

Public Abstract

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Graduation Term:SS 2017

Department:Chemistry

Degree:PhD

Title:

EXPLORING CHEMICAL REACTION COMPLEXITY:
APPLICATION TO HYDROGEN COMBUSTION

The aim of this research is to gain insight into hydrogen combustion as a prototype of complex chemistry via classical molecular dynamics (CMD) simulations given the presently available reactive force-field, ReaxFF. We focus on developing computational and theoretical methods to analyze CMD simulations of hydrogen combustion and glean the details of chemistry to identify major sequential elementary reactions connecting reactants to products.

In Chapter 1 we explain the problem exists in understanding complex chemistry followed by a brief overview of currently popular methods used to study complex chemical processes with an emphasis on hydrogen combustion. Then, we propose our approach that is based on CMD simulations to tackle the problem and elaborate on the goals of the study.

In Chapter 2 we introduce an algorithm that identifies every elementary molecular event such as reactions and formation/dissociation of hydrogen-bond complexes in CMD simulations of hydrogen combustion. After validating the ReaxFF force-field for the equation of state and interaction energy, we then present ReaxFF-based results of CMD simulations for the early chemistry of hydrogen combustion. The CMD simulations predict two major pathways for production of initial radicals; a termolecular elementary reaction $2O_2 + H_2 \rightarrow 2HO_2$ and the widely-accepted bimolecular reaction $O_2 + H_2 \rightarrow H + HO_2$. Later in Chapter 2, we present and discuss the effects of density on the early chemistry of hydrogen combustion; which show that at elevated density and low temperature the termolecular reaction dominates the chemistry. We describe a method based on collision gas theory that can be used with CMD simulations to explain the observed trends.

In Chapter 3, we provide results for Nudged Elastic Band method (NEB) to characterize potential energy profiles for the bi- and ter-molecular reactions predicted by ReaxFF. Then, we use state-of-the-art electronic structure calculations to examine accuracy of the ReaxFF predictions for the energies and stationary points of the reactions. Later in Chapter 3 we discuss the effect of temperature on the occurrence probability of the ter- and bi-molecular reactions based on the electronic structure predictions of the energy barriers. Lastly, we identify the steric requirements predicted by ReaxFF for each reaction based on the CMD simulations.

In Chapter 4, we present a method based on Tolman's interpretation of activation energy that can be applied to thermal and non-thermal chemical reactions in molecular dynamics simulations of bulk gases. We use Boyd's assumption of local equilibrium thermodynamics to generalize Tolman's concept for application to individual reaction clusters, which include all chemical species that participate in an isolated reaction, for which we define the reaction cluster local energy (RCLE). The RCLE is shown to be conserved during the course of a reaction. We identify the transition configuration (TC), which is the point where the local energy of the reactants crosses that of the products. The TC is a unique point that separates reactants and products and can be used as an estimation of the transition state in accordance with Marcus theory for proton transfer reactions. We demonstrate application of the method by computing activation energies of the several reactions in molecular dynamics simulations.