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Microscopic Experimental Approaches to High Pressure Chemistry

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Abstract: The experimental study of the chemistry related to the deflagration/detonation of energetic materials is extremely challenging due to the high pressure, high temperature, and time domain under which the chemical reactions occur. In addition, non equilibrium pressure and temperature conditions temporally effect the reaction pathways and rates during the reaction process. The multiple phases of material present (i.e. the heterogeneous nature of the problem), the multiple reaction pathways (both in series and in parallel), and the temporal dependency of the physical conditions make the assignments of the early reaction products, product sequence, and reaction mechanism an extremely difficult if not nearly unsolvable problem.

Recently, experimental approaches have been developed which permit the spectroscopic identification of products species, reaction sequences, and global reaction rates under simulated detonation conditions. Three experimental techniques: (1) high pressure matrix isolation (2) high pressure time-resolved absorption spectroscopy, and (3) high pressure time-resolved emission spectroscopy are used in conjunction with a gem anvil cell to probe the high pressure chemical processes.

1. INTRODUCTION

The detonation of a condensed explosive is a complex process involving extremely rapid mechanical, physical, and chemical changes. It is convenient to approximate or envision the detonation process in the following sequential steps. First, the materials is subjected to a stimulus, e.g. a shock wave, which transfers energy to the material. Second, the chemically excited material most likely proceeds through an endothermic process (termed reaction initiation) resulting in bond breaking at some threshold deformation and temperature condition. Third, a sequence of endothermic/exothermic processes occur resulting in the liberation of chemical energy. Finally, the released chemical energy supports the propagation wave and results in the continuum or hydrodynamic response of the reacted material. Historically, the last step is the one that has been most commonly studied. Very recently, work has also begun to develop techniques to experimentally access the first two steps. There is, however, little that is known about the third step of the chemical changes following reaction initiation.

The initiated material continues to react over an extended period of time through a variety of reaction pathways until some final product distribution is achieved or reaction quenching terminates the developing processes. This region following initiation is defined as the hot molecule zone. The hot molecule zone includes all endothermic and exothermic reactions after initiation. The hot molecule chemistry supports the detonation wave and is responsible for the conversion of chemical energy into the P/V work. This zone is on the order of nanoseconds to microseconds for an ideal explosive. For a nonideal explosive (such as a composite explosive), this region is on the order of nanoseconds to milliseconds. Despite the importance of the chemical reactions in the hot molecule zone, direct experimental measurements are lacking. All chemical reactions which occur during the detonation process take place under nonequilibrium temperature, pressure, and volume conditions. Our studies focus on the chemistry of the hot molecule region. We recognize that the chemical sequences must be probed under representative pressure, temperature, volume (density) and time conditions. A

microscopic experimental approach has been developed to spectroscopically probe the reaction products, reaction product sequence and global reaction rate related to deflagration/detonation. Three experimental techniques: (1) high pressure matrix isolation (HiPMI), (2) high pressure time-resolved UV/Vis absorption spectroscopy (HiPTRAS), and (3) high pressure time resolved emission spectroscopy (HiPTRES) are used in conjunction with a high pressure gem anvil cell (GAC).

2. BACKGROUND

In the past, the chemistry taking place in the hot molecule region has been described by applying basic chemical decomposition processes. This information provided the basis for more realistic estimations of thermodynamic parameters and product distributions to describe the explosive behavior. However, the extrapolations made are unreliable and lead to large uncertainties in thermodynamic parameters which are often used to support the theoretical descriptions of the explosion phenomenon. Given the complexity of the reactions involved and the observed temperature and pressure dependent effects an understanding of the hot molecule region is necessary for modeling explosion behavior. Unfortunately, such experiments are difficult to carry out, and therefore, only a few results have been reported. The effects of extreme conditions (high pressure/high temperature) has been applied to energetic materials over the last several years in an attempt to probe the hot molecule region. Several static experimental approaches have been employed to study the structural dependency, decomposition kinetics, and burn rate of energetic materials under high pressure. [1-4] In addition, detonation mass spectrometry has been employed to probe the chemical sequences of the third step. [5] The decomposition kinetics under static high pressures has provided kinetic and thermodynamic data on the decomposition of materials such as, HMX, RDX, and nitromethane. The high pressure decomposition kinetic studies do not provide any chemical information on the reaction intermediates, final products, or reaction mechanisms and the times associated with decomposition are on the orders of minutes to hours. Static high pressure burn rate studies provide a physical measurement of the affects of pressure on the combustion rate. Detonation mass spectrometry has provided limited chemical information on the reaction processes of a detonation. The temporal evolution of the products has been observed. Multiple products with similar masses and poor resolution make product identification a non-trivial process. These experimental approaches have provided a good first approximation to probe structural dependency, global reaction kinetics, burn rate and product formation of the chemistry of a deflagration/detonation. Further advances are necessary to provide additional information of reaction intermediates, product formation sequence and reaction rates under extreme conditions. The approach must probe the chemistry under representative pressure, temperature, volume (density) and time conditions to attempt to identify the dense state chemistry of the hot molecule region.

3. EXPERIMENTAL

The experimental techniques employed in the present work have been reported in detail elsewhere [6-11]. Only a brief description will be given for the sake of clarity.

3.1 High Pressure Cell:

The high pressure apparatus is either a Merrill-Bassett or NIST Anvil cell. [6,7] Two types of gem anvil materials (diamond and cubic zirconia) are employed. The UV/Vis spectroscopy or matrix isolation sample is prepared by compressing a 3-5 micron sample film between two KBr or NaCl salt windows. A tantalum or nickel gasket confines the sample under pressure. (Figure 1). The gasket hole diameter is 250 microns with a 100 or 200 micron thickness. A small ruby sphere, < 15 microns in diameter, is placed within the salt window. The entire sample (salt windows and sample) is compressed in the gem anvil cell (GAC) to the desired initial pressure. Initial temperature is measured by a chromel-alumel thermocouple with the thermocouple bead in contact with the gasket. In matrix isolation experiments the Merrill-Bassett GAC cell is clamped

Figure 1. Sample arrangement inside the GAC for HiPTRAS and HiPMI.

in thermal contact with a duplex refrigerator head. The GAC (and sample) is cooled to a constant initial temperature of ~ 40 -50 K. The temperature is measured with two gold/chromel thermocouples. One thermocouple is located in a hole drilled in the aluminum mounting plate between the refrigerator and the anvil cell. The second is attached to the gasket surrounding the sample in the GAC cell. Pressure inside the anvil cell is measured by the ruby fluorescence pressure measurement technique originally developed by NIST in 1972 [8,9] and calibrated against the compression of NaCl via the Decker equation of state in 1976.[9] Pressure is evaluated by a peak shift calculation or a line-shape model. The ruby fluorescence measurements are accurate to ± 0.05 GPa when they are made in a hydrostatic environment at room temperature. The material inside the anvil cell is laser heated with either an 8 ns or a 3.5-4.0 microsecond pulse using a visible laser pulse. A first approximation of the bulk thermal response is estimated to be between 700-1200 K.

3.2 High Pressure Matrix Isolation (HiPMI)

The matrix isolation apparatus consists of a closed-cycle helium refrigerator (Air products, Model DE-202) mounted inside a vacuum chamber, a pulsed Nd:YAG laser (Continuum, Model YG 581), and a Nicolet 60 SX FTIR spectrometer employing an MCT-A detector for improved sensitivity.[10]

A single pulse (8 ns) from the frequency doubled Nd:YAG laser (532 nm) is used to heat the sample. The typical laser energies are 15-20 mJ. The laser beam diameters were determined by measuring the spot size burned onto photographic paper loaded in the GAC. Typical values for the beam diameters are ~ 0.5 mm. The fluence of the laser is ~ 1 to 1.5 J/cm². Under these conditions, an initial temperature between 270 and 740°C (543 and 1013 K) is obtained within the sample. The lower temperature is the minimum required to thermally decompose the sample at this pressure. The higher temperature is the melting temperature of KBr, which is not exceeded. The background pressure of the chamber is $\sim 1.0 \times 10^{-7}$ torr. The sample pressure inside the anvil cell is 3.0 GPa. Vacuum conditions are required to eliminate condensation problems on the anvil cell at ~ 40 -50 K.

The infrared absorption spectra of the starting material and the reaction products are measured before and after the laser pulse. Typical spectra are collected with 500-1000 scans at 2 cm⁻¹ resolution. Separate samples are loaded with diamond and cubic zirconia anvils for a complete IR spectral analysis of products in the mid-infrared region (4000 - 600 cm⁻¹).

3.3 High Pressure Time Resolved UV/Vis and Emission Spectroscopy

The time-resolved apparatus consists of a microscope system employing a 20X Zeiss microscopic objective, a flash lamp pumped dye laser (Candela Model SLL 500), a single monochromator (SPEX 1681), a streak camera (Cordin 160 model No. 5B) and a CCD detector (SPEX Model Spectrum-One). [11]

A single pulse (3.5-4.0 μ s) from the flash lamp pumped dye laser, tuned to 514 nm, is used to heat the sample. Typical laser energies are 1.0-6.5 mJ and a measured spot size of ~ 0.14 - 0.20 mm. The UV/Vis absorption and emission spectra were collected into the single monochromator and temporally dispersed by the streak camera onto the CCD detector, thus providing an intensity measurement as a function of wavelength and time. The consumption of material by UV/Vis absorption spectroscopy and the detection of products by emission spectroscopy was monitored in the 380-550 nm wavelength region at a maximum temporal resolution of 110 ns.

4. RESULTS

4.1 Matrix Trapping at High Pressure

Matrix experiments have been carried out on hexanitrohexaazaisowurtzitan (HNIW) at 2.7 GPa. Infrared spectra were collected i) before the laser pulse; ii) after the laser pulse; iii) after warming the sample to room temperature at 2.7 GPa; and iv) after the pressure release from 2.7 GPa to ambient pressure. Figure 2 shows selected spectra from the laser initiated reaction of HNIW in a DAC. The same results are observed in the CZAC and DAC experiments. No starting material remains,

Figure 2. Selected spectra from the HiPMI of HNIW in a DAC.

indicating that the reactant is completely consumed. The products formed are identified by their infrared absorption frequencies. The tentative assignments for the observed reaction products are provided in Table 1. The products observed at 50 K (spectrum A) including unknown (Unk) absorption bands are: CO_2 , Unk 3040, H_2O , Unk 1413, NO_2 , CO , HNCO , Unk 2813, $\text{t}(\text{NO})_2$, Unk 2015, and N_2O . These products are listed roughly in order of their peak height intensity in the spectra without line strength corrections. The three unknown product absorption bands at 3117, 3040, and 1413 cm^{-1} are tentatively assigned to the formation of at least one product containing NH functionality. The two absorption bands detected at 2813 and 2015 cm^{-1} are assigned to at least one product containing CH and CN functionality. Upon warming the sample to room temperature and 2.7 GPa, the only observed changes (Spectrum B) are: the disappearance of the $\text{t}(\text{NO})_2$ band at 1765 cm^{-1} and the NO_2 symmetric stretching band at 1311 cm^{-1} , and the appearance of a band at 1873 cm^{-1} indicates NO monomer formation. All other products remain the same. After the temperature and pressure are returned to ambient conditions (Figure C) the reaction products observed at 50 K disappear. A visually dark film remains trapped in the matrix. The residue spectrum was determined to have the same functionality observed from decomposition and combustion. Therefore, all product absorption bands which disappear are either volatile products or reactive intermediates.

Table 1. IR Bands and Tentative Assignments of the Observed Products in the CZAC and the DAC.

ν (cm^{-1})	Species	Tentative Assignment (intensity)	in CZ	in DIA
3727	CO_2 or H_2O	$\nu_1 + \nu_2(39)$ or $\nu_3(200)$	Y	Y
3615	CO_2 or $\text{OHCN}(\text{?})$	$2\nu + \nu_3(30)$ or OH str	Y	Y
~ 3600 (broad)	H_2O	OH str	Y	Y
3117	$-\text{NH}^{\text{a}}$ or $-\text{CH}-$	NH str or CH str	Y	Y
3040	$-\text{NH}^{\text{a}}$	NH str , CH or $\text{CH}_2\text{ str}$	Y	Y
2813	CH or CH_2	$\text{CH}_2\text{ str}$	Y	Y
2342	CO_2	$\nu_3(2026)$	Y	Y(edge)
2291	HNCO or OHCN	NCO a-str or CN str	Y	
2232	N_2O	$\nu_3(1285)$	Y	
2140	CO	$1-0(235)$	Y	
2015	CH or $\text{CN}(\text{?})$		Y	
1765	$\text{t}(\text{NO})_2$	a-str	Y	Y
1413	$-\text{NH}^{\text{a}}$ or $\text{HINO}(\text{?})$ or $\text{CH}_3\text{NO}(\text{?})$ or $\text{H}_2\text{CN}(\text{?})$	NO str $\text{CH}_3\text{ a-def}$ $\text{CH}_2\text{ sciss}$		Y
1311	$\text{NO}_2(\text{?})^{\text{b}}$	s-str^{b}		Y
883				Y
742	$\text{CH}(\text{?})$			Y
~ 650	CO_2	$\nu_2^{\text{a}}(194)$		Y

^aSimilar to HN_3 decomposition products in Blau and Hochheimer, JCP, 34,1060 (1961) and JCP, 41, 1174 (1964).

^bNot seen in post-laser fire RT spectrum.

4.2 TIME RESOLVED MEASUREMENTS

4.2.1 UV/Vis Absorption:

High pressure time resolved absorption spectroscopy (HiPTRAS) was accomplished with a temporal resolution of 110 ns in the study of $C_6H_6N_{12}O_{12}$, (1,4 trinitroethylamine tetrazine). DTETZ was studied at 0.8, 2.0 and 3.4 GPa. The $\pi - \pi^*$ transition at atmospheric conditions at 411 nm of the tetrazine ring was monitored at a 110 ns temporal resolution. A pressure shift was observed for this band. The experiments at 0.8, 2.0 and 3.4 GPa were performed with comparable laser initiation energies. Similar results are observed for all pressures studied. Figure 3 shows selected spectra of the laser initiated DTETZ sample at 0.8 GPa. A decrease in the absorption band is detected after 580 ns and the absorption has reached its minimum value after 1.1 microseconds. The sample maintains a constant transmittance for 1.1 microseconds. After 1.1 microseconds, an increase in absorption is detected between 380-550 nm. The increase in absorption is detected throughout the remaining temporal window (0.66 microseconds) for the experiment.

Figure 3: HiPTRAS spectra with 220 ns temporal resolution of the DTETZ π to π^* transition laser initiated at 0.8 GPa.

4.2.2 Emission Spectroscopy:

High pressure time resolved emission spectroscopy (HiPTRES) at a temporal resolution of 110 ns was applied to monitor the reaction sequence for the reaction of $Al + H_2O$. The $Al + H_2O$ reaction was studied at < 0.1, 0.2, 0.4, and 0.7 GPa. Figure 4 shows selected spectra for the laser initiated $Al + H_2O$ reaction at a pressure < 0.1 GPa. A reaction sequence is identified by the order of appearance of product emissions. The observed emission lines were identified using tables compiled by Pearse and Gaydon. [12] Spectrum A shows the initial emission detected. Al emission superimposed on a low energy continuum spectral background is observed. This continuum spectral background is assigned to the heating process of the H_2O (l). A continuum spectral background equal in intensity is observed at the same time during laser heating of pure H_2O (l). Al atom emission disappears after 330 ns, with the appearance of AlO and AlH emission (Spectra B and C). AlH emission disappears after 220 ns. During the appearance of AlO and AlH, a large continuum background is also detected. An additional species is detected along with AlO and AlH which has not been identified at this time. AlO emission disappears in 1.1 microseconds. The unassigned emission product continues to emit for 0.5 microseconds after the disappearance of AlO. (Spectra D and E) This suggests that the unassigned emission may be produced by the further reaction of AlO. After the unknown emission has disappeared the continuum spectral background continues until the end of the temporal window of the experiment. (Spectrum E) Two products have been reported which may be identified with the continuum emission. [13] These products are Al_2O_2 and Al_2O_3 (l).

Figure 4: HiPTRES spectra with 110 ns temporal resolution of the laser initiated $Al + H_2O$ reaction at < 0.1 GPa.

5.0 CONCLUSIONS

The experimental approaches to the investigation of chemistry at high pressures has been described and preliminary results are presented for each technique. All experiments are initiated by a similar technique in an attempt to model the conditions associated with a deflagration/detonation. However, each experimental approach provides significantly different chemical information which helps to discern the complicated nature of the problem. Three experimental techniques: (1) high pressure matrix isolation (2) high pressure time-resolved UV/Vis absorption spectroscopy and (3) high pressure time-resolved emission spectroscopy have been demonstrated in a GAC. The combined experimental techniques provide multiple spectroscopic probes for the determination of unique chemical information related to the hot molecule zone. The products produced, product formation sequence, and global reaction rate are determined.

6. ACKNOWLEDGMENTS

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