Effect of Pressure on the Thermolysis of Nitroalkanes in Solution

Jiang Wang*,† and Kay R. Brower

Department of Chemistry, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801

Darren L. Naud

American University of Beirut (AUB), Beirut, Lebanon

Received March 27, 1997[⊗]

The effect of pressure up to 1.1 GPa on the rates of decomposition of two acidic nitroalkanes, nitromethane and 2-nitropropane, was measured. The mechanisms of thermolysis are inferred from kinetic studies and product analysis. The rate-controlling step for nitromethane decomposition in toluene at 230 °C at low pressures is homolysis of the C−N bond. Beyond 20% conversion, the decomposition is autocatalytic. At high pressure, nitromethane has another reaction path which supplants homolysis. It is proposed that nitromethane forms an intermediate by cyclization of its aci-form. The high-pressure process is characterized by a first-order rate law without primary kinetic isotope effect, a low activation energy (28.5 kcal/mol), a negative activation volume (−5.5 mL/mol), and formation of products which cannot be attributed to radical intermediates. At high conversion, the reaction becomes autocatalytic as a result of accumulation of water leading to formation of products explainable by the Nef reaction. 2-Nitropropane is less stable than nitromethane. Pressure powerfully accelerates its decomposition owing to its activation volume averaging −11.2 mL/mol from 0.1 to 1.1 GPa. It is believed to cyclize via the aci-form like nitromethane. 2,2-Dinitropropane does not have α hydrogen and cannot tautomerize. In earlier work it was found to have a homolytic mechanism at high pressure. Therefore, the decomposition pathways of nitroalkanes in aprotic solvents are determined not only by the conditions but also by the availability of α hydrogen.

Introduction

Nitromethane, the simplest of the aliphatic nitro compounds, is an explosive and monopropellant. Up to the present, many studies of its thermal stability under various conditions have been reported.[1−6] The pyrolysis of gaseous nitromethane at temperatures from 305−440 °C was investigated by Crawforth and Waddington.[7] The activation energy (E_a) was 55.5 kcal/mol which agrees well with C−N bond dissociation energy, 60 kcal/mol. The products in order of abundance are CO, CH_4, H_2O, N_2, CO_2, and small amounts of HCN and oxides of nitrogen. It was suggested that methyl radicals are generated by homolysis of the C−N bond and converted to methane by hydrogen abstraction:

$$CH_3NO_2 \rightarrow {}^{\bullet}CH_3 + NO_2 \qquad (1)$$

$${}^{\bullet}CH_3 + CH_3NO_2 \rightarrow CH_4 + {}^{\bullet}CH_2NO_2$$

Recently another mechanism involving methyl nitrite as an intermediate was proposed by Dewar et al.[8]

$$CH_3NO_2 \rightarrow CH_3ONO \rightarrow \text{products} \qquad (2)$$

They found that the activation energy for methyl nitrite rearrangement is 13 kcal lower than that of the C−N homolysis. Wodtke et al.[9] on the other hand found evidence there is only a small difference in activation energy between homolysis and rearrangement. They claimed that mechanisms 1 and 2 operate in parallel. Lee, Sanborn, and Stromberg[10] have studied effects of pressure on the rate of decomposition of various explosives, and nitroalkanes appear to be anomalous. Reported time-to-explosion measurements on nitromethane indicate that pressure decreases the time required to achieve an explosion while an opposite effect was found for 2,2-dinitropropane and other explosives. Engelke et al.[11] found that high pressure applied to nitromethane increases the concentration of the nitronate ion and proposed that sensitivity is directly related to this effect. Miller et al.[12,13] reported that pressure increased the decomposition rate of liquid nitromethane and a reduction of the frequency of the asymmetric stretching mode of NO_2 with increasing pressure was observed. They proposed a bimolecular mechanism which accounts for the observed products, ammonium formate and water. Naud and Brower[14] studied the products and rates of

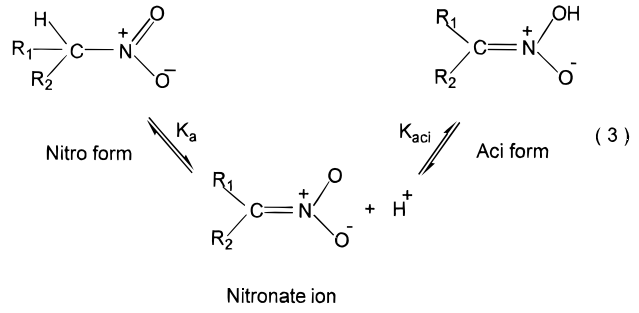
* Corresponding author.
† Current address: Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.
⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) Brasch, J. W. *J. Phys. Chem.* **1980**, *84*, 2084.
(2) Brower, K. R. *J. Org. Chem.* **1988**, *53*, 3776.
(3) Engelke, R.; Earl, W. L.; Rohlfing, C. M. *J. Chem. Phys.* **1986**, *84*, 142.
(4) Trocino, J. L. *Techniques for Sensitizing and Detonating Nitromethane-Based Explosive Systems, Bulletin JLTN-2, April 1972; Sixth Symposium (Intl.) on Detonation*, edited by Edwards, D. J., Ed. (Office of Naval Research, Washington D. C.), 1976, p 99.
(5) Engelke, R.; Earl, W. L.; Rohlfing, C. M. *Int. J. Chem. Kinet.* **1986**, *18*, 1205.
(6) Cook, M. D.; Haskins, P. J. *19th Intl. Annu. Conf. ICT* **1988**.
(7) Crawforth, C. G.; Waddington, D. J. *Trans. Faraday Soc.* **1969**, *65*, 1334.
(8) Dewar, M. J. S.; Ritchie, J. R.; Alster, J. *J. Org. Chem.* **1985**, *50*, 1031.
(9) Wodtke, A. M.; Hintsa, E. J.; Lee, Y. T. *J. Chem. Phys.* **1986**, *84*, 1044.
(10) Lee, E. L.; Sanborn, R. H.; Stromberg, H. D. *Proc. 5th Symp. (Intl.) Detonation*, **1970**, 331.
(11) Engelke, R.; Schiferl, D.; Storm, C. B.; Earl, W. L. *J. Phys. Chem.* **1988**, *92*, 6815.
(12) Miller, P. J.; Block, S.; Piermarini, G. J. *J. Phys. Chem.* **1989**, *93*, 457.
(13) Miller, P. J.; Block, S.; Piermarini, G. J. *J. Phys. Chem.* **1989**, *93*, 462.
(14) Naud, D. L.; Brower, K. R. *High-Pressure Res.*, **1992**, *11*, 65.

S0022-3263(97)00563-X CCC: $14.00 © 1997 American Chemical Society

decomposition of solutions of 2-nitropropane with an equimolar quantity of piperdine in THF at various hydrostatic pressures. They found that pressure accelerated decomposition and the principal products were acetone and acetone oxime in equimolar proportions. The key step is thought to be a bimolecular reaction of nitronate ion with the aci form of 2-nitropropane.

Nitroalkanes with α hydrogens are weak acids and have two tautomeric forms. It is well established that the acid tautomer (aci form) equilibrates with the nitro tautomer (nitro form) by way of the nitronate ion. The equilibrium for nitroalkanes is as follows:



(3)

$$K_a = \frac{[\text{Nitronate ion}]\,[H^+]}{[\text{Nitro form}]} \qquad (4)$$

$$K_{aci} = \frac{[\text{Aci form}]}{[\text{Nitronate ion}]\,[H^+]} \qquad (5)$$

$$K_T = K_a\,K_{aci} = \frac{[\text{Aci form}]}{[\text{Nitro form}]} \qquad (6)$$

Turnbull and Maron[15] measured the ionization constants for aci and nitro forms and the tautomeric equilibrium constants in aqueous solution. They found that the preferred tautomer is the nitro form. The equilibrium constants, K_T, for nitromethane and 2-nitropropane at 25 °C are 1.1×10^{-7} and 2.75×10^{-3}, respectively. Methyl substituents greatly increase the stability of the aci form.

In most of the published kinetics studies the only intensive variable was temperature, and the role of pressure on the rates and mechanisms of decomposition of nitroalkanes was essentially unknown. In this paper, we report the pressure and temperature effects on the decomposition of nitroalkanes in solution. Through a combination of measured activation volumes and identification of products of decomposition, we postulate their possible decomposition mechanisms.

Experimental Section

High pressure experimental work was performed using a piston-in-cylinder assembly described by Naud and Brower.[16] The decomposition temperature was maintained to within 1 °C in the range of 195 °C to 260 °C. Gas chromatography (GC) was used to measure the conversion of nitroalkane. Dilute solutions of nitroalkane (in toluene) were heated, and conversion of nitroalkanes ranged from 5−75%. For kinetic studies involving determination of reaction order, activation volume, and activation energy, the conversion was less than 25% to avoid autocatalysis.

For low-pressure thermolysis, 30-μL samples of 10 wt % nitromethane in toluene were sealed in 5.5 cm capillary tubes and heated at temperatures from 250 to 302 °C. The rate of thermal decomposition was followed by GC using a thermal conductivity detector (TCD). The pressure in the capillary tube depends on the volatility of the solvent, the amount of gas evolved, and the temperature. The tube was capable of containing 100 atm during thermolysis without bursting.

Activation volumes were obtained from plots of ln k versus P according to eq 7.

$$\Delta V^* = -\mathrm{RT}(\delta \ln k/\delta P)_T \qquad (7)$$

Their values in each case 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.

A Hewlett-Packard GC 5890A coupled to a Hewlett-Packard mass selective detector 5970 was employed for product analysis. Identification of products was achieved by comparing the mass spectra to those of the authentic samples or by interpretation of the fragmentation pattern. Gas-phase products, such as CH_4, CO, CO_2, N_2O, NO, and NO_2 were analyzed by Fourier transform-infrared spectroscopy (FTIR). No rigorous attempt was made to quantify the products of reaction.

Nitroalkanes and solvents were obtained either from Aldrich or Fluka Chemical Co. and used without further purification.

Results and Discussion

In contrast to previous work[10,12,13] using pure explosives, our experiments use solutions in aprotic solvents for the following reasons. A diluting solvent can suppress intermolecular reactions and scavenge highly reactive intermediates, such as NO and NO_2, which could otherwise lead to autocatalysis. Furthermore, it is convenient to measure reaction order by changing the reactant concentration.

From the pressure effect on the rates of decomposition it is possible to evaluate the molar volume difference between reactants and their transition state which is defined as the activation volume (ΔV^*):

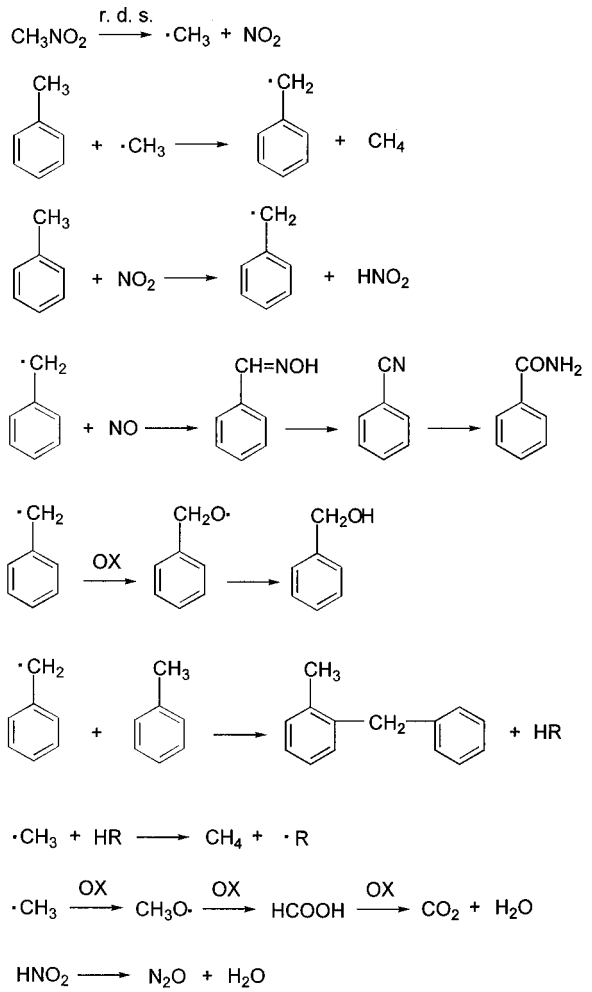
$$\Delta V^* = V^* - \Sigma V_r \qquad (8)$$

The activation volume can help to characterize transition states and elucidate reaction mechanism according to a review by Asano and le Noble.[17] The facts we rely upon to interpret the results of the effects of pressure are that (1) homolytic reactions have positive activation volume ranging from +5 mL/mol at low temperatures to +40 mL/mol at high temperatures; (2) reactions which lead to electrical polarization either by bond formation or bond breaking have large negative activation volumes; (3) the observed activation volume for a reaction having a preequilibrium step is the sum of the volume change for the equilibrium and activation volume of the rate determining step.

1. Thermal Decomposition of Nitromethane in Toluene at Pressure Below 100 Atmospheres. Decomposition of 10 wt % nitromethane in toluene followed a pseudo first-order rate law at low degrees of reaction (≤20%). This is ascribed to homolytic cleavage of the C−N bond as the rate-determining step in the thermal decomposition. The activation energy is 53.5 kcal/mol, and it was obtained from a straight line of Arrhenius plot. This activation energy is close to the dissociation energy

(15) Turnbull, D.; Maron, S. H. *J. Am. Chem. Soc.* **1943**, *65*, 212.
(16) Naud, D. L.; Brower, K. R. *J. Org. Chem.* **1992**, *57*, 3303.
(17) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 409.

Scheme 1



of the C−N bond, 60 kcal/mol. The activation entropy change (ΔS^*) calculated from the Eyring equation is $+3.1R$ (J/K mol). The high E_a and large preexponential factor (positive ΔS^*) suggest that decomposition is a unimolecular radical process and C−N bond homolytic scission is the rate-determining step. The gaseous products detected by FTIR for 30% decomposition, in order of abundance are CO_2, N_2O, CH_4, and CO. It is probable that methane is formed from methyl radicals by hydrogen abstraction and that methyl radicals are generated by homolysis of the C−N bond. The liquid products analyzed by GC/MS in order of abundance are benzonitrile, benzyl alcohol, benzyltoluene, water, and benzamide. The yield of these products reaches a plateau when the conversion of nitromethane is 20%. The involvement of toluene in the radical decomposition is shown in Scheme 1.

When nitromethane decomposition exceeds 20%, an increase in decomposition rate is observed in Figure 1, and the percentage yield of radical products such as C_6H_5-CN decreases. An insoluble tarry material was also formed. The radical mechanism is therefore overtaken by another mechanism at higher conversion. A trace amount of water added to a nitromethane solution was found to increase the rate of decomposition 30-fold. This suggests that water accumulating at high conversion catalyzes the decomposition of nitromethane and leads to autocatalysis through the Nef reaction shown in Scheme 2.

At higher conversion the ratio of CH_4 to N_2O decreased. Formaldehyde was not found. This may be due to its high reactivity in redox and condensation reactions leading to tarry products.

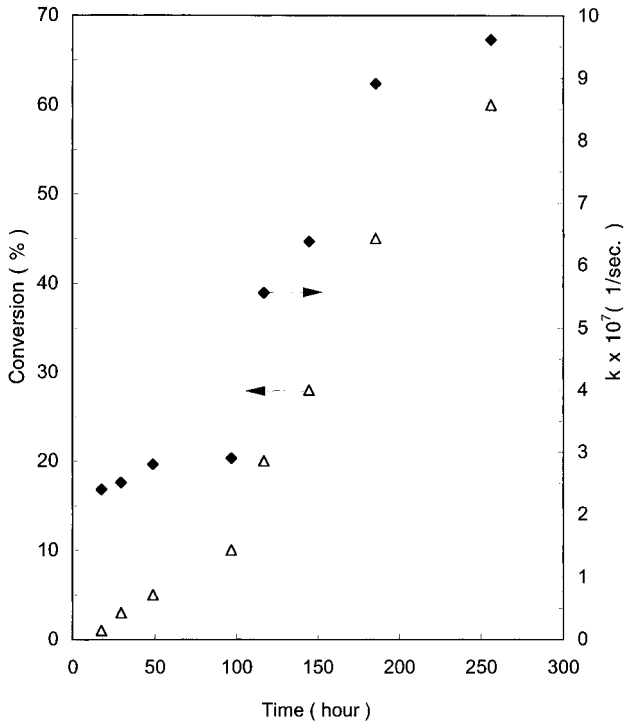
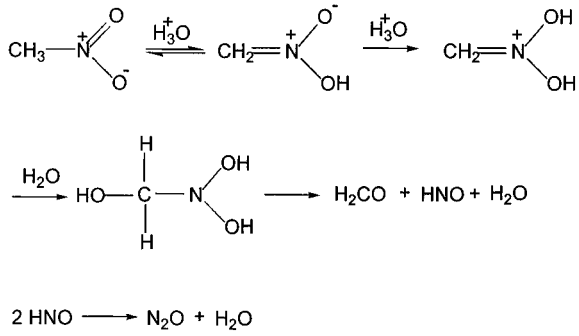


Figure 1. Rate constant and conversion of 10 wt % nitromethane decomposed in toluene under low pressure at 250 °C.

Scheme 2



2. Thermal Decomposition of Nitromethane in Toluene under High Pressure. At 0.7 GPa, the decomposition rate of 10 wt % nitromethane was measured at various temperatures, and the Arrhenius plot is a perfect straight line. The E_a and ΔS^* were 28.5 kcal/mol and −14.6R (J/K mol), respectively. These low activation parameters clearly demonstrate that the decomposition mechanism at higher pressure is different from that at low pressure. It is not a radical process. FTIR analysis did not give any evidence of CH_4 formation but CO_2, N_2O, and traces of water were found. A higher ratio of N_2O to CO_2 was found at higher conversion. The yield of black polymeric substance was greater at higher conversions. It varied in consistency from tar to powdery solid depending on conditions. The products in solution were analyzed by GC/MS after removal of the black tar. Water was formed, but no product derived from toluene could be detected. It is evident that toluene plays no direct chemical role at high pressure and that the radical decomposition mechanism can be ruled out. Acceleration of the decomposition rate by pressure was observed at pressures up to 1.1 GPa at 230 °C. The activation volume

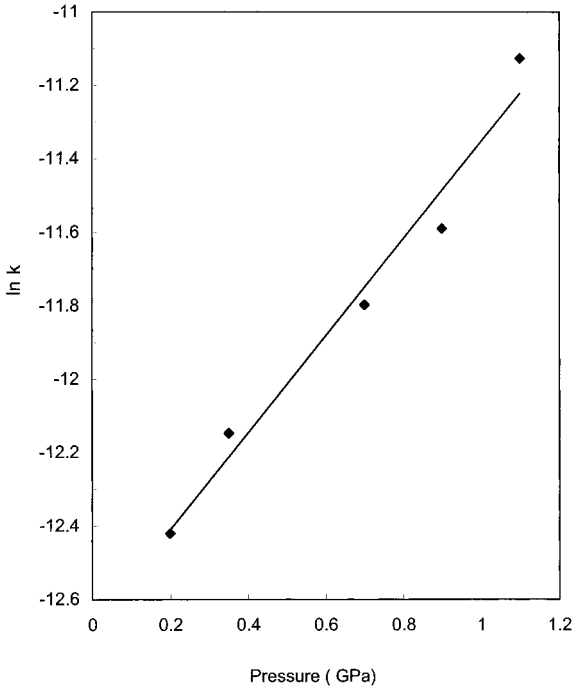


Figure 2. Activation volume profile of 10 wt % nitromethane decomposed in toluene at 230 °C.

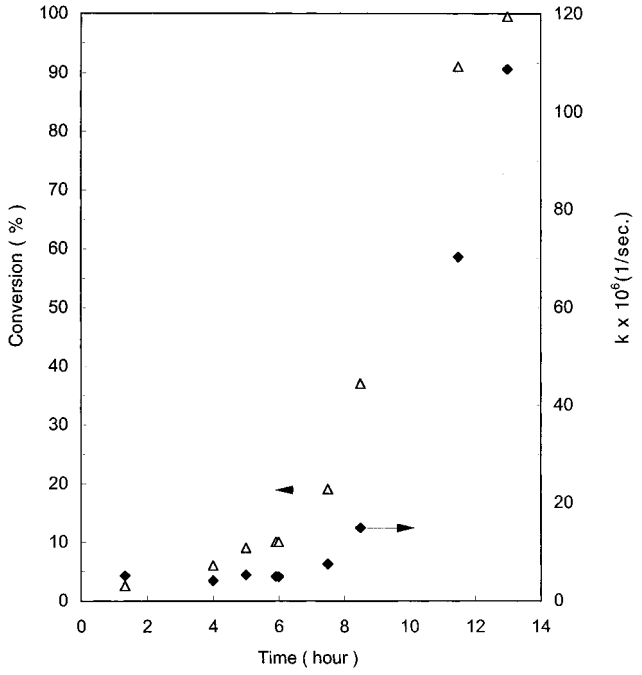


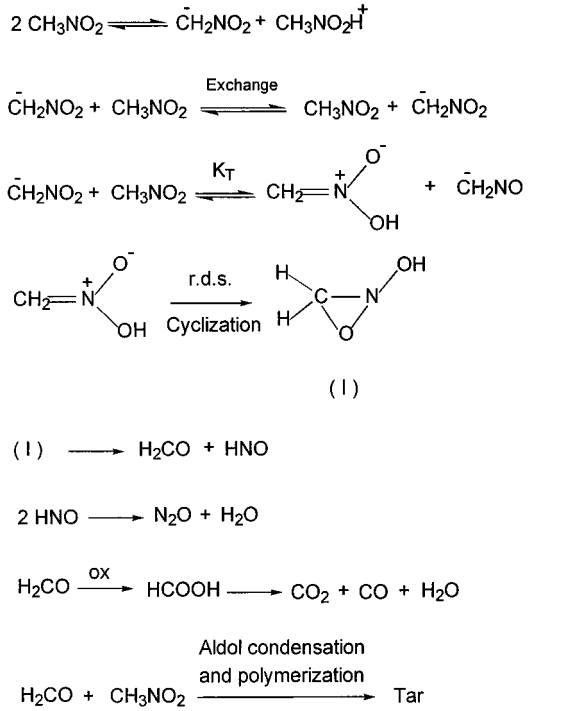
Figure 3. Rate constant and conversion of 10 wt % nitromethane decomposed in toluene at 230 °C, 0.7 GPa.

plot given in Figure 2 is a straight line, and the activation volume is −5.5 mL/mol. This also suggests that rate-controlling step at high pressure is not homolysis because homolysis is characterized by positive activation volume. Figure 3 is a relation between the pseudo-first order rate constant and reaction time. It is obvious that there is a gradual change in mode of decomposition. The first phase is from zero to about 8 h during which the rate of decomposition remains constant and follows first-order kinetics. The second is in the range of 8 h to 13 h where decomposition accelerates and follows an autocatalytic mechanism. This suggests that kinetic studies should be limited to the early stage of decomposition to avoid

Table 1. Pseudo First-Order Rate Constants for Thermolysis of Nitromethane at 230 °C, 0.7 GPa, and 2-Nitropropane at 195 °C, 0.9 GPa

sample no.	nitroalkane	solvent	k (s^{-1}) × 10^6 run 1	run 2
1	10% CH_3NO_2	benzene	1.00	
2	10% CH_3NO_2	toluene	4.95	5.68
3	5% CH_3NO_2	toluene	5.23	5.58
4	20% CH_3NO_2	toluene	6.00	
5	10% CD_3NO_2	toluene	5.25	5.65
6	5% 2-nitropropane	toluene	11.80	
7	10% 2-nitroporpane	toluene	13.50	

Scheme 3



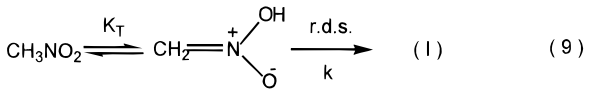
autocatalytic reaction. Table 1 gives the pseudo-first-order rate constants at 230 °C under 0.7 GPa. Sample 2 has a 2-fold higher concentration than sample 3, but both have the same rate constant. The same result is found for samples 2 and 4. The rate law thus appears to be first order in nitromethane. The results in Table 1 show that k_H/k_D is about 0.9−1.15. Clearly there is no primary kinetic isotope effect, and C−H bond cleavage is a fast preequilibrium step. An isotope exchange reaction was performed to test the rate of nitronate formation. A solution made up of 1:1 by volume of nitromethane and d_3-nitromethane was heated at 230 °C under 0.7 GPa for 50 min. It was found that exchange goes to completion with a mixture of h_3, h_2d_1, h_1d_2 and d_3-nitromethane in the statistical ratio of 1:3:3:1. The formation of nitronate ion is therefore not rate limiting because only 2% decomposition occurred during the isotope exchange. Pressure greatly accelerates the formation of nitronate ion, but this process does not control the rate of decomposition. It may, however, be an essential preequilibrium step. The mechanism shown in Scheme 3 is proposed.

The energy barrier for cyclization in Scheme 3 should be lower than that of isomerization of nitromethane to methyl nitrite, because nucleophilic addition of oxygen anion to a double bond with partial positive charge is normally facile as in saponification. This is probably the reason such a low activation energy was found. For the isomerization of nitromethane to methyl nitrite, a three-

Table 2. Effect of Additives on Thermal Stability of Nitromethane at 230 °C, 0.7 GPa

	k (s^{-1}) × 10^6	
sample	run 1	run 2
10% CH_3NO_2 in toluene	4.95	5.68
toluene dried by sodium	3.10	
addition of 3% water	343.3	
addition of 3% methanal	28.3	
addition of 3% pyridine	100.8	

membered cyclic transition state was proposed in which the carbon atom has to be five-coordinated[8] and the energy barrier is at least as high as 47.0 kcal/mol. A sequence involving a cyclization like that of Scheme 3 has been used in synthesis.[18] Compound I in Scheme 3 should readily decompose to form the major products, formaldehyde and N_2O. The first-order rate law can be derived from eq 9.



(9)

$$K_T = \frac{[\text{Aci form}]}{[\text{Nitromethane}]}$$

$$\text{Rate} = kK_T[\text{Nitromethane}]$$

$$k_{obs} = k K_T$$

When benzene was used as solvent instead of toluene, the apparent rate constant, k_{obs}, decreased by a factor of 5. This result may be attributed to a solvent effect on K_T. At relatively high nitromethane decomposition, the reaction was autocatalytic as under low pressure. Table 2 gives the effect of additives on the thermal stability of nitromethane. It is evident that substances capable of accelerating proton transfer can catalyze the decomposition.

3. Thermal Decomposition of 2-Nitropropane in Toluene at High Pressure. The pressure effect on the decomposition rate of 10 wt % 2-nitropropane in toluene was studied in the pressure regime from 0.10 GPa to 1.1GPa at 230 °C. The activation volume calculated from Figure 4 is −11.2 mL/mol. The extraordinary negative activation volume indicates that decomposition is not a radical process. It is unusual for an activation volume to maintain a large magnitude at high pressure. 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 high pressure. This large activation volume of 2-nitropropane may be indicative of an ionic preequilibrium such as autoprotolysis. The pressure effect on 2-nitropropane is greater than that on nitromethane (−5.5 mL/mol) and can arise from at least two reasons: (1) 2-Nitropropane has a longer chain structure and, consequently, its volume in a three-member transition state would be compact (i.e. ball-like) and (2) the K_T of 2-nitropropane was found to be lager in aqueous solution than for nitromethane; this means that 2-nitropropane exhibits greater charge separation and solvation effect than nitromethane in the preequilibrium process. The very low activation energy, 15.4 kcal/mol, was derived

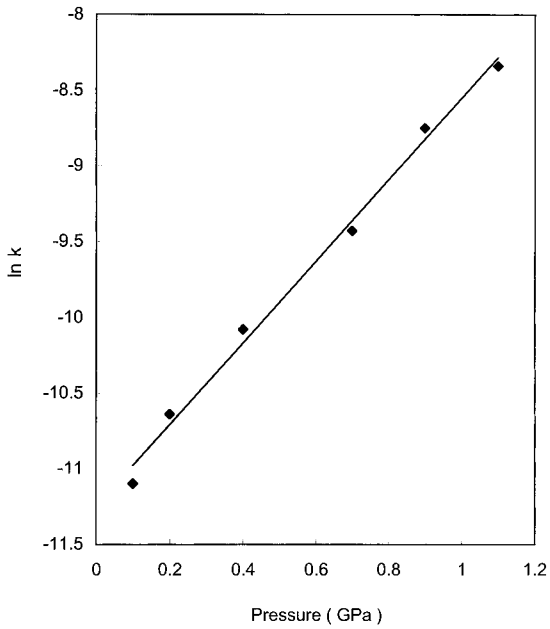
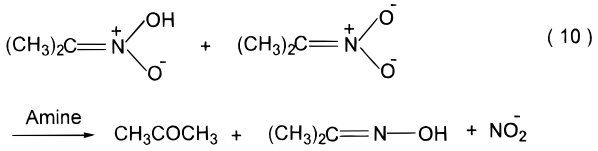


Figure 4. Activation volume profile of 10 wt % 2-nitropropane decomposed in toluene at 230 °C.

from kinetic data at 1.1 GPa which is an indication of the complex reaction. The rate law was determined to be the first-order. The products are acetone, water, N_2O, and tar. Acetone oxime was not found although it is stable under the reaction conditions. This indicates that the following bimolecular reaction for decomposition of 2-nitropropane catalyzed by amine does not occur in the absence of amine.



(10)

Figure 5 is a plot of rate constant k vs decomposition time. When the decomposition time is less than 100 min, the decomposition obeys first-order kinetics, but beyond 2 h, the rate increases substantially. Therefore, 2-nitropropane like nitromethane has different decomposition mechanisms at low and high conversion. The products in the gas phase are N_2O, CO_2, $(CH_3)_2CO$, and a small amount of CH_4. As in the case of nitromethane, it has been found that water dramatically catalyzed the decomposition of 2-nitropropane. Because of the similarities between nitromethane and 2-nitropropane, a parallel decomposition mechanism can be invoked.

At 230 °C and 1.1 GPa, the decomposition rate of 2-nitropropane is 16 times greater than that of nitromethane. The previously mentioned difference in tautomeric equilibrium constants may be a factor. The observed activation volume for the proposed mechanism is the sum of the volume changes of the equilibrium and subsequent rate-determining step. At high conversion of 2-nitropropane, the autocatalytic mechanism (addition of water to the aci-form yielding acetone and nitroxyl) dominates the decomposition.

In contrast to nitromethane and 2-nitropropane, 2,2-dinitropropane is an explosive compound without α hydrogen and cannot form the nitronate ion. In earlier work,[14] the activation volume was found to be +3.6 mL/

(18) Young, A.; Levand, O.; Luke, W. K. H.; Larson, H. O. *Chem. Commun.* **1966**, 230,

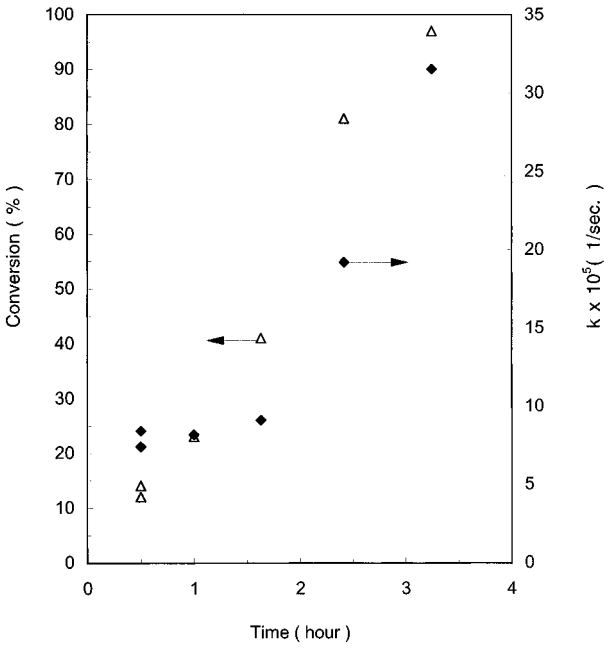
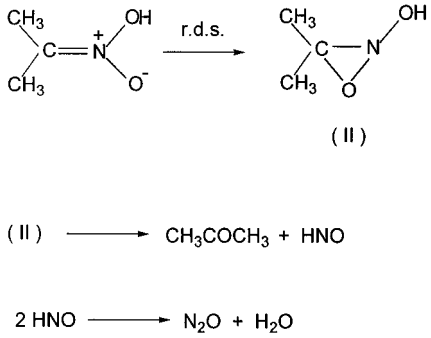


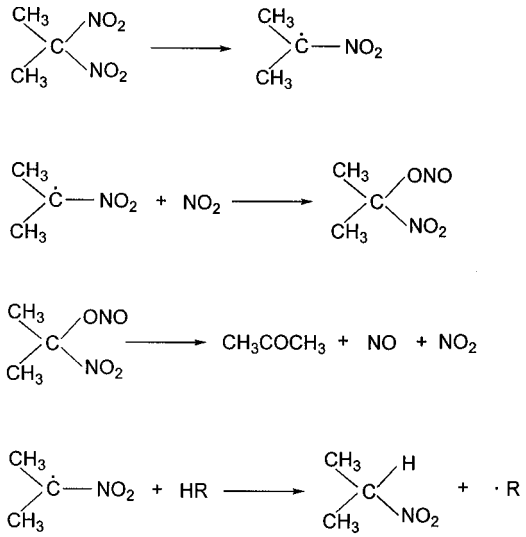
Figure 5. Rate constant and conversion of 10 wt % 2-nitropropane decomposed in toluene at 195 °C, 1.1 GPa.

Scheme 4



mol. The principal products are acetone, NO, and NO_2 with a small quantity of 2-nitropropane. It is interesting to note that the behavior of 2,2-dinitropropane in aprotic solution is very different from that of 2-nitropropane. The proposed mechanism is shown in Scheme 5.[14,19] This activation volume is appropriate for free-radical dissociation in the rate-determining step. Comparison of the activation parameters and the characteristics of mono- and dinitropropane makes it highly probable that the tautomeric equilibrium of the former plays a vital role in the mechanism of decomposition. If a link is to be made with the aforementioned reactions and the reactions of detonation of nitromethane (or any other acidic nitroalkane), one must consider the limits imposed by heat and mass transport on the rate of molecular collisions in the detonating material. Unlike other explosives (i.e. nitrate ester explosives) where part of the shock energy is consumed immediately by bond rupture, nitromethane might need one or more preequilibrium steps until a highly reactive intermediate is produced. An estimate of the number of molecular collisions during passage of the shock wave can be obtained from the diffusion length of nitromethane. The time for propagation of the pressure pulse and reaction heat in a detonation shock front is approximately 10^{-7} s. The diffusion

Scheme 5



coefficient for ordinary liquids at ambient conditions is approximately 10^{-9} m^2 s^{-1}, which probably would be reduced to ca. 10^{-11} m^2 s^{-1} under shock initiation conditions such as 10 GPa and 1000 K.[20] Under these conditions, the diffusion length for 10^{-7} s is 1 to 2 nm, which is approximately one to two molecular diameters of nitromethane. This is a length that could feasibly allow a number of rapid proton-transfer reactions to occur in the 10^{-7} s time span. Since nitromethane is usually detonated without extension by solvent and it is the principal reactant in both preequilibrium reactions that leads to the formation of the aci-form (first and third reactions of Scheme 3), the generation of the aci-form through the bimolecular reactions could be facile. The heat generated from the ensuing cyclization of the aci-form followed by secondary reactions could sustain the shock front or promote a low-order detonation process to full detonation. However, it must be noted that proton-transfer reactions involving carbon acids may be too slow even under the detonation conditions of pressure and temperature. By our mechanism, two successive proton-transfer reactions are needed before nitromethane reaches the aci-form intermediate. Therefore it is questionable whether the proposed cyclization pathway for the static thermal decomposition of nitroalkanes could be applied to the detonation process.

Conclusion

The observed pressure effects on the decomposition of nitroalkanes in aprotic solution have indicated that the dominant reaction channel can change with pressure.

At low pressure, nitromethane reacts by homolysis of the C−N bond while at high pressure, it adopts a mechanism with a negative volume, negative activation entropy, and low activation energy. A cyclic intermediate is proposed. The behavior of 2-nitropropane at high pressure is similar to that of nitromethane and very different from that of 2,2-dinitropropane.

At high conversion, both nitromethane and 2-nitropropane change mechanism to a Nef-like reaction with water formed in the first stage.

The solvent has four effects on the decomposition of nitroalkanes: (1) a polar solvent can facilitate conversion

(19) Flournoy, J. M. *J. Chem. Phys.* **1962**, *36*, 1107.

(20) Campbell, A. W.; Davis, W. C.; Travis, J. R. *Phys. Fluids*, **1961**, *4*, 498.

of tautomers; (2) dilution decreases intermolecular interaction and gives reliable information about the initial step; (3) the solvent can stabilize highly reactive intermediates such as NO_2 and retard autocatalytic decomposition; (4) if the solvent is protic it will accelerate the decomposition by Nef reaction. The large effect of pressure on the rate of thermal decomposition of nitromethane and 2-nitropropane points to the importance of the proton-transfer reactions leading to the formation of the aci-form. At least three other experiments suggest the same: (1) amine-catalyzed decomposition of nitroalkanes is promoted by pressure,[14] (2) time-to-explosion is decreased with increasing pressure,[10] and (3) compression of neat nitromethane in a diamond anvil cell accelerates decomposition.[12,13]

Pressure appears to be a principal factor in the chemistry of nitromethane decomposition and detonation.

The decomposition mechanisms for nitroalkanes are very complicated. It is evident from our study that the dominant reaction channel is determined not only by the experimental conditions such as temperature, pressure, and solvent properties, but also by the structural features of the nitroalkane.

Acknowledgment. This work was supported by the Research Center for Energetic Materials, an NSF/Industry cooperative venture. D. L. Naud is grateful for the financial support provided by the University Research Board of AUB.

JO9705632