Evidence of an Elimination Mechanism in Thermal Decomposition of Hexahydro-1,3,5-trinitro-1,3,5-triazine and Related Compounds under High Pressure in Solution

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The thermal decomposition of a number of six-membered cyclic nitramines and nitrosamines was studied under pressures up to 1.1 GPa in dilute solution (THF). The studied nitramines and nitrosamines include hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), hexahydro-5-methyl-1,3,5-trinitropyrimidine, hexahydro-1,3,5,5-tetranitropyrimidine, 1,3,3,5,5-pentanitropiperidine, and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TRDX). In all cases negative activation volumes have been found, indicating that thermolysis is not a homolytic process. On the basis of negative activation volumes, detection of aromatic products, low decomposition temperature (low E_a), and order of thermal stability, we propose that these cyclic nitramines and nitrosamines are thermally decomposed through the elimination of HNO_2 or HNO under high pressure. By summarizing our current and previous work, we find that the decomposition pathway of nitramines and nitrosamines is dependent not only on the reaction conditions but also on structural features.

Introduction

Nitramines are the most commonly used military explosives. A more complete understanding of their thermal stability is of great importance in the explosive industry. The relatively weak $N-NO_2$ chemical bond is responsible for their reactivity. In recent years, many systematic studies of their thermal decomposition have been reported. Some of the results are summarized in the review by Dubovitskii and Korsunskii.[1] Thermal decomposition of simple nitramines, such as dialkynitramines, has been unambiguously determined to result from homolysis of the $N-NO_2$ bond. The measured activation energies are usually larger than 40 kcal/mol and about equal to the $N-NO_2$ bond dissociation energy of 50 kcal/mol for the simple nitramines. In contrast to the simple nitramines, none of the studies performed on complex nitramines, such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), has provided a consistent interpretation for the mechanism of thermolysis. Further, the mechanism is believed to be highly dependent on the experimental conditions.[2−5] From our recent studies of the effects of pressure on the rate of thermal decomposition of nitramines, nitrosamines, and nitrate esters,[6] we believe that most of nitramines including octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrozocine (HMX) undergo homolysis of the $N-NO_2$ bond because their activation volumes are positive. However, in the thermolysis of RDX and 1,2,3,4-tetrahydro-6-nitro-1,4-dinitrosoquinoxaline, the rate accelerates as the pressure increases. Considering these contrasting pressure effects on the decomposition rates, we conclude that decomposition of RDX and 1,2,3,4-tetrahydro-6-nitro-1,4-dinitrosoquinoxaline is not a radical process under high pressure. To clarify this surprising divergence in mechanism, we studied the pressure effect on the decomposition rates of other six-membered cyclic nitramines and nitrosamines. All of these compounds have molecular structures which are able to produce aromatic intermediates through elimination of HNO_2 or HNO.

In every regime of temperature, pressure, and concentration, nitro compounds have a choice of reaction pathways. It is not always possible to guess which pathway will be preferred under the conditions of shock initiation of detonation with pressures near 10 GPa and temperatures near 1200 K. A recent study [7] has revealed some surprising intermolecular reactions of nitro compounds with solvent. The study of possible intermolecular reactions in shockwave decomposition of explosives without solvent is beyond our technical competence at present.

In this paper, we report the pressure and temperature effects on the thermal decomposition rates of six-membered cyclic nitramines and nitrosamines in THF solution. We propose an elimination mechanism for the thermolysis of these complex nitramines and nitrosamines under conditions of high pressure in solution.

Experimental Section

A piston and cylinder capable of achieving 2.0 GPa as described by Naud and Brower[6] was used to obtain pressures in the range of 0.2 to 1.1 GPa. Dilute solutions were placed in a Teflon capsule which can withstand about 1.4 GPa without leakage. The temperature was maintained within ±1 °C by a thermistor controller. Typically the conversion was limited to 30−60% to avoid autocatalysis. Consumption of starting material was followed by a Perkin-Elmer FTIR spectrometer,

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Model 1710. The asymmetric stretch of the nitro-group in the range of 1500−1650 cm^{-1} is highly absorbing and its absorbance obeys Beer's law for all nitramines within our concentration range. Dilute solutions were made up on the order of 0.02 M to avoid possible bimolecular reactions. FTIR was also used for gaseous products identification, such as CH_4, CO, CO_2, N_2O, NO, and NO_2. The Hewlett-Packard GC 5890A, coupled to Hewlett-Packard Mass Selective Detector, Model 5970, was used for liquid-phase product analysis. Identification of products was achieved by comparing the mass spectra to those of authentic samples or by interpretation of the fragmentation pattern. No rigorous attempt was made to quantify the products of reaction.

Hexahydro-5-methyl-1,3,5-trinitropyrimidine, hexahydro-1,3,5,5-tetranitropyrimidine, and 1,3,3,5,5-pentanitropiperidine were synthesized according to the method of Cichra and Adolph.[8] To synthesize these secondary cyclic nitramines, an N-blocking *tert*-butyl group was used to control the course of Mannich condensations. These three nitramines were synthesized in two steps. First, Mannich condensation of *tert*-butylamine was performed with the appropriate nitroalkanes. Second, nitrolysis of corresponding *tert*-butylamines by 100% nitric acid was carried out to obtain these cyclic nitramines. The pure products were obtained after purification by washing and recrystallization of the raw products.

THF, toluene, and acetone were obtained from either Aldrich or Fluka Chemical Co., and toluene and acetone were used without further purification. THF was distilled fresh from sodium metal. RDX was obtained from a commercial source, and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TRDX) was previously synthesized by our group.

Results and Discussion

There are several reasons for studying the decomposition of explosives in solution. First, dilution by solvent retards intermolecular reactions. Second, solvent stabilizes intermediates by quenching highly reactive species, such as NO_2, which would otherwise decompose the explosives autocatalytically. Third, the kinetic order with respect to starting material can be determined by changing the concentration. From the pressure effect on decomposition rates it is possible to evaluate the difference in molar volume between reactants and their transition states. These measured differences can help to characterize transition states and elucidate decomposition mechanisms. The following equation gives an isothermal relationship between activation volume, ΔV^*, and the pressure effect on reaction rate:

$$\Delta V^* = -RT(\delta \ln k/\delta P)_T$$

Its use has contributed to clarifying many reaction mechanisms.[9,10] The facts we rely upon to interpret the present results are that (1) homolytic reactions have positive activation volumes ranging from +5 mL/mol at low temperature to +40 mL/mol at high temperature and (2) reactions which lead to electrical polarization, either by bond formation or bond breaking, have large negative activation volumes.

Nitramines. The rates of decomposition of RDX under high pressures at 145 °C are shown in Figure 1. The activation energies are 42.5 and 35.0 kcal/mol at 0.2 and 0.7 GPa, respectively. These activation energies, especially at high pressure, are much lower than 66 kcal/mol,[11] the reported bond dissociation energy of the N−NO_2 bond in RDX, suggesting that the decomposition

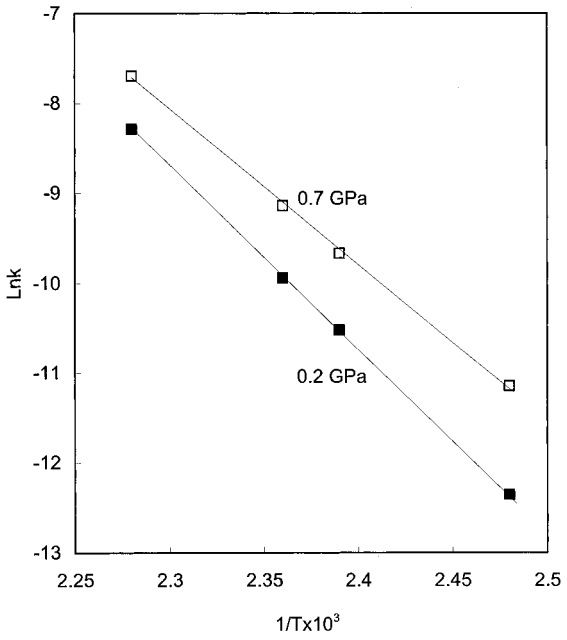

Figure 1. Arrhenius plots of RDX in THF solvent under 0.2 and 0.7 GPa.

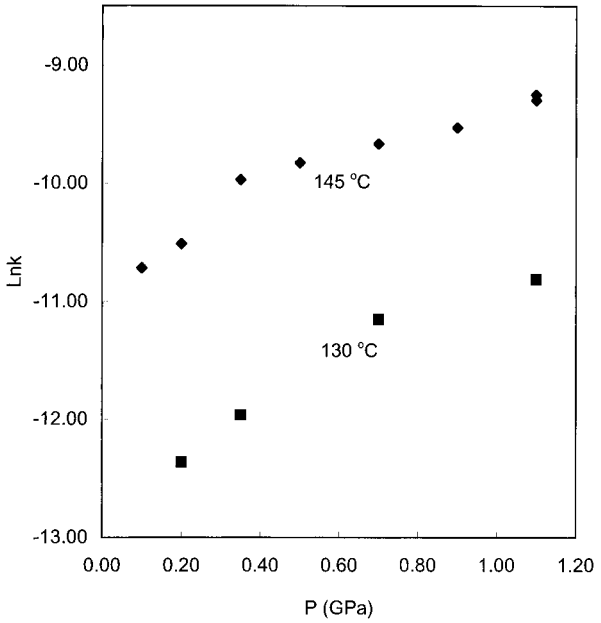

Figure 2. Activation volume profiles of RDX in THF solvent at 130 °C and 145 °C.

mechanism is not homolytic. The trend of decrease in activation energy with the increase in the pressure indicates that pressure has a great effect on the selection of decomposition channel for RDX. In our preceding paper[12] two quite different decomposition mechanisms of nitromethane under low and higher pressure have been found. Recently, Behrens and Bulusu[13,14] reported that condensed-phase RDX could decompose in four parallel channels, including the homolysis of the N−NO_2 bond and elimination of HNO_2. Therefore, it is possible that higher pressure makes the eliminative decomposition

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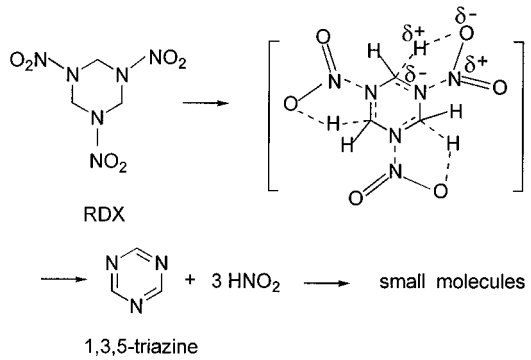
dominant and the other pathway minor as in the case of nitromethane decomposition. Any homolytic process will probably be hindered and suppressed by high pressure since it almost always has a positive activation volume. Figure 2 shows activation volume plots for 130 °C and 145 °C. It is evident that pressure accelerates the decomposition of RDX, and the activation volumes calculated from these plots are −11.0 mL/mol between 0.2 and 0.7 GPa and −3.5 mL/mol between 0.7 and 1.1 GPa, respectively, at both temperatures. This clearly indicates that the first step of decomposition is not homolysis of the $N-NO_2$ bond. The GC-MS did not detect 1,3,5-triazine in the liquid phase, perhaps because it was consumed in subsequent reactions. The gas-phase products identified by FTIR are N_2O and CO_2, rather than NO_2, CH_2O, and HCN which are said to result from $N-NO_2$ and C−N bond breakage in the thermolysis of RDX and HMX.[15] This implies that elimination is dominant under high pressures and that both homolytic cleavage of the $N-NO_2$ bond and decomposition by the concerted triple scission pathway[2] are suppressed. Even though CH_2O and NO_2 can be consumed in a subsequent gas-phase reaction, the final products, NO and CO, are still not found under our experimental conditions.

$$CH_2O + NO_2 \rightarrow NO + CO + H_2O$$

To reveal more information about the mechanism of decomposition, small amounts of different additives have been added to the RDX solutions. Toluene, which is a radical scavenger, was added to the THF solvent. The rate constants of RDX with and without addition of 3 wt % toluene are 1.8×10^{-4} s^{-1} and 1.9×10^{-4} s^{-1}, respectively, at 1.1 GPa and 145 °C, and no products related to toluene, such as benzyl toluene, were found. This product is usually formed substantially in the radical processes if toluene is present. By contrast, addition of 2 wt % acetone into the sample increased the decomposition rate to 3.4×10^{-4} s^{-1} under the same conditions, suggesting that the transition state is polar and stabilized by the acetone. In addition, we also found that decomposition of dilute RDX under a pressure of 0.1 GPa has a primary isotope effect of 1.4, indicating that C−H bond rupture is involved in the rate-determining step. In thermal decomposition of both liquid and solid RDX, Behrens and Bulusu[13] also observed primary isotope effect. On the basis of these results, we propose that RDX undergoes concerted elimination of HNO_2 through a five-center transition state under high pressure.



Partial aromatization of the transition state by concerted elimination will decrease the free energy of the transition state. Hence, a lowering in the activation energy is expected. In addition, the loss of freedom of movement for the NO_2 group and H in the transition state will cause a negative activation volume. The acidity of hydrogen in RDX and the elimination of nitrous acid have been shown clearly by Hoffsommer et al.[4] in the studies of aqueous alkaline hydrolysis of RDX. They observed a primary isotope effect due to elimination of HNO_2 and detected the elimination product, 1,3,5-triaza-3,5-dinitrocyclohexene, by mass spectrometry. The intermediate 1,3,5-triazine has been found in the thermolysis process of condensed RDX,[16] which is explained by the elimination of HNO_2. Recently, Ostmark[17] has clearly observed the 1,3,5-triazine as a decomposition intermediate of RDX by the combined laser ignition/mass spectroscopy method.

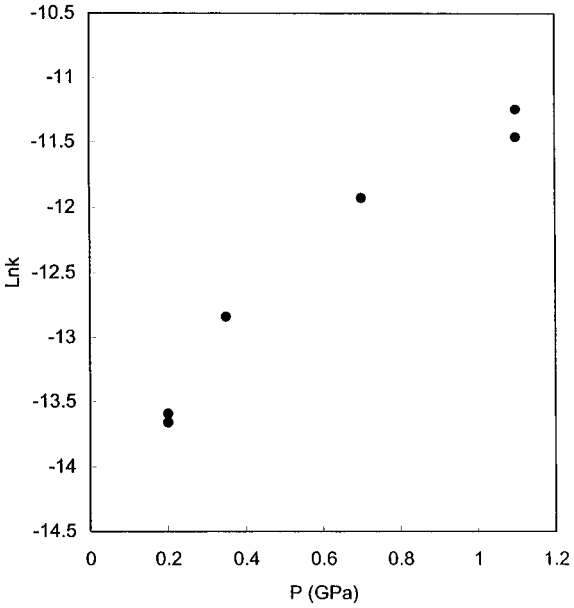


Figure 3. Activation volume profile of hexahydro-5-methyl-1,3,5-trinitropyrimidine in THF solvent at 145 °C.

Hexahydro-5-methyl-1,3,5-trinitropyrimidine was decomposed under different pressures in THF at 145 °C. The dependence of the rate of decomposition on the pressure is displayed in the Figure 3. Pressure accelerates the decomposition with activation volumes, −11.6 mL/mol between 0.2 GPa to 0.7 GPa, and −4.0 mL/mol between 0.7 and 1.1 GPa. Because of similarities between RDX and hexahydro-5-methyl-1,3,5-trinitropyrimidine, a mechanism parallel to that of RDX is proposed. At 0.2 and 1.1 GPa, the ratios of rate constant of RDX to that of hexahydro-5-methyl-1,3,5-trinitropyrimidine are 23 and 9, respectively. The thermal stability relative to RDX will be discussed hereafter.

The thermolysis of hexahydro-1,3,5,5-tetranitropyrimidine was studied in THF at 105 °C up to 1.1 GPa. Figure 4 shows the pressure effect on the rate of decomposition which, unlike RDX and hexahydro-5-methyl-1,3,5-trinitropyrimidine, shows a straight line with an activation volume of −3.5 mL/mol between 0.2 and 1.1 GPa. Even at 105 °C, its decomposition rate is still about 10 times faster than that of the RDX at 145 °C. This unusual instability can be understood by facile elimination of HNO_2 due to accumulation of NO_2 groups in its structure.

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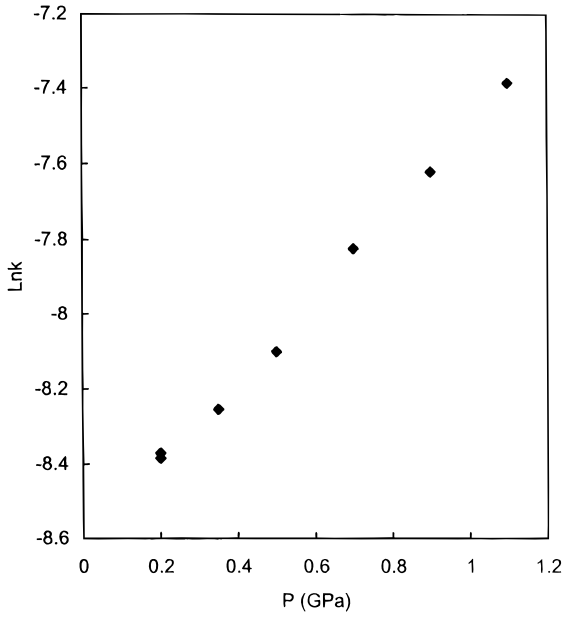


Figure 4. Activation volume profile of hexahydro-1,3,5,5-tetranitropyrimidine in THF solvent at 105 °C.

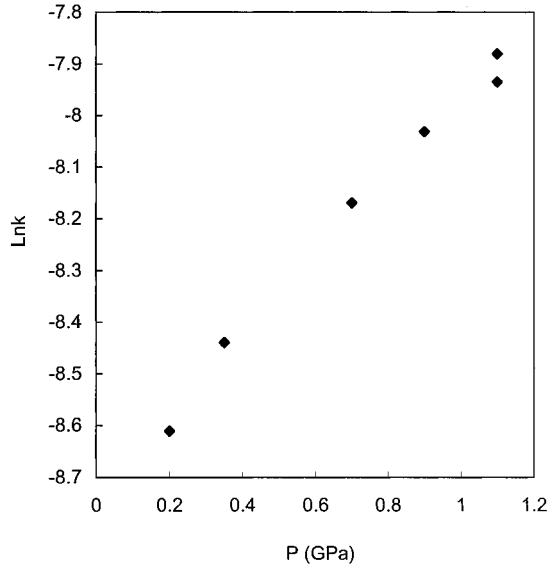
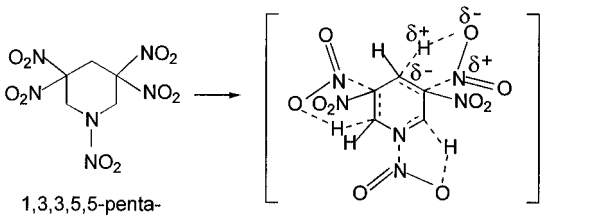
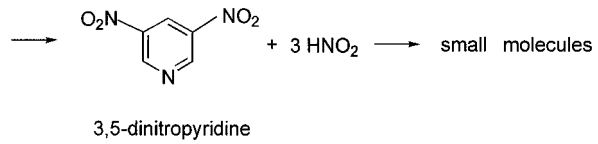


Figure 5. Activation volume profile of 1,3,3,5,5-pentanitropiperidine in THF solvent at 80 °C.

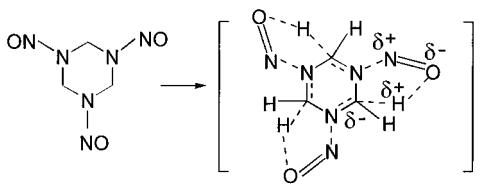
The decomposition of 1,3,3,5,5-pentanitropiperidine was studied in THF at 80 °C up to 1.1 GPa. The pressure effect on the rate of decomposition is displayed in Figure 5. It is also linear, and the activation volume is −2.2 mL/mol. At this relatively low temperature its rate of decomposition is still 10 times faster than that of RDX at 145 °C. The activation energy is estimated to be 21 kcal/mol with an activation entropy of −9R(J/K mol). The decrease in activation entropy suggests that the transition state has restriction of movement which could be associated with ring formation. The kinetic parameters suggest that its decomposition is a concerted elimination process. The small magnitude of ΔV^* could be explained by a concerted process with easy development of the transition state (an early transition state usually results in smaller activation volume and activation energy). We also detected 3,5-dinitropyridine with molecular weight of 169 amu by GC/MS. This result is a strong support for the elimination mechanism.



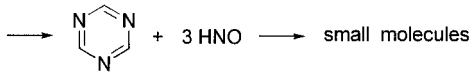


3,5-dinitropyridine

Nitrosamines. TRDX has a similar structure to that of RDX; the difference is that three NO_2 groups in RDX are replaced by three NO groups. TRDX was studied under the same experimental conditions as RDX. The activation volumes shown in Figure 6 are −11.7 mL/mol between 0.2 and 0.7 GPa, and −1.6 mL/mol from 0.7 to 1.1 GPa. The gaseous products are N_2O, CO_2, NO, and a small amount of CO. No 1,3,5-triazine was detected. Since a negative activation volume was observed, we ruled out the radical decomposition and proposed an elimination decomposition of HNO.

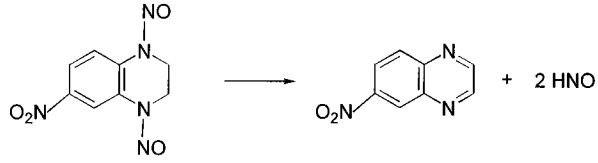


TRDX



TRDX is more stable than RDX. At 0.2 GPa, k_{RDX}/k_{TRDX} is 5 while at 1.1 GPa this ratio is 3. Its better thermal stability is due to the stronger N−NO bond in the TRDX, and a weaker attraction of the NO group for protons.

In the thermolysis of 1,2,3,4-tetrahydro-6-nitro-1,4-dinitrosoquinoxaline, we have found a negative activation volume of −3.5 mL/mol, and 6-nitroquinoxaline as a product.[6] It is noted that the temperatures to give equal rates of decomposition under the same pressure for 1,2,3,4-tetrahydro-6-nitro-1,4-dinitrosoquinoxaline and *N*-methyl-*p*-nitro-*N*-nitrosoaniline are quite different. The temperature for 1,2,3,4-tetrahydro-6-nitro-1,4-dinitrosoquinoxaline is 65 °C lower than that of *N*-methyl-*p*-nitro-*N*-nitrosoaniline. These results further illuminate and strengthen our proposed elimination mechanism.



1,2,3,4-tetrahydro-6-nitro-1,4-dinitrosoquinoxaline

6-nitroquinoxaline

The activation volume has been used to characterize many reaction mechanisms unambiguously including

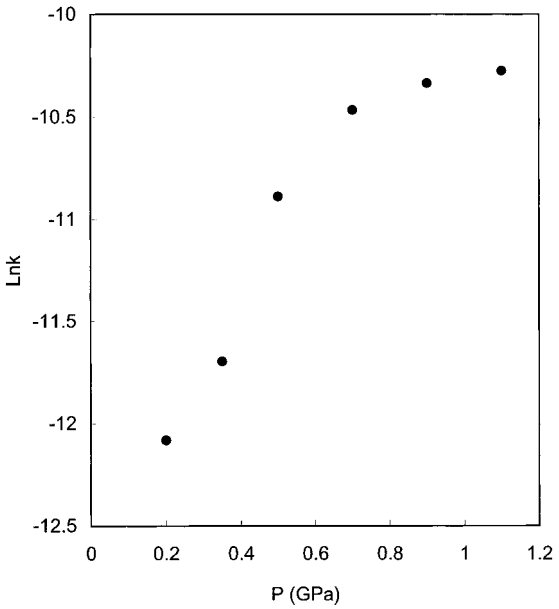


Figure 6. Activation volume profile of TRDX in THF solvent at 145 °C.

thermal decomposition of energetic materials.[6,9] Since activation volume can provide reliable information about the initial step of the activation process, it is extremely valuable for the studies of fast and complicated decomposition of practical explosives. These practical explosives, such as RDX and HMX, usually are large compounds with high density, and their decomposition mechanisms cannot be reliably inferred from product analysis and kinetic studies because of too many possible reaction channels, hardly detectable intermediates, and secondary reactions. Activation volumes of some nitramines and nitrosamines have been measured in our laboratory, and the results are listed in Table 1.[6] Most of the nitramines and nitrosamines in this table with positive activation volumes have been proved to decompose through radical processes by both kinetic studies and product analysis. The cyclic mononitramines, such as *N*-nitropyrrolidine and *N*-nitropiperidine, gave large positive activation volumes, indicating that the first step is homolysis of the $N-NO_2$ bond. Similarly, diisopropylnitramine shows a positive activation volume even though it has a labile tertiary hydrogen situated at α position to the nitro group. HMX, 1,3-dinitroimidazolidine, and hexahydro-1,3-dinitropyrimidine do not appear to undergo elimination as the first decomposition step. Therefore, positioning a methylene group at the α position to two strongly electron-withdrawing nitramine groups and formation of nonaromatic conjugated products do not play a key role in initiating concerted polarized elimination. Table 2 lists all nitramines and nitrosamines with negative activation volumes for thermolysis under high pressure in solution. A striking structural feature of all these compounds compared with those in Table 1 is that they are able to produce aromatic intermediates and products if they decompose through the elimination of HNO_2 or HNO. Because of observed negative activation volumes and detection of aromatic intermediates, we propose that thermal decomposition of these compounds is through the elimination of HNO_2 or HNO assisted by partial aromatization of the transition state. Under conditions of high pressure, the elimination pathway is highly preferred because the concerted transition state with five-center rings yields a negative activation volume.

Table 1. Nitramines and Nitrosamines with Positive Activation Volumes in the Thermolysis

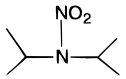
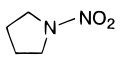
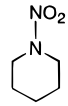
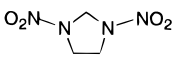
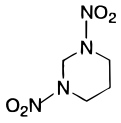
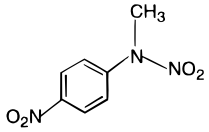
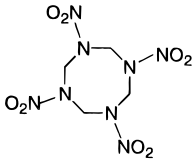
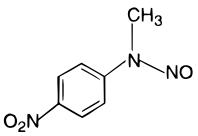
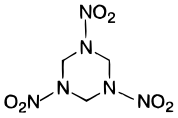
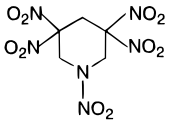
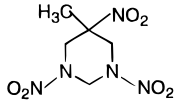
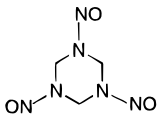
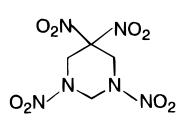
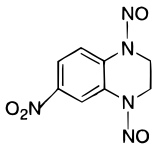
Structure Name	Activation volume ml/mol	Structure Name	Activation volume ml/mol
 Diisopropylnitramine	+47	 N-Nitropyrrolidine	+48
 N-Nitropiperidine	+34	 1,3-Dinitroimidazolidine	+18
 Hexahydro-1,3-dinitropyrimidine	+15	 N-Methyl-N, p-dinitroaniline	+39
 HMX	+25	 N-Methyl-p-nitro-N-nitrosoaniline	+12

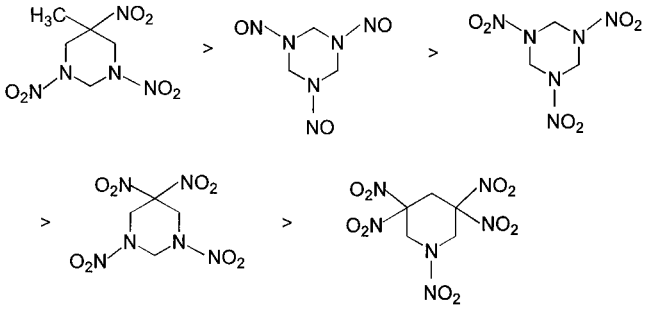
Table 2. Nitramines and Nitrosamines with Negative Activation Volumes in the Thermolysis

Structure Name	Activation volume ml/mol	Structure Name	Activation volume ml/mol
 RDX	-11.0	 1,3,3,5,5-Pentanitro-piperidine	-2.2
 Hexahydro-5-methyl-1,3,5-trinitropyrimidine	-11.6	 TRDX	-11.7
 Hexahydro-1,3,5,5-tetranitropyrimidine	-3.5	 1,2,3,4-Tetrahydro-6-nitro-1,4-dinitrosoquinoxaline	-3.5

Unlike the compounds in Table 1, the six-membered cyclic compounds in Table 2 decompose at markedly lower temperatures (ca. 145 °C and 80 °C) under high pressure. This suggests that the decomposition mechanism is not

direct homolysis of the nitramine bond because a homolytic process usually requires higher temperature for similar rates of reaction. This has been clearly demonstrated by the thermal stability of two very similar nitramines, RDX and HMX. RDX dissolved in THF solvent decomposed rapidly under 1.0 GPa and 167 °C, but decomposition of HMX in acetonitrile was not detectable at 200 °C and 1.0 GPa. The decomposition at low temperature can be attributed to the concerted polarized elimination of HNO_2 or HNO assisted by the aromatization of the transition state. It is well-known that aromatization of the transition state can significantly decrease the activation energy.

The reactivity of the six-membered cyclic compounds should be determined by the ease of elimination if the mechanism interpretation is right. The order of thermal stability determined by experiment is



This order of thermal stability is consistent with the order predicted by the elimination mechanism because it is well-known that electron-withdrawing groups, such as NO_2, in the molecule will make the hydrogen of α-methylene more acidic and the negative charge on the anionic carbon more stable. Therefore, the α-hydrogen will be abstracted more easily and the energy of the transition state will be lowered when the compounds contain more NO_2 groups. In contrast, a methyl group is an electron-donating group and has a destabilizing effect on the negative charge on the anionic carbon, and hence lowers the rate of elimination. These reasons explain why the 35 kcal/mol activation energy for RDX exceeds the 21 kcal/mol for 1,3,3,5,5-pentanitropiperidine and why the last two nitramines depicted above have smaller activation volumes and can decompose at such low temperatures.

Shaw[18] estimated that HMX has an activation energy greater than 38 kcal/mol when it undergoes five-center elimination of HNO_2. This is fairly consistent with our RDX results and supports our proposed elimination mechanism.

Conclusions

The pressure effect on the thermal decomposition rate of various nitramines and nitrosamines has been studied in this paper. Negative activation volumes, indicative of nonhomolytic decomposition, have been found for all of these six-membered cyclic nitramines and nitrosamines. These cyclic nitramines and nitrosamines have a structural feature leading to aromatic intermediates or products when elimination of HNO_2 and HNO occurs. On the basis of negative activation volumes, detection of aromatic intermediates, low decomposition temperature, and order of the thermal stability, we determined that these complex nitramines and nitrosamines decompose through the elimination of HNO_2 or HNO under high pressure.

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