAB and the C-C linkage between phenyl rings for HNB, and (d) purity and physical characteristics of the explosive, among which are particle size and crystal form.

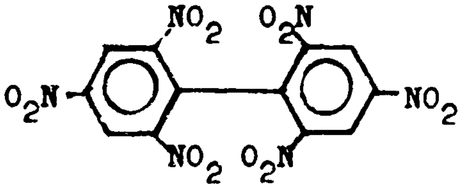
The task of attempting to relate the thermal stability of an explosive to its chemical structure may become seemingly hopeless when comparisons are made between explosives which differ widely. For example, the effects of crowding in polynitroaromatic amines and crowding in polynitropolyphenyls could be largely masked or distorted in the first case by the reactive amine groups. It would thus seem highly desirable to make thermal stability measurements between explosives which are similar chemically and differ structurally as little as possible.

The purpose of the present study is threefold: (a) to measure the thermal stabilities of HNB and HNAB by means of thin layer chromatographic analysis for undecomposed starting material, (b) to determine the products of HNAB and HNB decomposition when feasible in an attempt to gain insight into the mechanisms of slow thermal decompositions of explosives, and (c) to assess the importance of crystal lattice forces in an explosive molecule.

The two compounds chosen for this study were 2,2',4,4',6,6'-hexanitroazobenzene, I, (HNAB) and 2,2',4,4',6.6'-hexanitrobiphenyl, II, (HNB). They differ only by the -N=N- linkage of HNAB.



I, HNAB, m.p., 221° - 222°C



II, HNB, m.p., 242° - 243°C

The crowding of the ortho nitro groups of HNB is undoubtedly extensive. It is thus possible to separate biphenyl derivatives which contain bulky groups in these ortho positions as enantiomorphs (3). It has also been found by several workers that the nitro group exerts a larger effective radius for crowding than H, F, OH, COOH, NH_2, CH_3 and Cl groups and only slightly less than Br and I (4). In contrast, the nitro groups of HNAB are separated by an -N=N- linkage, and interaction between these groups should be absent or neglibible, especially in the preferred trans form for HNAB (5).

RESULTS AND DISCUSSION

Rates of Thermal Decomposition of HNAB and HNB, Chromatographic Method of Analysis

Thin layer chromatographic (TLC) analysis (6) was used to measure residual explosive after a specified time at a particular temperature for both HNAB and HNB. The results, listed in Appendix A, are expressed in terms of percent decomposition at time, t, and temperature, °C. These percentages are $\left[(A_o-A_t)/A_o\right]100$, where A_o is the initial amount of explosive, and A_t is the amount determined by TLC analysis at time, t. A typical plot of the percentage decomposition of explosive as a function of time is shown in Figure 1.

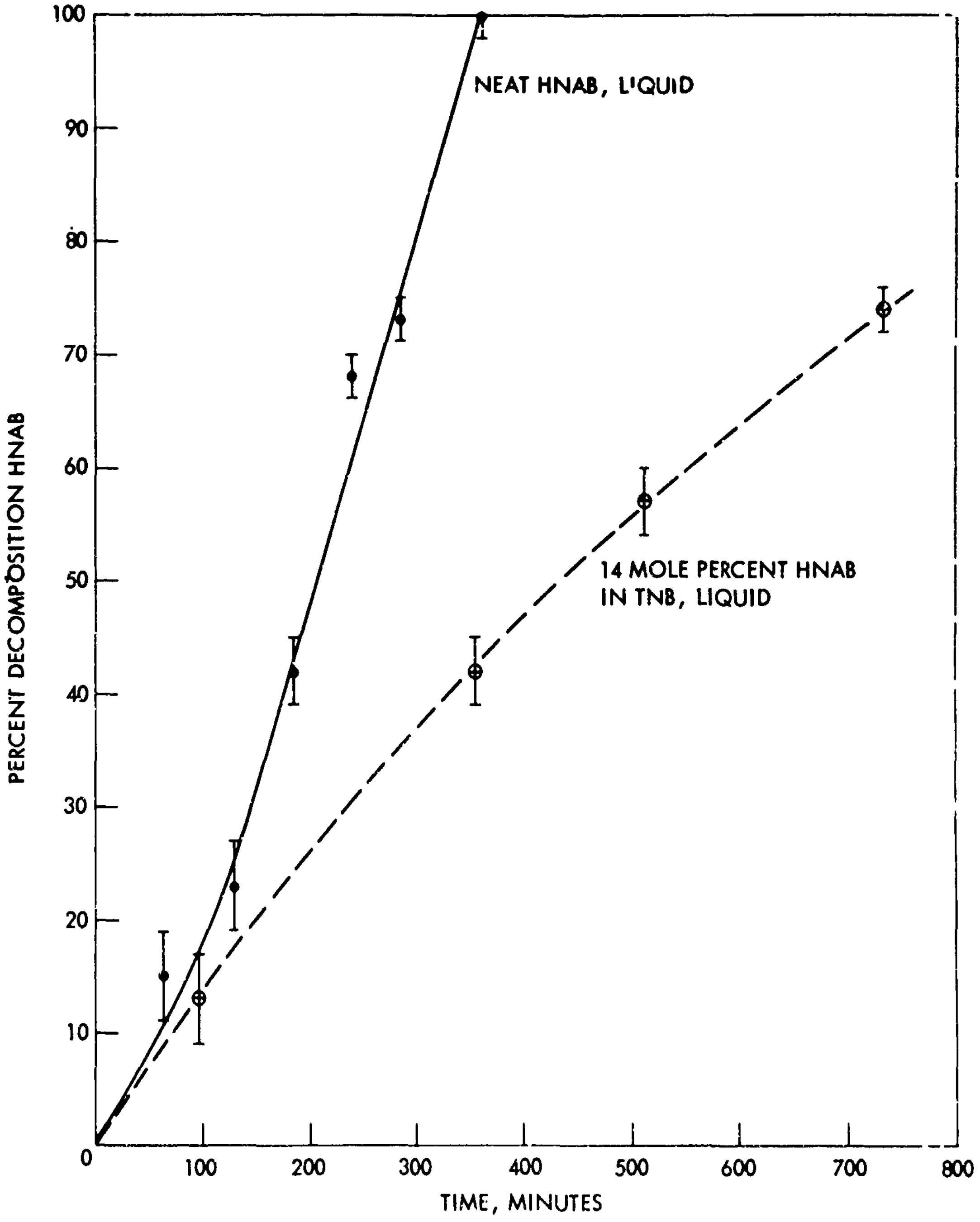


FIG. 1 THERMAL DECOMPOSITION OF HNAB ALONE AND IN TNB SOLUTION AT 260° C, CHROMATOGRAPHIC ANALYSIS

In all cases for both HNAB and HNB there is a nearly linear relationship between percentage decomposition and time. This linear relationship has already been observed (7) for the decompositions of picramide and PIPAM (3-amino-2,2',4,4',6,6'-hexanitrobiphenyl) as neat liquids at 250°C. Slopes of similar decomposition-time plots are listed in Table 1.

TABLE 1

Relative Rates of Decomposition for HNAB and HNB As a Function of Temperature

Temperature, °C	Percentage Decomposition/Minute Chromatographic Analysis HNAB	HNB	Relative Rate HNAB/HNB
230	0.022±0.002	0.012±0.006	18±5
245	0.10 ±0.01	-	-
250	-	0.019±0.002 (a)	-
260	0.31 ±0.04	-	-
280	1.0 ±0.05		4±1

(a) PIPAM. 3-amino-2,2',4,4',6,6'-hexanitrobiphenyl, decomposes over 10 times faster at 250°C (0.24% minute).

The uncertainty of the slopes, percentage decomposition/minute reflects the degree of accuracy of the chromatographic analysis. Results from two chromatographic plates usually agreed to within ± 5% for residual explosive. Since the percentages decomposition are based on the difference between the starting weighed explosive and that remaining determined by TLC analysis, it is to be expected that the greatest error would be in the first 5-10% decomposition. To avoid this error, measurements were made when possible at times where the explosives were 20 - 90% decomposed.

HNAB was found to much less stable than HNB, Table 1. Although the ortho nitro groups adjacent to the C-C bond between rings of HNB are much more sterically crowded than the nitro groups near the N=N linkage of HNAB, the greater ease of C-N cleavage must account for, in part at least, the more rapid HNAB decomposition. (See section on the Decomposition Products of HNAB and HNB.) By analogy, the C-N bond energy for azomethane is given as 46 Kcal/mole (8) while the C-C bond energy for ethane is 84 kcal/mole (9).

Gas Evolution as a Function of Decomposition at Several Temperatures for HNAB and HNB

Since HNAB and HNB are different chemically it would not necessarily be expected that their decomposition processes would be the same. That the two decomposition schemes are different is evident from the data obtained, Table 2. The (moles gas/moles explosive decomposed) ratios for both HNAB and HNB depend on temperature and time of heating. Generally, at a given temperature, these ratios increase with time. This would strongly indicate that decomposition products from the original explosive are themselves decomposing to yield gaseous products.

TABLE 2

Decomposition and Gas Evolution for HNAB and HNB As Functions of Time and Temperature

		Moles gas formed (a)/ Moles Decomposed		% Decomposition	
Time, Min.	Temperature, °C	HNAB	HNB	HNAB	HNB
720	230	1.2±0.3	-	14±4	-
342	245	1.2±0.1	-	32±3	-
540	245	1.9±0.1	-	44±3	-
1934	250	-	4.3±0.2	-	38±3
61	260	1.3±0.3	-	15±4	-
130	260	2.2±0.3	-	23±4	-
187	260	2.1±0.1	-	42±3	-
168	280	-	3.6±0.2	-	36±3
295	280	-	4.0±0.1	-	54±3

(a) On the assumption that 1 mole of gas at S.T.P. occupies 22.4 liters.

The average ratio, moles gas formed/moles explosive decomposed, for HNAB was found to be 1.6±0.4 over the temperature range 230-260°C contrasted to 4.0±0.4 from 245-280°C for HNB, up to about 50% decomposition for both compounds.

Decomposition of HNAB and HNB as Solids and Supercooled Liquids at the Same Temperature

It is well known that crystal lattice forces help stabilize molecules against thermal degradation. For example, malonic acid decomposes 22 times faster as a supercooled liquid at 110°C than the solid at the same temperature (10).

Garner interprets these results in terms of increased molecular mobility in the liquid relative to that in the solid, leading to a chain decomposition mechanism. Also, the "autocatalytic" decomposition of DATB taking place after extended heating at 280°C has been attributed to progressive melting caused by decomposition products of the overall decomposition process (11).

In the present study supercooled liquids of both HNB and HNAB were compared to their respective solids at the same temperature, Table 3. To the author's knowledge, this is the first example of a direct comparison between a supercooled neat liquid explosive and the solid material at the same temperature.

Samples of HNAB and HNB were melted slightly above their melting points, cooled, and heated as supercooled liquids at the temperature and time indicated. The supercooled liquids were observed not to crystallize during the entire heating period, but did crystallize after removal from the heating block at the conclusion of the experiment. No indication of any decomposition was observed during the initial melting process. Samples which had been melted, and then allowed to recrystallize at room temperature, were identical in regard to gas evolution and melting point behavior with untreated solid samples at the test temperature.

TABLE 3

Thermal Stabilities of Solid and Supercooled Liquids of HNAB and HNB

Compared at the Same Temperature

(HNAB, m.p. = 221-222°C; HNB, m.p. = 242-243°C)

Time min.	Compound	T, °C	State	ml/g/min(a)	Factor Decomposition Liquid/ Decomposition, Solid
1148	HNAB	215	solid	0.0016	3.3
1148	HNAB	215	liquid	0.0054	
1333	HNB	230	solid	0.00044	20
1333	HNB	230	liquid	0.0091	

(a) Approximately 0.1 g samples were used for HNAB and HNB.

Valid comparisons between the extents of decomposition in the solid versus decomposition in the liquid may be made from gas evolution data for the same compound at a single temperature. The factor, decomposition (liquid)/decomposition (solid), was found to be much greater for HNB than HNAB. The reason for this increased reactivity for HNB liquid is not completely known. It might be suggested that HNB is much more sterically crowded than HNAB and the increased intramolecular interactions of the ortho nitro groups of HNB in the liquid relative to HNAB would lead to greater instability. Similarly, Dacons has found from gas evolution measurements that the least sterically crowded 3',5',2,4,6-pentanitrobiphenyl (12) was the most stable of three pentanitrobiphenyl isomers. However, liquid HNAB decomposes much more rapidly than liquid HNB at the same temperature, as shown by the analytical data of Appendix A.

Decomposition Products of HNAB and HNB

a. Decomposition of HNAB. The Case for Picryl Radical Formation.

Decomposition residues of HNAB in the temperature range 230°-260°C were analyzed by means of a combination of thin layer and column chromatography. In several cases, 5 to 10 grams of HNAB were employed. The results obtained, Table 4, indicate that the decomposition mechanism is quite complex.

TABLE 4

Products of HNAB Decomposition

Products	Approximate Amount	Evidence, Comments
(1) 1,3,5-trinitrobenzene, TNB	< 1%	TLC(a); I.R.(b)
(2) Picramide, PAM	< 1%	TLC(a); isolation; M.W. = 227 ± 2 (PAM = 228)
(3) 2,2',4,4',6,6'-hexanitrobiphenyl, HNB	0	TLC spot corresponding to HNB standard absent
(4) 4.6-dinitrobenzfuroxane, DNBF(c)	0	TLC spot corresponding to DNBF standard absent
(5) Benzene Insoluble Fraction	67% of residue(d)	M.W. = 1066 ± 3; I.R. curve similar to TNB; aromatic nitro present
(6) Yellow compound	< 1%	M.W. = 316 ± 8
(7) 6-7 others	<< 1%, trace	Colors on TLC plates varied from orange to purple

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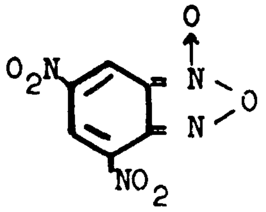
(a) Showed identical R_f values with authentic sample with several different developing solvents.

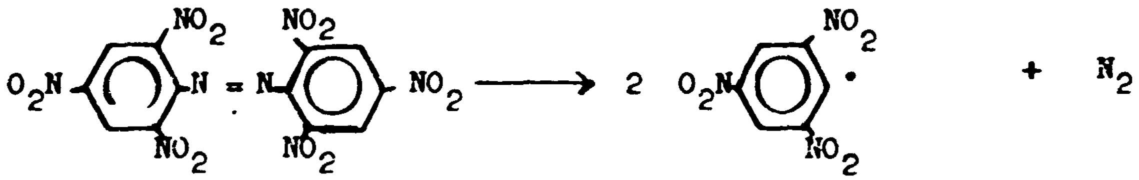
(b) Infra red curves were identical with authentic sample (attenuated total reflectance unit attachment used, ATR unit).

(c)

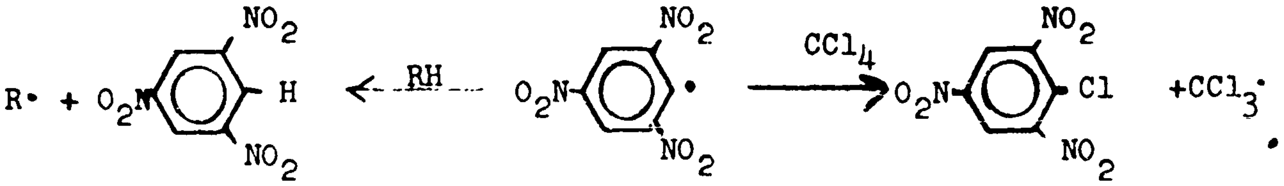


(d) From 5 grams HNAB. After 4 hours at 260°C, 3.91 grams of residue were obtained of which 2.62 grams was benzene insoluble.

In the early stages of HNAB decomposition, one mole of gas was formed for every mole of HNAB decomposed (Table 2). By means of vapor phase chromatography this gas was shown to be largely N_2 which is like decompositions of other azo compounds. Azobisisobutyronitrile and a host of other azo compounds are postulated to cleave thermally by a simultaneous rupture of both C-N bonds to form N_2 and two free radicals.(13). Similarly for HNAB,



Further proof for the existence of the picryl radical was obtained from decompositions of HNAB in the presence of CCl_4 in sealed tubes at 260°C. After 91 minutes, about a 1% yield of picryl chloride and a slightly lesser amount of trinitrobenzene were formed. These yields were based on the assumption that HNAB decomposition paralleled the decomposition of HNAB in CCl_4. HNAB is about 18% decomposed in 91 minutes at 260°C. During this time interval picryl chloride is stable. Picryl chloride and trinitrobenzene must evidently arise by some free radical scheme involving the picryl radical;



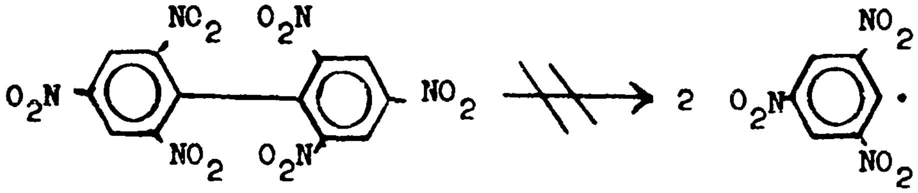
Trinitrobenzene Picryl Radical Picryl Chloride

The formation of the picryl radical must evidently be a rather high energy process. No picryl chloride or trinitrobenzene were formed when HNAB and CCl_4 were heated in sealed tubes for periods up to as much as 4 hours.

It is also interesting to note that no hexanitrobiphenyl which might arise by combination of two picryl radicals was found in any of the decompositions of HNAB, alone or in the presence of CCl_4.

b. Decomposition of HNB

No identifiable products were isolated or observed in the case of HNB decomposition in the temperature range 230-280°C. Trinitrobenzene, TNB, was especially looked for on thin layer plates but was not found. Residues from these HNB decompositions were extremely insoluble in organic solvents. No picryl chloride or TNB were formed when HNB was decomposed in the presence of CCl_4 (sealed tubes) at 260°C even for periods up to three hours. These results indicate that homolytic cleavage of the C-C bond between rings must be absent. The first steps of HNB thermal decomposition most likely involve the C-N or N-O bonds or both around the crowded ortho positions.



Further experiments are needed to elucidate the mechanism or first bond breaking steps in thermal decompositions of HNB.

c. Thermal Decompositions of HNAB in Trinitrobenzene Solutions

The fate of the picryl radical once formed in the decomposition of HNAB is not known exactly. Attack of the picryl radical on a molecule of HNAB would lead to higher molecular weight products. A mixture of products which could not be made to crystallize was isolated as a benzene insoluble fraction from the decomposition of 5 grams of HNAB (neat liquid) at 260°C for 4 hours. The overall decomposition of HNAB was about 70%, the average molecular weight of the product was 1066 ± 3 (Table 4).

If, however, attack of a picryl radical or other radical derived from HNAB was on another molecule, say for instance, trinitrobenzene, the overal stability of the HNAB would appear to be enhanced. Indeed HNAB was found to be "stabilized" in solutions of TNB (Table 5 and Figure 1).

TABLE 5

Thermal Stabilities of HNAB in Trinitrobenzene Solutions at 260°C

Mole Ratio: HNAB/TNB	Rate of Decomposition of HNAB, %/Min.
1/0[a]	0.33
1/1	0.14
1/2.1	0.061
1/6	0.10

(a) Neat HNAB

This "stabilization" by the solvent must evidently change in different solutions. HNAB is not "stabilized" in 1,4-dinitrobenzene solutions, and is actually decomposed faster in 1,3-dinitrobenzene solutions (Appendix B). Bartlett and Kwart (14) have shown a similar ordering of nitro compounds in their ability to inhibit the polymerization of vinyl acetate. These authors found that TNB inhibited the polymerization of vinyl acetate best, p-Dinitrobenzene next, with m-Dinitrobenzene least in the ratio: 890/267/105.

The thermal degradation of HNAB, alone and in TNB, is complex. The exact kinetic or chemical behavior of HNAB with TNB, other HNAB molecules, or degradation products formed in solution or in vapor phase can only be speculated upon at present. Thus the "stabilizing" influence of TNB toward HNAB decomposition in TNB-HNAB mixtures could also be interpreted as just a dilution effect. This concept, however, does not hold for solutions of HNAB in 1,3- or 1,4-dinitrobenzene.

The overall disappearance of HNAB (or HNB), which, after all, is the only quantity that is being measured, can be schematically represented by,

$$-d(\mathrm{HNAB})/dt = k_1(\mathrm{HNAB}) + k_2(\mathrm{HNAB})^n + k_3(\mathrm{HNAB})^m(\mathrm{TNB})^p \ \ldots k_4 \ldots k_z \sum_1^z (P)^r (\mathrm{HNAB})^s,$$

where P may be wide variety of various products. The major objectives of this study have been achieved and further refinements must await future experiments.

EXPERIMENTAL

Thin Layer Chromatographic Analysis

The thin layer chromatographic method of analysis has been reported (6) and will not be reviewed here. Samples ranging in size from 0.050 g to 0.100 g of HNAB and HNB were heated isothermally for a specified time in calibrated one piece glass tubes under a partial atmosphere of nitrogen (15). Pressure increases were noted when possible. The resulting residues were extracted with acetone and quantitatively transferred into a 50 ml volumetric flask and diluted to the mark. Typically, a 0.005 ml aliquot of this solution was spotted together with equal volumes of two standard solutions of HNAB or HNB onto a 300 micron thick silica gel G plate. After air drying, the plates were developed with a mixture of toluene/benzene/hexane in the ratio 2/2/4 (by volume) in the case of HNB, and benzene/toluene/n-pentane in the ratio 4/4/2 in the case of HNAB. Both these solvent mixtures will spearate TNB, HNB, and HNAB in a single chromatogram.

Chromatographed zones were visualized by spraying the plates with a 10% methanolic solution of potasium hydroxide. Zones appeared as bright red spots against a white background. These spots were photographed with 146L transparency film and projected by means of a lantern slide projector onto a white piece of paper. The resulting dark spots of the unknown and two standards were traced on the paper and their areas obtained with a precision planimeter. The linear relationship between the square root of the spot area and the logarithm weight of compound in the spot was used to calculate the amount of unknown either graphically or by interpolation. Two plates were determined in each analysis and the results agreed with ± 5%.

Nitrogen Analysis from HNAB Decomposition by Vapor Phase Chromatography

A half gram sample of HNAB was heated for 1 hour at 260°C in an evacuated tube, 13 ml capacity. The gas formed was vacuum transferred into a Beckman GC-2 Gas Chromatograph and developed on a 4 ft molecular sieve 5A column, isothermally, at 70,C. A peak was observed with a retention time of 4.64 minutes which was identical to a standard nitrogen gas sample developed under the same conditions.

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APPENDIX A

Thermal Decomposition of Hexanitroazobenzene (HNAB)

Time, Minutes	Temperature, °C	Weight, Grams	Decomposition, %	Gas Volume, ml(STP)±0.05
720	230	0.1052	14±5	1.15
4380	230	0.1063	100 *	-
342	245	0.1312	32±3	2.53
540	245	0.1088	44±3	4.61
61	260	0.1036	15±4	0.99
130	260	0.1155	23±4	2.98
187	260	0.1055	42±3	4.63
240	260	0.2048	68±2	-
288	260	0.1067	73±2	-
360	260	0.1201	100 *	-
30	280	0.1080	10±4	-
60	280	0.1035	49±3	-
92	280	0.1031	60±2	-
118	280	0.1031	100 *	-

*Detected only a trace of residual HNAB.

Thermal Decomposition of Hexanitrobiphenyl (HNB)

Time, Minutes	Temperature, °C	Weight, Grams	Decomposition %	Gas Volume, ml(STP)±0.05
1305	230	0.1119	5±4	-
7222	230	0.1169	9±4	-
1934	250	0.0501	38±3	4.30
168	280	0.0555	36±3	3.80
295	280	0.0561	54±2	6.40
389	280	0.0557	96±2	-

APPENDIX B

Thermal Decomposition of HNAB in TNB Solutions at 260°C

Time, Minutes	Grams HNAB	Grams TNB	Mole % HNB in TNB	% Decomposition HNB
96	0.1034	0.2972	14.2	13±4
352	0.1040	0.2992	13.9	42±3
513	0.1091	0.2945	14.8	57±3
731	0.1015	0.3034	13.6	74±2
175	0.1024	0.1024	32.2	11±4
175	0.1030	0.0507	49.0	25±3

Thermal Decomposition of HNAB in 1,4-Dinitrobenzene Solutions at 260°C

Time, Minutes	Grams HNAB	Grams 1,4-DNB	Mole % HNB in TNB	% Decomposition HNAB
187	0.1033	0.1032	27.1	40±3
187	0.2273	0.1032	45.0	47±3
187	0.1055	-	100	42±3

Thermal Decomposition of HNAB in 1,3-Dinitrobenzene Solutions at 260°C

Time, Minutes	Grams HNAB	Grams 1,3-DNB	Mole % HNAB	% Decomposition HNAB
213	0.100	0.039	49.0	69±2
176	0.104	0.200	10.8	100 *

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*Detected only a trace amount of residual HNAB.

Thermal Decomposition of HNB in TNB Solutions at 280°C

Time, Minutes	Grams HNB	Grams TNB	Mole % HNB in TNB	% Decomposition HNB
295	0.0521	0.6090	4.1	17±4
1399	0.0521	0.6059	4.1	35±3
295	0.0529	0.0267	49.8	53±2

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13. ABSTRACT

Rates of thermal decompositions for 2,2',4,4',6,6'-hexanitroazobenzene (HNAB) and 2,2',4,4',6,6'-hexanitrobiphenyl (HNB) were measured in the temperature range 215°C to 280°C by analysis for undecomposed explosive. HNAB decomposed 1.3%/hour at 230°C, about 18 times faster than HNB. At 280°C HNAB decomposed 60%/hour, 4 times faster than HNB. Supercooled liquids of both HNAB and HNB decomposed faster than the solids measured at the same temperature; however, the relative increase in liquid decomposition was much greater for HNB. Isolation and identification of several products from these decompositions indicate the presence of free radicals. Evidence for the formation of picryl radicals during HNAB decomposition is presented.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hexanitroazobenzene						
Hexanitrobiphenyl						
Stability						
Decomposition						
Chromatography						
Analysis						