

Probing the dynamics and bottleneck of the key atmospheric SO₂ oxidation reaction by the hydroxyl radical

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 SO_2 (Sulfur dioxide) is the major precursor to the production of sulfuric acid (H₂SO₄), contributing to acid rain and atmospheric aerosols. Sulfuric acid formed from SO₂ generates light-reflecting sulfate aerosol particles in the atmosphere. This property has prompted recent geoengineering proposals to inject sulfuric acid or its precursors into the Earth's atmosphere to increase the planetary albedo to counteract global warming. SO₂ oxidation in the atmosphere by the hydroxyl radical HO to form HOSO₂ is a key rate-limiting step in the mechanism for forming acid rain. However, the dynamics of the HO + $SO_2 \rightarrow HOSO_2$ reaction and its slow rate in the atmosphere are poorly understood to date. Herein, we use photoelectron spectroscopy of cryogenically cooled HOSO₂⁻ anion to access the neutral HOSO₂ radical near the transition state of the HO + SO₂ reaction. Spectroscopic and dynamic calculations are conducted on the first ab initio-based full-dimensional potential energy surface to interpret the photoelectron spectra of $HOSO_2^-$ and to probe the dynamics of the HO + SO_2^- reaction. In addition to the finding of a unique pre-reaction complex $(HO \cdots SO_2)$ directly connected to the transition state, dynamic calculations reveal that the accessible phase space for the HO + SO₂ \rightarrow HOSO₂ reaction is extremely narrow, forming a key reaction bottleneck and slowing the reaction rate in the atmosphere, despite the low reaction barrier. This study underlines the importance of understanding the full multidimensional potential energy surface to elucidate the dynamics of complex bimolecular reactions involving polyatomic reactants.

photoelectron | potential energy surface | polyatomic reactants | bimolecular reaction | spectroscopy

Sulfur dioxide (SO₂) is a major atmospheric pollutant. The main sources of SO₂ emissions are the burning of fossil fuels and the smelting of sulfur-rich ores. SO₂ is accepted as a major precursor to the production of sulfuric acid (H_2SO_4), contributing to acid rain (1–3) and atmospheric aerosols (4–7). Consequently, atmospheric SO₂ significantly impacts the environment, human health, and climate change. Furthermore, atmospheric sulfuric acid formed from SO₂ generates light-reflecting sulfate aerosol particles in the atmosphere. This property has prompted recent geoengineering proposals to inject sulfuric acid or its precursors into the Earth's atmosphere to increase the planetary albedo to counteract global warming (8–11).

The atmospheric conversion of SO₂ to sulfuric acid starts via SO₂ oxidation by the hydroxyl radical HO (12–16) or the Criegee intermediate in the presence of biogenic volatile organic compounds (17). The atmospheric formation of sulfuric acid via SO₂ oxidation by the ubiquitous hydroxyl radical occurs through three steps (12–16, 18, 19). The first step (R1) involves gas-phase oxidation of SO₂ by HO to form the HOSO₂ radical intermediate, which is further oxidized by O₂ to form SO₃ and HO₂ (R2) (12, 17). The final step (R3) corresponds to the hydration of SO₃ to produce sulfuric acid, which is one of the major components of acid rain:

$$HO + SO_2 \rightarrow HOSO_2,$$
 [R1]

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3,$$
 [R2]

$$SO_3 + nH_2O \rightarrow H_2SO_4 + (n-1)H_2O.$$
 [**R3**]

The first step to form the key $HOSO_2$ radical intermediate (R1) has been extensively studied both experimentally (13, 20–25) and theoretically (26–34). The existence of the $HOSO_2$ radical was first detected by mass spectrometry (35). The radical was trapped in lowtemperature matrices and studied by infrared spectroscopy (15, 16, 36). R1 and R3 are

Significance

The oxidation of SO₂ (Sulfur dioxide) in the atmosphere by the hydroxyl radical to form the HOSO₂ radical intermediate is the first and a rate-limiting step to the formation of acid rain and sulfate aerosols. Despite extensive kinetic studies, the underlying dynamics of this key reaction step is poorly understood. The current study provides a dynamic insight into the HO + SO₂ \rightarrow HOSO₂ reaction using a combination of a state-of-the-art experimental technique and theoretical calculations. The implications of this work extend to atmospheric chemistry, providing fresh insights into the mechanisms underlying acid rain formation. The current study also makes significant advances to probe the dynamics of complex bimolecular chemical reactions.

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Reaction coordinate

Fig. 1. Energetics for the photodetachment of $HOSO_2^-$ and reaction pathway for the HO + SO_2 system. The energies in kJ/mol are relative to the reactant asymptote HO + SO_2 at the UCCSD(T)-F12a/aug-cc-pV(T+d)Z level and are ZPE corrected values. RC: reaction complex. TS: transition state.

significantly slower than R2 and the production of H_2SO_4 requires a high concentration of water in the atmosphere (37). The reaction rate for the first step (R1) was comprehensively studied in the 1980s (21–23), and the rate coefficients were determined to be a function of pressure and temperature (20). Given the reaction rate for R1 and the atmospheric HO radical and SO₂ abundance profile, the atmospheric lifetime for SO₂ was estimated to be 13 d (38, 39). Recently, highly accurate ab initio theories have been used to construct the HO + SO₂ reaction pathways to predict the temperatureand pressure-dependent rate coefficients (26, 27).

Although the reaction rates and kinetics for reaction R1 have been investigated extensively, the dynamics of the HO + SO₂ \rightarrow HOSO₂ reaction remain poorly understood. For example, despite the fact that the potential barrier of this reaction is extremely low, the rate of the reaction is rather slow, leading to the relatively long lifetime of SO₂ in the atmosphere (38, 39). A key issue in chemical reaction dynamics is to understand how the transition state controls the reactivity (40). As shown in Fig. 1, the reaction path for R1 features several shallow pre-reaction wells (RC1, RC2, and RC3) and an extremely low barrier (TS1) (0.77 kJ/mol, zero-point corrected) for the formation of the HOSO₂ product (33, 34). A natural question is, how is this low barrier related to a slow reaction rate?

The key to understanding this question is the dynamics near the transition state. Experimentally, photoelectron spectroscopy of suitable precursor anions is a promising technique for probing the spectroscopy and dynamics of the transition state region (41, 42), especially when aided by reaction dynamics analyses on accurate potential energy surfaces. This approach has proven to be powerful for probing the dynamics of elementary chemical reactions, primarily involving hydrogen transfer reactions or reactions that can be effectively described by a one-dimensional reaction coordinate (43-52). However, R1 corresponds to an association reaction involving heavy reactants and potentially multi-dimensional reaction coordinates. To further advance our understanding of fundamental polyatomic reaction dynamics, such as R1, it is essential to go beyond one-dimensional systems. In particular, it is critical to understand the multidimensional potential energy surface of the $HO + SO_2$ reaction to gain dynamic insight and unravel the mechanisms of the slow reaction rate.

Herein, we report a photoelectron spectroscopy study of cryogenically cooled HOSO₂⁻ anion and ab initio calculations of the structures and multidimensional potential energy surfaces of the HOSO₂⁻ anion and the HOSO₂ radical. The experimental and theoretical investigations uncover the importance of the shape of the multidimensional potential energy surface near the transition state in controlling the dynamics of the HO + SO₂ reaction. This finding results from the analyses of the photoelectron spectra of the cold HOSO₂⁻ anion and the quantum mechanical and quasi-classical trajectory (QCT) calculations on a full-dimensional potential energy surface that is ab initio based.

Results

Photoelectron Spectroscopy. The experiment is conducted using an electrospray ionization (ESI) photoelectron imaging apparatus (53). Further details about the experimental methods and procedures are given in SI Appendix and the Materials and Methods section. The photoelectron spectra of cryogenically-cooled $HOSO_2^{-}$ anion obtained at photon energies ranging from 3.5399 to 4.1993 eV (341.55 to 405.17 kJ/mol) (Fig. 2A) exhibit wellresolved peaks (a to z) corresponding to detachment transitions from the anion ground state to low-lying vibrational levels of the neutral HOSO₂ radical. There is another nearly isoenergetic isomer (54, 55), HSO_3^- , in which the H atom is directly bonded to the S atom (SI Appendix, Figs. S1 and S2). In the current experiment, the contribution from the HSO3⁻ isomer can be excluded because of its high detachment threshold of 460.14 kJ/ mol, according to our ab initio calculations (*SI Appendix*, Fig. S1). The S atom in HSO_3^- is in its highest oxidation state of +VI, which is similar to that in HOSO₃⁻; HOSO₃⁻ has a known detachment threshold of 4.75 eV (458 kJ/mol) (56). The positions of peaks *a-z* are given in *SI Appendix*, Table S1. The observed peak *a* with the lowest binding energy of 3.367 eV (324.9 kJ/mol) defines the detachment threshold of HOSO2⁻ or the electron affinity of HOSO₂, which is in good agreement with the theoretical value of 320.04 kJ/mol (SI Appendix, Table S2). Peaks b-z correspond to excited vibrational levels of HOSO₂.

The low-energy wing of the photoelectron spectra is dominated by low-lying vibrational levels of HOSO₂. Our computed anharmonic frequencies for HOSO₂ are summarized in SI Appendix, Table S3 relative to previous theoretical values and experimental frequencies measured in low-temperature matrices (15, 16, 57). The atomic displacement vectors for the vibrational modes of $HOSO_2$ and $HOSO_2^-$ are presented in *SI Appendix*, Fig. S3. The simulated spectrum for the first few vibrational levels of HOSO₂ is compared with the measured photoelectron spectrum at 3.6042 eV (347.75 kJ/mol) in Fig. 2B. The calculated spectrum is obtained by a Franck-Condon model using the normal modes of $HOSO_2^{-}$ and $HOSO_2$ on the anion and neutral potential energy surfaces with the experimentally determined vibrational frequencies. The active modes, including the HO pseudo-rotation (ν_1 , 265 cm⁻¹), SO₃ umbrella (ν_4 , 515 cm⁻¹), and HO-SO₂ stretch $(\nu_5, 774 \text{ cm}^{-1})$, are consistent with the differences between the neutral and anion geometries (SI Appendix, Fig. S2).

At high binding energies, the photoelectron spectrum approaches the region near TS1. The reactants HO + SO₂ are 430.71 kJ/mol (4.4640 eV) above the ground state of HOSO₂⁻ (Fig. 1). To access the transition state region of the HO + SO₂ reaction, we obtain the photoelectron spectrum of HOSO₂⁻ at 4.661 eV (449.7 kJ/mol) (Fig. 2*C*), revealing the full Franck-Condon region for the detachment transition from HOSO₂⁻ to the HOSO₂ neutral final state. The vertical detachment energy of HOSO₂⁻ is determined to be 3.90 eV (376 kJ/mol) from the



Fig. 2. (*A*) Experimental photoelectron spectra of $HOSO_2^-$ at 10 photon energies ranging from 3.5399 to 4.1993 eV (341.55 to 405.17 kJ/mol). The observed features are labeled as *a-z*. (*B*) Experimental photoelectron spectrum of $HOSO_2^-$ at 3.6042 eV (347.75 kJ/mol) (Expt.), compared with the calculated Franck-Condon factors (FCFs). (*C*) Photoelectron spectra of $HOSO_2^-$ at 4.661 eV (449.7 kJ/mol) (red curve) compared with the calculated Franck-Condon (blue curve) and Wigner (black curve) profiles. The black arrow indicates the dissociation threshold energy of the $HOSO_2^-$ anion (to $HO + SO_2 + e^-$). TS denotes features near the transition state of the $HO + SO_2$ reaction.

maximum point of the 4.661 eV (449.7 kJ/mol) spectrum (Fig. 2C), which is in good agreement with the theoretical value of 384.40 kJ/mol (3.984 eV) (SI Appendix, Table S2). By using the full potential energy surface, built from machine learning [PIP-NN (permutational invariant polynomial-neural network)] with high-level ab initio data, we simulate the photoelectron spectrum with two methods (see SI Appendix, Theoretical Methods for further details). The overall spectral profile at 4.661 eV (449.7 kJ/ mol) is not well reproduced by the Franck-Condon model on the high-energy side presumably due to anharmonic effects; however, it can be reproduced using Wigner phase space sampling (Fig. 2*C*) (58). The Wigner method takes into account anharmonic effects in the final states and is more suitable for electronic transitions involving large geometry changes between the final state and the initial state (see SI Appendix, section II.D. for details). The latter spectrum is slightly broader than the experimental spectrum, mainly due to anharmonic effects.

Potential Energy Surface Calculations. Fig. 1 shows that a prereaction complex is formed before the submerged transition state (TS1) along the HO + SO₂ \rightarrow HOSO₂ reaction path. Previous studies (27, 34) have shown that the pre-reaction complex is a hydrogen-bonded complex between the H atom of HO and one of the O atoms of SO₂ (RC2, Fig. 1). RC2 in this work is at an energy of -7.72 kJ/mol with zero-point energy (ZPE) correction, which is consistent with the previous value of -7.2 kJ/mol (27). However, the intrinsic reaction coordinate (IRC) analysis on the current potential energy surface, built from the PIP-NN machine-learning method with high-level ab initio data (see SI Appendix, Fig. S5 and Theoretical Methods for further details), reveals a unique pre-reaction complex RC1 with a ZPE-corrected energy of -8.88 kJ/mol, in which the O atom of HO is pointed toward the S atom of SO2. Importantly, the structure of RC1 is close to TS1 (Fig. 1), and it is easier to reach TS1 from RC1 than from RC2 or RC3. A cyclic complex (RC3, Fig. 1) is found at a ZPE-corrected energy of -8.10 kJ/mol. The optimized geometry of TS1 on the potential energy surface is similar to the recent high-level calculation at the CCSD(T)-F12a/cc-pVTZ-F12 level (26). The ZPE-corrected energy of TS1 is 0.77 kJ/mol, which is consistent with the previous values of 1.2 kJ/mol and 1.1 kJ/mol at CCSD(T)/CBS (27) and CCSDT(Q)/CBS (26), respectively. The fitting error (E_{fit} - E_{target}) of the potential energy surface as a function of the ab initio energy is given in SI Appendix, Fig. S4. The potential energies along the minimum energy paths of TS1, TS2, TS2', and TS3 (SI Appendix, Fig. S1) on the potential energy surface are depicted in SI Appendix, Fig. S5. There is good agreement between the potential energy surface and the direct ab initio calculation at the UCCSD(T)-F12a/aug-cc-pV(T+d)Z level. Importantly, the intrinsic IRC analysis presented in *SI Appendix*, Fig. S5, shows that TS1 connects with the pre-reaction complex RC1 rather than the previously reported hydrogen-bonded RC2 (27, 34). Our calculated dissociation energy from HOSO2 to OH + SO2 is 111.83 kJ/ mol (SI Appendix, Table S4), which agrees well with the previous experimental reaction enthalpy of -113.3 ± 6 kJ/mol (20) and the benchmark calculation at the CCSDT(Q)/CBS limit (-111.54 kJ/mol) (26) for the HO + SO₂ \rightarrow HOSO₂ reaction. Interestingly, the photoelectron spectrum at 4.661 eV (449.7 kJ/mol) exhibits reproducible oscillatory structures in the high

binding energy side at approximately 4.5 eV (434 kJ/mol) (labeled as TS in Fig. 2*C*). These oscillatory structures occur in the same energy range predicted for the transition state of the HO + SO₂ reaction (calculated to be 431.48 kJ/mol or 4.472 eV above the $HOSO_2^-$ ground state, Fig. 1), strongly suggesting the existence of resonances. These resonances imply the existence of a narrow phase space bottleneck for the HO + SO₂ reaction. However, a definitive identification of these resonances requires quantum dynamic calculations beyond the state-of-the-art computational methods. Nevertheless, the full-dimensional global potential energy surface obtained from the PIP-NN method can provide critical insight into the dynamics of this reaction.

Discussion

The contour plot of the potential energy surface along the reaction pathway of R1 is shown in Fig. 3, displaying the positions and

energies of RC1, TS1, and HOSO₂. In addition, the conversion between HOSO₂ and its mirror image HOSO₂' via TS2 or TS2' is given. Despite the extremely low-energy barrier, the entrance channel for R1 is very tight, forming the key bottleneck responsible for its slow reaction rate. The tight entrance channel is clearly illustrated in Fig. 4*A*, where the potential contour is displayed as functions of the angle θ and the distance R_{OS} with other coordinates being relaxed (the definitions of θ and R_{OS} are shown in the *Inset*). The reaction proceeds through a narrow entrance with a small range for the acceptance angle θ . The tight reactive entrance channel is revealed by the potential contour along the R_{OS} and other angles, as depicted in *SI Appendix*, Fig. S6, resulting in the extremely low reactive encounters as shown in the trajectory calculations (vide infra).

By using the PIP-NN potential energy surface, we further simulate the bimolecular reaction rate for R1 at room temperature (within the zero-pressure limit) using a QCT method. As shown in *SI Appendix*, Fig. S1, the formation of HSO₃ is not possible under atmospheric conditions due to the large barriers (TS4 and TS5); nevertheless, the HOSO₂ intermediate can be readily formed. The calculated formation rate for HOSO₂ is 1.99×10^{-12} cm³ mole⁻¹ s⁻¹ using 9×10^5 trajectories, which is in reasonable agreement with the experimental values (24, 59) in the range of 7.10×10^{-13} to 3.61×10^{-12} cm³ mole⁻¹ s⁻¹. The trajectory calculations reveal that approximately 0.24% of the trajectories reach HOSO₂, due to the very narrow bottleneck for R1, illustrating how the shape of the entrance channel restricts the number of reactive encounters. Furthermore, our QCT calculations suggest that nascent HOSO₂ can survive a sufficiently long lifetime to experience collisional stabilization. As shown in Fig. 4B, the lifetime distribution has a bi-exponential behavior. Most of the trajectories have a relatively short lifetime (1.4 ps), but many other trajectories survive on the order of 57.0 ps. These long-lived trajectories are a direct result of the reaction bottleneck, which is conducive to resonances implicated in the photoelectron spectrum at 4.661 eV (Fig. 2C).

There is limited understanding of the dynamics and causes of the slow rate of SO_2 oxidation by HO in the atmosphere. By employing photoelectron spectroscopy of cryogenically cooled $HOSO_2^-$ anion, we have successfully accessed the neutral $HOSO_2$



Fig. 3. Contour plot for the potential energy surfaces (energy in kJ/mol) along the HO + SO \rightarrow HOSO₂ reaction pathway as functions of θ and R_{OS} , with the other coordinates being relaxed. R_{OS} is the distance between O2 and S3, and θ is the dihedral angle of H1-O2-S3-O4.



Fig. 4. (A) Potential energy contours (in kJ/mol) for the HO + SO₂ system as functions of θ and R_{OS} , with all other coordinates being relaxed. (B) Semilogarithmic plot of QCT survival probabilities as a function of time and the least-square fits at 298 K.

radical near the transition state of the HO + SO₂ reaction. By comparing these observations with the first ab initio-based full-dimensional potential energy surface, we have made a significant breakthrough in understanding the dynamics of the HO + SO₂ reaction. We find that the accessible phase space for the HO + SO₂ \rightarrow HOSO₂ reaction is exceptionally narrow, resulting in a major bottleneck and contributing to the sluggish reaction rate in the atmosphere, despite the low energy barrier. Our findings demonstrate that the rate of the HO + SO₂ reaction is influenced by the multidimensional reaction dynamics rather than by only the reaction energetics.

The implications of our study extend to atmospheric chemistry, providing fresh insights into the mechanisms underlying acid rain formation. The findings of this work on elucidating the dynamics of the HO + SO_2 reaction underscore the crucial role of a full-dimensional potential energy surface in unravelling the intricate details of bimolecular reactions involving polyatomic reactants. It is highly probable that such dynamics-driven phenomena are ubiquitous in complex bimolecular reactions, emphasizing the importance of explicitly considering dynamics when characterizing and interpreting complicated reaction mechanisms.

Materials and Methods

Experimental Method. Experiments were carried out using an ESI photoelectron spectroscopy apparatus equipped with a cryogenically cooled three-dimensional Paul trap and high-resolution photoelectron imaging. The photoelectron spectra of cryogenically-cooled HOSO₂⁻ anions were taken at photon energies ranging from 3.5399 to 4.1993 eV (341.55 to 405.17 kJ/mol), and at 4.661 eV (449.7 kJ/mol). Further details are available in *SI Appendix*.

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Theoretical Method. The geometries, energies, and harmonic frequencies of all stationary points were determined at the explicitly correlated unrestricted coupled-cluster singles, doubles, and perturbative triples level [UCCSD(T)-F12a] with the augmented correlation-consistent polarized split-valence set aug-cc-pV(T+d)Z using the 2020 version of the MOLPRO package. The aug-cc-pV(T+d) Z basis set is the improved version of the standard aug-cc-pVTZ set and can provide more accurate results for systems containing sulfur atoms. Full-dimensional potential energy surfaces were built from the PIP-NN machine-leaning method with high-level ab initio data. The FCclasses3 code with time-independent strategies was employed to calculate the photoelectron spectrum within the normal mode approximation. The photoelectron spectrum was also calculated using the Wigner phase space sampling approach. The QCT calculations were performed to obtain the rate coefficient of the OH + SO₂ reaction at room temperature. Further details are available in *SI Appendix*.

Data, Materials, and Software Availability. All study data are included in the article and/or *SI Appendix*.

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