**Kinetics.** The procedure was generally the same as for the kinetic studies of the methanolysis. The solution initially placed in the spectrophotometer cell contained the thiol, as well as $CF_3SO_3H$ and $CF_3SO_3Li$. The progress of the reaction was followed by monitoring the decrease in the absorbance of the solution at 405 nm. Plots of log $(A - A_\infty)$ vs time were linear, and the experimental first-order rate constant for a run was obtained from the slope of such a plot.

**Measurement of the Basicity of Sulfenamides. $^1$H NMR Method.** For **1a** in $CD_3CN$–$CD_3OD$ (5.0 or 8.2 M) the chemical shift for the $(CH_3)_2N$ protons occurs at $\delta$ 2.91. Addition of trifluoromethanesulfonic acid to such a solution initially causes this signal to move to higher $\delta$, but after enough acid has been added, further addition of acid has no effect on $\delta$, the reason being that once sufficient excess acid has been added **1a** is present entirely as **1a**-$D^+$, $ArSND^+(CH_3)_2$, and the chemical shift for the $(CH_3)_2N^+$ protons in **1a**-$D^+$ is not affected by addition of further acid to the medium.

Other studies, where a small amount of $(CH_3)_2ND_2^+$ $CF_3SO_3^-$ was also present in the solution, showed that the chemical shift ($\delta$ 2.63) for the $(CH_3)_2ND_2^+$ protons in this solvent was invariant with trifluoromethanesulfonic acid concentration and could therefore serve as a suitable internal standard.

Sulfenamide **1a** (5 mg) was dissolved in 5 mL of $CD_3CN$–5.0 M (or 8.2 M) $CD_3OD$. To 0.8 mL of this solution was added a measured amount (10–100 $\mu$L) of a 0.7 M stock solution of trifluoromethanesulfonic acid in $CD_3CN$. Also present in the solution was a sufficient amount of $(CH_3)_2ND_2^+$ $CF_3SO_3^-$ ($\delta$ 2.63) to serve as an internal standard. Immediately after injection of the acid the $^1$H NMR spectrum of the solution was recorded.

The fraction ($\alpha$) of the sulfenamide present as **1a**-$D^+$ is related to $K_b^D$ (eq 4-*d*) and $[D^+]$ as follows:

$$K_b^D = \alpha/(1 - \alpha)[D^+]$$

$$(1/\alpha) = 1 + (1/K_b^D[D^+]) \qquad (13a)$$

We define $\Delta\delta$ as the difference between the chemical shift for the $Me_2N$ protons in a particular acid solution and the chemical shift for the same protons in unprotonated **1a** ($\delta$ 2.91). Studies[17] of other protonation equilibria of the general type of eq 4-*d* have shown that

$$\alpha \sim \Delta\delta$$

Introducing $Y$ as the constant of proportionality between $\alpha$ and $\Delta\delta$ gives $\alpha = Y(\Delta\delta)$ and

$$1/(\Delta\delta) = (Y/K_b^D)(1/[D^+]) + Y \qquad (13b)$$

Regression analysis of plots of the data according to eq 13b gives $Y$ as the intercept and $(Y/K_b^D)$ as the slope. Such plots ($r \geq 0.996$) gave $Y = 2.1 \pm 0.05$ for the data for **1a** in MeCN containing 5.0 or 8.2 M $CD_3OD$ and slopes leading to the $K_b^D$ values for **1a** shown in Table III.

**UV Method.** Addition of sufficient $CF_3SO_3H$ to solutions of either **1a** or **1b** in MeCN–MeOH leads to an *immediate* decrease in the absorbance of the solution at 382 nm ($\lambda_{max}$ for **1**). This change has nothing to do with the absorbance change associated with the methanolysis of **1**; it is due to the fact that the UV absorption spectrum of **1**-$H^+$ is different from that of **1**. If $A_o$ is the optical density for the particular solution with **1** unprotonated, $A_{inf}$ is the optical density for the same solution with **1** completely protonated, and $A$ is the measured optical density for a particular concentration of added $CF_3SO_3H$, then

$$\alpha = (A_o - A)/(A_o - A_{inf})$$

For each **1** and methanol concentration, measurements were made using solutions containing $1.0–2.0 \times 10^{-4}$ M **1a** or **1b** and three to five different concentrations of added $CF_3SO_3H$ sufficient to give a conveniently measurable spread of $\alpha$ values. The data for each sulfenamide in a particular MeCN–MeOH solvent mixture were then plotted according to eq 13a. In each case such plots were linear ($r \geq 0.993$) and had an intercept on the $1/\alpha$ axis of $1.0 \pm 0.1$. Their slope is equal to $1/K_b^H$; those values are tabulated in Table III. The agreement for **1a** between $K_b^D$ (measured by the $^1$H NMR method) and $K_b^H$ (measured by the UV method), when account is taken of the anticipated solvent isotope effect,[3] provides reassurance that the UV method measures $K_b^H$ accurately.

The degree of protonation of two of the weak base amine indicators (*o*- and *p*-nitroaniline) used to establish the $H_o$ acidity scale[5] in dilute aqueous sulfuric acid was also measured by an analogous UV procedure for MeCN–MeOH mixtures containing from 1.0 to 8.2 M MeOH. The change in $K_b$ with changing [MeOH] in both cases paralleled very closely the changes found for **1a** and **1b** for the change in solvent. The measurements in MeCN–8.2 M MeOH gave the following $pK_a$'s for the two amines: *p*-nitroaniline, +1.70; *o*-nitroaniline, +0.41. These are 0.70 $pK$ units more positive than their $pK_a$'s in dilute aqueous solution, indicating that $a_{H^+}f_B/f_{BH^+}$ is five times *larger* for a given $[H^+]$ in MeCN–8.2 M MeOH than in water.

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# Pressure Effects on the Thermal Decomposition of Nitramines, Nitrosamines, and Nitrate Esters

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Solutions of nitramine and nitrate ester explosives and model compounds were thermolyzed at various hydrostatic pressures and their rates of decomposition were measured. The effects of pressure on their rates were used to infer the mechanism of their initial decomposition steps. Most nitramines, including the explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), appear to undergo homolysis of the N–$NO_2$ bond, because their reaction rates decrease with increasing pressure. Exceptions are hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and the model compound, 6-nitro-1,2-dinitroso-1,2,3,4-tetrahydroquinoxaline, which react faster with increasing pressure. These two compounds can aromatize by elimination of $HNO_2$ and HNO, respectively. Secondary nitrate esters shift their major decomposition pathway from homolysis of the O–$NO_2$ bond to elimination of $HNO_3$ in the pressure range of 0.4 to 0.8 GPa. The elimination reaction resembles carboxylate ester pyrolysis with E1 character.

## Introduction

There is an abundance of kinetic and mechanistic data pertaining to the decomposition of explosives with very little attention to the effect of pressure. The practical application of energetic materials usually involves exposure to intense shock waves or high dynamic pressures, and there is not much basis for theoretical prediction of their behavior under these conditions. Our aim is to increase

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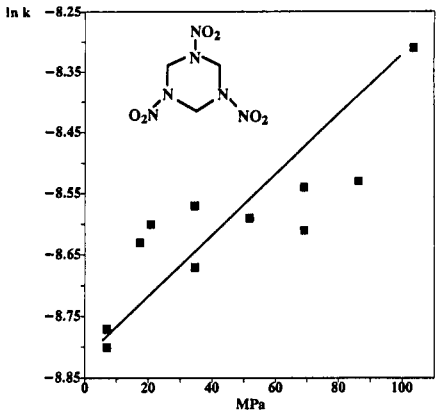


**Figure 1.** Activation volume plot of **3** in THF solvent.

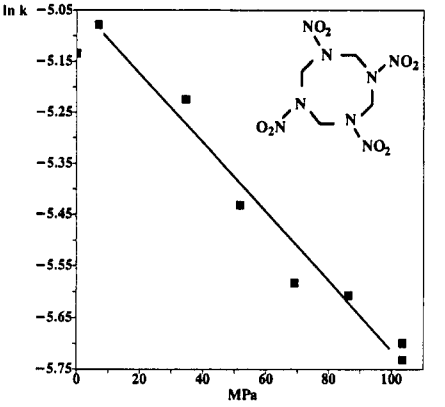


**Figure 2.** Activation volume plot of **2** in acetonitrile solvent.

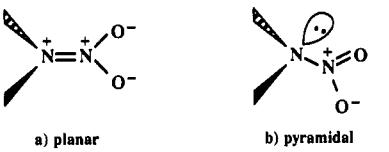


**Figure 3.** Two structural conformations of the *N*-nitro group.

the knowledge of pressure effects on the kinetics and mechanisms of explosive decomposition.

Bowden et al.[1] have found that heating pentaerythritol tetranitrate (**1**) at a constant rate resulted in explosion at a higher temperature when the pressure was increased to 2 GPa. In a similar study, Lee, Sanborn, and Stromberg[2] applied static pressures of 1 and 5 GPa to selected explosives and measured the time to explosion as a function of temperature. Under isothermal conditions, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (**2**) and **1** exhibited a decrease in time to explosion with higher pressure. Piermarini, Block, and Miller[3] found a 20-fold decrease of rate of decomposition for **2** in a diamond anvil cell when the pressure was raised from 3.0 to 6.6 GPa. In all of these studies, no chemical interpretation of the results was given.

A great effort has been devoted to clarifying thermal decomposition mechanisms of nitrate esters and nitramines, and most of the results are discussed in two reviews.[4-5] For primary and secondary nitrate esters, homolytic scission of the $O-NO_2$ bond is the first and rate-determining step at ambient pressure conditions.[6-9] Tertiary nitrate esters undergo an elimination reaction rather than homolysis.[10] Dimethylnitramine, the prototype of organic nitramines, follows a similar homolytic pathway in the gas phase.[11,12] However, for more complex nitramines, no experimental study has provided conclusive evidence as to whether the first step is homolysis, HONO elimination, or a mixture of both.[4]

## Results and Discussion

Explosives and model compounds were thermolyzed in solution for several reasons. First, a diluting solvent retards intermolecular reactions of the energetic compounds. Second, solvent stabilizes intermediates by quenching highly reactive species, such as $NO_2$, which would otherwise autocatalytically decompose the starting material. 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. Equation 1 gives an

$$\Delta V^* = -RT(\delta \ln k/\delta P)_T \quad (1)$$

isothermal relation between activation volume, $\Delta V^*$, and pressure effect on kinetic rates. Its use has contributed to clarifying many reaction mechanisms. Examples are discussed in a current book by Isaacs.[13] The facts we rely upon to interpret the present results are that (1) homolytic reactions have positive activation values 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 negative activation volumes.

**Nitramines and Nitrosamines.** The rates of decomposition of hexahydro-1,3,5-trinitro-1,3,5-triazine (**3**) and **2** in solution at various pressures are shown in Figures 1 and 2. Their respective activation volumes are −12 and +25 mL/mol. A negative value for compound **3** is suggestive of an ionogenic process and is ascribed to an elimination mechanism. On the other hand, the decomposition of **2** appears to involve homolytic scission only. There are two possible reasons why such closely related compounds show a surprising difference in their rate-controlling steps. The first is that differences in energy associated with the conformation of the nitro group show a significant dependence on ring size. It is well-known that the *N*-nitro group has two structural conformations, planar and pyramidal, and they are pictured in Figure 3. The sum of the angles for the ring nitrogens of $\alpha$ and $\beta$ polymorphs of **2** is approximately 360°, and the nitramine groups are said to be planar.[14] For **3**, the environment of the methylene groups is tetrahedral, one nitramine is planar and the remaining two have pyramidal conformation.[15]

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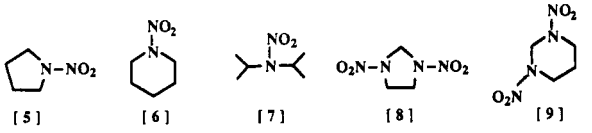
**Table I. Activation Volumes Measured for Nitramines and Nitrosamines over a Pressure Range of 0 to 100 MPa[a]**

| compound | solvent | decompostn temp (°C) | $\Delta V^*$, mL/mol |
|---|---|---|---|
| hexahydro-1,3,5-trinitro-1,3,5-triazine | THF | 170 | −12 |
| octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine | $CH_3CN$ | 205 | +25 |
| diisopropylnitramine | benzene | 203 | +47 |
| *N*-nitropiperidine | benzene | 240 | +34 |
| *N*-nitropyrrolidine | benzene | 235 | +48 |
| 1,3-dinitro-1,3-diazacyclopentane | THF | 163 | +18 |
| 1,3-dinitro-1,3-diazacyclohexane | THF | 205 | +15 |
| *N*-methyl-*N*,*p*-dinitroaniline | toluene/base | 100 | +39 |
| *N*-methyl-*N*-nitroso-*p*-nitroaniline | toluene/base | 140 | +12 |
| 6-nitro-1,4-dinitroso-1,2,3,4-tetrahydroquinoxaline | toluene/base | 85 | −3.5 |

[a] The solvent mixture, toluene/base, is a volumetric ratio 95:5 of toluene and piperidine base.

These explosives and other model compounds representing the different conformations have been studied by Burov and Nazin,[16] and they have found that the gas-phase decomposition of the conformational groups differ in reaction rate by a factor of 25 at 220 °C.

The second possible reason is that aromatization is the driving force for **3** to eliminate $HNO_2$ and form 1,3,5-triazine (**4**) as shown in eq 2. Compound **4** has been identified as a reaction product in pyrolysis of neat **3** under ambient pressure.[4,17] To determine the factors which favor elimination, the effects of pressure on the rates of thermolysis of various model arylnitramines and arylnitrosamines and cyclic mono- and dinitramines were measured and are given in Table I. The cyclic mononitramines, *N*-nitropyrrolidine (**5**) and *N*-nitropiperidine (**6**), gave large positive activation volumes, indicating that the first step is homolysis of the N–$NO_2$ bond. Likewise, diisopropylnitramine (**7**) shows a positive activation volume even though it has a labile tertiary hydrogen situated $\alpha$ to the nitramine group. Like **2**, the cyclic compounds 1,3-dinitro-1,3-diazacyclopentane (**8**) and 1,3-dinitro-1,3-diazacyclohexane (**9**) do not undergo elimination. Positioning a methylene group $\alpha$ to two strongly electron withdrawing nitramine groups does not appear to induce an ionogenic reaction.

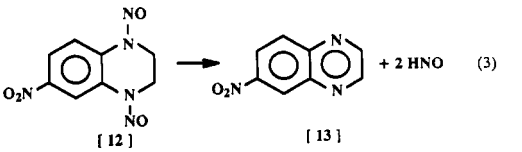


The activation volumes for the above nitramines are larger than usual for the general run of homolytic reactions (5 to 10 mL/mol range), and the magnitude can be partly attributed to a desolvation effect when the polar *N*-nitro bond undergoes homolysis to generate two less polarized products, the amino and $NO_2$ radicals. To exemplify such electrostrictive effect by polar compounds, the molar volumes at infinite dilution for *o*-, *m*-, and *p*-hydroxy-*N*,*N*,*N*-trimethylanilinium hydroxide inner salts in methanol and water are given in Table II.[18] It can be seen that the difference of the molar volumes of the inner salts dissolved in water and methanol ($V^\circ_{(water)} - V^\circ_{(MeOH)}$) suggests a strong solvent dependence. This is characteristic of the electrostrictive effect and is a consequence of the higher compressibilities of the less polar solvents. It can also be seen from Table II that the magnitude of the effect by electrostriction increases as the distance between charge centers increases. Therefore, we have reason to believe that *N*-nitro compounds, especially those having a planar structural conformation with significant charge separation (Figure 3a), may have a significant electrostrictive effect on nonpolar solvents. Furthermore, high temperatures of reaction have the effect of increasing activation volumes, which is easily understood as a consequence of the thermal expansion of solvent (i.e. increase in free volume). For example, the activation volume for homolytic scission of *tert*-butylperoxide was determined by Luft et al.[19] to be +13.4 mL/mol, which most interpreters would consider to be normal. On the other hand, the activation volume for the dissociation of bibenzyl at 395 °C is +31 mL/mol.[20] The difference in activation volumes can only be understood if the effect of temperature on free volume is considered. For the nitramines studied, the high temperatures have the effect of increasing their reaction volumes.

**Table II. Partial Molar Volumes at Infinite Dilution of Hydroxy-*N*,*N*,*N*-trimethylanilinium Hydroxide Inner Salts at 25 °C[18]**

| isomer | dipole length, Å | solvent | $V^\circ$ (mL/mol) | $V^\circ_{(water)} - V^\circ_{(MeOH)}$ |
|---|---|---|---|---|
| ortho | 2.85 | water | 129 | |
| ortho | 2.85 | methanol | 114 | 15 |
| meta | 4.27 | water | 123 | |
| meta | 4.27 | methanol | 105 | 18 |
| para | 5.70 | water | 120 | |
| para | 5.70 | methanol | 85 | 35 |

Arylnitramines and arylnitrosamines were pyrolyzed in toluene containing 5% piperidine. An excess of amine was necessary to avoid the acid-catalyzed Fischer Hepp rearrangement, which would have proceeded autocatalytically during the course of reaction. The activation volume for the decomposition of *N*-methyl-*N*,*p*-dinitroaniline (**10**) is +39 mL/mol and is ascribed to homolysis of the arylnitramine bond. The mechanism is in agreement with Barnes and Hickinbottom's study of thermal rearrangement of the same compound.[21] Thermolysis of *N*-methyl-*N*-nitroso-*p*-nitroaniline (**11**) has an activation volume of +12 mL/mol, which again suggests homolysis of the N–NO bond. In both cases, the products *N*-methyl-*p*-nitroaniline and *N*-nitrosopiperidine (from the reaction of $NO_x$ radical and excess piperidine) were detected and identified by GC-MS. Contrariwise, the activation volume for 6-nitro-1,4-dinitroso-1,2,3,4-tetrahydroquinoxaline (**12**) is −3.5 mL/mol, which is attributed to an elimination mechanism driven by aromatization as shown in eq 3. The mechanism is further revealed by the



(15) Choi, C. S. *Acta Crystallogr. B.* **1972**, *28*, 2857.
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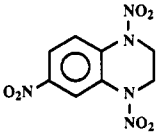
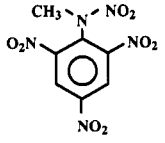
**Table III. Severe Reaction Conditions for Various Solutions of Nitramines and Their Outcomes**

| nitramine | conditions | outcome |
|---|---|---|
| diisopropyl-nitramine | 1.0 GPa; 205 °C; 18 h | no reaction |
| *N*-nitropiperidine | 1.0 GPa; 200 °C; 21.5 h | no reaction |
| 1,3-dinitro-1,3-diazacyclohexane | 1.2 GPa; 204 °C; 50 min | no reaction |
| octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine | 1.0 GPa; 200 °C; 90 min | no reaction |
| hexahydro-1,3,5-trinitro-1,3,5-triazine | 1.0 GPa; 167 °C; 100 min | complete reaction |

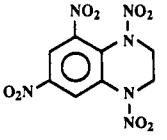
detection and identification of 6-nitroquinoxaline (13) as a decomposition product. It must also be noted that the temperatures selected to give equal rates of decomposition for compound 11 and 12 in solution differ by 65 °C. This large disparity strongly suggests different activation energies associated with different mechanisms of decomposition. Attempts to oxidize compound 12 to its nitramine counterpart, 1,4,6-trinitro-1,2,3,4-tetrahydroquinoxaline (14), by ozonolysis and with dimethyldioxirane failed. However, oxidation and possible nitration of compound 12 with 98% nitric acid yielded a yellow solid. Dissolved in a 95:5 toluene/piperidine mixture, the material degraded fairly rapidly at 25 °C to give an unidentified product and *N*-nitrosopiperidine. Such reactivity in solution made structural analysis by NMR an impossibility. An FTIR spectrum of the solid was nearly identical to that of *N*-methyl-*N*,2,4,6-tetranitroaniline (15), an explosive commonly known as "tetryl". It is suspected that the unidentified compound was 1,4,6,8-tetranitro-1,2,3,4-tetrahydroquinoxaline (16) and has a similar structure to those of 14 and 15. Its reactivity is assigned to a double elimination reaction with low activation energy.



[14]



[15]



[16]

In a final effort to measure the effects of pressure on nitramine decomposition, solutions of various model compounds and the explosives 2 and 3 were pyrolyzed under severe conditions of pressure. Table III gives the conditions of pressure, temperature, and time of reaction for the compounds with their respective qualitative outcomes. Compound 3 decomposed to completion, generating many gas products and an intractable black polymer. Decomposition of the remaining nitramines was completely prevented by high pressure.

In conclusion, we postulate that 3 is capable of concurrent decomposition by elimination of HONO and homolysis of the N–$NO_2$ bond. Evidence of homolysis has been demonstrated by the generation of the three nitroso intermediates of 3 in benzene solvent.[22] Also, from the temperatures of decomposition of 3 and other nitramines, the activation energy for concerted elimination appears to be comparable to that of homolysis.

**Nitrate Esters.** Pressure effects on the decomposition of cyclohexanol nitrate, propyleneglycol dinitrate, 1-pentanol nitrate, nitroglycerin (17), and *cis,cis*-3,5-cyclohexanetriol 1,3,5-trinitrate (18) in toluene and tetralin solvents were studied. Figure 4 gives the activation volume

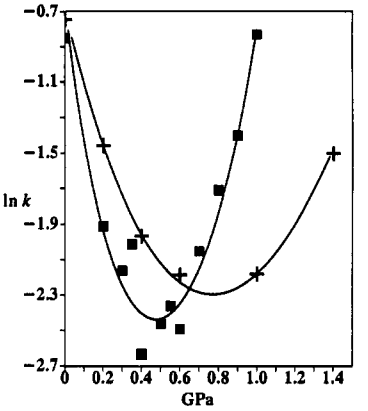



**Figure 4.** Activation volume profile of cyclohexanol nitrate in tetralin (■) and toluene (+) solvents.

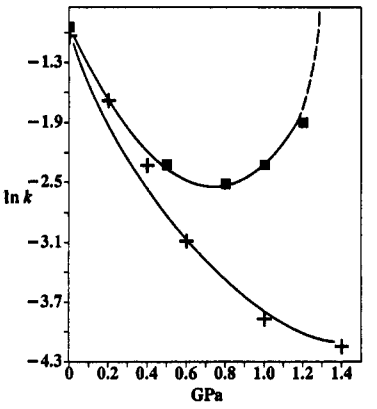



**Figure 5.** Activation volume profile of propylene glycol dinitrate in tetralin (■) and toluene (+) solvents.

profiles of cyclohexanol nitrate in both solvents at 170 °C. In tetralin solvent, the positive activation volume, +12 mL/mol between 0 and 0.5 GPa, is attributed to homolytic scission and diffusive separation of the O–$NO_2$ bond. The parent alcohol, cyclohexanol, is the principal reaction product in the low pressure regime. At higher pressures, however, an elimination mechanism is favored over homolysis. Above 0.5 GPa, cyclohexene is the major product and the apparent activation volume takes on a negative value of −10 mL/mol. Cyclohexanol nitrate dissolved in toluene behaves somewhat differently despite the chemical similarity of the solvents. The low and high pressure products from the two mechanisms are observable, but, as can be seen in Figure 4, the ascendancy of elimination over homolysis is gradual. The rate–pressure profiles in Figure 5, propylene glycol dinitrate in toluene and tetralin solvents, show a similar result. With toluene solvent, no reversal in the activation volume is seen at pressures approaching 1.4 GPa. On the other hand, tetralin solvent promotes the elimination process at pressures above 0.7 GPa. The solvent dependence is believed to be caused by either hydride or hydrogen atom donation from tetralin to the nitrate ester group preceding elimination, as shown in eqs 4 and 5. Decomposition rates of propylene glycol dinitrate in tetralin and deuterated tetralin were measured at 0, 0.8, and 1.2 Gpa at 155 °C. A negligible deuterium isotope effect was found at 0 GPa; homolysis is the principal route and solvent plays no part as reactant. At 0.8 and 1.2 GPa, $k_H/k_D$ ratios of 2.14 and 2.88 were found, respectively, confirming the participation of solvent as a reactant. In a similar kinetic isotope study, the rates of cyclohexanol nitrate decomposition in toluene and deuterated toluene were measured at 0, 0.4, 0.6, 1.0, and 1.4 GPa at 170 °C. There was no isotope effect at 0 and 0.4

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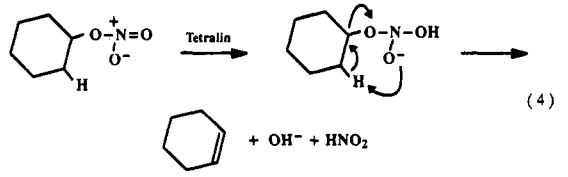
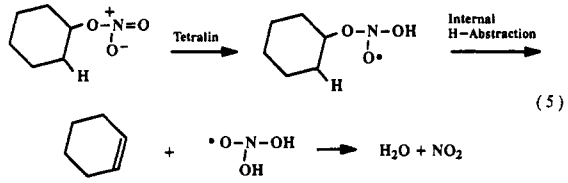
Hydride donation by tetralin




(4)

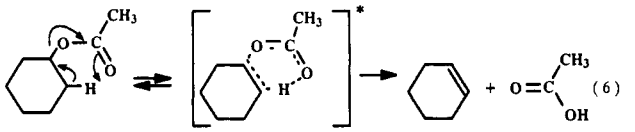
Hydrogen atom donation by tetralin



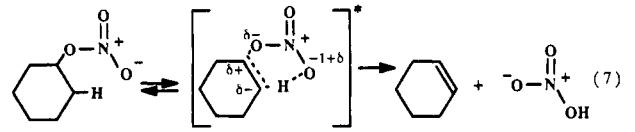

(5)

GPa, as expected for homolysis. At 0.6, 1.0, and 1.4 GPa, the $k_H/k_D$ ratios were 1.61, 1.38, and 1.37, respectively. These low values suggest that toluene is a poorer hydride or hydrogen atom donor than tetralin and that cyclohexanol nitrate undergoes concurrent decomposition by an elimination mechanism and one of the bimolecular routes shown in eqs 4 and 5. Additional evidence indicates that hydride, rather than hydrogen atom donation, is the more plausible route. Propylene glycol dinitrate rapidly increases its rate of decomposition between 1.0 and 1.4 GPa, with an activation volume of approximately −25 mL/mol. Measuring the rate of decomposition at 1.4 GPa proved difficult since it reacted too quickly. Electrostriction of the transition state by hydride donation would result in a large acceleration in decomposition with increasing pressure. A similar ionic bimolecular mechanism has been postulated for the reaction of coal and tetralin.[23]

The mechanism of nitrate ester elimination is thought to be similar to that of ester pyrolysis, shown in eq 6. The



(6)



(7)

effect of pressure on the decomposition rate of cyclohexanol nitrate in toluene implies that the mechanism is ionogenic. The apparent activation volume is −5 mL/mol in the range of 1.0 and 1.4 GPa. It therefore appears that the mechanism of elimination for nitrate esters has some E1 character, eq 7. It is unusual to have a reaction with a large activation volume at high pressures (i.e. the pressure regime where the free volume of a solvent is small). Activation volumes for some Diels–Alder reactions have been measured in excess of −50 mL/mol for the first 0.1 GPa, but they rapidly decrease with reduction of free volume at the higher pressures. The glycerolysis of 2-bromopropane between 0 and 8.2 Gpa is an exceptional example where the reaction continues to be significantly accelerated by pressures above 1.0 GPa. Cameron et al.[24] determined its activation volume to be −30 mL/mol when extrapolated to zero pressure. Between 1.0 and 2.0 GPa, the volume takes on a smaller value of approximately −2 mL/mol.

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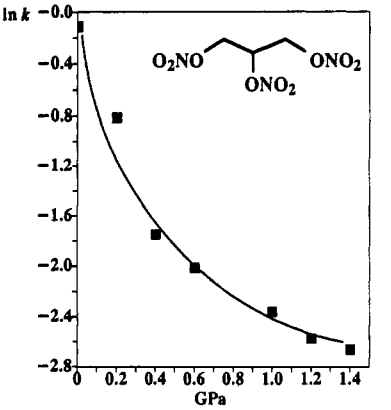


**Figure 6.** Activation volume profile of compound 17 in toluene solvent.

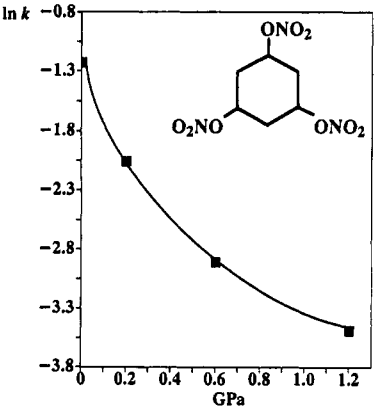


**Figure 7.** Activation volume profile of compound 18 in toluene solvent.

When electron-withdrawing groups are situated near the nitrate ester, their effect is to destabilize the transition state by induction and to retard the elimination reaction. This is seen from the activation volume profiles of propylene glycol dinitrate, (17), and (18) in toluene solvent, Figures 5, 6, and 7, respectively. There is no reversal in the sign of the activation volume profiles up to 1.4 GPa, giving no apparent indication of change in mechanism from homolysis. However, product analysis of 18 at low and high pressure conditions demonstrated the existence of a crossover from homolysis to elimination. Compound 18 decomposes to undeterminable products at 0 GPa but gives exclusively benzene, an elimination product, at 1.4 GPa. More evidence of E1 character in the elimination mechanism comes from the pressure effect on the decomposition of 1-pentanol nitrate. From 0 to 1.4 GPa, the chief decomposition product of 1-pentanol nitrate is its parent alcohol, *n*-pentanol. The primary carbon sufficiently destabilizes the transition state, disallowing the elimination route for primary nitrate esters. Such observations are comparable to those found in pure E1 eliminations.

## Experimental Section

**General Procedure.** GC-MS was performed with a Hewlett Packard GC 5890A, coupled to a Hewlett Packard mass selective detector, Model 5970. Infrared analyses were done on a Perkin-Elmer FTIR spectrophotometer, Model 1710. $^1$H NMR spectra were obtained on a Varian EM 360A instrument at 60 MHz, and melting points were determined with a Mel-Temp apparatus and are uncorrected.

**Materials.** The preparation of 1-pentanol nitrate with mixed acids is given by Pattison and Brown.[25] Cyclohexanol nitrate,

(25) Pattison, F. L. M.; Brown, G. M. *Can. J. Chem.* **1956**, *34*, 880.

propylene glycol dinitrate, and compound 18 were obtained by nitrating the parent alcohols with acetyl nitrate as described by Soffer, Parotta, and DiDomenico.[26] Compounds 17 and 3 were synthesized following the methods of Davis.[27] Nitramines 5 and 6 were prepared by catalytic dehydration of the nitrate salts.[28] 7 was obtained by direct nitration of the amine with dinitrogen pentoxide.[29] 8 and 9 were synthesized in a four-step process described by a number of authors.[30-33] Highly purified 2 was obtained from a commercial source. Deuteration of tetralin was performed by base-catalyzed exchange with $D_2O$ and NaOD.[23] The arylnitramine, 10, was prepared following the method of Hughes and Jones.[34]

**6-Nitro-1,4-dinitroso-1,2,3,4-tetrahydroquinoxaline (12).** The aryldinitrosamine was synthesized by direct N-nitrosation and aromatic nitration, preceded by Fisher Hepp rearrangement, of 1,2,3,4-tetrahydroquinoxaline (19) with $NO_2$. Compound 19 was prepared by reduction of quinoxaline with $LiAlH_4$.[35] 19 (1.5 g) was dissolved in 50 mL of benzene and fed dropwise into a reaction flask by means of a separatory funnel. The addition required approximately 30 min. The flask contained a well stirred solution of 30 mL of benzene, into which a stream of $NO_2$ was bubbled at a rate of 0.05 L/min. Upon addition, the benzene solution was stirred for an additional 30 min, and the remaining unreacted and dissolved $NO_2$ was purged by a stream of air. The solution was neutralized to litmus with several washings of 5% $NaHCO_3$, and the product was collected by evaporation of solvent. Recrystallization from MeOH afforded red crystals of 12, mp 141–2 °C dec. FTIR (KBr): 1612, 1598, 1520, 1470, 1343, 1304, 1208, 1181, 1079, 947, 851, 815, 751 $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 4.23 (s, $CH_2CH_2$, 4 H), 8.40 (s, aromatic, 2 H), 8.97 (s, aromatic, 1 H).

***N*-Methyl-*N*-nitroso-*p*-nitroaniline (11).** The method described above was utilized, but with 1.2 g of *N*-methylaniline as the amine reactant. Recrystallization from MeOH yielded pale yellow crystals of 11, mp 100 °C (lit.[36] mp 102–3 °C). $^1H$ NMR ($CDCl_3$): $\delta$ 3.47 (s, $CH_3$, 3 H), 7.67–8.43 (m, aromatic, 4 H).

**Pressure Apparatus.** Two devices were available for pressurizing reaction solutions. With the first, a maximum pressure of 100 MPa and maximum temperature of 350 °C were achieved. The reactor was a heavy-walled stainless steel tube with one end sealed. It is 130 mm long, with 6.4 mm o.d. and 2.3 mm i.d. This tube held a reaction mixture contained in a glass melting point capillary, and it was connected to a hydraulic pump. The heavy-walled reactor tube was heated by inserting it into a massive aluminum block, in which a matching hole was drilled. The temperature of the block was maintained constant to within ±0.3 °C by means of a thermostat. The reactor tube was experimentally determined to have a time constant of 40 s and allowance was made in the calculation of reaction rates. Glass capillary tubes, measuring 90 mm long, 1.8 mm o.d., and 1.5 mm i.d., were heated and slightly drawn to form a constriction near the open end. These tubes were filled with approximately 50 μL of a 1–2% solution, and a 15–20 μL bead of mercury was placed above the constriction to serve as a seal and transmitter of hydraulic pressure. The large surface tension of mercury permitted it to remain above the constriction. When the concentration of the reaction solution was too high, the gaseous decomposition products blew the mercury seal out upon release of the hydraulic pressure. Therefore, only dilute reaction solutions could be used with this technique.

The second pressure vessel originated from a monoblock design by Lavergne and Whalley[37] and was capable of achieving pressures up to 2.0 GPa. A casing of Astroloy or Carpenter's steel rod stock, 2.5 in. in diameter, was cut to a height of 2 in., and the center was drilled and lapped to approximately 0.25 in. A piston and plug set were machined from drill rod steel to match the bore's dimension with a tolerance of 0.0005 in. All metal components were heat treated for optimum hardness. Sample containers were 1-in. lengths of PFTE tubing (0.25 in. o.d. and 0.125 in. i.d.) capped with PFTE plugs, which plastically deformed into reliable gaskets. Teflon was ideal for containing reactions due to its inertness; however, severe extrusion occurred when temperatures approached 230 °C. After reaction, the sample was collected by removing the piston, drilling a $^1/_{32}$ in. hole through the Teflon plug, and extracting the fluid with a syringe for analysis. The cell fitted snugly into an aluminum block of large mass and was mounted onto a Carver hydraulic press. The temperature of the block was maintained to within 1 °C by means of a heat controller. To prevent large thermal gradients within the cell, the press anvils were also heated.

**Analysis.** A special technique was developed for kinetic measurements of nitrate ester and nitramine decomposition by use of FTIR spectrophotometry. The nitro group's asymmetric stretch (1650–1620 $cm^{-1}$ for nitrate esters and 1600–1530 $cm^{-1}$ for nitramines) is highly absorbing, and its rate of disappearance was followed. Special effort was made to decompose these compounds without interference from bimolecular reactions; therefore dilute solutions were made up such that they had approximately 0.7 absorbance units with a NaCl cell having a path length of 0.25 mm. Typical concentrations were on the order of 0.02 M. Solvent choice was critical for reliable FTIR data. Tetrahydrofuran, acetonitrile, benzene, toluene, and tetralin were often used, since they are relatively transparent in the N=O stretching regions. Typically, a solution was reacted for a given time and pressure such that 80 to 50% remained. The solution was collected and transferred to the infrared cell and analyzed. The ratio of final to initial absorbances gave the fraction of starting material remaining. It was determined that nitramines and nitrate esters followed Beer's law within a range of 0.18 to 0.85 absorbance units, and no adjustments to the absorbances were deemed necessary.

**Activation Volume Measurements.** The activation volumes, $\Delta V^*$, were obtained from plots of ln $k$ versus $P$ according to eq 1. Figure 1 and 2 represent such a plot for the decomposition reactions of 2 and 3. In the cases of nitrate esters, $\Delta V^*$ values were calculated for specific pressure ranges where the slope of ln $k$ versus pressure is approximately linear. All kinetic calculations were based on a (pseudo) first-order rate law.

**Error.** On the basis of reproducibility, we estimate that the relative error in rates of nitramine decompositions is ±10%. For cyclohexanol nitrate in tetralin, where the rates were obtained by GC-MS, an error of ±15% is estimated. The rates of all other nitrate esters, obtained by FTIR spectrometry, have an error of ±8%.

**Acknowledgment.** Financial support for this work was provided by Research Center for Energetic Materials, a joint National Science Foundation/Industry supported research center.

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