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Simulations of highly reactive fluids

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Abstract: We report density functional molecular dynamics simulations to determine the early chemical events of hot (T = 3000 K) and dense (1.97 g/cm^3, $V/V_0 = 0.68$) nitromethane (CH_3NO_2). The first step in the decomposition process is an intermolecular proton abstraction mechanism that leads to the formation of CH_3NO_2H and the aci ion $H_2CNO_2^-$, in support of evidence from static high-pressure and shock experiments. An intramolecular hydrogen transfer that transforms nitromethane into the aci acid form, CH_2NO_2H, accompanies this event. This is the first confirmation of chemical reactivity with bond selectivity for an energetic material near the condition of fully reacted specimen. We also report the decomposition mechanism followed up to the formation of H_2O as the first stable product.

Keywords: Density Functional Theory, Molecular Dynamics, Energetic Materials, Nitromethane, Reaction mechanisms

PACS: 71.10, 71.15, 71.20, 61.20

1. Introduction

The reaction chemistry of energetic materials at high pressure and temperature is of considerable importance in understanding processes that these materials experience under impact and detonation conditions. Basic questions such as: (a) which bond in a given energetic molecule breaks first, and (b) what type of chemical reactions (unimolecular versus bimolecular, etc.) that dominate early in the decomposition process, are still largely unknown. The most widely studied, and archetypical example of such materials is nitromethane (CH_3NO_2), a clear liquid with mass density 1.13 g/cm^3 at 298°K. Static high-pressure experiments[1] showed that the time of explosion for deuterated nitromethane is approximately ten times longer than that for protonated materials, suggesting that a proton or hydrogen atom abstraction is involved in the rate determining step. Isotope-exchange experiments, using diamond cells methods, also gave evidence [2] that the aci ion concentration ($H_2CNO_2^-$) increases with increased pressure. Other studies[3] also suggested that reactions occur more rapidly and are pressure enhanced when small amount of bases are present, giving further support to the aci ion production. Shock wave studies of the reaction chemistry are still inconclusive and at odds: mass spectroscopic studies suggesting condensation reactions[4], time-resolved Raman spectroscopy suggesting a bimolecular mechanism[5], UV-visible absorption spectroscopy indicating no sign of chemical reaction[6], or the production of $H_3CNO_2^-$ intermediate for amine-sensitized nitromethane[7]. It was noted, however, that part of the discrepancy is due to the fact that the ring-up experiments are mapping lower temperature regimes (≈1000 °K) than experienced under detonation conditions (T≈2500-5000 °K)[4].

In this work, we use spin-polarized, gradient corrected density-functional calculations to determine the interatomic forces, and simulate the initial decomposition steps of hot (T = 3000K) dense (1.97 g/cm^3, $V/V_0 = 0.68$) nitromethane at constant-volume and temperature conditions. The studied state is in the neighborhood of the Chapman-Jouget state, which is achieved behind a steady detonation front when the material has fully reacted. This state could be achieved through a sudden heating of nitromethane in a diamond anvil cell under constant volume conditions. Our results emphatically show that the first chemical event is a proton extraction to form CH_3NO_2H, the aci ion $H_2CNO_2^-$, and the aci

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acid H_2CNO_2 H. These results are uniquely associated with the condensed-phase rather than the energetically favored C-N decomposition expected in the gas-phase.

2. Computational Approach

The electronic structure calculations of the molecular forces were performed using density functional theory (DFT).[8] For the exchange-correlation potential, we used the spin-polarized generalized gradient corrected approximation of Perdew -Wang (PW91)[9]. Electron-ion interactions were described by Vanderbilt-type ultrasoft pseudopotentials,[10] and orbitals were expanded in a plane wave basis set with kinetic energy cutoff of 340 eV. We used two k-point spacing in the Brillouin zone, each with a total number of 2921 plane waves. Minimization of the total density functional from DFT utilized the charge density mixing scheme[11]. Calculations on a single unit cell were performed using the CASTEP program [12], while those on larger cells employed the VASP program.[11,13]

Molecular dynamics simulations were carried out under constant volume and temperature using a Nose thermostat. For each MD run, random initial velocities were chosen, and a first-order Verlet extrapolation of the wave functions was used. Periodic boundary conditions, whereby a particle exiting the cell on one side is reintroduced on the opposing side with the same velocity were imposed. A dynamical time step of 0.25 fs was employed for all runs, the longest of which was 4.5 ps. Simulations were performed at a constant temperature of 3000 K using either one unit cell of nitromethane crystal (4 molecules, 28 atoms), a supercell with 8 molecules, and a supercell with 16 molecules. The unit cell was fully optimized at the reduced (compressed) volume, V = 205.36 Å^3.

3. Results and Discussion

The initial configuration at density 1.974 g/cm^3 was determined by compressing the simulation cell and performing full relaxation of all atomic coordinates. From this initial structure, molecular dynamics were performed using the Nose-Hoover thermostat at 3000K.

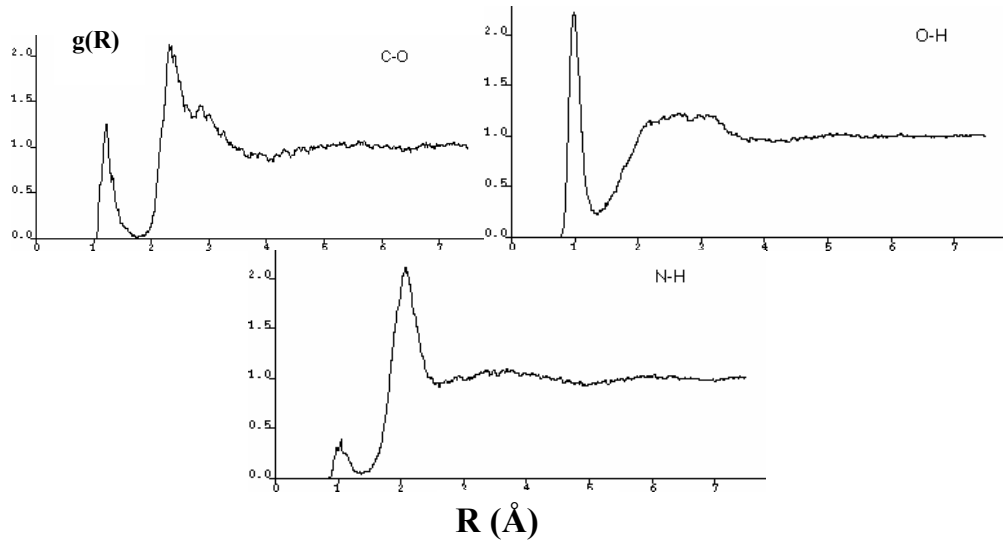

Figure 1. Calculated radial distribution functions g(R) for various intra and intermolecular bonds.

Here, we report the results obtained from the simulation using the largest supercell, consisting of four unit cells of nitromethane molecules with a repetition of 2x2x1 of the unit cell and corresponding to a volume of 821.5 Å^3. The total time of this simulation was 1.16 ps.

Figure 1 shows the C-O, O-H, and N-H radial distribution functions obtained over the total time of the simulation. It is evident from the distributions for the C-O, O-H and N-H that significant rearrangement of the bonds have occurred and chemistry has ensued. For C-O, the dominant population around 1.2 Å is due mainly to the formation of CO_2, while for N-H, the small population around 1.0 Å

is due to the formation of radical intermediates of CH_2NHO. Most interestingly is the significant population growth of O-H at 1.0 Å, which encompasses the formation of H_2O, and in the early stages, to inter and intramolecular hydrogen bonding that leads to proton transfer.

A snapshot of the MD simulation at 59 fs where the formation of CH_3NO_2H and CH_2NO_2 takes place is shown in Figure 2. This process of proton transfer is initially facilitated by enhancement in the C-N double bond character, and an accelerated rotation of the methyl groups (CH_3), rotations that are omnipresent even at ambient temperatures. [14]

The proton transfer process described above is uniquely associated with the condensed fluid phase of nitromethane. This bond specificity is remarkable, since in the gas phase the C-N bond is the weakest in the molecule (D_0 = 60.1 kcal/mol) [15], and is therefore expected to be the dominant dissociation channel and the initial step in the decomposition of nitromethane even at high temperature. In contrast, the C-H bond is the strongest in the nitromethane molecule. In the condensed phase, however, vibrational energy is the highest in the C-H mode. Due in part to a caging effect, this vibrational motion eventually leads to a proton extraction.

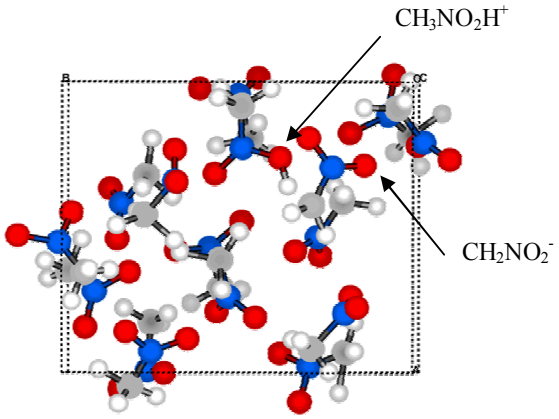

Figure 2. A snapshot of the MD simulation at 59 fs. The formation of CH_3NO_2H and CH_2NO_2 due to intermolecular hydrogen abstraction is shown.

The formation of CH_3NO_2H and CH_2NO_2 via proton extraction was observed in all three simulations of different supercell sizes. In the simulation on a single unit cell, the event occurs at 785 fs of the simulation time. We performed Mulliken charge analysis and determined the net charges on the two moieties CH_3NO_2H and CH_2NO_2. We notice that the negative charge on the carbon atom of CH_2NO_2 is larger than in CH_3NO_2H, while the opposite trend is exhibited for the positive charge on nitrogen. This is a manifestation of electronic charge redistribution in the region between the C and N atoms.

It is noteworthy that all three simulations (one, two and four unit cells) have yielded the same results in the formation of CH_3NO_2H, $H_2CNO_2^-$, and CH_2NO_2H. Experimental concurrence for the production of the aci ion in highly pressurized and detonating nitromethane abound. Shaw et al.[1] observed that the time to explosion for deuterated nitromethane is about ten times longer than that for the protonated materials, suggesting that a proton or hydrogen atom) abstraction is the rate-determining step. Isotope-exchange experiments provided evidence that the aci ion concentration is increased upon increasing pressure[2], and UV sensitization of nitromethane to detonation was shown to correlate with the aci ion presence. [16] Finally, we note that a recent electronic structure study of solid nitromethane determined a significant C-H stretch upon compression, which eventually lead to proton dissociation[17].

4. Conclusion

We studied the early chemical events of hot (T = 3000 K) and dense (1.97 g/cm^3, V/V_0 = 0.68) nitromethane using density functional molecular dynamic simulations. Three simulations on one, two , and four unit cells of crystal nitromethane have shown that the first step event in the decomposition process is an intermolecular proton abstraction mechanism that leads to the formation of CH_3NO_2H and

the aci ion $H_2CNO_2^-$, which lends support to experimental results from static high-pressure and shock experiments. An intramolecular hydrogen transfer that transforms nitromethane into the aci acid form, CH_2NO_2H, accompanies this event. This is the first confirmation of chemical reactivity with bond selectivity for an energetic material near the condition of fully reacted specimen.

Acknowledgments

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