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What we can learn from quantum molecular dynamics simulations of detonation chemistry: extracting reaction rates, and the search for intermediates

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The chemistry of energetic materials (EM) is characterized by rapid exothermic reactions that lead to dramatic increase of the pressure and temperature on the pico- to nanosecond timescales. Under these conditions, experiments have struggled to provide detailed insights into early and intermediate processes, and simulations have thus become a valuable tool to help interpret experiments and parameterize mesoscale models. We have performed molecular dynamics (MD) cook-off simulations of EM with DFTB, a parameterized form of DFT that allows to simulate systems with hundreds of atoms, over hundreds of picoseconds, with explicit treatment of the electronic interactions and an accuracy close to that of DFT. We find drastically different times-to-explosion, even for the same initial T/P conditions, due to multiple complex and competitive chemical pathways. However, a simple effective reaction rate can be extracted, as long as multiple simulations are performed at each T/P to account for the stochastic component of detonation chemistry in EM. We apply this methodology to nitromethane and RDX, and determine pressure-dependent activation energies and volumes that can be compared to experimental results and used in higher scale models. Additionally, the atomistic MD resolution allows us to simulate time-resolved IR spectra, that are compared to experiments, and can be used to guide the search for metastable intermediates during the reaction.