

**P1.2 THEORETICAL CORROBORATION OF RECENT EXPERIMENTAL RESULTS
IN THE OH RADICAL REACTION WITH DIMETHYLSULFIDE**

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1. INTRODUCTION

The atmospheric fate of sulfur is determined by the gas phase reactions of sulfur containing compounds with constituent gases of the atmosphere. In particular, the atmospheric fate of dimethylsulfide (DMS, CH₃-S-CH₃) is of interest due to its role as an important contributor to the global sulfur concentration from biological sources. Interactions with hydroxyl radical (OH) drives the primary pathway for the degradation of DMS in the gas phase and will serve as our focus.

Experimental measurements of the kinetics and products of the reaction of OH radical with DMS have been made for many years. Theoretical studies of these reactions have also been conducted over the last decade or so, with a division of opinion on the likelihood of the formation of the adduct. Recent experiments support a two-channel mechanism, summarized in Figure 1, that involves abstraction of H (DMS_1) and adduct formation (DMS_2). In the troposphere adduct formation leads to a reaction with O₂ and the formation of dimethylsulfoxide (DMSO). Experimental studies of the branching ratio (k_{addition} / k_{abstraction}) have yet to form a consensus and yield a wide range of values, hence further theoretical study can aid in the interpretation of experimental results.

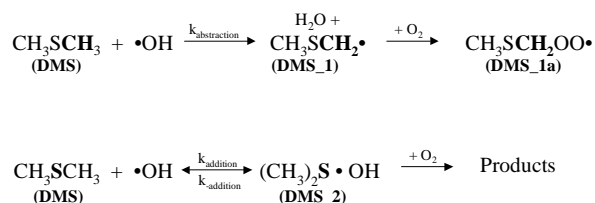


Figure 1. Schematic of initial step in DMS oxidation.

In determining the atmospheric fate of DMS, the importance of understanding whether adduct

formation occurs and the branching ratio is seen from the conceptual framework for mechanism development shown in Figure 2. Here, we summarize the three interrelated aspects of the methodology used to develop such chemical reaction mechanisms. These include mechanism formulation, rate constant determination (e.g., experimental chamber studies, theoretical computational chemistry), and sensitivity analysis. Mechanism formulation entails predicting all conceivable transformation products and pathways (Burns, 2001). Fundamental principles of atmospheric chemistry are used to propose possible reaction pathways for the degradation of DMS including abstraction and adduct formation as the first step in the pathway.

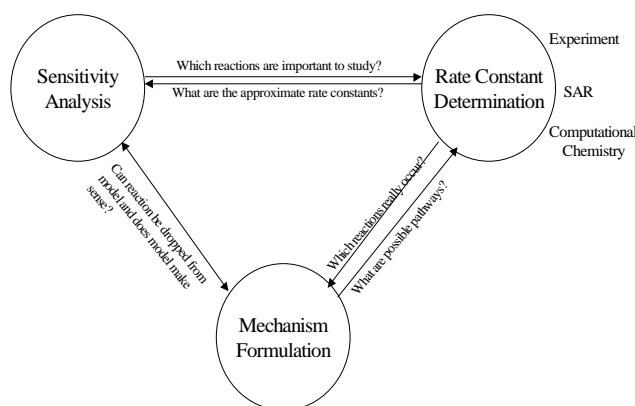


Figure 2. Interrelated aspects of mechanism development.

Experiments in the past decade have focused on the role of adduct formation in the reaction of OH with DMS in the atmosphere. Observations in the laboratory and the field have been made (Hynes 2001; Ravishankara, 1995). The former group finds that the adduct forms with a binding energy of 13±3 kcal/mol while the latter group finds the binding energy to be 10.7±2.5 kcal/mol. Work prior to the past decade is well summarized (Nielsen, 1989) and points out that as of 1989, 14 investigations of the OH + DMS reaction had been published, most of which focused on hydrogen abstraction.

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Theoretical investigations in the past decade have also focused on adduct formation, however, they have not been as univocal as the experimental data. Standard computational chemistry techniques, found the adduct to be bound by 9.3 or 8.7 kcal/mol dependent on the style and level of calculation, in good agreement with the experimental results cited above (McKee, 1993). The S-O bond length was found to be 2.047 Angstroms for the adduct. He also found an activation barrier for abstraction of 1.8 kcal/mol, a result somewhat greater than the range of the experimental activation barriers, generally found to be within 0.3 kcal/mol of zero. Turecek (1994), who also used standard computational chemistry techniques, though they were subtly different from McKee, found that the adduct was not stable and ruled out finding the adduct having any role in the atmospheric fate of DMS. However, Turecek found an activation barrier for the abstraction reaction that was about 1 kcal/mol, closer to the experimental results than McKee.

More recently, density functional theory and a variant of the G2 extrapolation procedure were used to study the adduct (Wang, 2001). The adduct was found to be stable with an S-O bond length of 2.326 Angstroms and a binding energy of about 7.4 kcal/mol. The abstraction pathway was not examined.

In light of the variety of interpretations of experimental and theoretical results, the present work focuses on the use of computational chemistry and a novel dynamics approach (Runge, 2001) to predict reaction rate constants. In this study, we illustrate how state-of-the-art theoretical computational chemistry techniques can be used to map out the energetics of a proposed reaction mechanism. Calculation of the energetics involves determination of the activation energies of the abstraction reaction and the binding energies of the adduct formation. Subsequent calculation of the rate constant for the abstraction reaction (k_{OH}) uses the previously determined energetics, as well as information about the reaction path, to drive the dynamics calculation. A similar theoretical analysis was described for dimethyl ether (Burns, 2002).

2. METHODS

2.1 Computational Chemistry - Energetics

Calculations were carried out using either the Gaussian 98 (G98) (Frisch, 1998) suite of

quantum chemistry programs running on a Silicon Graphics Inc. Origin 2000 or the ACES II program (Bartlett, 1998) running on a Cray SV-1. The stationary points (minima and 1st order saddle points) along the minimum energy path (MEP) of the DMS compounds were fully optimized and characterized at the CCSD level using the 6-311++G** (MED) basis set. Restricted Hartree Fock reference functions (for the closed-shell systems) and Unrestricted Hartree Fock reference functions (for the open-shell systems) were used. The core orbitals were frozen for both the CCSD and MBPT(2) calculations. In addition, optimization was also performed using the 6-311++G(2dp,3df) (LRG) basis set.

G2MP2 (Curtiss, 1993) is a method, available in G98, for computing accurate total energies of molecular systems. We have found that for the G2MP2 method to yield accurate E_A 's for these systems, the protocol has to be modified. That is, the reference structure must be obtained at a higher level of chemical theory than that specified in the literature (Curtiss, 1993). We use CCSD/MED as opposed to the MP2/6-31G* called for by the G2MP2 method. The Zero Point Energy (ZPE) correction is also computed at the CCSD/MED level, or, to decrease the computational requirements, extrapolated to the CCSD/MED level from CCSD/MED//MP2/MED results. We call this the CCG2MP2 method.

Other necessary information required for a SCFFAF dynamics calculation (other than the E_A) includes a description of the MEP connecting reactants to products and the rotational moments of inertia for the reactants and the TS structure (Runge, 2001).

The SCFFAF method requires a reasonably good description of the barrier in the neighborhood of the saddle point. That is, the curvature of the repulsive mode for 0.4 Å to either side of the barrier, as well as the curvatures of any "soft-modes" that can channel off energy otherwise available to drive the reaction, needs to be described adequately. This information is generated using a NDDO (Neglect of Differential Diatomic Overlap) semi-empirical quantum chemical Hamiltonian parameterized specifically for the particular chemical reaction of interest. (Truhlar, 1995) In this work we modified the semi-empirical Hamiltonian such that, to the extent possible, it reproduces a CCSD/MED level result for approximately 100 points spaced along the 0.8

Å segment of the MEP described above.

The rotational moments of inertia are computed for the CCSD/MED structures and are used in the pre-exponential partition functions of the SCFFAF dynamics model (Runge, 2001).

2.2 Computational Chemistry - Dynamics

Thermal rate constants typically are described by the Arrhenius expression as shown in Equation 1

$$k(T) = A \exp\left(-\frac{E_A}{RT}\right) \quad \text{Eq 1}$$

where E_A is the activation energy and A is the preexponential factor which is also a function of temperature. This expression illustrates the importance of an accurate E_A to getting good rate constants as it appears in the exponent of the exponential.

The rate constants are calculated using the Semi-classical Flux-Flux Autocorrelation Function (SCFFAF) approach and are described elsewhere (Runge, 2001).

3. SUMMARY OF RESULTS

Results are presented for the degradation of DMS ($\text{CH}_3\text{-S-CH}_3$). Rate constants determined via SCFFAF for abstraction are compared to published experimental data. In addition, comparisons of the energetics and structural properties of the adduct are also presented.

3.1 Abstraction Reaction

Figure 3 shows abstraction rate constants for hydrogen abstraction from DMS by OH radical obtained from a semi-classical flux-flux autocorrelation function (SCFFAF) calculation and compared to experimental results and the often used structure activity relation (SAR) (Atkinson, 1995). The abstraction barrier was obtained from a CCG2MP2 calculation, a variant of the G2 procedure that is distinct from the technique employed by Wang and Zhang (2001). The activation barrier obtained is 0.45 kcal/mol in better agreement with experimental activation barriers than previous calculated results. Interestingly, the published experimental measurements for the abstraction reaction have a decreasing trend and the most recent data are in agreement with the theoretical k_{abs} values we have determined.

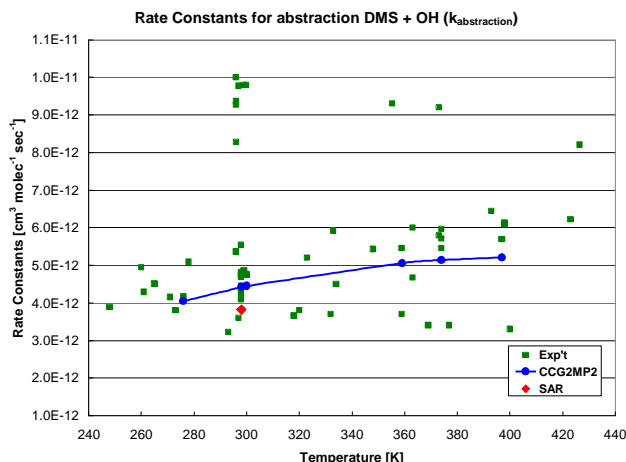


Figure 3. Comparison of $k_{\text{abstraction}}$ by SCFFAF, Experiment, and SAR as $f(\text{Temp})$ for DMS.

3.2 Adduct Formation

Table 1 shows energetic and geometric parameters that characterize the adduct formation. MBPT[2] and CCSD energetics calculations are consistent with data recently published by Hynes (2001) and Ravishankara (1995) suggesting a small energy well associated with reversible adduct formation between DMS and OH. This leads to an equilibrium process that favors adduct formation and the addition reaction channel under colder conditions.

Figure 4 is a representative illustration of the small energy well associated with formation of the DMS-OH adduct. These data were calculated at the MBPT[2]/MED level of theory and determined by fixing the S—O distance and allowing the rest of the system relax to its lowest energy. As summarized in Table 1 and Figure 4, there is a 1.31 kcal/mol stabilization at an S—O bond length of 2.11 Å. The structure of the adduct is shown.

Increasing the size of the basis set from MED to LRG at the MBPT[2] level, leads to a decrease in the predicted S—O bond length from 2.11 to 2.02 Å. There is a corresponding increase in the stabilization of the adduct relative to the reactants from -1.31 to -7.67 kcal/mol. These results are in agreement with McKee's observation that increasing the basis set size tends to stabilize the adduct. In particular, the role of diffuse functions in the stabilization of compounds with relatively long bonds is essential. Further, we see that the addition of functions with higher angular momenta,

d function on hydrogen and f functions on non-hydrogenic atoms, further stabilizes the adduct by more than 6 kcal/mol and reduces the bond length substantially.

Table 1. Comparison of predicted energies and structures for DMS-OH Adduct

Level	Basis Set	S-OH length	Relative Energy ($E_{\text{adduct}} - (E_{\text{DMS}} + E_{\text{OH}})$)
		[Å]	[kcal/mol]
MBPT[2]	MED	2.11	-1.31
	LRG	2.02	-7.67
CCSD	MED	2.40	In progress
	LRG	TBD	In progress
^a B3LYP	cc-pVTZ	2.326	-7.4
^b QCISD(T)	6-31+G(2d,p)	2.047	-8.7 to -9.3
Exp't	Hynes, 2001		-13±3
	Ravashankara, 1995		-10.7±2.5

a. Wang, 2001.

b. McKee, 1993.

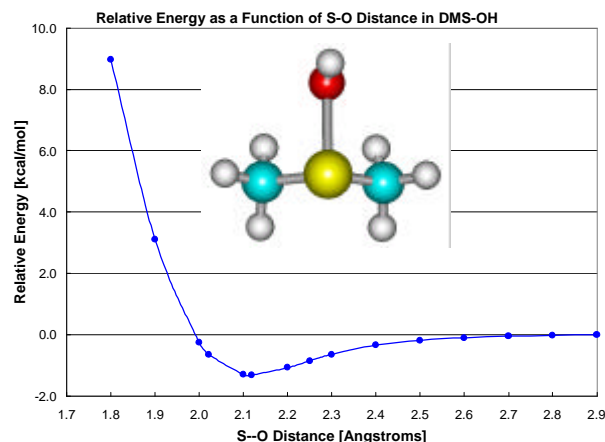


Figure 4. MBPT[2]/MED Structure and Relative Energy (kcal/mol) of DMS-OH adduct as a function of S—O distance (Å).

4. SUMMARY

This study indicates the capacity of current computational method to elucidate the most difficult chemical processes involved in the

atmospheric fate of sulfur. It also indicates the need to occasionally revisit difficult cases when new advances are made in the theory of electronic structure and dynamics. An overview of a theoretical approach for computing gas-phase reaction rate constants was described and illustrated for DMS. The energetics and rate constants determined from CCG2MP2 calculation (i.e., CCSD/MED structures used in the described CCG2MP2 / NDDO-SRP / SCFFAF methods) are consistent with experiment ($E_{A,\text{abstraction}} = 0.45$ kcal/mol) are able to predict accurately $k_{\text{abstraction}}$ with the proper temperature dependence.

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