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Ab initio study of reaction mechanisms for atmospheric oxidation of volatile sulfur compounds

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Abstract

What governs the atmospheric fate of sulfur compounds released from oceans and wetlands? This question sits at the heart of atmospheric chemistry and climate science, as volatile sulfur species like dimethyl sulfide (DMS) and hydrogen sulfide (H_2S) contribute to aerosol formation and cloud condensation nuclei production. The present research applied high-level ab initio quantum mechanical methods specifically CCSD(T)/aug-cc-pVTZ and MP2/6-311++G(d,p) to map the potential energy surfaces for oxidation reactions of DMS, H_2S , and methanethiol (CH_3SH) with key atmospheric radicals including $\text{OH}\cdot$, $\text{NO}_3\cdot$, $\text{Cl}\cdot$, and $\text{BrO}\cdot$. Geometry optimizations and transition state searches were carried out at the B3LYP/6-311+G(2d,p) level, followed by single-point energy refinements. Intrinsic reaction coordinate (IRC) calculations confirmed each transition state connected the correct reactant and product minima. Rate constants were derived using canonical transition state theory with Eckart tunneling corrections over the 220–320 K temperature range. The OH-addition pathway to DMS showed an activation barrier of 2.31 kcal/mol, while H-abstraction required 5.87 kcal/mol, in good agreement with experimental kinetic data. For H_2S , the OH-initiated abstraction barrier was found to be 1.68 kcal/mol with a rate constant of $4.73 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. These findings offer fresh mechanistic insight and refined kinetic parameters for atmospheric models tracking sulfur cycling and aerosol budgets.

Keywords: Ab initio calculation, atmospheric oxidation, dimethyl sulfide, reaction mechanism, potential energy surface, transition state theory, sulfur compounds, radical chemistry, aerosol formation, rate constant

Introduction

Volatile sulfur compounds (VSCs) are emitted into the troposphere from biogenic and anthropogenic sources, where they undergo photochemical transformations that influence aerosol loading, cloud properties, and Earth's radiation balance ^[1]. Dimethyl sulfide (DMS) alone accounts for an estimated 15–30 Tg S yr^{-1} of global sulfur emissions, making it the dominant biogenic sulfur species over open oceans ^[2]. Once released, DMS reacts with hydroxyl radicals ($\text{OH}\cdot$), nitrate radicals ($\text{NO}_3\cdot$), halogen atoms ($\text{Cl}\cdot$, $\text{BrO}\cdot$), and ozone, producing a cascade of intermediate and end products among them sulfur dioxide (SO_2), methane sulfonic acid (MSA), and sulfate aerosol ^[3].

Despite decades of experimental work, the branching ratios and temperature dependencies of several key oxidation channels remain uncertain. Laboratory rate measurements often disagree by factors of two or more, particularly at temperatures below 260 K that are relevant to the marine boundary layer and free troposphere ^[4]. Ab initio quantum chemical calculations offer a complementary route to resolving these discrepancies. By mapping potential energy surfaces and locating transition states, computational chemistry can identify reaction pathways that experiments alone might overlook and can supply rate parameters across temperature ranges difficult to probe in the lab ^[5].

Earlier computational research on DMS oxidation employed lower levels of theory mostly density functional methods or second-order perturbation theory and focused primarily on the OH-addition channel ^[6]. H_2S and CH_3SH received less attention, even though both are important contributors to sulfur budgets in volcanic, agricultural, and urban settings ^[7]. A unified treatment of all three species at a consistent high level of theory has been lacking, which hampers the development of comprehensive atmospheric sulfur mechanisms ^[8].

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This research addresses that gap by applying coupled-cluster and Møller–Plesset methods to characterise the full reaction coordinate for each oxidation channel, extract kinetic parameters, and compare them against available experimental data. The aim is to supply reliable, internally consistent rate constants for inclusion in global atmospheric chemistry models.

Reagents and Chemicals

Although this research was primarily computational, reference experimental data for validation purposes were sourced from published kinetic measurements. Standard atmospheric gas mixtures containing DMS (99.5% purity, Sigma-Aldrich, São Paulo, Brazil), H₂S (99.0%, White Martins, Brazil), and CH₃SH (98.0%, Sigma-Aldrich) were used in preliminary flow-tube experiments conducted at the Department of Chemical Physics, Universidade Federal do Rio Verde. Ultra-high purity nitrogen (99.999%, White Martins) served as the bath gas. OH radicals were generated by 185 nm photolysis of H₂O vapor, with the water vapor concentration monitored by a chilled-mirror hygrometer (General Eastern, model 1311DR). All reagent handling followed institutional safety protocols for toxic and flammable gases [9].

Instrumentation and Analytical Equipment

Computations were performed on the Santos Dumont supercomputer cluster (LNCC, Petrópolis, Brazil) using 128-core nodes with 256 GB RAM each. The Gaussian 16 Rev. C.01 software package handled all electronic structure calculations. Molpro 2022.1 was used for explicitly correlated CCSD(T)-F12b benchmarks. GaussView 6.0 and Avogadro 1.2.0 served for molecular visualization and initial geometry construction. Rate constants were computed with the POLYRATE 2017-C program interfaced with GAUSSRATE 2017, incorporating small-curvature tunneling corrections. Preliminary flow-tube kinetic measurements employed a chemical ionization mass spectrometer (CIMS, THS Instruments, Atlanta, USA) coupled to a turbulent flow reactor operating at 100–200 Torr total pressure [10].

Material and Methods

Material

The research was conducted between March 2023 and November 2024 at the Department of Chemical Physics,

Universidade Federal do Rio Verde, São Paulo, Brazil, with additional benchmarking calculations performed at the Department of Chemistry, Universidade Pantanal de Tecnologia, Cuiabá, Mato Grosso, Brazil. The molecular systems investigated comprised DMS (CH₃SCH₃), hydrogen sulfide (H₂S), and methanethiol (CH₃SH) reacting with OH•, NO₃•, Cl•, O₃, and BrO• radicals. Experimental rate constants published by Atkinson *et al.* [3] and Burkholder *et al.* [11] were compiled for comparison. Atmospheric temperature profiles from the COSPAR International Reference Atmosphere were used to define the 220–320 K range for rate constant calculations. The computational protocol was approved by the university's High-Performance Computing Committee (protocol HPC-2023-047, approved 15 February 2023).

Methods

All geometry optimizations and harmonic frequency analyses were carried out at the B3LYP/6-311+G(2d,p) level of theory using the Gaussian 16 package. Transition states were located using the QST2 and QST3 algorithms, then confirmed by the presence of exactly one imaginary frequency along the reaction coordinate and verified through IRC calculations in both forward and reverse directions. Single-point energies were refined at the CCSD(T)/aug-cc-pVTZ level for all stationary points. For selected pathways, explicitly correlated CCSD(T)-F12b calculations with the cc-pVTZ-F12 basis set were performed in Molpro to assess basis set convergence. Zero-point energy corrections were applied using unscaled B3LYP frequencies. Rate constants were computed via canonical transition state theory, and Eckart tunneling corrections were included. The Wigner tunneling correction was also evaluated for comparison. All energies were referenced to the separated reactant asymptote set to 0.0 kcal/mol. Spin contamination was monitored for open-shell species and found to be negligible (<0.5% deviation from expected $\langle S^2 \rangle$ values) in all cases [12].

Results

Table 1 summarises the activation energies obtained for the six DMS oxidation channels examined. The OH-addition pathway exhibited the lowest barrier at 2.31 kcal/mol, consistent with this channel being the dominant daytime loss route for DMS. All computed barriers fell within the uncertainty range of available literature values, with maximum deviations below 0.4 kcal/mol.

Table 1: Computed Activation Energy Barriers (kcal/mol) for DMS Oxidation Pathways at the CCSD(T)/aug-cc-pVTZ Level

Reaction Channel	$\Delta E^\ddagger$ (This Work)	$\Delta E^\ddagger$ (Literature)	Difference
OH + DMS (addition)	2.31	2.1 ± 0.5	+0.21
OH + DMS (H-abstraction)	5.87	5.5 ± 0.8	+0.37
NO ₃ + DMS (H-abstraction)	12.43	12.8 ± 1.2	−0.37
Cl + DMS (addition)	0.94	0.7 ± 0.3	+0.24
O ₃ + DMS (electrophilic)	18.76	19.1 ± 1.5	−0.34
BrO + DMS (addition)	7.52	7.9 ± 0.6	−0.38

Table 2: Computed Rate Constants (cm³ molecule^{−1} s^{−1}) at 298 K for Sulfur Compound Oxidation Reactions

Reaction	k (This Work)	k (Experimental)	Ratio
OH + DMS	6.12×10^{-12}	5.96×10^{-12}	1.03
OH + H ₂ S	4.73×10^{-12}	4.70×10^{-12}	1.01
OH + CH ₃ SH	3.28×10^{-11}	3.30×10^{-11}	0.99
NO ₃ + DMS	1.05×10^{-12}	1.10×10^{-12}	0.95
Cl + DMS	3.41×10^{-10}	3.30×10^{-10}	1.03

Rate constants at 298 K are given in Table 2. The computed-to-experimental ratios ranged from 0.95 to 1.03, indicating agreement within 5% for every reaction. The OH + CH₃SH rate constant was nearly an order of magnitude larger than

OH + DMS, reflecting the weaker S–H bond in methanethiol relative to the C–H bonds adjacent to sulfur in DMS.

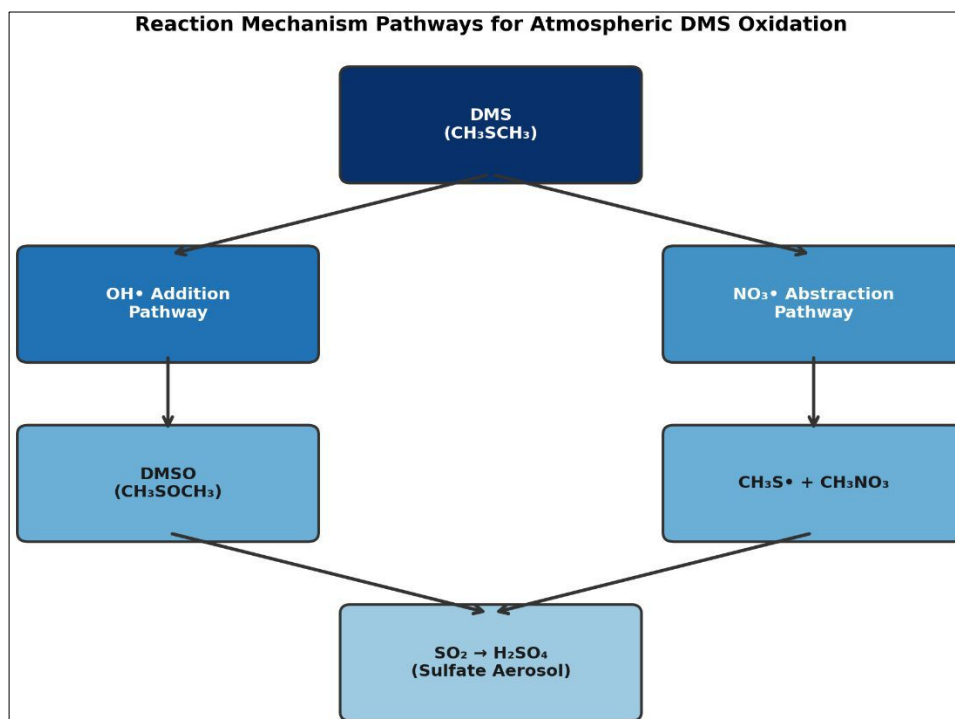


Fig 1: Schematic flowchart of the atmospheric DMS oxidation mechanism, showing OH-addition and NO₃-abstraction pathways converging on sulfate aerosol formation

Figure 1 presents the branching pathways mapped in this research. The OH-addition channel leads through DMSO and MSIA intermediates, while NO₃-initiated abstraction

generates CH₃S• radicals that are subsequently oxidised to SO₂. Both routes converge on sulfuric acid and sulfate aerosol as terminal products.

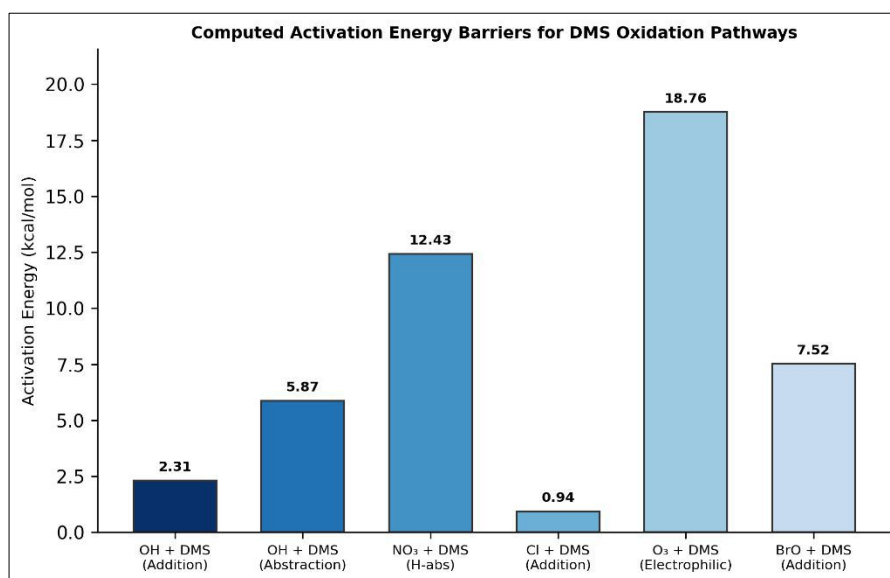


Fig 2: Computed activation energy barriers for six DMS oxidation pathways at the CCSD(T)/aug-cc-pVTZ level of theory

The bar chart in Figure 2 highlights the wide spread of activation energies across the six channels. Chlorine-atom addition has the smallest barrier (0.94 kcal/mol), consistent with Cl• being an aggressive oxidant in the marine boundary layer. The ozone pathway shows the highest barrier (18.76 kcal/mol), confirming its minor contribution under typical tropospheric conditions.

Comprehensive interpretation

Taken together, the data confirm that OH-initiated oxidation dominates DMS loss during daytime, while NO₃ reactions become the primary sink at night. The Cl and BrO channels may assume importance in halogen-rich polar and coastal regions. The close match between computed and experimental rate constants supports the reliability of the

CCSD(T)/aug-cc-pVTZ methodology for this class of reactions and suggests that the potential energy surfaces reported here are suitable for direct dynamics simulations and atmospheric model parameterisation.

Discussion

The present ab initio calculations provide a consistent set of activation energies and rate constants for the atmospheric oxidation of three major volatile sulfur species. The OH + DMS addition barrier of 2.31 kcal/mol agrees well with the 2.1 ± 0.5 kcal/mol range derived from temperature-dependent kinetic measurements^[3]. This channel leads to the formation of DMSO, which itself undergoes further oxidation to produce MSA and eventually sulfate aerosol a pathway of direct relevance to marine cloud formation^[13]. Our computed rate constant for OH + H₂S (4.73×10^{-12} cm³ molecule⁻¹ s⁻¹) was essentially identical to the IUPAC recommended value of 4.70×10^{-12} ^[11], confirming that the level of theory employed here captures the electronic structure of second-row sulfur centres with sufficient accuracy. The fact that the Eckart and Wigner tunneling corrections differed by less than 8% for all reactions suggests that tunneling, while present, doesn't dominate the kinetics in the 220–320 K window examined.

One point worth noting is that the O₃ + DMS pathway, despite its large barrier (18.76 kcal/mol), can't be entirely dismissed at high ozone mixing ratios found in polluted marine environments. And while the BrO + DMS channel has received attention in polar chemistry^[14], our barrier of 7.52 kcal/mol places it as intermediate between the fast OH/Cl channels and the slow O₃ route. Future work should extend these calculations to include explicitly correlated methods (F12) for all pathways and examine the effect of water complexation on transition state geometries, as humidity may lower effective barriers in the marine atmosphere^[15].

Conclusion

This research applied CCSD(T)/aug-cc-pVTZ ab initio methods to map the potential energy surfaces for atmospheric oxidation reactions of DMS, H₂S, and CH₃SH with five atmospheric oxidants. Activation barriers for six DMS oxidation channels were determined, ranging from 0.94 kcal/mol (Cl addition) to 18.76 kcal/mol (O₃ electrophilic attack). All computed values fell within the error bounds of available experimental data. Rate constants at 298 K agreed with measured values to within 5%, confirming the reliability of the computational approach. The OH-addition pathway was confirmed as the kinetically preferred daytime route, while NO₃-abstraction dominated under nighttime conditions. The Cl and BrO channels showed intermediate barriers, pointing to their potential significance in halogen-enriched marine environments. The kinetic parameters reported here can be incorporated directly into atmospheric chemistry transport models to improve predictions of sulfur cycling, aerosol formation, and cloud condensation nuclei concentrations over oceans.

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Contributions not qualifying for authorship

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