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 CH₂ and NO₂ fragments. As density and pressure rise approaching the Chapman-Jouguet detonation conditions (~30% compression, >2500K) the dominant mechanism switches to the formation of the CH₂NO 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

Nitromethane 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

Summary of Reaction mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NO₂ → CH₃ + NO₂</td>
<td>High</td>
</tr>
<tr>
<td>CH₃NO₂ → CH₃NO + OH</td>
<td>High</td>
</tr>
<tr>
<td>CH₃NO₂ → CH₃NO + O</td>
<td>High (at higher pressures)</td>
</tr>
<tr>
<td>C₂H₅NO₂ → CH₃NO + CH₂O</td>
<td>High (at higher pressures)</td>
</tr>
<tr>
<td>OH + NO → HNO₂</td>
<td>Medium</td>
</tr>
<tr>
<td>H + NO₂ → HNO₃</td>
<td>Medium</td>
</tr>
<tr>
<td>HNO₂ → H₂O + NO</td>
<td>Medium</td>
</tr>
<tr>
<td>CH₃NO₂ (or CH₃ + NO₂) → CH₂O + NO</td>
<td>Medium (at higher pressures)</td>
</tr>
<tr>
<td>C₂H₅NO₂ → CH₃NO₂ + CH₄</td>
<td>Medium (at higher pressures)</td>
</tr>
<tr>
<td>CH₄O → CH₂O + H</td>
<td>Low</td>
</tr>
<tr>
<td>CH₃NO₂ → CH₂O + NO</td>
<td>Low (at higher pressures)</td>
</tr>
<tr>
<td>CH₃NO₂ → CH₂O + NO₂</td>
<td>Low (at higher pressures)</td>
</tr>
<tr>
<td>CH₃O + CH₂NO₂ → CH₂O + CH₂NO₂</td>
<td>Low (at higher pressures)</td>
</tr>
<tr>
<td>CH₃NO₂ + O → CH₂NO₃</td>
<td></td>
</tr>
<tr>
<td>CH₂NO₂ + OH → CH₃NO₃</td>
<td></td>
</tr>
<tr>
<td>CH₃O + NO₂ → CH₂NO₃</td>
<td></td>
</tr>
</tbody>
</table>

Additional autocatalytic reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NO₂ + CH₃ → C₂H₄NO₂</td>
<td>Low</td>
</tr>
<tr>
<td>CH₃NO₂ + H → CH₃NO₂</td>
<td>Low</td>
</tr>
<tr>
<td>2 CH₃NO₂ → CH₃NO₂ + CH₂NO₂</td>
<td>Low</td>
</tr>
<tr>
<td>CH₃NO₂ + O → CH₂NO₃</td>
<td>Low</td>
</tr>
<tr>
<td>CH₂NO₂ + OH → CH₃NO₃</td>
<td>Low</td>
</tr>
<tr>
<td>CH₃O + NO₂ → CH₂NO₃</td>
<td>Low</td>
</tr>
</tbody>
</table>

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

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

FIG. 3: Initial and intermediate fragments obtained in 3000K and 4000K simulations at various densities. Dashed vertical lines are tₘₚₐₓ (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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