

Advances in Automatic Reaction Mechanism Generation for Sulfur Systems: A Case Study of Dimethyl Sulfide Oxidation

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Highlights

- Development of sulfur thermochemistry group additivity values, including for highly oxygenated organic sulfur species
- Implementation and adaptation of reaction templates, kinetics, and resonance types for sulfur species
- Comparison of automatically generated mechanism to experimental dimethyl sulfide oxidation results

1. Introduction

Automatic reaction mechanism generation is a powerful tool to understand complex reactive systems. The Reaction Mechanism Generator (RMG) software is an implementation of this concept that allows the user to create detailed kinetic models for use in the design, optimization, or understanding of reactors, engines, or fuels.¹ This work describes the expansion of the RMG software to higher valence sulfur species with a case study examining the partial oxidation of dimethyl sulfide. Previous efforts had allowed the modeling of low valence sulfur species,² but many industrially important processes involve highly oxidized, high valence, sulfur species. This work represents progress toward modeling these systems.

2. Methods

This work uses the Reaction Mechanism Generator software to create detailed kinetic models. The RMG software creates kinetic models by iteratively adding species and reactions, starting from user specified initial conditions. The reactions are automatically generated using known reaction templates and their corresponding kinetics are estimated using a hierarchical tree of rate estimation rules. The thermochemistry of each species is estimated using a combination of published libraries and group additivity methods.

Due to the large numbers of species and reactions present in most reactive systems and the difficulty of isolating these species and reactions, quantum chemical calculations were extensively used to generate estimations for both the group additivity methods and the kinetic parameters. In general the complete basis set method CBS-QB3 was used to evaluate the geometries, frequencies, and energies of species and transition states. From these calculated values the thermochemical and kinetic parameters were evaluated using the Cantherm software (packaged with RMG).

The validity of these models was tested by comparing an RMG generated model to experimental work that measured the concentration of major species during the hydroxyl radical initiated oxidation of dimethyl sulfide.³

3. Results and discussion

Thermochemical group values were determined in two steps. First, groups involving sulfur with a valence of two were fit primarily using species libraries published by Vandeputte and Class. Second, groups involving sulfur of a higher valence were fit using molecules calculated at CBS-QB3. In all, approximately 200 molecules were used to determine thermochemical group values for about 120 groups. The validity of these group values is supported by parity plots comparing the thermochemistry estimated by group additivity and the calculated thermochemistry.

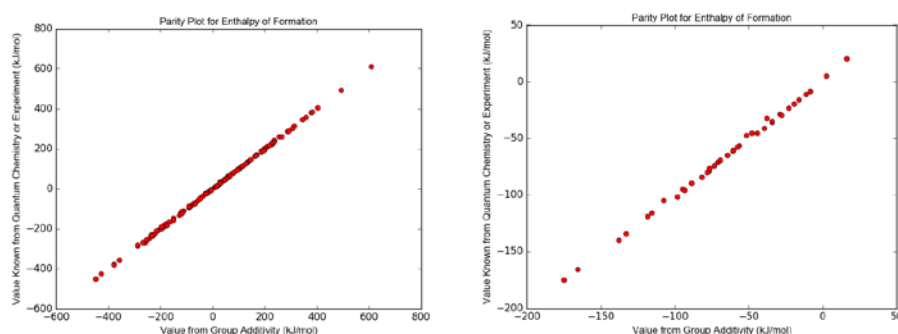


Figure 1. Estimated Enthalpies of formation compared to calculated enthalpies of formation for sulfur groups with a valence of two (left) and a valence higher than two (right)

While only enthalpies are displayed in the figures above, the remaining thermochemical parameters are similarly well fit by the group values. In addition to group additivity values, relevant kinetic and resonance additions allowed the modeling of complex sulfur-containing oxidation systems.

The RMG generated model for dimethyl sulfide oxidation compares well to the experiments in many respects while still containing many discrepancies. For example, the final concentrations of dimethyl sulfide and dimethyl sulfoxide approximately match those observed experiments. However, some species, such as sulfur dioxide and methyl thiol formate (CH_3SCHO), are less well predicted. These discrepancies suggest specific reaction classes and molecule types are being incorrectly described by the limited dataset.

4. Conclusions

Methods for estimating thermochemical and rate parameters for a wide range of C/H/O/S species were incorporated into the Reaction Mechanism Generator (RMG) software suite. These results illustrate that RMG is now capable of automatically creating models for predicting the reaction kinetics of systems containing highly oxidized sulfur species. However, comparison to experiment shows some discrepancies, pointing to areas where further improvements in understanding and in modeling techniques are needed.

References

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Keywords

Automatic Mechanism Generation; Sulfur