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ABSTRACT

The study of chemical transformations that occur at the reactive shock front of energetic materials provides important information for the development of predictive models at the grain-and continuum scales. A major shortcoming of current high explosives models is the lack of chemical kinetics data of the reacting explosive in the high pressure and temperature regimes. In the absence of experimental data, long-time scale atomistic molecular dynamics simulations with reactive chemistry become a viable recourse to provide an insight into the decomposition mechanism of explosives, and to obtain effective reaction rate laws. These rates can then be incorporated into thermo-chemical-hydro codes (such as Cheetah linked to ALE3D) for accurate description of the grain and macro scales dynamics of reacting explosives. In this talk, I will present quantum simulations of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) crystals under thermal decomposition (high density and temperature) and shock compression conditions. This is the first time that condensed phase quantum methods have been used to study the chemistry of insensitive high explosives. We used the quantum-based, self-consistent charge density functional tight binding method (SCC_DFTB)[1] to calculate the interatomic forces for reliable predictions of chemical reactions, and to examine electronic properties at detonation conditions for a relatively long time-scale on the order of several hundreds of picoseconds.[2] For thermal decomposition of TATB, we conducted constant volume-temperature simulations, ranging from 0.35 to 2 nanoseconds, at ρ=

2.87 g/cm^3 at T= 3500, 3000, 2500, and 1500 K, and ρ= 2.9 g/cm^3 and 2.72 g/cm^3, at T = 3000 K. We also simulated crystal TATB's reactivity under steady overdriven shock compression using the multi-scale shock technique.[3] We conducted shock simulations with specified shock speeds of 8, 9, and 10 km/s for up to 0.43 ns duration, enabling us to track the reactivity of TATB well into the formation of several stable gas products, such as H_2O, N_2, and CO_2. Although complex chemical transformations are occurring continuously in the dynamical, high temperature, reactive environment of our simulations, a simple overall scheme for the decomposition of TATB emerges: Water is the earliest decomposition products to form, followed by a polymerization (or condensation) process in which several TATB remaining fragments are joined together, initiating the early step in the formation of high-nitrogen clusters, along with stable products such as N_2 and CO_2. Remarkably, these clusters with high concentration of carbon and nitrogen (and little oxygen) remain dynamically stable for the remaining period of the simulations. Our simulations, thus, reveal a hitherto unidentified region of high concentrations of nitrogen-rich heterocyclic clusters in reacting TATB,[4] whose persistence impede further reactivity towards final products of fluid N_2 and solid carbon. These simulations also predict significant populations of charged species such as NCO^-, H^+, OH-, H_3O^+, and O^{-2}, the first such observation in a reacting explosive. Finally, A reduced four steps, global reaction mechanism with Arrhenius kinetic rates for the decomposition of TATB**,** along with comparative Cheetah decomposition kinetics at various temperatures has been constructed and will be discussed.

References:

1- M. Elstner et al., *Phys. Rev. B* **1998**, *58*, 7260.
2- E. J. Reed et al., *Nature Phys.* **2008**, 4, 72.
3- E. J. Reed et al., *Phys. Rev. Lett.* **2003**, 90, 235503.
4- M. R. Manaa et al., *J. Am. Chem. Soc.* **2009**, 131, 5483.

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