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TITLE CHEMISTRY OF NITROMETHANE AT VERY HIGH PRESSURE

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CHEMISTRY OF NITROMETHANE AT VERY HIGH PRESSURE

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Decomposition of nitromethane is reported over the range of 115-180°C and 0.6-8.5 GPa. About 5 µg of nitromethane is compressed with a diamond-anvil cell, heated to the point that reaction occurs, and held typically 10-20 minutes at the reaction temperature. The cell is cooled and the volatile contents of the cell are frozen as a thin layer in vacuo and an infrared absorption spectrum is recorded. The three volatile products observed are N₂O, CO₂, and water, with N₂O production peaking at 1.5 GPa, 135°C, and 35% of NME; CO₂ production peaking at 3.5 GPa, 135°C, and 65% of NME, and water yields at 20-50% of NME at the highest pressure measured, 8.5 GPa and 175°C. Water yields were difficult to quantify due to background contamination. Results indicate three different reactions for solid NME dependent primarily on the pressure of the reaction, and that fluid NME does not decompose at 0.6 GPa and 175°C, although the solid decomposes readily at 1.1 GPa and 120°C. The authors conclude that, while various decomposition mechanisms are possible, the initial step $\text{CH}_3\text{NO}_2 \rightarrow \cdot\text{CH}_3 + \cdot\text{NO}_2$ is very unlikely.

INTRODUCTION

The tendency for energetic materials, both high explosives and propellants, to undergo inadvertent detonation is a serious and not well understood problem. Detonations can be thought of as self-driven shock waves and are initiated by a variety of stimuli or insults. The initial chemistry that drives the deflagration (or fast burning) to detonation transition is of primary importance to understanding the initiation event, and a good amount of activity is occurring with regards to trying to understand the reactions that are important for this chemistry.

In order to obtain a better understanding of the kinds of chemistry that might be important for initiation events, we are studying reactions of simple energetic materials, e.g. nitromethane, under conditions of confinement at very high pressure. We have chosen these conditions for two reasons: 1) The reactions

that are expected to be important in deflagration to detonation transitions are, under low pressure conditions, solid to gas reactions. These reactions drive the energetic decomposition that leads to detonation and are reactions that produce small, stable, and hot molecules. Since these reactions are both fast and not diffusion limited, they will probably involve many concerted steps. Performing measurements at high pressure allows us to choose of the phase of the products, which, since we can choose the pressure, can be either fluid or solid. This allows a control over diffusion and mixing that is impossible by any other method. 2) We expect the initiation reactions to be extremely pressure dependent. The very notion of a detonation wave is one that involves pressure- and temperature induced chemical events that lead to further pressure and temperature increase until finally a dissipative process limits the energy release rate and a steady state is reached.

The concept of an activation energy for a given reaction and the role of temperature in surmounting it is well understood and the traditional Arrhenius activation is normally assumed to be valid even at very high density. Pressure-induced reactivity, on the other hand, does not involve overcoming the activation barrier in a dynamical sense. It is more subtle and involves actually *changing* the activation energy, now more properly considered the activation enthalpy. It is then reasonable to expect that we must, from the very start, consider the activation enthalpy instead of only the activation energy, E_a . The activation enthalpy will be a natural function of pressure as $\Delta H^\ddagger = \Delta E^\ddagger + P\Delta V^\ddagger$, and pressure-induced reactivity should really, by all rights, be called "pressure-catalyzed" reactivity. This emphasizes the very different role that pressure has compared to temperature and the critical parameter in describing the pressure dependence of the reaction rate or branching ratios then becomes the activation volume, ΔV^\ddagger .

An initial reaction or transition state with a substantial volume decrease ($-\Delta V$ or $-\Delta V^\ddagger$), increases the reaction rate and the presumption is that with energetic materials, the initial reactions do possess $-\Delta V^\ddagger$. Otherwise, increasing pressure would not increase the reaction rate, and may actually decrease it. While the initial reaction must involve $-\Delta V$, the overall reaction must, on the other hand, have a $+\Delta V$ in order to sustain the detonation. Thus, we expect to find (and must look for) reactions that have these two important characteristics.

Studying the reactions of energetic materials at high density allows us to probe chemistry that is slow or even nonexistent at low pressure. In particular, concerted intermolecular reactions should become very important at high density, whereas at low pressure, one often sees volatilization of the material prior to any actual chemistry. With the aid of pressure, then, we can hold molecules in their lattice to much higher temperature than would otherwise be possible. Another important factor in condensed phase reactions is that of the solvent cage and its effect on reaction rates. Cage effects are extremely important in solution reactions and they certainly will be even more important at high density. Furthermore, reactions of energetic materials ultimately will have more in common with solid state chemistry than with solution chemistry. Thus, for energetic materials the solid state chemical notion of *reactive* cages and also concerted intermolecular reactions will be very important.

We are trying to understand the very complicated reactions at high density for an energetic material undergoing deflagration or detonation. We must find ways of understanding these reactions, despite their complicated natures, in order to predict and possibly control such properties as sensitivity,

performance, and burn rate. The obvious limitations of performing experiments on such materials while they are reacting and the small amount of information that is obtained from those experiments means that we will always have to resort to some kind of approximation in order to understand the chemistry associated with initiation. With this work, we hope to establish at the very least, some general principles for the kind of chemistry that is associated with detonation initiation.

EXPERIMENT

We have used diamond-anvil cells of the Merrill-Bassett design¹ to compress nitromethane and have used the position of the C-N stretch infrared absorption, calibrated versus the ruby fluorescence standard, as a measure of pressure. Optical microscopy was used to observe the onset of reaction while the cell was heated with an external heater. For many of the samples, infrared absorption microscopy was used to determine the extent of reaction and also to determine the reaction products that accumulated within the cell. The release apparatus is shown in Fig. 1 and allowed

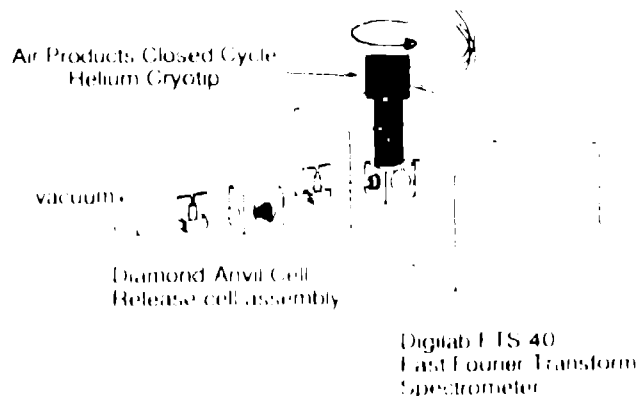


FIGURE 1. DIAGRAM OF THE RELEASE APPARATUS

the release and freezing of the contents of the diamond anvil cell onto a CsBr window mounted on an Air Products closed cycle helium refrigerator (a displax) and held at 20°K. Following deposition, the cryotip was rotated 90° within its shroud and an absorption spectrum was recorded at 2 cm^{-1} resolution and 256 scans. Such a procedure allowed the determination of absorption peaks on the order of 0.005 Å, although this apparatus had a large water background due to outgassing. Water also did not evaporate readily from the cell when the cell pressure was released and, as a consequence, only very qualitative data was obtained on the amount of water that evolved from the experiment.

A Digilab FTS-40 spectrometer was used for the thin layer experiments with a Bio-Rad infrared microscope installed in an auxiliary sample compartment to record the spectrum of nitromethane and/or products while under compression within the diamond-anvil cell.

When we release the contents of the diamond-anvil cell following reaction, freeze the volatiles in a thin layer, and measure the infrared absorption of that thin layer (Fig. 3), we have found that N_2O , CO_2 , and water

RESULTS

At pressures less than 0.8 GPa, the nitromethane melted about 80°C and showed very little reaction up to 175°C for over two hours. However, at 1.1 GPa, the NME did not melt on increasing temperature, but began to react at 120°C as evidenced by the nucleation and growth of bubbles. Infrared spectra in Fig. 2 show the spectra of the

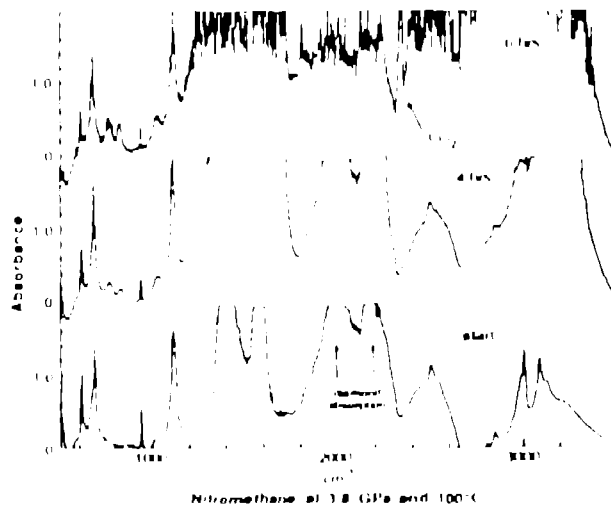


FIGURE 2. NITROMETHANE BEFORE AND DURING REACTION WITHIN DIAMOND ANVIL CELL.

nitromethane within the diamond anvil cell before reaction, after four hours, and after six hours at the temperature and pressure indicated. As the sample reacted, the infrared signal became progressively weaker, but new features are evident and are, 1) a broad, saturated absorption at 3200-3400 cm^{-1} , 2) a broad saturated band for the $-NO_2$ group symmetric and antisymmetric stretches in place of the two features that were evident before reaction, 3) and two absorption bands at 2220 and 2250 cm^{-1} that are partially obscured by the diamond second order absorption. Little spectral information is available for the reacting sample, implying that the products are absorbing completely at the nucleation sites. Eventually, as the reaction proceeds to completion, the infrared signal completely disappears.

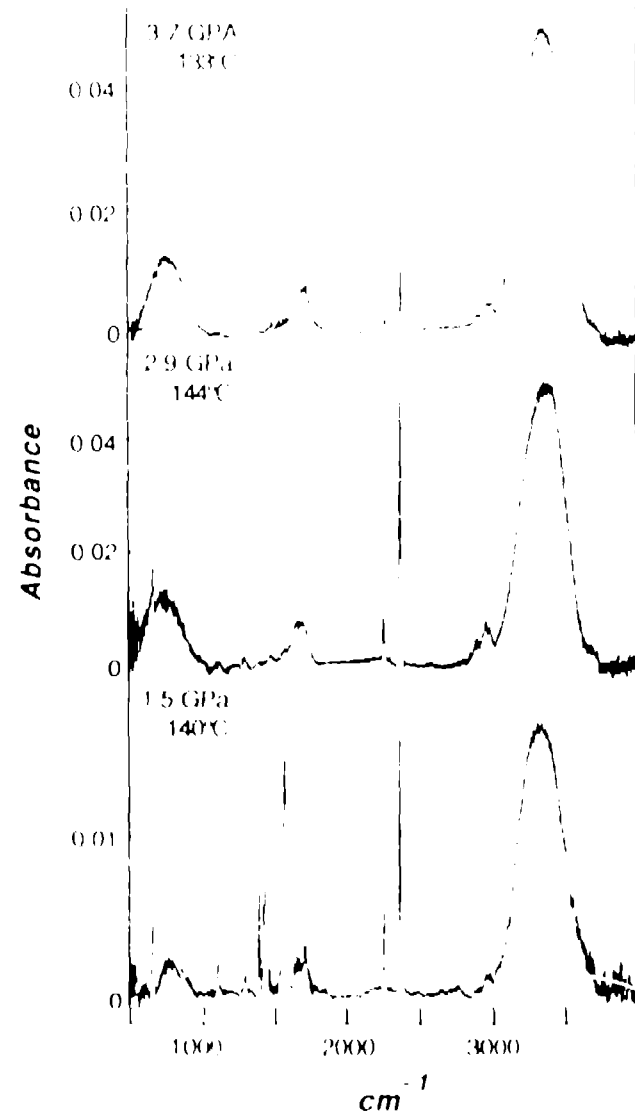


FIGURE 3. INFRARED ABSORPTION SPECTRA OF THIN LAYER OF NME REACTION PRODUCTS AT VARIOUS PRESSURES AND TEMPERATURES.

are the dominant volatile products. Their relative amounts depend on the particular temperature and pressure at which the reaction was performed as shown in Fig. 4. One can see that these volatile

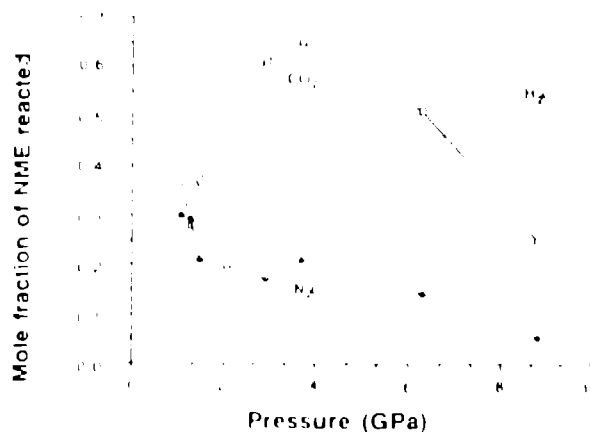


FIGURE 4. REACTION YIELDS OF CO₂, N₂O, AND WATER FOR NME DECOMPOSITION AS A FUNCTION OF PRESSURE AND TEMPERATURE OF ONSET OF REACTION

products are substantial fractions of the starting material. We know that water is present in significant amounts among the products, but have been unable to quantify it very well. (Evidently, water escapes from the cell upon release in variable amounts, since our results with releasing pure water from a diamond cell under identical conditions were subject to a large error.) Whenever NME melts before the temperature reaches ~120°C, no appreciable reaction occurs up to 175°C. We conclude, then that fluid nitromethane does not react appreciably over a period of 30 minutes at the pressure and temperature noted on the diagram. A P-T reaction diagram is shown in Fig. 5 and shows that between 1.0 and 2.5 GPa (reaction regime A), nitromethane is solid at 120°C, while the N₂O and CO₂ products are fluid, and nucleation and growth centers can be readily observed in the solid nitromethane involving these fluid products. Thus, the reaction is assisted by topochemical control of the crystal lattice (i.e., the relative orientations of the NME molecules in the solid). There is time for subsequent dissolution of some NME into these reaction product bubbles, but we feel that any reaction that takes place subsequently in the solution may follow a different pathway, since fluid NME itself shows no reaction at this temperature and slightly lower pressure.

Between 2.5 and 5.0 GPa (reaction regime B), CO₂ becomes the dominant product, consuming nearly 65 mole% of the NME at 3.5 GPa, and then decreasing with increasing pressure. In both regimes B and C, we expect that N₂O and CO₂ will be solid, and we do not observe the bubble growth that was so

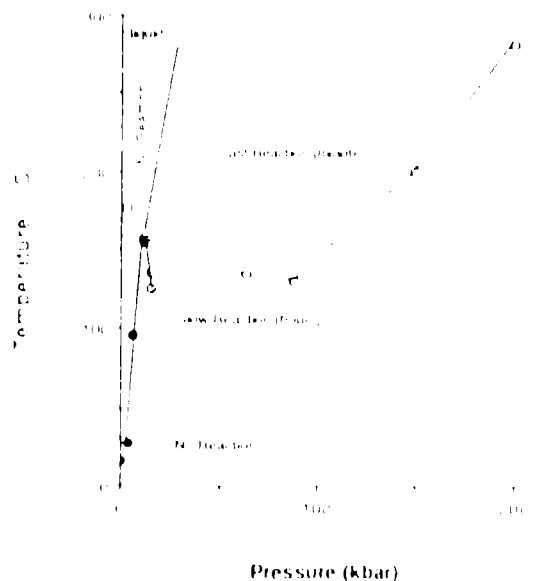


FIGURE 5. PRESSURE-TEMPERATURE REACTION DIAGRAM FOR NME DECOMPOSITION SHOWING THE TEMPERATURE FOR THE ONSET OF REACTION AT VARIOUS PRESSURES.

pronounced at lower pressure. The temperature at which the reaction begins is increasing with increasing pressure, indicating that very high pressure suppresses all NME chemistry. At pressures >5.0 GPa (reaction regime C), both N₂O and CO₂ become much less pronounced and water is the primary volatile product, and we have qualitatively determined that with pressure in excess of 20 GPa, NME is stable to 300°C. The solid residue that remains following chemistry at all of these pressures and temperatures qualitatively reflects the trends noted with the volatile products. In reaction regime A and B with the highest yields of CO₂ and N₂O, there is very little residue, and that which remains has an oily nature. On the other hand, at the highest pressure that we have measured, reaction regime C, a solid residue fills our gasket completely and there is much less CO₂ and no N₂O.

DISCUSSION

There have been many different kinds of studies of NME decomposition including studies under conditions of photolysis,^{2,3} pyrolysis,⁴ and high pressure.^{5,6,7} We believe that the decomposition chemistry in compressed nitromethane found for reaction regime A is different from any that has been previously reported for this molecule. This chemistry therefore does not involve radical production, $\text{CH}_3\text{NO}_2 \rightarrow \cdot\text{CH}_3 + \cdot\text{NO}_2$, which is typical of most of nitromethane's pyrolytic and photochemical reactions.

Although we have not yet determined our limits of detectivity for methane, ethane, or NO_2 , we do not observe any of these products and their absence would mean that the radical reaction is not the dominant decomposition pathway.

The three basic reaction regimes that we observe can be categorized as the nitrogen coupling regime (A), carbon oxidation regime (B), and dehydration regime (C). We suggest that the nitrogen coupling reaction necessary for N_2O production (regime A) involves either an N-nitroso or an N-nitrate intermediate, but we have no information yet to confirm that. The relatively small amount of residue would then be a polymer, possibly similar to polyvinyl alcohol (PVA). Regime B involves oxidation of the carbon and presumably, simultaneous reduction of the nitrogen to amine. Direct attack of the oxygen on the carbon and then hydrogen transfer to the nitrogen site is a plausible route to produce hydroxylamine formate, a likely precursor to CO_2 evolution. It is notable that even under condition that produce the largest amounts of CO_2 , neither formaldehyde (as a volatile) nor paraformaldehyde (detected in the residue) are observed among the products.

Finally, in regime C a notable amount of orange colored solid remains after the reaction, with water as the only volatile detected. This dehydration product could be related to the methazonate polymer that is known to result following further reaction of the ac-ion. On the other hand, there are reports^{5,6,8} that this solid is largely either ammonium formate or ammonium oxalate, with the orange color then due to small amounts of other minor products.

These results are consistent with the hypothesis that, for nitromethane initiation, reactions that produce small, stable molecules are going to be important. These reactions will release the large amount of compressive energy that is necessary to drive subsequent chemistry. Therefore, we consider both reactions A and B to be important in the initiation process. Reaction C, however, largely results in solid products and should consume compressive energy due to its $-AV$, thereby quenching any initiation chemistry that might occur.

These reactions occur in the solid state and are therefore quite complicated, but one must study these types of neat phase reactions if a better understanding of the chemistry of initiation is to follow. We feel that even a crude understanding of many of the reactions is preferable to no understanding of the neat, condensed phase reactions at all. It is obvious that extreme caution must be used, for example, if one wishes to relate these condensed phase reactions to gas phase pyrolytic chemistry or photochemistry. The implication is that concerted reactions will more often than not

dominate over the bond-breaking reactions that dominate at low density in the gas phase.

Both HMX(cyclo tetramethylene tetranitramine) and RDX(cyclo trimethylene trinitramine), which are very important military high explosives, produce N_2O in their thermal decomposition at low pressure.⁹ It has been shown¹⁰ that RDX, under isolated molecule pyrolysis, undergoes a concerted ring breaking step to first produce methylene nitramine, subsequently decomposing to formaldehyde and N_2O as $1/3\text{RDX} \rightarrow \text{CH}_2=\text{N}-\text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{CH}_2\text{O}$. Ammonium nitrate, the primary component of industrial high explosives, also produces N_2O upon decomposition.¹¹ This latter N_2O production has been explained as due to the initial dehydration to produce nitramine as $(\text{NH}_4)(\text{NO}_3) \rightarrow \text{H}_2\text{N}-\text{NO}_2 + \text{H}_2\text{O}$, followed by further dehydration of nitramine with an HNO dimer intermediate as $\text{H}_2\text{N}-\text{NO}_2 \rightarrow (\text{HNO})_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$. Key in both of these schemes is the nitramine intermediate, and we suggest that nitromethane decomposition most likely involves a dimerization or reaction between the nitrogens of adjacent nitromethanes. This could be due to unimolecular rearrangement of NME to hydroxylamine formate, $\text{HCOO}-\text{NH}_2$, with subsequent attack on another nitromethane to produce $\text{H}_2\text{COOCH}_3 + \text{NH}_2-\text{NO}_2$, simultaneous isomerizations of adjacent NME's to methyl nitrite with a coupling reaction to produce CH_3OCH_3 and N_2O , or unimolecular formation of a $(\text{H}_2\text{CO})(\text{HNO})$ intermediate for adjacent NME's with reaction of two HNO's to form N_2O and water, as shown above. All of these mechanisms must in turn be controlled by the solid state phase that we know is important for the reaction to proceed.

Another possible initial reaction is the isomerization to the nitrite form, $\text{CH}_3-\text{NO}_2 \rightarrow \text{CH}_3-\text{O}-\text{NO}$, with subsequent reaction to produce the observed products. This reaction would presumably result in N_2O and CO_2 production through an intermolecular coupling reaction, although one expects significant amounts of methanol or perhaps formaldehyde to result. A recent report¹² on supercritical nitromethane pyrolysis also suggests this reaction is a first step under those conditions. However, we have independently found that formaldehyde polymerizes readily under these conditions to form paraformaldehyde, which is directly characterizable in the infrared. Since we find no evidence for either formaldehyde, formalyn, or paraformaldehyde among the reaction products of nitromethane, the suggestion is that there is another pathway to both N_2O and CO_2 . Also, there is no reason to expect the isomerization to be inhibited in the fluid phase, at slightly lower pressure. The fact that we do not observe significant NME decomposition in the fluid then implies that the nitrite isomerization is not the initial reaction leading to decomposition.

Much previous work has been performed^{1,2} on the role of the aci-ion of nitromethane in the sensitization of nitromethane to shock initiation. We therefore consider the activation of nitromethane by means of either water or hydroxide ion to be a logical first reaction step. Since it is well established that the aci-ion dimerizes readily under ambient conditions to form the methazonate ion, it is hard to believe that the aci-ion itself would lead to the chemistry that we observe, since subsequent reaction of the methazonate produces an ill-defined colored polymer. That is, the aci-ion form evidently activates the carbon center for further reaction. In order to produce N₂O, we must have a nitrogen activation.

The exact nature of this nitrogen coupling reaction will have to wait for further experiments. We are currently working to improve our apparatus by increasing the heating rate and decreasing the contamination level of water. Such an improved apparatus should allow us to improve our measurements significantly.

CONCLUSION

Very different decomposition reactions occur for solid nitromethane at high pressure as compared with ambient or low pressure conditions. These reactions are evidently concerted intermolecular reactions, and three very different reaction regimes occur as a function of pressure and temperature. We suggest that the first two reaction regimes, those that produce N₂O and CO₂, are most closely related to the chemistry of initiation. Moreover, we expect that, in general, reactions in energetic materials that very quickly produce small, stable molecules (i.e. +ΔV overall), but are nevertheless associated with -ΔV[‡] (a decrease in volume for the activated complex) will be most important for determining the initiation of the material.

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