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STATIC AND DYNAMIC PRESSURE EFFECTS ON THE THERMOLYSIS OF NITROALKANES IN SOLUTION

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We have measured the effects of static and shock-induced pressures on the decomposition rates and mechanisms of various nitroalkanes dissolved in different solvents with and without organic amine catalysts. While nitroalkanes without α -hydrogen decompose by homolysis of the C-NO₂ bond over a wide range of conditions, the decomposition pathway of nitroalkanes having α -hydrogens (i.e. acidic nitroalkanes) is complicated and follows different decomposition mechanisms depending on the availability of organic base and reaction pressure. The Nef reaction is also an important reaction pathway. The five known decomposition pathways, homolysis of the C-NO₂ bond, bimolecular reaction between the aci-form and aci-ion, cyclization of the aci-form, elimination of nitrous acid, and the Nef reaction, are highly dependent on the reaction conditions, such as pressure, presence of organic amines, water, alcohols, and polarity of solvent. We discuss the results of several tests used to support these various decomposition mechanisms.

INTRODUCTION

There has been a tendency in explosives literature to discuss the C-NO₂ bond as a discrete moiety for which some characteristic behavior is implied for the entire class of compounds containing this functional group. There have been claims of a single chemical process dominant under conditions ranging from gas-phase combustion and slow thermal decomposition up to the von Neumann spike. Our research clearly shows that this is not the case. Experimental evidence reveals that the decomposition chemistry of these compounds is incredibly rich, with strong dependence on the chemical environment of the nitro-bearing carbon atom, the physical conditions under which the reaction is studied, and the identity of other compounds present in the reaction medium. In this paper

we focus exclusively on aliphatic compounds, since the decomposition chemistry of nitroaromatic and vinylic compounds is known to be different.

We study solution-phase behavior because the solvent inhibits autocatalysis and simplifies kinetic analysis. Changing the reactant concentration provides a simple and reliable method of determining reaction order, and solvent effects provide valuable extrakinetic information about the reaction mechanism. Product analysis is useful in that intermediates may be trapped, particularly through their interaction with solvent molecules, and yield detailed information about the mechanism through the identification of key intermediates. Generally the most information is obtained from early-stage intermediates unique to a particular path. In the

experiments discussed here, we document the effect of replacing an acidic α -hydrogen with an alkyl group. It is important to realize, however that modifying the compound of interest may also introduce unexpected effects, and care is required to ensure that results are interpreted judiciously.

Principal tools of this work include characterization of the activation volume profile, detailed analysis of the reaction product distribution, substituent effects, and solvent effects. Activation volumes are useful in determining the character of the transition state, and changes in reaction mechanism due to increased pressure alone have been discussed previously. Until recently, the usefulness of activation volume measurement in elucidating mechanism has not often been exploited.

Isothermal decomposition experiments at low pressure have been conducted in sealed glass ampoules immersed in Wood's metal. For high static pressure experiments, we use two devices that have been described previously.¹⁻³ At pressures to 0.1 GPa and temperatures to 650 K we use a stainless reactor vessel that contains glass capillaries. Pressure is transmitted to the reaction mixture through a mercury seal, and the assembly is heated by immersion in a massive block thermostatted to provide temperature control to $\pm 0.3^\circ$ C. For hydrostatic experiments at pressures up to 2 GPa and temperatures to 600 K we employ a monoblock apparatus similar to that described by Lavergne and Whalley.¹ Recently we have found that relatively thin aluminum disk seals at the ends of the PTFE sample container enable temperatures to be increased significantly without extrusion of the polymer.

We have also performed shock recovery experiments in the study of nitroalkane chemistry. We use capsules fabricated from either aluminum or steel round stock, which are sealed and suspended in an explosive charge. After detonation of the explosive, the capsules are recovered and the liquid, solid, and gaseous contents analyzed. The development and characterization of this method has been discussed elsewhere.⁴⁻⁶ For reactions where the mechanism is clearly understood and kinetic parameters are available, shock temperatures in the sample bulk were calculated from the observed extent of reaction and the reaction time (1 μ s) by use of the rearranged Arrhenius equation (1) where T is temperature, E_a is activation energy, A is the pre-exponential factor, R is the gas constant, and $k_{\text{obs}} = 10^6 \ln(C_0/C)$; the initial and final concentrations of reactant are C_0 and C respectively.

$$T = \frac{-E_a}{R \ln\left(\frac{k_{\text{obs}}}{A}\right)} \quad (1)$$

More recently, Forest has evaluated the shock temperature in these experiments by numeric integration of equation (2) using an adaptive 8-point Legendre-Gauss algorithm.^{7,8}

$$T_h(v)G(v) = T_0G(v_0) + \frac{1}{c_v} \int_0^u \frac{G(v_h(u))u^2 dU_s}{U_s(u)du} \quad (2)$$

Here T is temperature as before, the subscript h denotes Hugoniot, the subscript 0 denotes the initial state, u is particle velocity, v is specific volume, U_s is shock velocity, and the integrating factor $G(v) = e^{\int \frac{\Gamma}{v} dv}$ with Γ being Grüneisen's gamma as usual. The degree of agreement between experiment and theory, shown in Table 1, compares favorably with the results of other studies.^{9,10}

Table 1. Measured and calculated shock temperatures.

Pressure (GPa)	T_{measured} (K)	$T_{\text{calculated}}$
6.9	910	733
9.4	1090	980
11.1	1210	1178
13.4	1400	1405

2,2-DINITROPROPANE

Decomposition under a wide range of conditions occurs through homolysis of one of the C-NO₂ bonds, followed by a variety of steps. Hydrogen abstraction from solvent by the resulting 2-nitropropyl radical intermediate forms 2-nitropropane, which decomposes to acetone, water, and other products as discussed in a subsequent section. Acetone may also be formed more directly by rearrangement and recombination of the caged radical pair to form the nitrite ester, through subsequent O-NO homolysis followed by loss of NO₂. There is no clear method of distinguishing whether acetone is formed from 2-nitropropane or through the nitrite ester. The activation volume has previously been reported as +3.5 mL/mol over the range 0 to 0.6 GPa.² In shock recovery experiments, the extent of reaction is small, with 2-nitropropane, acetone, and N₂O being the dominant reaction products. It appears that this compound is atypical in that its decomposition chemistry is simple and consistent. With other compounds, particularly acidic nitroalkanes, this is not the case and mechanistic changes are induced both by increased temperature and pressure.

2-NITROPROPANE

Decomposition of 2-nitropropane in the gas phase has been studied previously¹¹⁻¹³ and found to proceed by elimination of nitrous acid to form propene. This mechanism has also been shown for nitroethane and 1-nitropropane. In previously reported results^{2,3} of a series of experiments with an equimolar quantity of piperidine present as a catalyst, a remarkably large negative activation volume profile, -60 mL/mol between 0 and 0.2 GPa, and -18 mL/mol between 0.2 and 1.3 GPa, was found, which excludes C-NO₂ homolysis. An effect of this magnitude is unusual and strongly suggestive of an ionogenic pre-equilibrium step, such as autoprotolysis or abstraction of a proton by base. Product analysis shows acetone, water, N₂O, and tar, which can be readily explained by a bimolecular reaction between the aci-form and the aci-anion. This hypothesis is bolstered by the following facts: (1) that the two non-acidic nitroalkanes in this study, 2,2-dinitropropane and 2-methyl-2-nitropropane, exhibit completely different behavior, (2) by the cross-product reaction with nitrocyclopentane discussed previously² and in a subsequent section, and (3) by the inhibition of the reaction by Proton Sponge®, (N,N,N',N'-tetramethyl-1,8-naphthalenediamine), which is a stronger base than triethylamine, but does not easily yield the proton it acquires due to steric constraints. Isotopic labeling shows that a mixture of d₃-nitromethane and h₆-2-nitropropane is stable under ambient conditions, but that upon the addition of base, complete isotopic scrambling of the hydrogen atoms occurs within minutes.

In experiments conducted without base under the same reaction conditions, Wang¹⁴ found the same product distribution, and similar activation volume profile, indicating that pressure-driven autoprotolysis occurs in this compound. A remarkably low activation energy, only 15.4 kcal/mol, was observed for the decomposition of 2-nitropropane in toluene at 500 K and pressures to 1.3 GPa, indicating the complexity of the dominant mechanism. Decomposition becomes autocatalytic at high conversion. Both with and without base catalysis, water was found to accelerate the rate of reaction greatly. The Nef reaction, addition of water to the double bond in the aci-anion, yields acetone, water, and N₂O from 2-nitropropane. It is well documented in standard texts.¹⁵

In shock experiments the dominant product is propene, as in the gas phase, with trace amounts of acetone also present. Since both the five-center electrocyclic elimination of nitrous acid and the bimolecular reaction between the aci-form and the aci-anion are accelerated by pressure, this result is ascribed to

a number of factors. The low activation energy for this bimolecular reaction prevents it from competing with the high temperature elimination process which has an activation energy of 41.5 kcal.

The activation entropy under these shock conditions favors unimolecular processes that yield multiple products, and the bimolecular reaction is a diffusion controlled process that is retarded by the high pressure. It seems that for 2-nitropropane, the gas-phase elimination mechanism is supplanted by the condensation reaction at high pressure and moderate temperature, and is again overtaken by elimination at higher temperatures and pressure.

NITROCYCLOPENTANE

Results of cross-product condensation studies between the aci-form and aci-anion of nitrocyclopentane and 2-nitropropane with base catalyst have been reported previously² and help to illustrate the bimolecular reaction of these compounds at ca. 1 GPa pressure and temperatures around 500 K. Because the concentration of the aci-form is small compared to the aci-anion, a mixture with a large initial concentration of nitrocyclopentane, and smaller amount of 2-nitropropane, yields primarily cyclopentanone and cyclopentanone oxime via a bimolecular reaction. Likewise, under these same concentration conditions, the principal mode of reaction of 2-nitropropane is the bimolecular reaction between the aci-anion of 2-nitropropane and the aci-form of nitrocyclopentane to give acetone and nitrocyclopentane oxime. Only a trace of acetone oxime is produced. When the proportions are reversed, the dominant product is cyclopentanone, with very little cyclopentanone oxime. We performed the same experiments under shock loading, and found a small amount of acetone from the 2-nitropropane, but found no cyclopentanone, cyclopentanone oxime, nor acetone oxime. Shocked nitrocyclopentane exhibited an extent of reaction consistent with the measured rate law of nitrous acid elimination from 2-nitropropane and nitroethane, with cyclopentene as the main product. As with 2-nitropropane we believe this may be attributed to a low activation energy for the condensation reaction compared to elimination, and to entropy considerations.

NITROETHANE

At ambient pressure and 533 K a 10% solution of nitroethane in benzene, with an equal volume of piperidine, produces N-ethylpiperidine, N-nitrosopiperidine, N-formylpiperidine, N-acetylpiperidine, and

3,4,5-trimethylisoxazole.² At 1.3 GPa and 373 K the product distribution consists only of 3,4,5-trimethylisoxazole and N-nitrosopiperidine. It is believed that the 3,4,5-trimethylisoxazole is formed from a condensation reaction of acetaldehyde and the aci-anion of nitroethane. As with 2-nitropropane, the elimination of nitrous acid is seen both in the gas phase and in shock recovery experiments at ca. 11.1 GPa and 1210 K.

NITROMETHANE

Although it has the simplest structure of any nitroalkane, nitromethane has more complex chemical behavior than any other compound we have studied. Unlike higher nitroalkanes, the gas-phase behavior is dominated by C-NO₂ homolysis.¹⁶ This behavior persists in toluene solution at low pressure.¹⁴ Under high pressure, especially in the presence of bases, its behavior changes completely, with an activation volume in acetonitrile of -85 mL/mol and an entirely different product distribution. An activation volume of this magnitude clearly indicates ionization in the transition state. Piperidine in solution gives a nucleophilic displacement of nitrite ion, forming N-methylpiperidine, N-nitrosopiperidine, and N-formylpiperidine. When the extent of reaction exceeds 20% the process becomes autocatalytic, probably due to the formation of water. Trace amounts of water have been shown to accelerate the rate of decomposition by a factor of 30 under static conditions. In detonation experiments addition of 2 vol. % water reduces the failure diameter by 5.5 mm.^{17,18} Engelke dried nitromethane over Linde 3A molecular sieves, reducing the water content from 0.06 vol. % to 6×10^{-4} vol. % and found the failure diameter increased by 1.6 mm.¹⁹ Because all of the intermediates formed in the decomposition of nitromethane are highly reactive, its mode of decomposition is more difficult to elucidate.

At hydrostatic pressures up to a few GPa and temperatures approaching 700 K the activation volume is large and negative, and product analysis shows that radical intermediates may be categorically excluded.^{2, 14, 20} The activation energy is 28.5 kcal/mol and the activation entropy is -14.6R (J/K·mol); comparison to the gas-phase process activation energy of 53.5 kcal/mol and activation entropy of +3.1R (J/K·mol) clearly shows a change in decomposition mechanism. In gas phase, the product distribution contains primarily CH₄, CO₂, CO, and N₂O. Under high pressure there is little or no methane, and HCN is formed as well. It is possible that HCN may be formed as a result of a condensation reaction, as in 2-nitropropane and nitrocyclopentane, between the aci-form and the aci-

anion by elimination of water from the oxime; it may also result from reduction of nitromethane to nitrosomethane by formaldehyde or other reactive intermediate.

To account for the low activation energy, negative activation entropy and volume, and observed product distribution, we propose that cyclization of the aci-form occurs in the rate-determining step, followed by rearrangement to formaldehyde and nitroxyl. Due to the probability that decomposition of this proposed intermediate would be considerably faster than the rate of formation, it seems unlikely that a sufficient concentration would exist for its observation by Raman spectroscopy, and the electronic structure suggests a UV transition at shorter wavelength than the strongly absorbing $n-\pi^*$ transition of nitromethane. Cyclization may operate in parallel with the condensation reaction. The radical anion intermediate discussed by Gruzdkov and Gupta²¹⁻²³ is not formed under the conditions of our hydrostatic experiments, as evidenced by the lack of products that would result from the presence of methyl radicals.

Piermarini, Block, and Miller²⁴ observed an overall negative activation volume, and commented that their data seems to indicate at least three different mechanisms operative under different conditions of temperature and pressure, with the onset of the third regime beginning above ca. 5 GPa. In shock recovery experiments using perdeuterated nitromethane in benzene without amine catalysis, the extent of reaction is ca. 23% and there is a nearly stoichiometric yield of CD₃H, apparently formed from methyl radicals. A similar result is obtained when perhydro-nitromethane is used with perdeuterated benzene, indicating the absence of a primary deuterium isotope effect. When amine catalyst is present and all other reaction conditions are unchanged, the extent of reaction is more than doubled. We attribute scrambling of the deuterium isotope label to the autoprotolysis of nitromethane, resulting in formation of the aci-anion, which appears to occur simultaneously with formation of methyl radicals under these conditions. Due to the presence of CH₂D₂ it is not clear whether the methyl radicals are formed directly, or through the radical anion intermediate, via either electron or hydrogen atom transfer, as discussed elsewhere.²¹⁻²³

We find further evidence of autoprotolysis in the spectra of both pure and amine-sensitized nitromethane obtained by Constantinou, Winey, and Gupta.²⁵ Reversible red shifting of the absorption band edge seen between 300 and 400 nm was observed by these workers and attributed to the effect of pressure on the system. This interpretation is acceptable, but the fundamental nature of

the pressure effect that results in this red shift is not discussed. It has long been known that high pressure drives autoprotolysis of acidic compounds, because electrostriction lowers the free energy of the ions relative to the associated molecule.²⁶⁻²⁸ Acetone is a particularly good example, since it is a carbon acid and similar to nitromethane in this respect; but it is a much weaker acid, having a pKa of 20 in comparison to the value of 10.2 for nitromethane. Hamann²⁸ found evidence of autoprotolysis in acetone more than forty years ago. Yakusheva, Yakushev, and Dremmin²⁹ observed progressive opacification of acetone behind a 10 GPa shock front. More recently we identified products of a Claisen condensation reaction in shocked acetone (4-methylpent-3-en-2-one and 4-hydroxy-4-methylpentan-2-one) resulting from autoprotolysis. We have been able to duplicate this red shift of nitromethane under ambient conditions by the addition of an organic amine, in this case triethylamine, as shown in Figure 1.

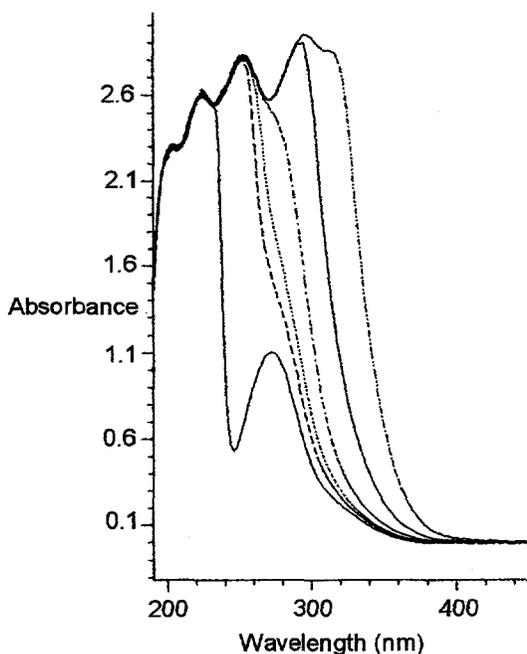


FIGURE 1. ABSORPTION BAND EDGE SHIFT AS A FUNCTION OF ACI ION CONCENTRATION; SPECTRA FROM LEFT TO RIGHT ARE APPROXIMATELY 0, 80, 110, 181, 386, AND 891 μ MOL/L ACI ION.

Engelke et al. has shown³⁰⁻³² that the only new chemical species formed on the addition of an amine to nitromethane is the aci-ion, that high pressure drives the formation of this tautomer as well as ultraviolet light, and that it is a rate-controlling intermediate. Assignment of the

reversible shift in the absorption band edge to formation of the nitromethane aci anion is made with the support of several additional quantitative tests. Figure 2 shows that at different wavelengths the change in absorbance with respect to the concentration of the aci anion of nitromethane is linear, as expected from the Beer-Lambert law. Only wavelengths from 290 to 330nm in 5nm increments were selected for clarity. Figure 3 shows that the plot of the logarithm of the change in absorbance divided by the change of aci anion concentration is linear over the wavelength range of interest.

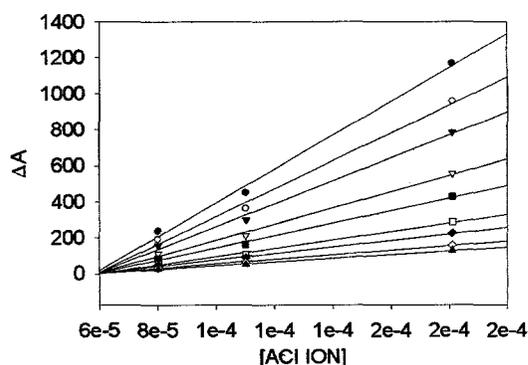


FIGURE 2. ABSORBANCE CHANGE VERSUS CALCULATED ACI ION CONCENTRATION AT DIFFERENT WAVELENGTHS; FROM TOP TO BOTTOM 290, 295, 300, 305, 310, 315, 320, 325, AND 330 NANOMETERS.

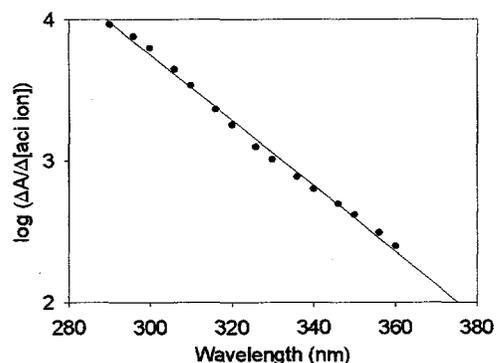


FIGURE 3. LOGARITHM OF ABSORBANCE CHANGE DIVIDED BY CHANGE IN ACI ION CONCENTRATION, PLOTTED VERSUS WAVELENGTH.

Electrical conductivity measurements provide a method for obtaining useful estimates of pK_b values for organic bases in nitromethane, which is preferable to using values obtained in water. We use Equation 3 with the understanding that, in practice, the electrical mobility of an ion μ_B is a function of the square root of concentration, c_B , as noted by Kohlrausch.

$$\kappa = \sum_B |z_B| \mathcal{F} \mu_B c_B = \sum_B \kappa_B \quad (3)$$

Here \mathcal{F} is the Faraday constant, κ is conductivity, and z is the charge on the ion. For pure anhydrous nitromethane, the only significant charged species present are the aci anion and protonated nitromethane, we make the assumption that the electrical mobilities of these are equal due to their comparable size, shape, and charge density; this permits the electrical mobility to be determined from the dissociation constant. As in water, proton jumping is a conceivable mechanism of charge transport in nitromethane but these measurements show that it is much less facile, as expected. In water the organic amine Proton Sponge® has a pK_a of 12.34, and acetic acid has a pK_a of 4.74, so we expect an equimolar combination of these in nitromethane to exist primarily as the protonated amine and the acetate ion, and that the electrical mobility of the acetate ion is comparable to the nitromethane aci ion. We then evaluate the electrical mobility of Proton Sponge®, and have determined its pK_b to be 3.7 in nitromethane. For triethylamine and diethylenetriamine we obtain pK_b values of 6.3 and 4.9 respectively. Engelke³³ has suggested that a plot of failure diameter versus electrical conductivity or resistance for different concentrations of diethylenetriamine would yield a straight line, further demonstrating the intermediacy of the aci anion as a rate-controlling intermediate in the shock initiation and detonation chemistry of nitromethane. That result is illustrated in Figure 4.

Under hydrostatic experiments with 2-nitropropane we found that the addition of Proton Sponge® inhibited the reaction, which supports the bimolecular reaction between the aci anion and the aci form. In failure diameter experiments with nitromethane this is not the case; on a molar basis sensitization is comparable or slightly greater than reported for diethylenetriamine.³⁴ This result had been obtained previously³⁵ but was not widely known. It is possible that rotational modes of the amine groups of Proton Sponge®, while strongly hindered by adjacent molecules, are more active at the temperatures in shock initiation facilitating proton transfer away from the protonated amine as with any other base. However, the absence of products characteristic of the bimolecular reaction indicates that in shock experiments the aci anion reacts by another path.

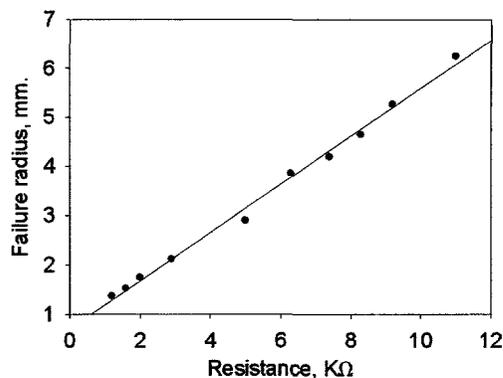


FIGURE 4. RADIUS OF FAILURE VERSUS ELECTRICAL RESISTANCE FOR DIETHYLENETRIAMINE IN NM.

Blais, Engelke, and Sheffield³⁶ used time-of-flight mass spectroscopy to study the chemistry of the detonation reaction zone of nitromethane, and found substantial amounts of high-mass products. Initially it was believed that these compounds resulted from a condensation reaction forming 1-nitroethan-2-oxime, but isotopic labeling experiments seem to show that these reactive intermediates arise from a condensation reaction not previously documented. In our hydrostatic and shock recovery experiments there is no significant deuterium isotope effect, which contrasts sharply with the observed near-doubling of failure diameter seen for perdeuterated nitromethane.³⁷ Given the complexity of nitromethane chemistry, it is reasonable to suppose that fully developed detonation will prove to have additional reaction channels which have not been seen in the shock initiation stage.

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