

LIQUID-PHASE MECHANISM GENERATION FOR APPLICATION TO FUEL OXIDATION

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Abstract

The oxidation of liquid fuels poses storage and transportation issues for the automotive industry, leading to decreased fuel efficiency and increased pollutant formation over time. Consideration of all radical propagation pathways is necessary to fully understand the oxidation process. In this study, the Reaction Mechanism Generator (RMG) software was used to generate detailed kinetic models for the oxidation of alkane fuels. A molecular structure group-based method, derived from quantum calculations on a set of training reactions, was used to correct gas-phase reaction rates in the model to account for the reactions occurring in the liquid-phase. Model simulations were performed before and after altering the reaction rates, and the results were compared to experimental measurements of the oxidation of these fuels.

Keywords

Automatic mechanism generation, oxidation, fuels, kinetic modeling

Introduction

The oxidation of liquid fuels causes degradation of the fuel over time and may increase the potential for pollutant formation. Additives, such as fatty acid methyl esters (FAME), alter the oxidation properties of the fuel (Ben Amara et al., 2013). Although many reaction pathways contribute to radical propagation in these chemical systems, typically only the main reaction channel, consisting of hydrogen abstractions with alkyl peroxy radicals, is considered (Shaich, 2012). Building detailed kinetic models can help elucidate these reaction pathways, leading to better understanding of the oxidation of fuels, especially when the effect of additives is unknown. Automatic mechanism generators such as the Reaction Mechanism Generator (RMG) are used to generate these models faster and minimize their errors. This work adds

to ongoing efforts to use RMG to generate liquid-phase reaction mechanisms, specifically for fuel oxidation.

RMG can build detailed chemical mechanisms for combustion and pyrolysis of hydrocarbons in the gas phase well, but requires additional functionality to build mechanisms for liquid-phase systems. Thermodynamic and diffusion effects due to solvation have been previously added to RMG (Jalan et al., 2013), but solvation also affects intrinsic reaction rates, an effect which has not yet been implemented. To date, this kinetic solvent effect has been investigated for relatively small sets of reactions and solvents, but so far no systematic corrections to the gas-phase reaction rates exist in automatic mechanism generators.

The change in reaction rate due to solvation occurs in part because solvents affect reactants and transition states differently, resulting in changed activation energy of the reaction. However, calculating the energy of the reactant and transition state structures for every reaction in a large model during the course of the simulation, in both the gas-phase and in the solvent, is not feasible. In this work, a method to predict, on the basis of the molecular structure, the effect of solvent on activation energy has been developed, and implemented in RMG for two reaction families that commonly occur in these fuel oxidation models. The method has been used to alter reaction rates in detailed kinetic models for n-paraffins. The resulting models were compared with experimental data from the oxidation of these liquid fuels.

Methods

To determine trends in the difference in activation energy between reactions occurring in solution and gas phase, $\Delta E_A = E_A^{\text{solvent}} - E_A^{\text{gas}}$, a set of reactions for each reaction family was investigated using quantum chemistry. To facilitate the calculation of many transition states, an automated method for predicting transition state geometries via group additivity, developed by Bhoorasingh and West (2015), was used to generate the transition state geometries for these reactions. Both reactant and transition state geometries were optimized with the M06-2X/MG3S density functional and basis set., The continuum solvation model SMD (Marenich, 2009) was used to calculate single point energies in each of eight solvents, where n-octane was the solvent used to represent the alkane fuels studied in this work.

The ΔE_A values determined for these reactions were used to train group-additive values for the reacting functional groups, via linear least squares regression. The group values are stored in hierarchical trees within each reaction family, so that the estimate is based on the most specific functional group for which data are available, falling back to a more general group definition if necessary. Different trees are fitted for each category of solvent; in this study, all reactions are occurring in alkane fuels, so the same tree is used throughout (the one trained on octane). The contribution for each reactant is added together to obtain ΔE_A for a given reaction.

Using the method for determining ΔE_A , the reaction rate was modified for each hydrogen abstraction reaction

in fuel oxidation models that had previously been generated using RMG. The resulting models, with updated E_A for each reaction, were used to perform reactor simulations in Cantera, an open-source reactor modeling software. The results of the simulations were compared to simulations using the original models at the same conditions, and to experimental data for a range of C₈-C₁₆ alkanes.

Conclusions

Model simulation revealed that adding ΔE_A to the activation energy of the gas-phase hydrogen abstraction and intra-molecular hydrogen migration reactions changes the oxidation behavior for liquid hydrocarbon fuels. These results highlight the importance of modifying the reaction rates to account for a solvent, and show that using a group contribution method can quickly generate estimates of this difference in reaction barrier between gas and liquid phases. Further work to include the solvent effect on other reaction types may further change fuel oxidation models, leading to improved predictions of the stability of liquid fuels

Acknowledgments

Financial support is acknowledged from the Department of Chemical Engineering at Northeastern University.

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