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Thermochemistry Prediction and Automatic Reaction Mechanism Generation for Oxygenated Sulfur Systems: A Case Study of Dimethyl Sulfide Oxidation

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Abstract

Automatic mechanism generation is a powerful approach to understanding complex chemical mechanisms. Here we describe the expansion of an open source mechanism creating software, the Reaction Mechanism Generator or RMG, to oxygenated sulfur systems. This principally involved the expansion of thermochemistry estimation techniques for higher valence oxygenated sulfur molecules.

As a demonstration of this new tool, we present an automatically generated mechanism describing the oxidation of dimethyl sulfide. This mechanism is then compared to several experimental studies of dimethyl sulfide oxidation. This case study provides insight into the transformation of sulfur species in the atmosphere, especially the formation pathways of sulfoxides, sulfones, and sulfur dioxide. However, the applications of the newly enhanced mechanism generation tool extend far beyond this single system with obvious use in understanding a variety of atmospheric, petrochemical, and other industrial chemistries.

1. Introduction

Chemical systems often resist simplification because the number of important species and reactions far exceeds anyone's definition of simple. However in spite of the inherent complexity, understanding the detailed chemistry of reacting systems is crucial in a wide variety of pursuits, both academic and commercial. Entwined within this detailed chemistry lie key combustion

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characteristics such as the ignition delay[1], extinction strain rate[2], octane number[3], or flame speed[4]. Other natural systems are also better understood with a knowledge of the chemistry, including the formation pathways and fates of species in the atmosphere[5]. Similarly, biological systems are often described in complex reaction networks[6] that attempt to predict or describe the behavior of feedback loops [7] that control the behavior of cells and organisms. Industrially, the conditions leading to desired products, such as a biocrude from biomass[8], and the conditions that lead to unwanted products, such as particulate matter[9] within a furnace or combustion engine, can be clarified with the detailed chemistry. These are just a few examples of the very practical knowledge that come from detailed chemical mechanisms.

Automatic reaction mechanism generation is a powerful tool to understand complex reactive systems and describe the detailed chemistry. The Reaction Mechanism Generator (RMG) software[10] 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.[11]

Sulfur chemistry is an area that is not well explored by automatic mechanism generation. There are many inherent challenges when modeling sulfur systems including their variable oxidation and valence, the unique reactions in which they participate, and the only limited experimental characterization of the kinetics and thermodynamics of sulfur species, especially radicals. Previous efforts have allowed for the modeling of low valence sulfur species,[12] [13] but many important systems involve highly oxidized, high and changing valence, sulfur species.

Automatic mechanism generation methods require rapid evaluations of the thermochemistry of individual molecules. Accurate quantum chemical calculations are far too time intensive to be practical in this setting, requiring other methods of predicting thermochemistry. An older relatively simple solution is to use a linear model known as Benson group additivity[14]. This method assigns each heavy atom thermochemical values based on its characteristics and the characteristics of the atoms to which it is bonded. A molecule's thermochemistry is then predicted by summing over each heavy atom. Newer, more nuanced machine learning methods promise greater predictive power, albeit with less transparency[15] [16].

This work describes the expansion of the RMG software to higher valence sulfur species, with an emphasis on thermochemistry prediction for high valence sulfur molecules. This focus involves the creation of a sulfur species database, and the implementation of a simple prediction method to estimate

the thermochemistry for an arbitrary molecule. The paper closes with a case study demonstrating the new functionality, examining the partial oxidation of dimethyl sulfide. The validity of the automatically generated model was tested by comparing the model to experimental work that measured the concentration of major species during the hydroxyl radical initiated oxidation of dimethyl sulfide.[17]

2. Methods

2.1. Quantum Chemical Calculations and Dataset Creation

First, 47 sulfur species with experimentally measured enthalpies of formation were used to test the accuracy of the calculation methods.[18] [19] [20] [21] [22] [23] [24] [25] The molecules in this validation set were selected because they both had experimental measurements for enthalpy of formation and were comprised of 10 or fewer heavy atoms. An approach using b3lyp/CBSB7 for the geometry optimization, frequency calculation, and hindered rotor scans along with CBS-QB3 for the energy calculation was selected. The thermochemistry and rate calculations were performed using the rigid-rotor harmonic oscillator (RRHO) approximation with corrections for internal rotors, using the Arkane software in the RMG package[10]. Each rotating dihedral within the molecule was treated as a 1-dimensional independent rotor and stepped in 10 degree increments through the full rotation. An optimization constrained by the stepped dihedral was performed at each of these steps. Additional details on the hindered rotor treatment can be found in the work of Sharma et al[26]. Rate calculations were performed using conventional Transition State Theory (TST) with Eckart tunnelling corrections.[27] Constraints on computational resources required the use of different versions of Gaussian for these calculations. The majority of the calculations used Gaussian03[28], with several exceptions noted in detail in the Supporting Information.[29][30] Bond additivity corrections (BAC) were determined with a least squares fit to the 47 validation molecules for C-S, S-S, S-H, S-O, and S=O bonds. All other BAC corrections came from the work of Paraskevas et al.[31]

The validated procedure was then used to calculate 255 oxygenated sulfur molecules. These 255 molecules were combined with 185 molecules from Class[32] and Vandeputte[8]. This combined list of 440 molecules was used to derive group additivity values for the prediction of the thermochemistry of sulfur containing molecules.

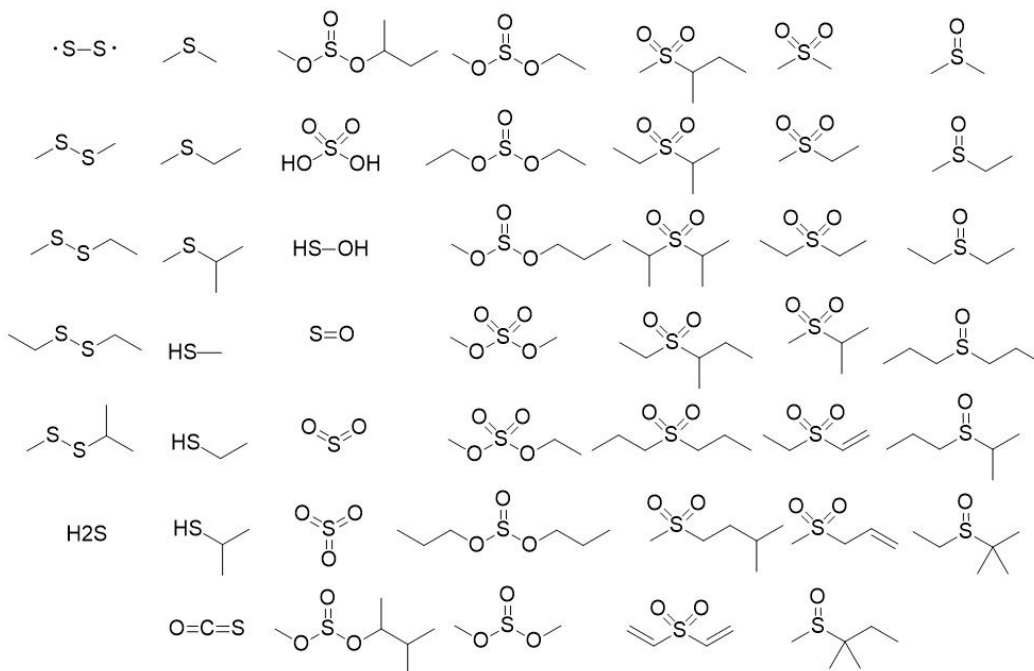


Figure 1: The molecules in the validation set.

2.2. Mechanism Generation

The second section of the work uses the Reaction Mechanism Generator software with the augmented thermochemistry predictions to create a detailed kinetic model. 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. A detailed description of the algorithm can be found in the work of Gao. [10]

The detailed chemical mechanism was created based on the conditions studied by Barnes et al.[17]. Specifically, a concentration of 25 ppm hydrogen peroxide and 15 ppm dimethyl sulfide in a bath of artificial air at 1 bar total pressure and a temperature of 298K was used in model generation. The input file annotated to include the RMG-Py and RMG-database version numbers used in mechanism generation is supplied in the supporting information.

3. Results

3.1. Benchmarking of the Calculation Procedure

Before creating a dataset, we validated our methods for oxygenated sulfur molecules. This was done by comparing calculated enthalpies of formation to experimentally measured enthalpies for 47 molecules. The lack of experimental data precludes similar comparisons to entropies and heat capacities.

First, bond additivity corrections (BACs) for C-S, S-S, S-H, S-O, and S=O bonds were calculated using a least squares fitting from these 47 molecules. These BAC values were combined with those suggested by Paraskevas[31] for molecules containing carbon, hydrogen, and oxygen. The BAC corrections and their effect on the accuracy of the test set is shown in Tables 1 and 2.

Table 1: Bond additivity corrections fit from the 47 molecules in the validation set (all values in $\frac{kcal}{mol}$)

Bond Additivity Corrections (CBS-QB3)				
S-O	S=O	C-S	S-H	S-S
0.07	-1.03	1.08	-0.69	-1.46

Table 2: Deviations between the calculated (CBS-QB3) and experimental enthalpy of formation values with and without the newly calculated sulfur BACs (all values in $\frac{kcal}{mol}$)

Summary Statistics		
	w/out Sulfur BACs	w/Sulfur BACs
RMSD	1.70	1.23
MAD	1.42	1.08
Avg. Deviation	1.09	0.03

Naturally, the newly fit BACs lowered the deviation between calculated and experimental values. However, they also noticeably corrected a persistent overprediction of the enthalpy in oxygenated sulfur compounds by the CBS-QB3 method. A histogram of deviations between the calculations and experiment is shown below in Figure 2. A detailed list of the deviation between each experimental and calculated value is included in the Supporting Information.

This set of 47 molecules excluded 2 potential experimental data sources. Divinyl sulfoxide and methane sulfenic acid each had only a single experimental enthalpy measurement source[33] [34] and the measured value for

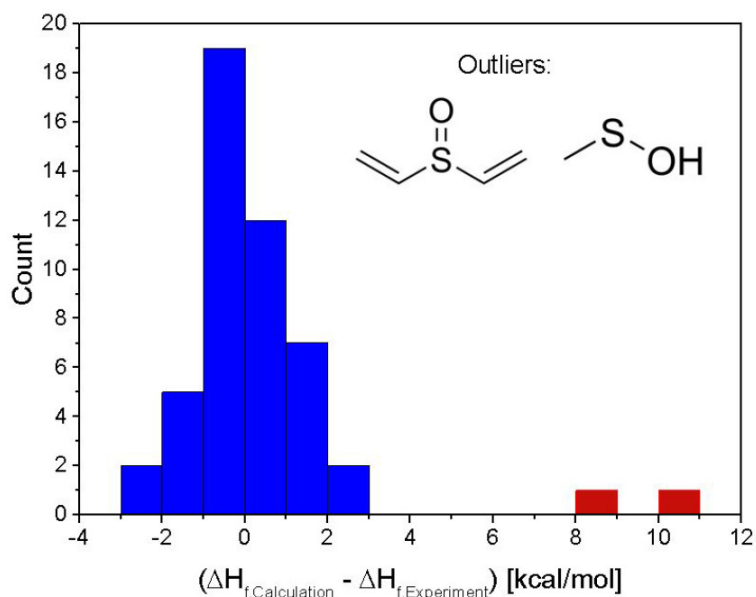


Figure 2: A histogram sorting the deviations between experiment and calculation for 49 sulfur and oxygen containing molecules. The two outliers were excluded when determining the BAC values.

each deviated wildly from our calculated values (8.33 and 10.15 kcal/mol off respectively). This could be due to a weakness of our calculation method or it could be from inaccurate experimental numbers. Either way, these values were excluded from the least squares fit for bond additivity corrections.

3.2. Dataset

Content with the accuracy of the method, we selected 255 primarily oxidized and high valence sulfur molecules to supplement existing sulfur species thermochemistry data. When considering what molecules should be included in this dataset, we balanced representation of typical highly oxygenated sulfur molecule motifs with very unstable, semi-randomly generated, molecules. The emphasis on unstable molecules might seem odd. However, thermochemistry prediction from a dataset is inherently limited by the nature of the molecules in the training data, and both experimental and computational studies often focus on relatively low energy molecules. In contrast, automatic mechanism generation, in combinatorial fashion, generates a wide range of structures, from the stable to the extremely unstable. If the datasets used to predict thermochemistry are disproportionally filled with low energy

molecules, then the predictions for the energy will necessarily skew low. Thus, there is an important, and largely unfilled, gap in knowledge about the thermochemical nature of high energy and high valence sulfur species. For this reason, about 150 molecules that we calculated for this study were randomly generated, usually creating high energy structures. This was done by starting with a structure such as a sulfur atom double bonded to an oxygen atom and iteratively adding atoms in a semi-random manner.

Once a list of molecules was selected, their geometries, frequencies, hindered rotor scans, and CBS-QB3 energies (including BACs) were computed. The thermochemical descriptors (enthalpy, entropy, and heat capacities) were then calculated using the Arkane software as described in the Methods section. We combined these 255 molecules (240 stable, 15 radical) with the low valence sulfur thermochemistries calculated by Class[32] and Vandeputte[12] to create a dataset with 440 molecules (368 stable, 72 radical). Using this combined dataset a group additivity scheme was created and implemented in the Reaction Mechanism Generator software. The thermochemical descriptors of all 440 molecules in the dataset are found in Supporting Information. Additionally, the 255 molecules that were calculated as a part of this work have their geometries, frequencies, and zero-point energies reported.

3.3. Thermochemistry Prediction

After compiling a dataset of sufficient size, we turned to the problem of predicting thermochemistry from this information. In this work we fit the data to a group additivity scheme, not because we believe it is the most accurate prediction method, but rather because it integrates well with the automated mechanism generating software that we will use in the creation of a dimethyl sulfide oxidation mechanism. However, the information provided could and should be integrated into more sophisticated prediction schemes. The 368 stable species were fit by adjusting 200 sulfur containing group additivity values.[35] Non-sulfur containing groups present in the molecules were assigned values according to the RMG-database used in mechanism generation. The 200 group values are included in the Supporting Information along with the anticipated uncertainties for their enthalpy component. Summary and fitting statistics are included in Table 3. The quality of the fit is emphasized in the parity plots comparing the calculated and fit enthalpy and entropy of formation shown in Figure 3.

The 72 radical species were used to generate hydrogen bond increment (HBI) corrections as defined by Lay et al.[36] This information is organized

Table 3: Summary statistics for the GAV fit to the calculated values (units of $\frac{kcal}{mol}$, $\frac{cal}{mol K}$)

	$\Delta H_f(298 K)$	$\Delta S_f(298 K)$	$C_p(300 K)$	$C_p(500 K)$	$C_p(1000 K)$
MAD	0.73	0.99	0.36	0.31	0.22
RMSD	1.18	1.62	0.59	0.49	0.39

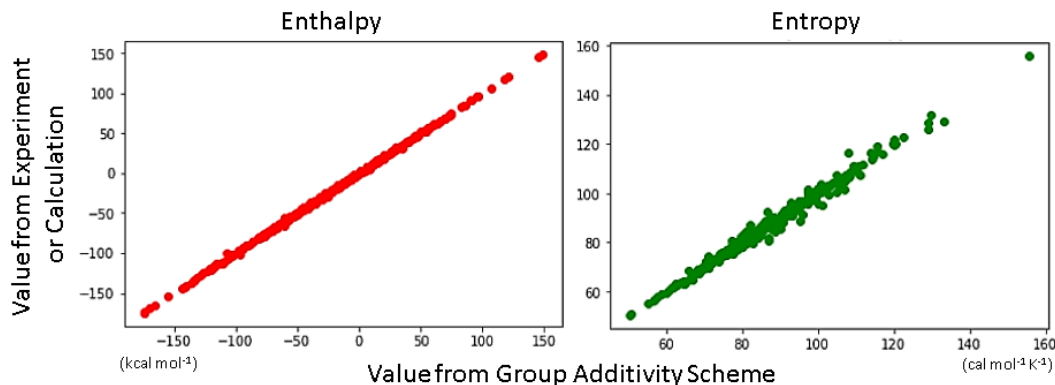


Figure 3: Parity plots comparing the calculated thermochemical value and the linear model prediction

in a tree structure in the version of RMG used in mechanism generation and conveniently accessible through the Molecule Search Tool at rmg.mit.edu. Together the stable species group additivity scheme and hydrogen bond increment corrections allow thermochemistry prediction for a variety of sulfur species.

3.4. Dimethyl Sulfoxide Oxidation

3.4.1. Experiment and Motivation

As a test for our new thermochemistry estimation scheme, we selected the OH initiated oxidation of dimethyl sulfide. This system was chosen because the primary products of the reaction span a wide range of highly oxygenated sulfur structures, from sulfoxides to sulfones to carbonyl sulfide and more. Further, this is an important system for understanding the formation of sulfuric acid in the atmosphere. Thus, this test case itself provides value and insight for pollutant formation. Finally, there are many experimental studies on this system which provide ample experimental validation and comparison for the system. [37] [17] [38] [39] [40] Among these the work by Albu, Barnes et al.[17] will be most rigorously compared, because they provide the largest

amount of quantitative information about a variety of products across a range of temperature conditions. A review of the system by Barnes et al. provides a convenient aggregation of known kinetic and thermodynamic parameters of the system as well as a general reaction scheme with which to compare our automatically generated mechanism.[41]

While dimethyl sulfide oxidation seems an ideal comparison system, it does have challenges. Because the oxidation is at low temperatures small errors in estimates of transition state energies have large effects on the estimates of the rate constants. Further, there is some uncertainty about the efficiency of the hydrogen peroxide photolysis by the lamps used in the experiments. The lamp forces the reaction as it continuously creates hydroxyl radicals from hydrogen peroxide. To model this behavior the concentration of hydroxyl radical was held fixed while solving the concentration profiles. This precludes any validation of the time scale of reaction (dependent on the intensity of the lamps), but still allows product profiles and selectivities to be tested. This also creates uncertainty as the photolyzing lamps could have affected the chemistry of more than just the hydrogen peroxide species. The Supporting Information has detailed information about the kinetic information, from literature or newly calculated, supplied in the mechanism generation process.

3.4.2. Dimethyl Sulfide Reaction Mechanism

The automatically generated mechanism contains 43 species and 122 reactions (included in full with the Supporting Information). A limited set of the major reaction pathways are illustrated below in Figure 4. Consistent with previous studies the model identifies two primary pathways by which the dimethyl sulfide reacts. They differ in importance based on temperature, with low temperature conditions favoring the addition pathway and its production of dimethyl sulfoxide, and the high temperatures favoring hydrogen abstraction leading to sulfur dioxide products.

3.4.3. Experimental Validation

The selectivity of the four major species observed and quantified by Albu, Barnes et al.[17] (dimethyl sulfoxide, dimethyl sulfone, sulfur dioxide, and methyl thiolformate) were compared to the model's predictions in Figure 5. Relatively good agreement is found between the experimental results and the model predictions for 3 of the 4 major species. The remaining sulfur-containing species that were observed but not quantified by Albu, Barnes et

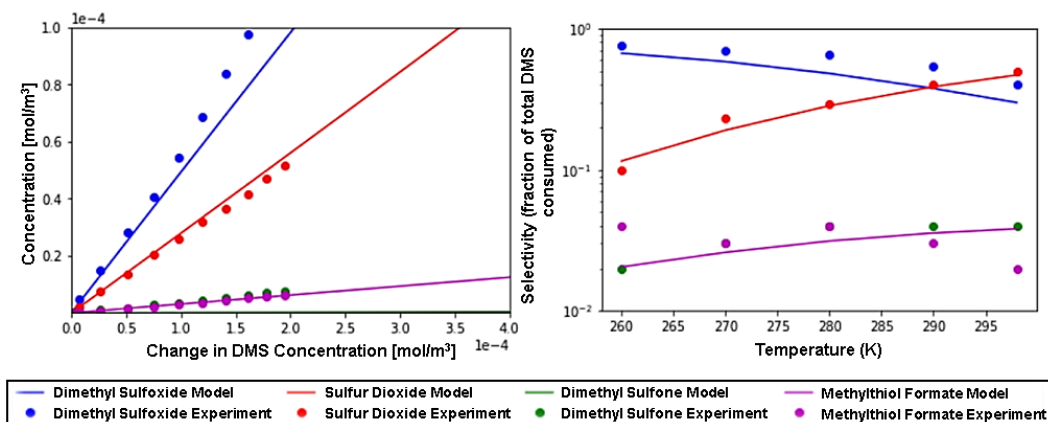


Figure 5: A. Comparison of the experiment and model at 280K and 1 bar of synthetic air over the course of the experiment. B. Comparison of the terminal selectivities of the experiment and model at 260K, 270K, 280K, 290K, and 298K.

6 and the sensitivity analysis in Fig. 7. The transition states and kinetic details for each of the computed reactions along these pathways can be found in the Supporting Information. Due to the low temperature of the reaction system, dimethyl sulfone formation is especially sensitive to barrier heights. Which, if any, of these paths to dimethyl sulfone is the significant pathway remains an ongoing question.

Additionally, the model predicts the formation of significant amounts of thioformaldehyde. This is a product that is not observed in any of the experimental works. [17] [37] [41] The sensitivity analysis (Figure 8) suggests that perhaps the hydrogen abstraction of methylthiyl radicals by O_2 is being significantly over-predicted. Alternatively, the reactivity of the CH_2S species could be underpredicted or the species could have been missed by the experimental analysis technique.

Finally, there are several minor discrepancies between the experiments and the model. For example, some experiments have suggested that sulfur dioxide is produced by both the hydroxyl addition and hydrogen abstraction pathways.[37] This is not reflected in our model, with the overwhelming majority of the sulfur dioxide formed through the hydrogen abstraction pathway. The missing addition pathways are thought to occur through the formation and decomposition of methanesulfinic acid.[41] Experiments performed in the absence of oxygen[17] are also not accurately represented by

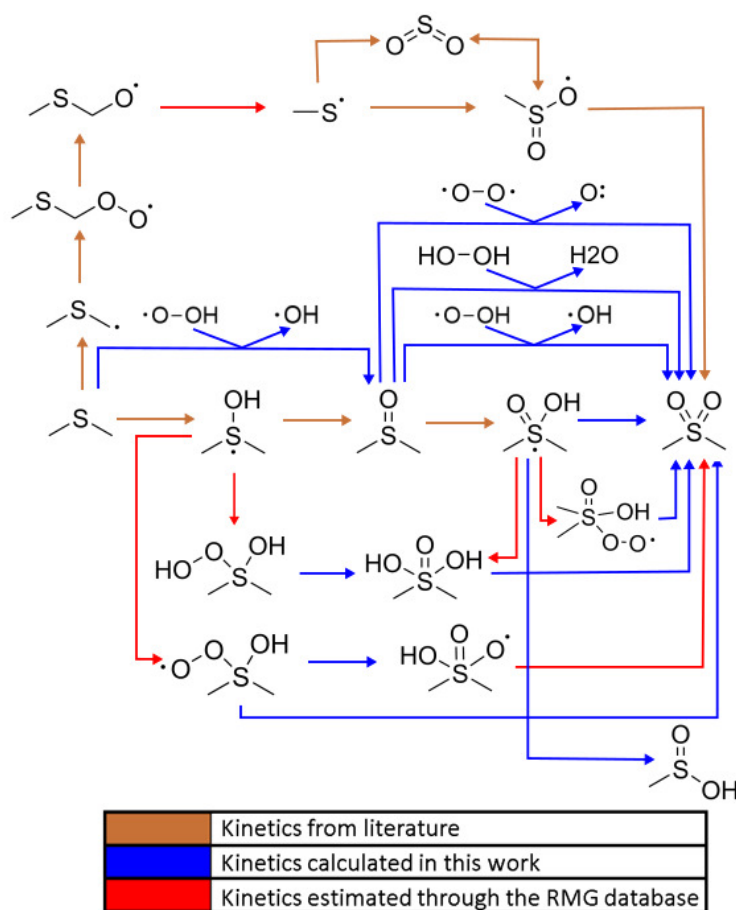


Figure 6: Pathways for dimethyl sulfone formation in the model. None fully explained the dimethyl sulfone formation observed in the experiments.

the model presented here as many of the crucial model oxidation pathways require molecular oxygen.

4.2. Sensitivity Analysis of Major Species

As has been seen with thioformaldehyde, sensitivity analysis provides insight into what kinetic parameters and species thermochemistries have the largest effects on the concentrations of model species. In Figures 9 and 10, sensitivity analysis reveals the most important species and kinetic factors for the highest concentration observable species, dimethyl sulfoxide and sulfur dioxide, respectively. The reactions and species on these lists of most

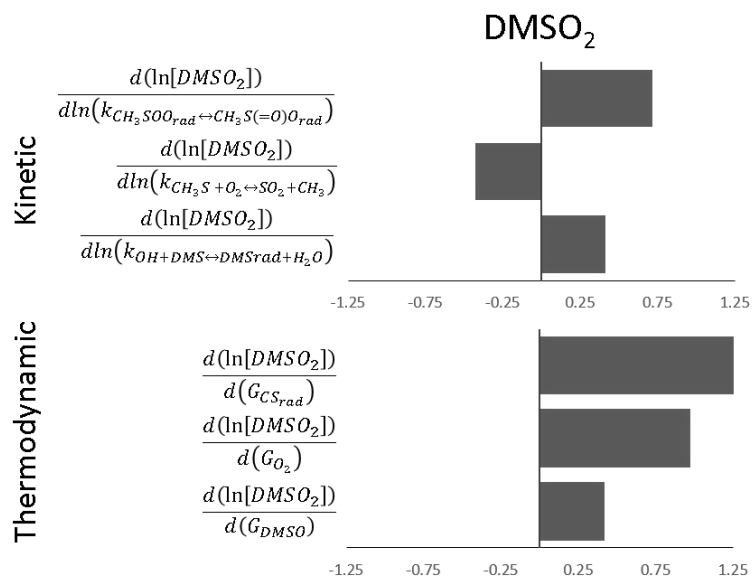


Figure 7: Top three most sensitive kinetic and thermodynamic parameters for dimethyl sulfone formation. Thermodynamic sensitivities are reported in units of $\frac{mol}{kcal}$.

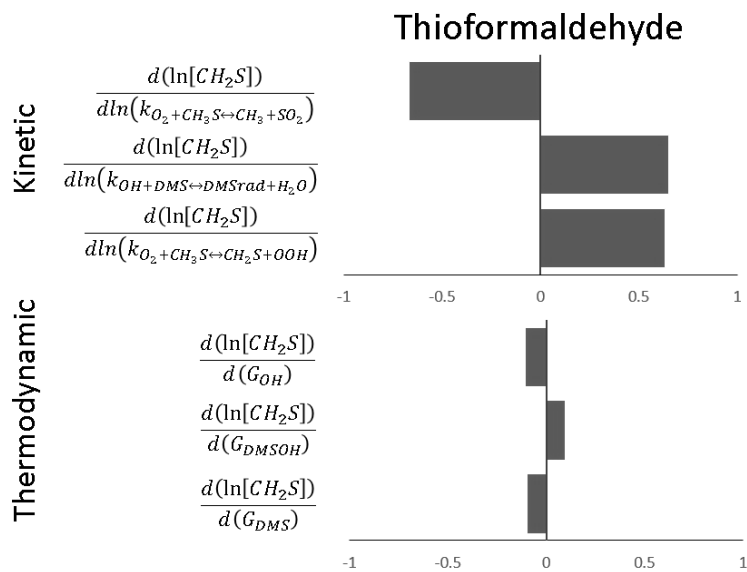


Figure 8: Top three most sensitive kinetic and thermodynamic parameters for thioformaldehyde formation. Thermodynamic sensitivities are reported in units of $\frac{mol}{kcal}$.

sensitive parameters have either experimentally determined or explicitly calculated kinetics and thermochemistry. As such, we believe the uncertainties in their parameters to be relatively small.

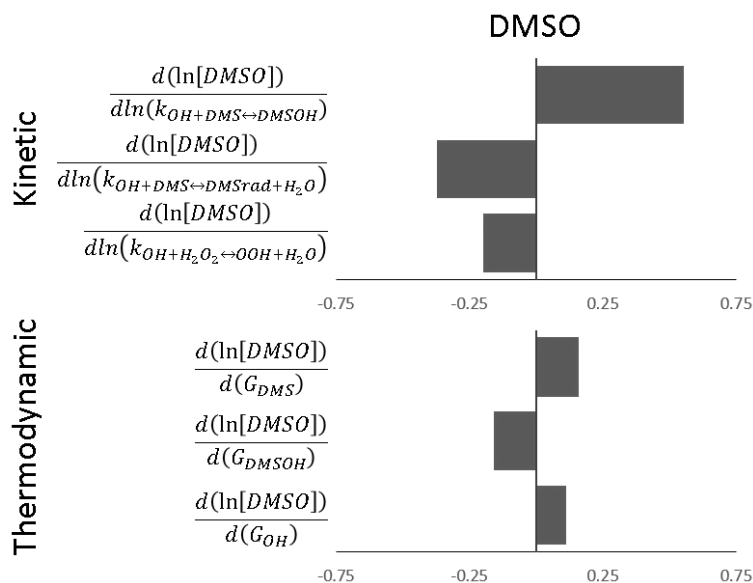


Figure 9: Top three most sensitive kinetic and thermodynamic parameters for dimethyl sulfoxide formation. Thermodynamic sensitivities are reported in units of $\frac{mol}{kcal}$.

5. Conclusion

Methods for estimating thermochemical 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 reasonable kinetic models for systems containing highly oxidized sulfur species. Further, this work illustrates how **automatic mechanism generation** software **could** be further expanded to other systems of interest.

A detailed kinetic model of dimethyl sulfide oxidation was also created and analyzed. While generally validated by experimental observations, a few discrepancies were observed. **These discrepancies** invite the creation of models of even further complexity, **especially exploring the low temperature generation of dimethyl sulfone.**

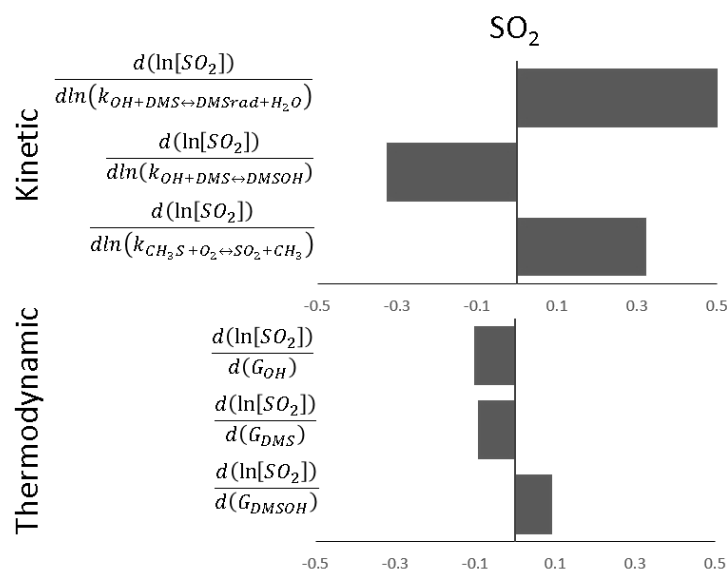


Figure 10: Top three most sensitive kinetic and thermodynamic parameters for sulfur dioxide formation. Thermodynamic sensitivities are reported in units of $\frac{mol}{kcal}$.

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Keywords: Automatic Mechanism Generation, Computational Chemistry, Dimethyl Sulfide, Kinetics, **Thermochemistry**

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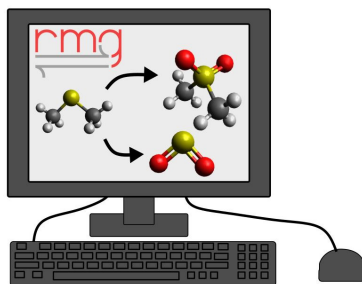
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Graphical Abstract

Here we present a thermochemistry prediction scheme for oxygenated sulfur molecules and the application of this scheme in the automatic creation of a reaction mechanism describing the oxidation of dimethyl sulfide.

Keywords: Automatic Mechanism Generation, Computational Chemistry, Dimethyl Sulfide, Kinetics, Thermochemistry