Change of mechanism in the decomposition of hot dense liquid nitromethane as a function of density: MD simulations

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Abstract

Decomposition mechanism of hot liquid nitromethane at various compressions was studied using reactive force field (REAXFF) molecular dynamics simulations. A competition between two different initial thermal decomposition schemes is observed, depending on compression. At low densities unimolecular C-N bond cleavage is the dominant route, producing CH_3 and NO_2 fragments. As density and pressure rise approaching the Chapman-Jouget detonation conditions (~30% compression, >2500K) the dominant mechanism switches to the formation of the CH_3NO fragment via H-transfer and/or N-O bond rupture. The change in initial decomposition mechanism of hot liquid NM leads to different kinetic and energetic behavior, as well as product distribution. The calculated exothermicity as a function of density reflects the changes in decomposition reactions mechanisms, thus it is a convenient and useful global parameter for the detection of reactions dynamics.

Relevance

Niromethane is a good, relatively simple model of a liquid explosive. The detailed understanding of its initiation and the chemical reactions which take place during a sustainable detonation are a template for other nitro based explosives. The information obtained in these simulation shade light on the detailed mechanism of the detonation process and allows on to obtain a more accurate equation of state to describe the explosion using hydrodynamic approach.

Mechanism of nitromethane decomposition at high density and temperature

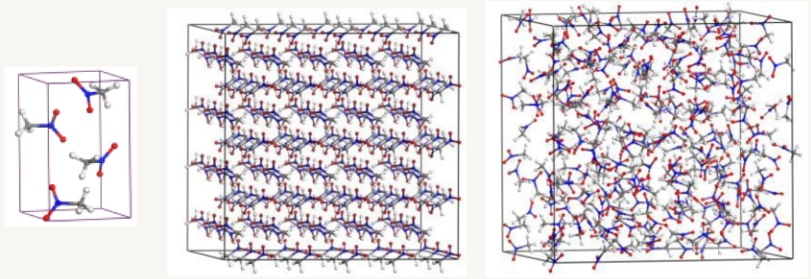

FIG. 1: Nintrometane Crystal. (a) unitcell (b) 5x4x3 energy minimized supercell and (c) liquid NM supercell at ambient conditions

Summery of Reaction mechanism

$CH_3NO_2 \rightarrow \mathbf{CH_3} + NO_2$
$CH_4NO_2 \rightarrow \mathbf{CH_3NO} + OH$
$CH_3NO_2 \rightarrow \mathbf{CH_3NO} + O$ (at higher compressions)
$C_2H_6NO_2 \rightarrow \mathbf{CH_3NO} + CH_3O$ (at higher compressions)
$OH + NO \rightarrow HNO_2$
$H + NO_2 \rightarrow HNO_2$
$HNO2 \rightarrow HO + NO$
CH_3NO_2 (or $CH_3 + NO_2$)$\rightarrow CH_3O + NO$
$CH_2NO_2 \rightarrow CH_2O + NO$ (at higher compressions)
$C_2H_6NO_2 \rightarrow CH_2NO_2 + \mathbf{CH_4}$
$CH_3O \rightarrow CH_2O + H$
$CH_2NO_2 \rightarrow CH_2O + NO$ (at higher compressions)
$CH_2NO_3 \rightarrow CH_2O + NO_2$ (at higher compressions)
$CH_3O + CH_3NO_2 \rightarrow CH_2O + CH_4NO_2$ (at higher compressions)

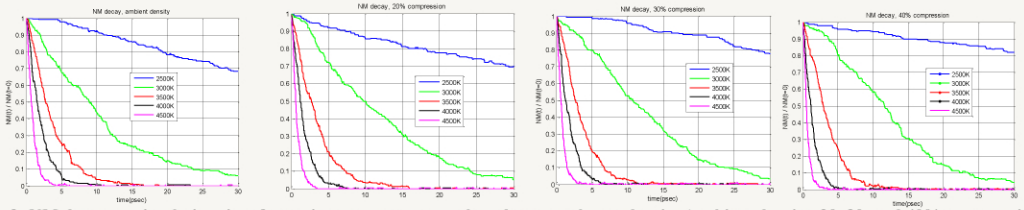

FIG. 2: NM decay vs. simulation time for various temperatures, plotted separately per density (ambient density, 20, 30, and 40% compressions.

Additional autocatalytic reactions

$CH_3NO_2 + CH_3 \rightarrow C_2H_6NO_2$
$CH_3NO_2 + H \rightarrow CH_4NO_2$
$2\ CH_3NO_2 \rightarrow CH_4NO_2 + CH_2NO_2$
$CH_3NO_2 + O \rightarrow CH_3NO_3$
$CH_2NO_2 + OH \rightarrow CH_3NO_3$
$CH_3O + NO_2 \rightarrow CH_3NO_3$

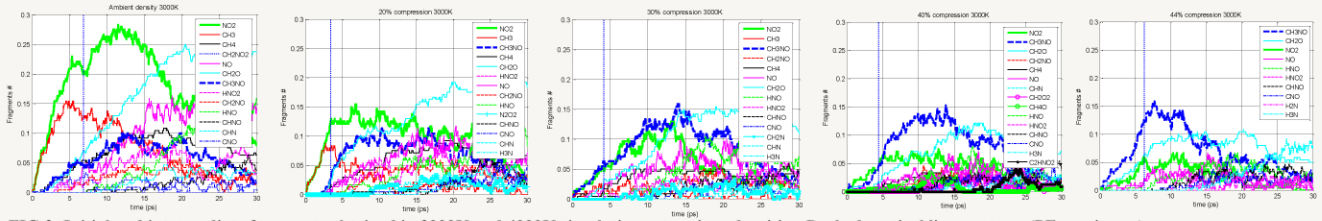

FIG.3: Initial and intermediate fragments obtained in 3000K and 4000K simulations at various densities. Dashed vertical lines are t_{max} (PE maximum). Shown are fragments reaching >3% of initial NM molecules, normalized relative to 240 initial NM molecule.

Accomplishments Through Current Year

This study is the first to obtain the detailed decomposition intermediate species of a liquid explosive. We find a change of mechanism when the density reached detonation conditions.

Future Work

We intend to explore other common explosives with the aim to figure out theoretically their safety features. In addition, similar simulation for mixtures of Nitromethane with various “fuels” or inhibitors will be carried out to understand the sensitivity and detonation mechanism of such mixtures.

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