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PROPOSED MECHANISM FOR NITRIC OXIDE DETONATION

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STATIC HIGH PRESSURE STUDY OF NITRIC OXIDE CHEMISTRY:

PROPOSED MECHANISM FOR NITRIC OXIDE DETONATION

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Los Alamos, New Mexico

The chemistry of nitric oxide under static high pressure conditions has been studied using diamond anvil cells and spectroscopic methods. Pressurized samples warmed rapidly to room temperature undergo facile disproportionation to form N_2O, N_2O_3, N_2O_4 and $NO^+NO_3^-$. Nitric oxide maintained at 90 K is observed to react at ca. 2.5 GPa to form, dominantly, N_2, O_2 and $NO^+NO_3^-$. The complex chemistry of nitric oxide is best explained in terms of two competing primary reaction mechanisms involving the direct formation of N_2 and O_2, and disproportionation to form N_2O and $NO^+NO_3^-$. The disporportionation reaction, which is favored under higher temperature conditions, releases two-thirds of the total energy content, and is believed to be important in the early chemistry accompanying shock-initiation of nitric oxide. Laboratory scale detonation studies, where the gaseous products are analyzed spectroscopically, show evidence for, dominantly, disproportionation and a small amount of N_2/O_2 production. This study points to the importance of condensed phase concerted reactions as well as ions and ionic reaction mechanisms in the shock initiated detonation of HE's.

INTRODUCTION

The macroscopic properties of a large variety of high explosives have been studied extensively in the past. However, it is still not possible to describe and verify the microscopic phenomena leading to shock-initiated detonation. Shock propagation in condensed-phase materials is expected to induce the transfer and localization of energy leading to chemical transformations on an extremely short time scale. Our intent in this work is to clarify those early chemical transformations that are important in the energy release accompanying shock-initiated detonation of nitric oxide. In large measure, the problem of developing a microscopic understanding of shock-initiated detonation results from the difficulty in detecting transient chemical intermediates within the shock front. While there has been considerable effort and success in developing time-resolved optical probes of chemical species behind shock fronts [1-4], these methods have not yet been successfully applied to real explosives. The experimental difficulties are compounded by the absence of information on what intermediates are likely to be important and the paucity of data on the behavior of such transients under extreme pressure and temperature. We report here static high pressure studies which provide direct insight into the early chemical transformations associated with detonation of nitric oxide.

Nitric oxide, although stable in the gas phase, is a high explosive in the condensed phase with an enthalpy [5] of 0.72 kcal/g relative to O_2 and N_2 at 298 K. It is one of the simplest known high explosives and is, therefore, an attractive model explosive for detailed theoretical and experimental studies. The molecular form of NO and the expected detonation products, N_2 and O_2, are tractable to both ab initio electronic structure calculation and hydrodynamic modeling. In order to study nitric oxide detonation, a multidisciplinary study entitled the Fundamental Research on Explosives (FRE) program has been established at Los Alamos National Laboratory. Our part in this program has been to provide a data base to guide theory, planning, and interpretation of time-resolved spectroscopic studies of shock-initiated detonation of NO by means of static high pressure studies of the various oxides of nitrogen. The focus of this report is the chemistry of NO and its reaction products under high pressure conditions.

Previous studies [6] on gas-phase nitric oxide have shown evidence for slow disproportionation, which is third order in [NO]. Other investigators [7,8] have also noted problems in obtaining thermodynamic information on pure NO at high pressure. We will show that NO undergoes facile and complex pressure-induced chemistry at low temperature. The disproportionation of nitric oxide at 176 K and 1.5 GPa to form N_2O, N_2O_4, and N_2O_3 has already been reported [9]. The unusual behavior of pure N_2O_4 at elevated pressures, including formation of $NO^+NO_3^-$, has also been reported [10]. This autoionization of N_2O_4 has been implicated [11] in the solution chemistry of N_2O_4 and observed for the nitrite isomer in low temperature N_2O_4 films as well [12,13]. In this work, we report new observations of pressure-induced chemistry of NO to form N_2, O_4, and $NO^+NO_3^-$ at 80 K as well as identification of the products resulting from laboratory scale samples of solid NO shocked at 15 K.

EXPERIMENTAL

A. High Pressure Spectroscopic Studies: Merrill-Bassett diamond-anvil cells with either hardened beryllium or beryllium-copper backings and type IIa diamonds were loaded with the indium-dam technique previously described [9]. Two different types of experiments have been performed. First, high-purity nitric oxide was condensed into the diamond-anvil cells at 115 K (which is within the liquid range of N_2O_4) pressurized to form a clear solid, and then warmed to room temperature at high pressure. The contents of the cells were then interrogated using vibrational (IR and Raman) and UV-visible absorption spectroscopies. In the second type of experiment, the NO was loaded into a cell mounted to the cold finger of an Air Products Displex cryostat equipped with a tailpiece that allowed access to adjust pressure. This permitted the measurement of the pressure dependence of the Raman features at 90 K.

Raman spectra were obtained on a SPEX Model 1403 double monochromator by use of a back-scattering technique. The resolution was 3 cm^{-1} and, typically, ten or more spectra were signal-averaged using a Nicolet 1180E Raman data system. Spectra-Physics Model 171 Ar^+ and Kr^+ ion lasers were employed with incident power of 30 mW or less at the sample. Infrared spectra were obtained with a Nicolet 7000-series Fourier-transform spectrometer using a liquid nitrogen cooled mercury-cadmium-telluride detector. Typically, 9000 scans with a 2 cm^{-1} resolution were signal averaged. Absorption of the diamonds obscured the IR spectra over the approximate ranges 1300-1350 and 1900-2500 cm^{-1}. Visible absorption spectra were obtained with a Perkin Elmer 330 spectrometer equipped with a beam condenser and the Model 2600 data station. Pressures were measured by the ruby fluorescence method, assuming the R_1 line shift to be 0.1322 GPa/cm^{-1}. The known temperature shift of the R_1 ruby fluorescence was used to correct the R_1 line shift for the low temperature studies.

B. Laboratory Scale Studies of Shocked No: The experiments were carried out in an evacuable firing chamber containing a detonating device mounted behind a thin foil. Solid NO was deposited from a stream of gaseous NO directed to the surface of the foil, which was maintained at 15 K by a Air Products Displex cryostat. The detonating device consists of an electrically energized device that propels a 1.3 mm diameter X 0.05 mm long cylinder piece of plastic through a ruby barrel at a velocity of several km/s (a slapper), which impacts at a 5 mg pellet of pentaerithratol tetranitrate (PETN) that is glued to the end of the ruby barrel (Fig. 1). Two isotopic compositions of NO were used to distinguish N_2 originating from NO from either the PETN booster or inadvertent air leaks. The entire assembly was housed in a bell jar connected to two liquid nitrogen traps in series to capture the expected products, the first an empty common stainless steel U-trap, and the second packed with activated 5X molecular sieve. The products N_2O, NO_2, N_2O_3, N_2O_4, CO_2 (from PETN), and unreacted NO are found in the first trap and are determined by gas-phase IR spectrophotometry. The N_2 and CO (from PETN) are found in the second trap and measured by mass spectrometry.

RESULTS

A. High Pressure Studies: The results obtained from studies of nitric oxide at high pressure in diamond anvil

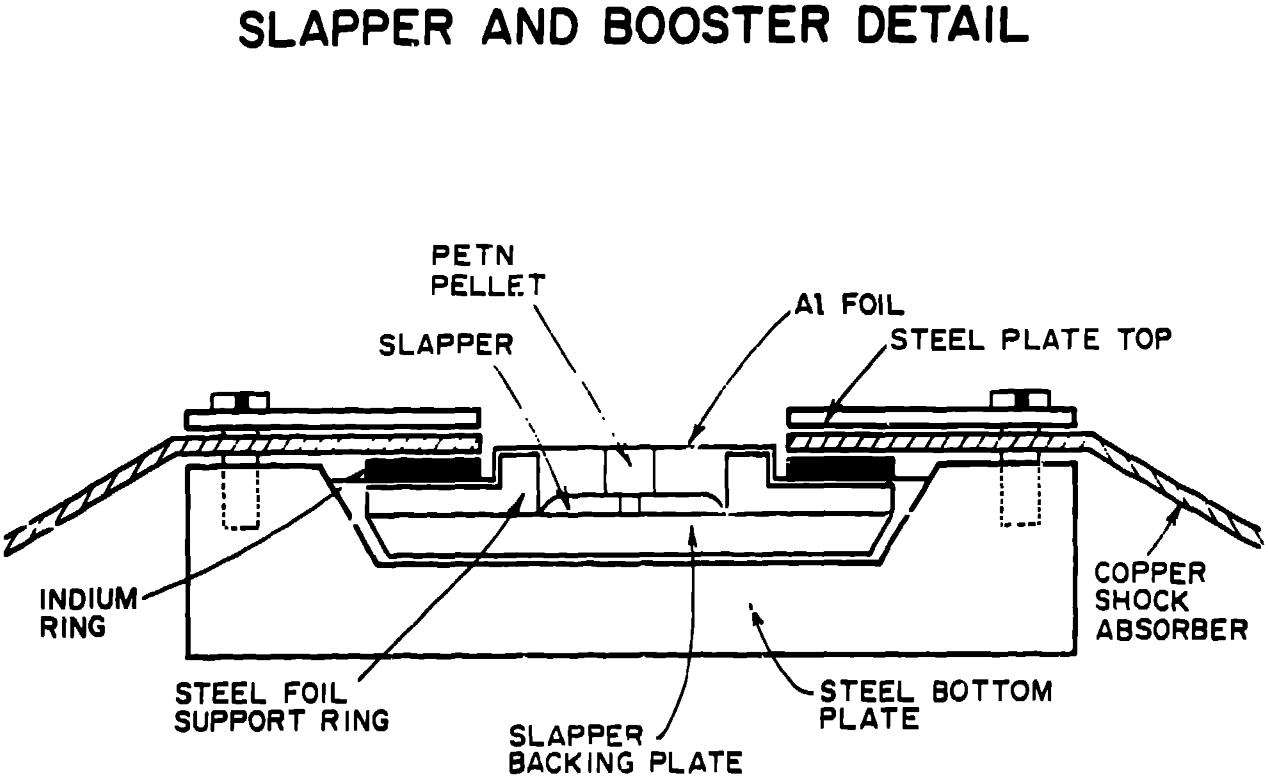


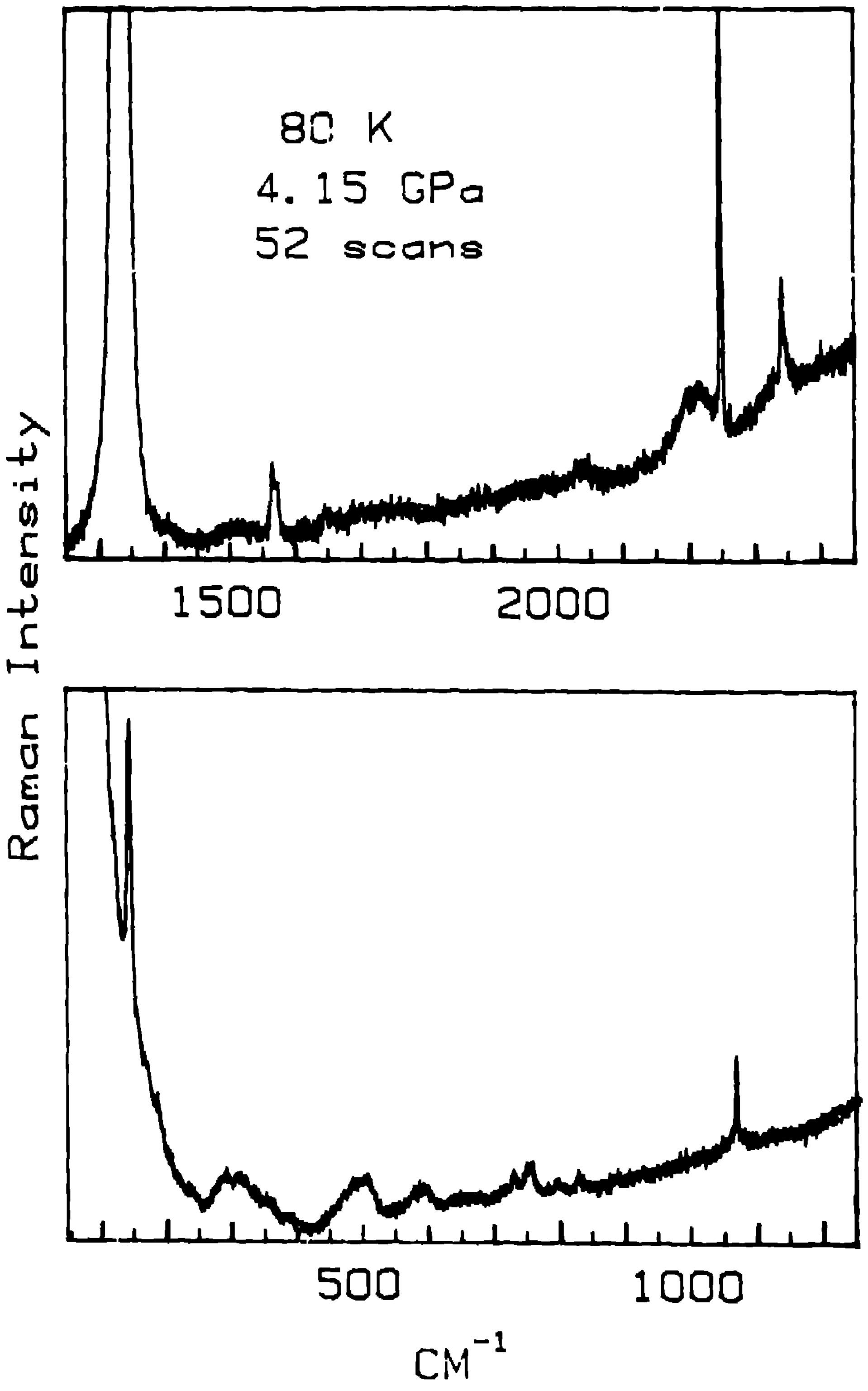
Fig. 1 - Diagram of slapper and booster used in PETN-driven NO reaction.

cells which were warmed to room temperature have been described elsewhere [9] and will be summarized here. Upon warming, the sample remains clear and colorless until ca. 170 K where the reaction begins. The sample first turns deep red, then black, and finally becomes transparent, exhibiting either a straw-yellow fractured solid or a mixed straw- yellow or blue solid.

Detailed IR, Raman and UV-visible spectroscopic studies of the cell contents have revealed the presence of varying amounts of N_2O, N_2O_4, N_2O_3 molecular species as well as the ions NO^+, NO_2^+ and NO_3^-. The above species show complex equilibria as a function of pressure and temperature. At low pressure in the fluid phase (ca. 1.9 GPa) only molecular species are observed while the ions are more prevalent at higher pressures in the solid phase. Both molecular and ionic species are present in the original solid samples upon warming to room temperature. It is stressed that no N_2 or O_2 could be observed in any of the samples which had been allowed to react by warming to room temperature. Raman spectral analysis of the cell contents was made [illegible] by the photolysis of N_2O_4 and N [illegible] which resulted in the formation of [illegible] isomers of each species, as well as the formation of NO_2^+, NO_3^- and N_2O_5 by [illegible]ysis of N_2O_4.

B. Pressure Dependence at Low Temperature: Nitric oxide entrapped in a diamond-anvil cell and maintained at 80 K was found to be stable at pressures below ca. 2.5 GPa. The zero bar vibrational phonon features at [illegible] and 53.2 cm^{-1} are consistent with those previously reported [14] in studies of solid N_2O_2 condensed on a cold surface. The internal modes appear at [illegible] cm^{-1} (ν_4, torsion), 185.2 cm^{-1} ([illegible], N-N stretch), 263.4 cm^{-1} (ν, symmetric bend), and 1865.1 cm^{-1} (ν_1, symmetric N-O stretch). Survey scans showed no evidence of any other features in the range 50-2450 cm^{-1}.

The spectrum in Fig. 2 was taken after a 2.43 GPa spectrum in Fig. [illegible] and indicated that a dramatic transformation had taken place with the NO sample. The


80 K
4.15 GPa
52 scans
Raman Intensity
1500
2000
500
1000
CM^{-1}

phonon region changed and the internal modes for NO disappeared. We did observe very weak features indicating the presence of several particular species. They include $NO^+NO_3^-$ by 108.6 cm^{-1} (interionic), 722.7 cm^{-1} (ν_4, NO_3^- bend), 1063.7 cm^{-1} (ν_1, symmetric NO_3^- stretch), and 2246.7 cm^{-1} (NO^+ stretch), O_2 by the 1565.8 and 1572.9 cm^{-1} doublet, N_2 by the 2339.3 cm^{-1} N-N stretch, N_2O_4 by the 822.9 cm^{-1} (ν_2 scissor) and 286.7, 308.4 cm^{-1} doublet (ν_3 N-N stretch), and N_2O by 589.1 cm (ν_2 bend). The features at 2035.7 and 2206.9 cm^{-1} could be due to an as yet unknown complex of the NO^+ ion and the band at 1644.9 cm^{-1} could be the associated $-NO_2$ symmetric stretch for such a species.[2] The band at 500 cm^{-1} remains unexplained. The pressure increased dramatically for this sample from 2.3 to 4.1 GPa after this transformation occurred and the intensity of the N_2 and O_2 peaks indicate that a substantial amount of these species had formed. It should be noted that this is the first indication of either O_2 or N_2 in the NO reaction products for any cell that we observed that had been loaded by the previous technique, which always involved a fairly rapid warming to room temperature before any analysis took place.

Following this transformation, the optical quality of the cell did not change noticeably as viewed through a microscope, although the cell contents had become pale yellow with increasing pressure. Not until the cell had been warmed to 200 K and the pressure released to under 0.5 GPa did a noticeable transformation occur. A clear to pale yellow solution finally resulted which, when cooled to 190 K produced the spectrum in Fig. 3. Very prominent features are now evident for N_2O , N_2O, N_2, and O_2, with no evidence for any remaining unreacted nitric oxide. Also present in this spectrum are features due to NO_3^-, NO_2^+, and NO^+, although they are much weaker than before.

C. Laboratory Scale Studies of Shocked NO: Initially, it was thought that a slapper alone would detonate solid NO and several attempts were made to achieve this. However, less than 1% decomposition of the deposited NO (ca. 100 mg), was observed, and indeed, under the same conditions the slapper could not even detonate a 6 mg pellet of PETN. With the pellet of PETN glued directly to the slapper, however, the PETN did detonate and the solid NO deposited on the opposite side of the foil that covered the PETN decomposed into a variety of products. Five experiments have been done in this configuration. Molecular nitrogen is the only expected detonation product common to both PETN and solid NO. However, both the small amount of N_2 that results from the PETN (0.04 mmol) as well as the fact that ^{15}NO was used to label the nitrogen source, allowed unambiguous determination of the nitrogen yield from the nitric oxide.

The products collected from the PETN-driven nitric oxide reaction were N_2O, N_2, NO_2, N_2O_3, N_2O_4 and unreacted NO. Presumably any O_2, which is formed due to the NO decomposition, would subsequently react with NO in the gas phase to form additional NO_2. Thus, oxygen may or may not have formed originally from the shock-induced reaction. In addition, the various gas-phase equilibria involving NO_2, as well as its substantial loss by reactivity with CO, metal surfaces, O-rings, etc., complicate the determination of the NO_2 in the original products. The product yields measured from five separate experiments are presented in Table 1. In all cases a substantial portion (29-53%) of the nitric oxide reacted and, of that amount, most ended up as N_2O, with a smaller amount ending up as N_2+NO_2. The N_2 result was corrected for the N_2 produced by PETN, which was determined by means of isotopically labeled NO.

All the experiments in Table 1 except Experiment 3 were done with the bell jar evacuated. Experiment 3 was done with 1 torr of He in the chamber to prevent reshock of the products at the wall. Reshock may have caused the product N_2O and NO_2 to further react, thereby producing N_2. The amount of N_2 produced was indeed the smallest of all the experiments, suggesting that some of the N_2 observed in the other experiments was produced by reshock at the walls of the apparatus.

DISCUSSION

Prior to our work on the chemistry of nitric oxide under static high pressure conditions, it was suspected that shock-initiated detonation of NO proceeds through a single chemical reaction to produce N_2 and O_2. We have shown, on the other hand, that the reaction chemistry under both static high pressure and shock conditions is much more complex involving, most likely, several distinct mechanisms and chemical intermediates. The static high pressure studies demonstrate that nitric oxide reacts rapidly under even modest pressure and temperature conditions to

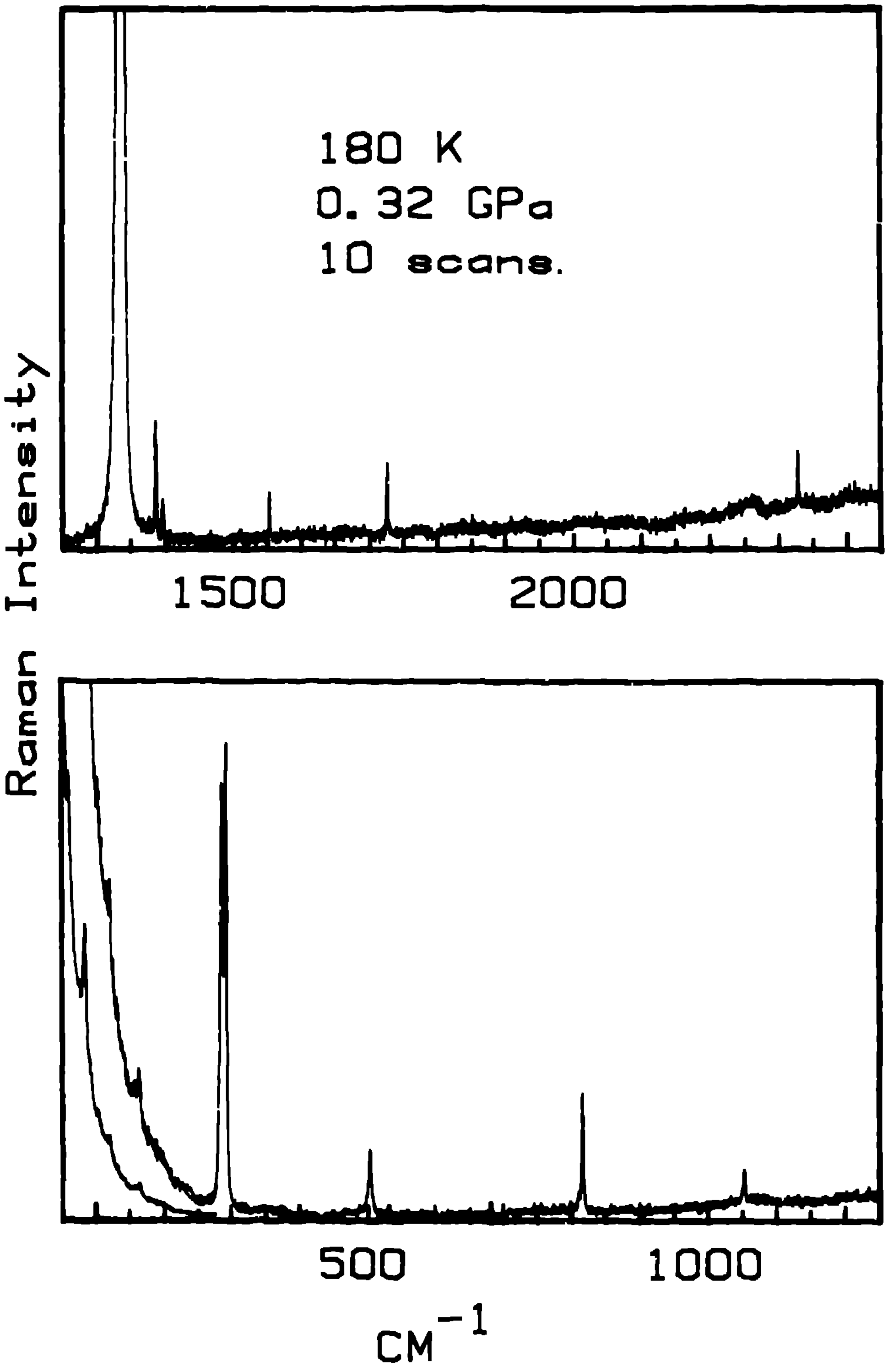


Fig. 3 - Raman spectrum of NO reaction products at 180 K after annealing at [illegible] K and lowering pressure to 0.32 GPa.

TABLE 1

Products from Solid NO Shocked with 6 mg of PETN

	Experiment Number				
	1	2	3	4	5
NO gas used,[a] mmol	3.4	4.6	6.3	10.0	11.2
NO accounted for,[b] mmol	3.3	3.4	4.2	7.5	8.9
NO unreacted, mmol (%)	2.3 (70)	1.6 (47)	3.0 (71)	4.9 (64)	4.4 (50)
N_2O found, mmol	0.33	0.43	0.37	0.60	1.17
N_2 found, mmol	–[c]	0.13	0.03	0.23	0.23

[a] [illegible] NO escapes while forming the solid.

[b] Assuming the overall reaction stoichiometries,

$$3\ NO \longrightarrow N_2O + NO_2 \qquad (i)$$
$$4\ NO \longrightarrow N_2 + 2\ NO_2 \qquad (ii)$$

to account for the N_2O and N_2 observed. The small amount of NO tied up as N_2O_3 is ignored.

[c] N_2 not measured and not accounted for in collected material.

produce a multitude of molecular and ionic species. The fact that this pressure-induced chemistry is quite facile and releases significant amounts of energy strongly suggests that similar reactions dominate the chemistry of shock-initiated detonation of nitric oxide.

The chemistry of samples warmed rapidly to room temperature can be explained to arise from three possible disproportionation reactions

$$2(N_2O_2) \longrightarrow N_2O + N_2O_3 \qquad (1)$$

$$3(N_2O_2) \longrightarrow 2N_2O + N_2O_4 \qquad (2)$$

$$3(N_2O_2) \longrightarrow 2N_2O + NO^+NO_3^- \qquad (3)$$

While the low-temperature high-pressure NO samples as well as the PETN driven NO decomposition show evidence for yet another reaction pathway,

$$N_2O_2 \longrightarrow N_2 + O_2 \qquad (4)$$

The presence of N_2O_3 in the reaction products could arise from its direct production via equation (1) or from reaction of N_2O_4 with excess NO. Equations (2) and (3) differ only in that (2) involves a molecular reaction mechanism while (3) involves the direct production of ionic species. The ions NO^+ and NO_3^- could result from their direct production via equation (3) or through the autoionization of N_2O_4 at high pressures. We have previously shown [10] that molecular N_2O_4 does autoionize at elevated pressures. However, on the basis of the ubiquitous presence of ions in all of the samples reacted under high static pressures and the observation of deep red color (indicative of NO^+ in N_2O_4) in the initial reaction, we presently favor the ionic mechanism (eq. 3).

The studies of pressure-induced chemistry under low temperature conditions further complicated the situation. Whereas N_2 or O_2 could never be detected for samples warmed rapidly to room temperature, the low temperature reaction produces significant and equal amounts of N_2 and O_2. Despite the rather weak relative intensities of the O_2 and N_2 features in the Raman spectra (Figs. 2 and 3) these species are in significant concentration as their Raman cross sections are known to be substantially less than that of the other species present. While it has not been possible to quantify the amounts of N_2 and O_2 production relative to the production of disproportionation products (dominantly [illegible]) it is clear that N_2 and O_2 are produced in nearly equal concentrations. The PETN-driven NO decompositon suggest that the predominant reaction of shocked NO is (3) with reaction (4) present as a minor pathway. This is certainly consistent with the results of static high-pressure measurements upon rapid warming. The implication of the low-temperature high-pressure work (i.e., the importance of reaction (4)) is not yet completely clear, but the PETN-driven NO reaction does show evidence for reaction (4) as well.

The overall reactions depicted above do not necessarily represent the primary reactions, and one could imagine many different possible schemes. One possibility, which we believe can be eliminated, is that the primary reaction involves direct production of N_2 and O_2. The ubiquitous formation of disproportionation products (N_2O, N_2O_4, $NO^+NO_3^-$) would then result from subsequent reactions of N_2, O_2 and excess NO. The formation of N_2O_4 and $NO^+NO_3^-$ is easily explained to arise from

$$N_2 + N_2O_2 \longrightarrow N_2O_4 \rightleftharpoons NO^+NO_3^- \qquad (5)$$

However, the formation of N_2O is more difficult to explain. While gas phase radical reactions are known to result in the formation of N_2O, these are unlikely to occur under low-temperature high-density conditions. In addition, several observations mitigate against this single primary reaction mechanism. First, the nearly equal concentration of N_2 and O_2 in the low temperature experiment is difficult to rationalize because the facile reaction of O_2 and excess N_2O_2 would be expected to deplete the O_2 concentration to a much greater extent than that of N_2. Furthermore, no N_2 or O_2 could be detected in the samples warmed to room temperature; it is extremely unlikely that all of the N_2 could be converted to N_2O under these modest high density conditions. Finally, the observation that the thermodynamically more stable products, N_2/O_2, are formed under low temperature conditions and not formed under higher temperature conditions is counter-intuitive. If a single primary reaction to produce N_2 and O_2 is operative, one should certainly observe these species in cells which were allowed to warm to room temperature.

At present, the results presented here are best explained in terms of two, and possibly more, primary reaction mechanisms. In effect, one mechanism leads to the production of N_2 and O_2 while the other proceeds to form the disproportionation products.

$$N_2O_2 \longrightarrow [\text{Intermediate}] \begin{array}{l} \nearrow N_2 + O_2 \\ \searrow 2N_2O + NO^+NO_3^- \end{array} \qquad (6)$$

The branching between these two primary reactions is then quite sensitive to temperature and pressure. It is possible, for example, that the relative rates of these two global reactions diverge significantly as temperature is changed with disproportionation proceeding more rapidly at elevated temperatures. Additional work is needed to fully understand the complex reaction chemistry of nitric oxide under high density conditions, and work is underway to follow the static high pressure chemistry by careful control of both temperature and pressure.

Implication Regarding Shock-Initiated Detonation of Nitric Oxide: While a detailed chemical mechanism is not yet available for the pressure-induced chemistry of nitric oxide, several conclusions can, nonetheless, be inferred. First, condensed phase concerted reactions appear to dominate the chemistry of nitric oxide under static and dynamic high density conditions. By analogy, gas phase radical type mechanisms known from studies of gaseous NO at low density are not important in the early chemistry of shock initiation of nitric oxide. Second, the present results strongly suggest that disproportionation to form N_2O and $NO^+NO_3^-$ dominates the early chemistry under shock conditions. This reaction would account for 2/3 of the total enthalpy content of nitric oxide and the accompanying energy release could, in turn, drive subsequent reactions to form N_2 and O_2. Finally, the ubiquitous presence of ions such as NO^+ and NO_3^- at high densities points to the importance of ions and ionic reaction mechanisms in shock-initiated detonation. The thermodynamic driving force for the formation of ions at high density presumably derives from the strong inter-ionic interactions and the attendant volume reduction relative to molecular species.

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