

A New Mechanism of Acid Rain Generation from HOSO at the Air-Water Interface

Manuel F. Ruiz-López,^{[a],*} Marília T. C. Martins-Costa,^[a] Josep M. Anglada^[b] and Joseph S. Francisco^[c]

[a] Laboratoire de Physique et Chimie Théoriques, UMR CNRS 7019, University of Lorraine, CNRS, BP 70239, 54506 Vandoeuvre-lès-Nancy, France

[b] Departament de Química Biològica (IQAC), CSIC, c/ Jordi Girona 18, E-08034 Barcelona, Spain

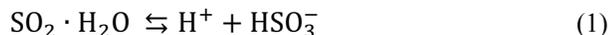
[c] Department of Earth and Environmental Science and Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA 19104-6316

Supporting Information Placeholder

ABSTRACT: The photochemistry of SO₂ at the air-water interface of water droplets leads to the formation of HOSO radical. Using first-principles simulations, we show that HOSO displays an unforeseen strong acidity (pK_a = -1) comparable with nitric acid, and is fully dissociated at the air-water interface. Accordingly, this radical might play an important role in acid rain formation. Potential implications are discussed.

The two major acid rain components are H₂SO₄ and HNO₃. SO₂ is the main precursor of H₂SO₄ and oxidation of S(IV) to S(VI) can take place in the gas phase or in the aqueous phase.^{1,2} Gas-phase oxidation of SO₂ is at the origin of new particle formation mechanisms. Reaction of SO₂ with OH and O₂ leads to SO₃, which then reacts with water or water dimer³ to form sulfuric acid. The high hygroscopicity of H₂SO₄ favors the formation of small water clusters that grow by condensation of further water molecules, possibly promoted by ammonia or small amines.⁴⁻⁵

Aqueous-phase oxidation of SO₂ is, however, the most important pathway to sulfate on a global scale, and the process is even considered as the most important chemical transformation in cloud water.^{1,6} Nevertheless, despite numerous theoretical and experimental studies, SO₂ oxidation mechanisms are not yet fully understood. The process is believed to start by uptake of SO₂ in water followed by fast ionization:⁷



The pK_a of aqueous SO₂ is 1.86.⁸ In equations 1-2 (and below), the proton is notated H⁺ for simplicity though the relevant species in water is H₃O⁺. The equilibrium

formally involves H₂SO₃ but this species has never been isolated and calculations showed that it corresponds to a loosely bonded complex SO₂(H₂O).⁹ The main species at usual atmospheric pH (pH=2-7) is HSO₃⁻. Transformation of S(IV) to S(VI) is facilitated by oxidants such as O₃, O₂ (uncatalyzed or catalyzed by transition metal ions), OH or HO₂, but reaction with H₂O₂ is particularly efficient because it readily reacts with HSO₃⁻ and its concentration is relatively high.^{2,6} The reaction leads to SO₂OOH⁻, which in acid media finally forms sulfuric acid.¹



According to *ab initio* calculations in water clusters,^{9,11} hydrolysis of SO₂ is a thermodynamically unfavorable process with high activation barrier.¹² Water-assistance may decrease the barrier¹³ but *ab initio* Molecular Dynamics simulations of SO₂ in liquid water could not detect the formation of hydrolyzed species at the time-scale of the simulation.¹⁴ Theoretical studies⁹⁻¹² are consistent with pump-probe experiments on SO₂(H₂O)_n clusters (n=1-5), which suggested that formation of HSO₃⁻ ions is a slow process.¹⁵

Other experiments have argued that key steps in atmospheric SO₂ hydrolysis and oxidation occur at the surface of liquid water,¹⁶⁻¹⁸ ice^{10, 19-20} or dust,²¹ trying to explain why simulations of homogeneous reactions typically underestimate sulfate production. Indeed, experiments¹⁷ and calculations²² have demonstrated that SO₂ adsorption at the air-water interface is thermodynamically favorable (ΔG_{ads} ~ 5 kcal·mol⁻¹). Mass-accommodation coefficient measurements in water droplets¹⁶ concluded that an interfacial contact ion pair is formed, which might be HSO₃⁻-H⁺. This result was confirmed by

second-harmonic generation¹⁷ and vibrational sum-frequency spectroscopy.¹⁸ Electrospray-ionization mass spectrometry studies of SO₂ oxidation at the surface of microdroplets²³⁻²⁴ reported four major ions, HSO₃⁻, SO₃⁻, SO₄⁻ and HSO₄⁻ at acidic pH without addition of oxidants other than oxygen. Some experiments have been carried out on ice surface too. FTIR spectroscopy of SO₂ on the surface of ice nanoparticles displayed a band that was assigned to HSO₃⁻.¹⁹ Reactive-ion scattering and low-energy sputtering techniques in conjunction with temperature-programmed desorption mass spectrometry of SO₂ on ice films showed that charged molecular species were formed with very low or negligible activation barriers,²⁰ and both SO₂⁻ and HSO₃⁻ anions were identified.¹⁰

In this communication, we show that SO₂ hydrolysis at the water surface may take place photochemically through a process in which S(IV) sulfur dioxide is reduced to S(III) sulfur dioxide radical anion, whose oxidation to bisulfite and bisulfate completes the acid rain formation mechanism. Our study has been carried out using different theoretical methods described in the SI, in particular, Molecular Dynamics (MD) simulations with state-of-the-art quantum-classical (QM/MM) force-fields.

The initial step is the formation of a HOSO radical through reaction of the lowest SO₂ triplet (³B₁) with water. The reaction has recently been observed in gas-phase experiments²⁵⁻²⁶ and described through calculations in gas phase²⁶⁻²⁷ and at the air-water interface.^{22, 27} The long-living ³SO₂ state is reached either directly from the ground state or (most probably) by intersystem crossing from the lowest excited singlet states (¹A₂ and ¹B₁) within an absorption band extending between 240 nm and 330 nm.^{22, 26}



In process (8), S(IV) is reduced to S(III), an unusual sulfur oxidation state in the atmosphere, and water is oxidized, making this reaction a potential new source of OH radicals, as first suggested by Kroll et al.²⁶ The reaction could have implications for the formation of OH in volcanic plumes and in planetary atmospheres deficient in oxygen or ozone.²⁶ Estimation of OH production rates led to the conclusion that the impact of the reaction at the surface of water droplets in the Earth's troposphere could be significant.²² Further work has confirmed that the reaction mechanism involves a proton-coupled-electron-transfer mechanism that is favored by water solvation, so that the activation free energy at the air-water interface is predicted to be low (<1 kcal·mol⁻¹

at 298K) and the triplet is predicted to be rapidly hydrolyzed.²⁷ The atmospheric chemistry of HOSO is poorly known though some studies in gas phase have been reported.^{22, 26, 28-40}

The outcome of HOSO following (8) is unknown despite the atmospheric relevance of related species such as HONO.¹ To get insights into HOSO chemistry at the air-water interface, QM/MM MD simulations have been carried out in which HOSO and one water molecule are described quantum mechanically (B3LYP/6-311+G(d) level⁴¹), while the rest of water molecules are described classically (TIP3P⁴² force field). We found that the radical undergoes spontaneous ionization through proton transfer to H₂O (Figure 1) after less than 30 ps of production run. The proton transfer itself occurs in a very short time-scale (few tens of femtosecond) characteristic of strongly hydrogen-bonded systems.⁴³ Figure 2 displays some snapshots along the simulation. Throughout the transfer, HOSO and water approach to each other, the two O-H distances being short and similar (~1.1-1.2 Å), and the incipient ion-pair is stabilized by strong hydrogen-bonds with surrounding classical water molecules.

To get a deeper insight into the ionization mechanism, we have carried out B3LYP/6-311+G(d) calculations in a (H₂O)₂₁ cluster.⁴⁴ The results confirm the ease of HOSO dissociation, the relative energy between the reactant and final ion-pair complex being +1.6 kcal·mol⁻¹ (Figure 3). Detailed analysis of the mechanism shows an asynchronous process involving several proton transfers that starts, as in the MD simulation, by a transfer in a closely linked HOSO-water complex (see SI).

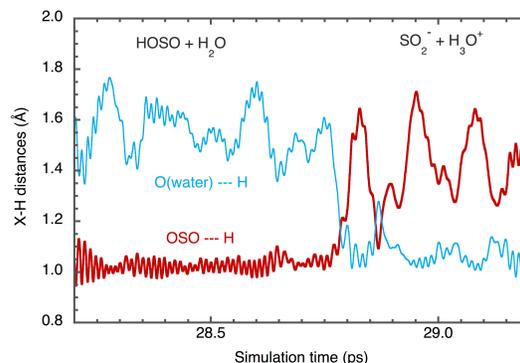


Figure 1. Time evolution of OH distances in the H₂O...HOSO system from QM/MM simulations at the air-water interface.

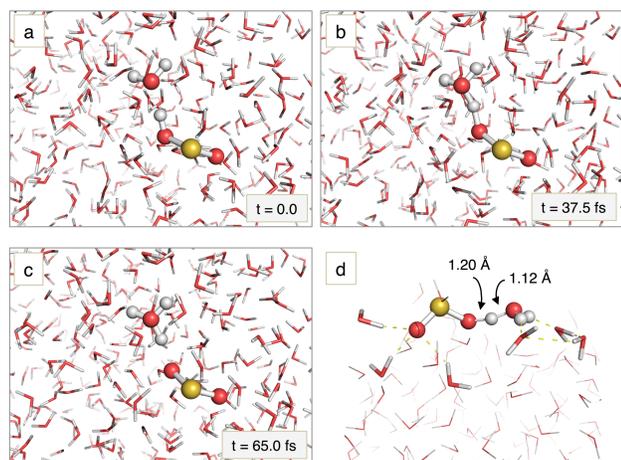


Figure 2. (a-c) Snapshots showing the HOSO ionization process at the air-water interface (top view) and relative time. (d) Detail of HOSO-water QM system and TIP3P solvation shell from snapshot b.

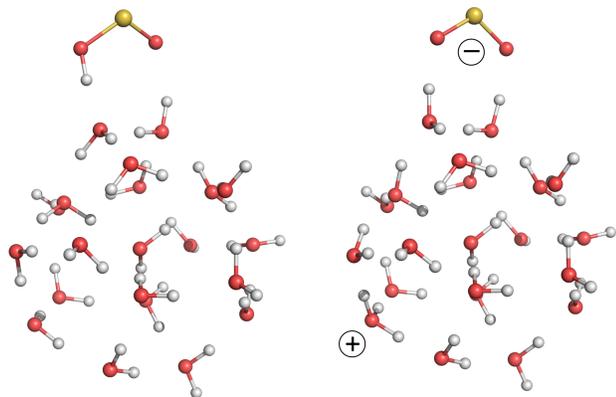


Figure 3. HOSO(H₂O)₂₁ and (SO₂⁻)(H₃O⁺)(H₂O)₂₀ structures optimized at B3LYP/6-311+G(d) level.

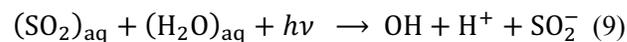
Whether an acid can dissociate can be assessed by its pK_a value, with lower pK_a favoring dissociation. The present simulation indicates that HOSO behaves like a strong acid that dissociates as soon as formed through reaction (8) at the water surface, contributing to acidify the medium. The acidic character of the related species HONO and HOCO is well documented ($pK_a^{\text{HONO}} = 3.16^{45}$, $pK_a^{\text{HOCO}} = 3.4^{46}$) but HOSO acidity in either gas or aqueous phase is unknown. Hence, we have made an estimation through *ab initio* computations at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory using an implicit solvation model. The results for gas phase acidity and pK_a in water solution are summarized in Table 1. In this Table, we include calculations and experimental data for HONO, for comparison.

The calculated gas phase acidity for HONO is very close to experiment⁴⁷ and to previous calculations.⁴⁸ Remarkably, the gas phase acidity of HOSO is ~ 10

kcal·mol⁻¹ lower than that of HONO. Analysis of gas phase ionization processes in terms of the thermodynamic cycle in Figure 4 provides some explanation for this finding. The experimental electron affinities of NO₂ and SO₂ are, respectively, 52.4 and 25.5 kcal·mol⁻¹,⁴⁹ and the homolytic bond dissociation energy of HONO (H+ONO) amounts 78.4 kcal·mol⁻¹ (using reported heats of formation⁴⁹). There is no experimental dissociation energy value for HOSO but there are several *ab initio* calculations reporting similar values.^{35, 39} For instance, Grant et al⁵⁰ obtained 39.7 kcal·mol⁻¹. By comparing these quantities, it clearly appears that the greater acidity of HOSO with respect to HONO is due to its much lower O-H bond dissociation energy, which is partially compensated by a significantly lower electron affinity of SO₂ compared to NO₂.

A strong HOSO acidity is also found in liquid water, with $pK_a = -1$ (see Table 1). This pK_a value is more than 4 units smaller compared to HONO and is comparable to the pK_a of nitric acid ($pK_a = -1.38$). Such a strong acidity explains and corroborates the results obtained in the simulations at the air-water interface (note that effective pK_a at the interface may be slightly different from bulk).⁵¹ HOSO is therefore expected to spontaneously and completely dissociate in water.

At this stage, the net photochemical process initiated by the absorption of sunlight by aqueous SO₂ can be written as:



which results in the formation of the radical anion SO₂⁻ at the interface. Very interestingly, this anion has been identified in SO₂ hydrolysis experiments on ice surfaces,¹⁰ as mentioned above, and this correlation supports the mechanism studied here. Ascertaining the atmospheric impact of (9) will require further studies, and experiments under SO₂ irradiation in the absence of oxidants are appealing. We present here a qualitative analysis based on the present results and previously reported reaction rates.

Since HOSO is much more acidic than SO₂, process (9) leads to acidification of the medium, eventually boosted by subsequent oxidation of SO₂⁻ to sulfate. A rough estimation of the upper limit for the formation rate of SO₂⁻ and H⁺ is (see SI) $0.2 \times 10^{10} \text{ molecule} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ (ppb [SO₂]_{gas})⁻¹. On the other hand, conventional S(IV) to S(VI) conversion by usual atmospheric oxidants in the pH range 3-6 spreads between 10^8 - $10^{13} \text{ molecule} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ (ppb [SO₂]_{gas})⁻¹, with H₂O₂ providing the highest values.¹⁻² Thus, HOSO contribution could become significant for SO₂ peaks attaining several hundreds of ppb and environments depleted in H₂O₂.

Moreover, oxidation of SO₂⁻ formed in (9) to S(VI) should also contribute to decrease the pH. Arguably, the atypical radical anions SO₃⁻, SO₄⁻ or SO₅⁻ might easily

be formed from the parent radical SO_2^- through reactions with common atmospheric oxidants such as O_2 , O_3 , H_2O_2 , OH or HO_2 . This is a key feature because those species lead to free radical chain reactions that have been shown to be involved in non-catalyzed SO_2 oxidation by O_2 at the surface of microdroplets and provide a significant contribution to the net sulfate formation in the atmosphere.²³⁻²⁴ The process is supposed to be initiated by the sulfite radical anion SO_3^- but generation of this species remains unclear.²⁴ Since SO_2^- has been detected in flash photolysis studies of these chain reactions,⁵² one may infer that photochemistry of SO_2 at the air-water interface might also contribute to sulfate formation by triggering the oxidation mechanism by O_2 .

Note finally that reaction with OH leads to bisulfite:



so that the overall reaction in that case is equivalent to (1), and that reaction with HO_2 (or O_2^-) directly leads to S(VI) in form of bisulfate (11) or sulfate (12):

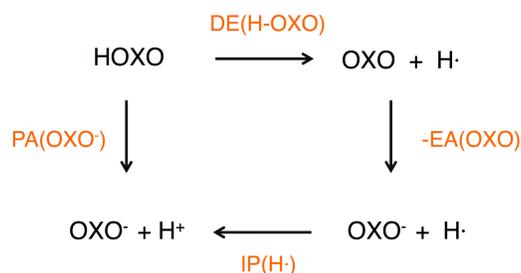


Figure 4. Thermodynamic cycle connecting HOXO ionization with other thermodynamic quantities (DE= dissociation energy, EA=electron affinity, IP=ionization potential, PA=proton affinity)

Table 1. Calculated gas-phase acidities (ΔG_a), solvation energies (ΔG_s^Y) and pK_a in water for HONO and HOSO.¹

	ΔG_a	ΔG_s^{HOXO}	$\Delta G_s^{\text{OXO}^-}$	ΔpK_a	pK_a
HONO	333.6	-2.43	-64.45	0.0	3.16
	<i>333.7</i> ²				<i>3.16</i> ³
HOSO	323.2	-3.60	-61.10	-4.16	-1.0

¹Calculated pK_a is given relative to HONO. Energies at 298K, in $\text{kcal}\cdot\text{mol}^{-1}$ at CCSD(T)/MP2 level. Experimental values are in italics. ²Reference.⁴⁷ ³Reference.⁴⁵

In summary, we have shown that the photochemistry of SO_2 can be an important ingredient in the overall mechanism of acid rain formation not yet considered by current atmospheric models. The key step in this mechanism is the population of the lowest triplet state, which

at the surface of water droplets undergoes a fast redox reaction with water producing HOSO and OH radicals. The role of the former in the troposphere is still poorly known but we have shown that HOSO is a strong acid that completely dissociates in aqueous media forming the reactive S(III) radical anion SO_2^- . An important finding from this work is that HOSO, the intermediate resulting from the hydrolysis of triplet SO_2 , can directly contribute to atmospheric acid formation, in addition to the two well-known components: sulfuric acid (H_2SO_4) and nitric acid (HNO_3). This finding significantly broadens the atmospheric chemistry of aqueous SO_2 .

ASSOCIATED CONTENT

Details on computational methods and calculations are provided as Supporting Information. The Supporting Information is available free of charge on the ACS Publications.

AUTHOR INFORMATION

Corresponding Author

Manuel.Ruiz@univ-lorraine.fr

ORCID

Manuel F. Ruiz-López:0000-0002-2784-6319

Marilia T. C. Martins-Costa: 0000-0003-4957-2248

Josep M. Anglada: 0000-0003-4526-3624

Joseph S. Francisco: 0000-0002-5461-1486

Notes

The authors declare no competing financial interest.

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