Theoretical Study of the Auto-catalyzed Hydrolysis Reaction of Sulfur Dioxide

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Abstract

The hydrolysis reaction of sulfur dioxide (SO_2) to form sulfurous acid involving additional sulfurous acid (H_2SO_3) was investigated using high-level computational methods. With H_2SO_3 , the reaction takes place via a double proton transfer process with a cage-like structure, which is different from the planar ring structure involved in a corresponding process with an additional water molecule (served as a catalyst). Our results show that H_2SO_3 is a better catalyst than water, as the barrier height for the H_2SO_3 -catalyzed reaction is only 5.5 kcal/mol, compared to over 25.0 and 15.0 kcal/mol for the reaction without a catalyst and the H_2O -catalyzed reaction, respectively. In addition, the sulfurous acid dimer from the H_2SO_3 -catalyzed reaction is more stable than hydrated H_2SO_3 from the H_2O -catalyzed reaction. Considering the existence of sulfurous

acid in the aqueous phase and acidic aerosols, as well as the importance of SO₂ and H₂O in the atmosphere, our results will have potentially significant implications on the homogeneous and heterogeneous nucleation processes.

Keywords: SO₂ hydrolysis; Auto-catalytic reaction; Sulfurous acid; DFT; CCSD(T); Kinetics.

Introduction

Sulfur dioxide is one of the most important atmospheric pollutants, which is mainly from volcano eruption and the burning of fossil fuels [1]. The reactions of SO₂ in the atmosphere contribute to various environmental issues, including acid rain, formation of sulfate aerosols, and production of secondary organic aerosols [2]. As a result, substantial efforts have been dedicated to the understanding of the chemical processes of SO₂ in the atmosphere [3-9]. A critical step in many atmospheric processes is the adsorption of SO₂ on the gas-liquid surface [10-13]. However, the chemical mechanism for the subsequent reactions of SO₂ after adsorption is still poorly understood. The high solubility in water leads to the “wet” deposition of SO₂, in which the hydrolysis reaction plays a major role. The hydrolysis reaction of SO₂ in the atmosphere has a profound impact on the environment. The reaction contributes to the production of hygroscopic species which will act as seed molecules for aerosol formation [9]. In view of this, the sulfurous acid product may serve as either a donor or an acceptor of hydrogen bond, and thus provide as a precursor capable of oligomers and ultimately condense into atmospheric aerosols [14,

15]. The hydrolysis reaction of SO_2 is kinetically and thermodynamically unfavorable in the gas phase[16, 17], and the complete process has been poorly understood for the past decades.

In the hydrolysis reaction of SO_2 , an additional water molecule may act as a proton transmitter or serve as a micro solvent, effectively reducing the energy barrier of reaction [18]. Recent efforts have been devoted to finding other species with similar effects in promoting the hydrolysis reaction of SO_2 . Ammonia, an important ingredient of atmospheric aerosols, has been identified as a better proton transmitter than water in promoting the hydrolysis reaction of SO_2 [9]. More specifically, recent computational studies on the hydrolysis reactions of sulfur trioxide [19] and glyoxal [20], for example, suggested that atmospheric acid can dramatically lower the energy barriers of the hydrolysis reactions. Acid catalysis may also be important in the hydrolysis reaction of SO_2 .

The solution of SO_2 is comprised of hydrated SO_2 , sulfurous acid (H_2SO_3), and sulfonate ion (HSO_3^-) [6,11,14]. As a hydrolysis product, sulfurous acid is also expected to be contained in the acidic aerosols [14]. The characterization and isolation of H_2SO_3 is still a challenge in inorganic chemistry due to the kinetic instability of sulfurous acid. However, H_2SO_3 has been successfully generated in a neutralization–reionization mass spectrometric experiment [21]. In addition, the solvated sulfurous acid $\text{H}_2\text{SO}_3\cdot 5\text{H}_2\text{O}$ is predicted to be more stable than hydrated sulfur dioxide $\text{SO}_2\cdot 6\text{H}_2\text{O}$ [6]. In addition, the half-life of H_2SO_3 is estimated to be 24 hours at room temperature, and Voegelé et al.

suggested that the dimeric H_2SO_3 is thermodynamically more stable than isolated SO_2 and H_2O molecules at 77 K [22].

In the present work, the hydrolysis reaction of SO_2 in the presence of sulfurous acid is studied using theoretical computation. Our primary objective is to know whether or not H_2SO_3 could act as an auto-catalyst for the formation of itself. Our next objective is to understand any potential effects of this reaction on the characterization and isolation of H_2SO_3 in laboratory. Natural Bonding Orbital (NBO) analysis will be performed to evaluate the nature of the catalytic effect. Kinetic simulations will be conducted over the temperatures 200~320 K. Atmospheric implications of this study will be discussed, particularly on atmospheric aerosol formation and particulate growth.

Computational methods

Quantum chemical calculations were performed using Gaussian 09 suite of program [23]. Equilibrium geometries corresponding to all local minima and transition states were optimized using the popular B3LYP hybrid density functional method with the cc-pV(T+d)Z basis set. The B3LYP/cc-pV(T+d)Z method has shown to provide reliable results for reactions of hydration of sulfuric acid [24] and the hydrolysis reactions of sulfur trioxide, catalyzed by formic acid [25] and sulfuric acid [19], respectively. Intermolecular interactions, particularly hydrogen bonding, may play an important role in the catalytic effect of H_2SO_3 in the hydrolysis reaction of SO_2 . Second-order Moller-Plesset perturbation method (MP2), which is known reliable in describing

noncovalent interactions [26-29], was also employed to confirm the adequate treatment of intermolecular interactions. All molecular geometries at the stationary points were re-optimized using MP2/cc-pV(T+d)Z method. Harmonic vibrational frequencies were obtained to verify each equilibrium geometry either at a local minimum or at a first-order saddle point. Furthermore, intrinsic reaction coordinate (IRC) calculations were performed to confirm each transition state that connects the desired reactant and product. Using B3LYP equilibrium geometries, electronic energies were further refined by the single point energy calculations using coupled-cluster theory with single, double, and perturbative triple excitations, CCSD(T), in conjunction with the extrapolation to the complete basis set limit (CBS) from augmented cc-pVDZ and cc-pVTZ energies. The KiSThelP program [30] was used for the kinetic calculations.

Results and Discussion

Figures 1 and 2 present the equilibrium geometries involved in the H₂O- and H₂SO₃-catalyzed reactions from B3LYP/cc-pV(T+d)Z and MP2/cc-pV(T+d)Z calculations. It is clear that the geometric parameters from B3LYP calculations are in good agreement with those from MP2 calculations. Overall, the deviations between the two methods are within 0.04 Å in hydrogen-bond lengths and 2.1° in hydrogen-bond angles. The results confirm that B3LYP/cc-pV(T+d)Z method gives an adequate description of the hydrogen bonds for the systems considered in this work. For simplicity, only the B3LYP geometries will be quoted in the following discussions.

H₂O-catalyzed reaction

The catalytic effect of a single water molecule on the gaseous hydrolysis reaction of SO₂ was studied previously with quantum chemical methods [9,16,18]. In the present study, we recalculated the reaction with a single H₂O as the catalyst, as well as the reaction without a catalyst, in order to compare consistently with the new reactions to be considered in the study. The potential energy surface (PES) profiles for the naked reaction and for the reactions with the catalysis of a single water molecule, along with the geometries of the stationary points on PES are drawn in Figure 1.

Our calculations have reproduced the catalytic effect of a single water molecule as reported previously. Compared with the naked reaction, the water molecule contributes to a reduction of 14.5 kcal/mol for the energy barrier, which is in good agreement with the previous reported values in the range of 12.5 ~ 15.4 kcal/mol [9, 16, 18].

H₂SO₃-catalyzed reaction

Figure 2 shows a schematic PES along with the geometries of the stationary points. The hydrolysis reaction of SO₂ in the presence of sulfurous acid is initiated from a bimolecular collision, either between SO₂-H₂O and H₂SO₃ or between H₂SO₃-H₂O and SO₂, similar to other three body reactions [19, 31-34]. Both channels involve the reactant complex SO₂-H₂O-H₂SO₃. The formation of reactant complex SO₂-H₂O-H₂SO₃, is 7.6 kcal/mol more exothermic than that of the corresponding reactant complex for the water-catalyzed reaction. The formation of the cage-like hydrogen bonding networks is responsible for the added stability in the SO₂-H₂O-H₂SO₃ complex. As seen in Figure 2,

the reaction proceeds from $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$ to the dimeric sulfurous acid $(\text{H}_2\text{SO}_3)_2$ through the transition state TS_{SA} . The pre-existing H_2SO_3 acts as a proton transmitter via a cage-like ring for the double proton transfer process. The reaction mechanism is similar to that for the water-catalyzed reaction. With H_2SO_3 , however, the energy barrier of the reaction is merely 5.5 kcal/mol. The barrier is dramatically reduced from the naked reaction ($\Delta E_{\text{barrier}} = 32.0$ kcal/mol) and from the H_2O -catalyzed reaction ($\Delta E_{\text{barrier}} = 17.5$ kcal/mol). It is worth mentioning that H_2SO_3 is even more effective than a union of five water molecules in reducing the energy barrier for the hydrolysis of SO_2 . In addition, the pre-existing H_2SO_3 is also effective in stabilizing the product, as the product complex $(\text{H}_2\text{SO}_3)_2$ is thermodynamically more stable than $\text{H}_2\text{SO}_3\text{-H}_2\text{O}$. In conclusion, sulfurous acid is a superior catalyst for the hydrolysis of SO_2 .

The catalytic effect of H_2SO_3

The high catalytic efficiency of H_2SO_3 may reside in the increased stabilization in the reactant complexes, which facilitates the proton transfer in the hydrolysis process. The stability of the reactant complexes are enhanced in the order of $\text{SO}_2\text{-H}_2\text{O}$, $\text{SO}_2\text{-(H}_2\text{O)}_2$ and $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$. The enhanced stability may be attributed to the favorable hydrogen bonding and certain geometric arrangement. The number of hydrogen bonds increases as a catalyst such as H_2O or H_2SO_3 , is added in the reactant complex. In addition, it is clear from Figure 3 that the quasi hexagonal hydrogen bonding networks in $\text{SO}_2\text{-(H}_2\text{O)}_2$ and $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$, respectively, have reduced tension from the quadrilateral network of $\text{SO}_2\text{-H}_2\text{O}$. It is worth mentioning that the transition state has a similar geometry as the

corresponding reactant complex. The superior catalytic effect of H_2SO_3 may originate from the hydrogen bond networks of the reactant complexes. A linear hydrogen bond $\text{X-H}\cdots\text{Y}$ (180.0°) is the most favorable, and any deviation from linearity decreases the stability as a result of poor delocalization of electrons from the donor (Y) to the acceptor (X) atom [31]. The delocalization of electrons for the hydrogen bond facilitates the proton transfer to form a covalent H-Y bond. Figure 3 shows that all hydrogen bonds in $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$ are closer to linearity than those in $\text{SO}_2\text{-(H}_2\text{O)}_2$. For example, two of the hydrogen bonds in $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$ have bond angles of 168.5° and 169.5° , which are in contrast to 144.3° and 162.6° in $\text{SO}_2\text{-(H}_2\text{O)}_2$. In addition, the stronger hydrogen bonds or the better delocalization of electrons are reflected by the shorter hydrogen bond lengths in $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$ than those in $\text{SO}_2\text{-(H}_2\text{O)}_2$.

In order to further understand the physical origin of high catalytic efficiency of sulfurous acid, we conducted the NBO analysis of the donor-acceptor interactions in the reactant complexes $\text{SO}_2\text{-H}_2\text{O}$, $\text{SO}_2\text{-(H}_2\text{O)}_2$, and $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$, respectively. Figure 4 shows three pairs of interacting molecular orbitals: the O_a lone pair orbital and the S-O antibonding orbital ($\text{LP}(\text{O}_a) \rightarrow \pi^*(\text{S-O})$), the O_b lone pair orbital and $\text{O}_a\text{-H}$ antibonding orbital ($\text{LP}(\text{O}_b) \rightarrow \delta^*(\text{O}_a\text{-H})$), and the O_c lone pair orbital and O-H_d antibonding orbital ($\text{LP}(\text{O}_c) \rightarrow \delta^*(\text{O-H}_d)$). Figure 4 shows the second-order stabilization energies which reflect the strength of the donor-acceptor interactions. The stabilization energies of the $\text{LP}(\text{O}_a) \rightarrow \pi^*(\text{S-O})$ interactions in $\text{SO}_2\text{-H}_2\text{O}$, $\text{SO}_2\text{-(H}_2\text{O)}_2$, and $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$ are 1.5, 3.2, and 5.2 kcal/mol, respectively. The energy values are in the order of $\text{SO}_2\text{-H}_2\text{O} <$

$\text{SO}_2\text{-(H}_2\text{O)}_2 < \text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$. The ordering of the stabilization energies is reflected by the trend in the orbital overlaps (see Figure 4), and is consistent with the intermolecular $\text{S}\cdots\text{O}_a$ bond distances of the three reactant complexes (see Figure 3). In the meanwhile, the $\text{LP}(\text{O}_b)\rightarrow\delta^*(\text{O}_a\text{-H})$ and $\text{LP}(\text{O}_c)\rightarrow\delta^*(\text{O-H}_d)$ interactions in $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$ (14.4, 8.2 kcal/mol) are also stronger than those in $\text{SO}_2\text{-(H}_2\text{O)}_2$ (13.9, 1.6 kcal/mol). The enhancement of the $\text{LP}(\text{O}_b)\rightarrow\delta^*(\text{O}_a\text{-H})$ and $\text{LP}(\text{O}_c)\rightarrow\delta^*(\text{O-H}_d)$ interactions is also consistent with the shortening of the $\text{O}_b\cdots\text{H-O}_a$ and $\text{O}_c\cdots\text{H}_d\text{-O}$ hydrogen-bond distances. On the other hand, the $\text{O}_a\text{-H}$ and O-H_d covalent bonds are weakened as the hydrogen bonds are strengthened, and ultimately the cleavage of $\text{O}_a\text{-H}$ and O-H_d bonds is facilitated to promote the proton transfer in the hydrolysis processes. In conclusion, the presence of sulfurous acid promotes the formation of the S-O_a bond and the transfer of a proton in the hydrolysis reaction. Sulfurous acid is shown more effective than a water molecule as a catalyst in promoting the hydrolysis reaction of SO_2 .

Kinetics analysis

The hydrolysis reaction of SO_2 in the presence of H_2O or H_2SO_3 as a catalyst can be characterized by Eq. 1,

Applying the steady-state approximation for the reactant complexes $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$ and $\text{SO}_2\text{-(H}_2\text{O)}_2$, and assuming that reactant complexes are in equilibrium with the reactants, the overall rate constant for this reaction can be expressed as

$$k_{tot} = \frac{k_1 k_{uni}}{k_{-1} + k_{uni}} \quad (2)$$

If $k_{uni} \ll k_{-1}$, the rate constant is expressed as

$$k_{tot} = \frac{k_1 k_{uni}}{k_{-1} + k_{uni}} = K_{eq} k_{uni} \quad (3)$$

where K_{eq} and k_{uni} are the equilibrium constants for the formation of reactant complex and the rate constant for the unimolecular isomerization, respectively. K_{eq} can be obtained by Eq. 4,

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{Q_{RC}}{Q_{reactants}} \exp\left(-\frac{E_{RC} - E_{reactants}}{RT}\right) \quad (4)$$

The unimolecular rate constant k_{uni} was calculated using the transition state theory (TST) with Wigner Tunneling corrections [35], as by Eq. 5,

$$k_{uni} = \Gamma \frac{k_B T}{h} \frac{Q_{TS}}{Q_{RC}} \exp\left(-\frac{E_{TS} - E_{RC}}{RT}\right) \quad (5)$$

In Eqs. 4 and 5, Q_{RC} , $Q_{reactants}$ and Q_{TS} are the total partition functions of the reactant complexes, reactants, and the transition states, respectively. E_{RC} , $E_{reactants}$, E_{TS} denote the total energies of the reactant complexes, reactants and transition states, respectively. Γ is the corresponding Wigner tunneling correction factor at temperature T , which was estimated by Eq. 6 [36],

$$\Gamma = 1 + \frac{1}{24} \left(\frac{h\nu^\ddagger}{k_B T} \right)^2 \quad (6)$$

where $\nu^\ddagger$ is the imaginary frequency of the transition state. Note that k_{-1} is much larger than k_{uni} for the two reaction channels of H₂O-catalyzed reaction and the SO₂ + H₂SO₃-H₂O reaction. As a result, the total rate constant is obtained by Eq. 3, i.e., $k_{\text{tot}} = K_{\text{eq}}k_{\text{uni}}$. However, in the case of the SO₂-H₂O+H₂SO₃ reaction, k_{uni} is larger than k_{-1} , and the overall rate constant is thus evaluated according to Eq. 2, in which k_I is evaluated by hard-sphere collision theory and k_{-I} is obtained from the expression $k_{-1} = k_1 / K_{\text{eq}}$. The values of the calculated rate constants for the H₂O-catalyzed and H₂SO₃-catalyzed reactions over the temperature range of 200 - 320 K are listed in Table 1. The kinetic data demonstrate that the two channels for the H₂O-catalyzed reaction have similar rate constants, about $10^{-25} \sim 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the temperature range of 200~320 K. In the H₂SO₃-assisted reaction, the reaction of H₂SO₃ with SO₂-H₂O is dominant, with the rate constant varying from 3.41×10^{-10} to 2.3×10^{-10} under the temperature range of 200 - 320 K. From Table 1, it is clear that the rate constants for the H₂O-assisted reaction are far slower than the H₂SO₃-catalyzed reaction, as the rate constants are about 15~12 orders of magnitude slower than that of SO₂-H₂O + H₂SO₃ reaction. In fact, sulfurous acid is kinetically unstable under the atmospheric conditions, which restricts the significance of the title reaction in the gas phase. However, given the importance of SO₂ and H₂SO₃ in contributing the aerosol formation and particle growth, the H₂SO₃-assisted reaction is important on surfaces of particles and in the bulk-phase droplets. In addition, in an

aqueous or surface environment, the produced sulfurous acid with oxygen atoms and hydrogen atoms serving as either proton donor or acceptor of hydrogen bonds are capable of forming hydrogen bonds with other aerosol contributors such as water, sulfuric acid or VOC(s), to provide a precursor capable of oligomers, which will provide a potential implication for the particle growth.

Conclusion

Sulfurous acid is shown to have more effective catalytic roles than water molecule in the gaseous hydrolysis reaction of SO_2 . In the presence of H_2SO_3 , the energy barrier is calculated to be only 5.5 kcal/mol, which is a significant drop of more than 20 kcal/mol relative to the naked reaction. The enhanced stability is attributed to the favorable hydrogen bonding and other geometric properties. In addition, the NBO analysis shows enhanced second-order stabilization energies from the donor-acceptor intermolecular interactions of the reactant complexes in the presence of sulfurous acid with respect to the reactant complexes involving only additional water molecules, a further demonstration of the strong catalytic effect of H_2SO_3 . The kinetic calculations indicate that the hydrolysis reaction of SO_2 is an autocatalytic reaction. The results of the present study may have significant implications on a detailed chemical mechanism for the formation of atmospheric sulfate aerosols.

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References

- [1] C. N. Hewitt, The atmospheric chemistry of sulphur and nitrogen in power station plumes, *Atmos. Environ.* 35 (2001) 1155-1170.
- [2] R. Zhang, A. Khalizov, L. Wang, M. Hu, W. Xu, Nucleation and growth of nanoparticles in the atmosphere, *Chem. Rev.* 112 (2012) 1957-2011.
- [3] Y. Zhou, E. P. Rosen, H. Zhang, W. Rattanavaraha, W. Wang, R.M. Kamens, SO₂ oxidation and nucleation studies at near-atmospheric conditions in outdoor smog chamber, *Environ. Chem.* 10 (2013) 210-220.
- [4] T. Kurten, J. R. Lane, S. Jorgensen, H.G. Kjaergaard, A Computational study of the oxidation of SO₂ to SO₃ by gas-phase organic oxidants, *J. Phys. Chem. A* 115 (2011) 8669-8681.
- [5] Y.-Y. Zhao, Y. Zeng Eddy, X.-H. Zhang, F.-M. Tao, Theoretical study of small Water clusters of sulfur dioxide, *Chin. J. Struct. Chem.* 29 (2010) 499-508.

- [6] R. Steudel, Y. Steudel, Sulfur dioxide and water: structures and energies of the hydrated species $\text{SO}_2 \cdot n\text{H}_2\text{O}$, $[\text{HSO}_3]^- \cdot n\text{H}_2\text{O}$, $[\text{SO}_3\text{H}]^- \cdot n\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_3 \cdot n\text{H}_2\text{O}$ ($n = 0-8$), *Eur. J. Inorg. Chem.* 10 (2009) 1393-1405.
- [7] S.-d. Jiang, Z.-h. Wang, J.-h. Zhou, Z.-c. Wen, K.-f. Cen, A quantum chemistry study on reaction mechanisms of SO_2 with O_3 and H_2O_2 , *J. Zhejiang Univ. Sci. A* 10 (2009) 1327-1333.
- [8] T. L. Tarbuck, G. L. Richmond, Adsorption and reaction of CO_2 and SO_2 at a water surface, *J. Am. Chem. Soc.* 128 (2006) 3256-3267.
- [9] J. Liu, S. Fang, W. Liu, M. Wang, F.-M. Tao, J.-y. Liu, Mechanism of the gaseous hydrolysis reaction of SO_2 : effects of NH_3 versus H_2O , *J. Phys. Chem. A* 119 (2015) 102-111.
- [10] E. S. Shamay, K. E. Johnson, G. L. Richmond, Dancing on water: the choreography of sulfur dioxide adsorption to aqueous surfaces, *J. Phys. Chem. C*, 115 (2011) 25304-25314.
- [11] S. T. Moin, L. H. V. Lim, T. S. Hofer, B. R. Randolph, B. M. Rode, Sulfur dioxide in water: structure and dynamics studied by an ab initio quantum mechanical charge field molecular dynamics simulation, *Inorg. Chem.* 50 (2011) 3379-3386.
- [12] M. Baer, C.J. Mundy, T.-M. Chang, F.-M. Tao, L.X. Dang, Interpreting vibrational sum-frequency spectra of sulfur dioxide at the air/water interface: A comprehensive molecular dynamics study, *J. Phys. Chem. B* 114 (2010) 7245-7249.
- [13] T. L. Tarbuck, G. L. Richmond, $\text{SO}_2\text{:H}_2\text{O}$ surface complex found at the vapor/water

interface, J. Am. Chem. Soc. 127 (2005) 16806-16807.

[14] T. M. Townsend, A. Allanic, C. Noonan, J.R. Sodeau, Characterization of sulfurous acid, sulfite, and bisulfite aerosol systems, J. Phys. Chem. A 116 (2012) 4035-4046.

[15] J. Herb, Y. Xu, F. Yu, A.B. Nadykto, Large hydrogen-bonded pre-nucleation $(\text{HSO}_4^-)(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_k$ and $(\text{HSO}_4^-)(\text{NH}_3)(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_k$ clusters in the earth's atmosphere, J. Phys. Chem. A 117 (2013) 133-152.

[16] W.-K. Li, M. L. McKee, Theoretical study of OH and H₂O addition to SO₂, J. Phys. Chem. A 101 (1997) 9778-9782.

[17] E. Bishenden, D. Donaldson, Ab initio study of SO₂ + H₂O, J. Phys. Chem. A, 102 (1998) 4638-4642

[18] T. Loerting, K. R. Liedl, Water-mediated proton transfer: A mechanistic investigation on the example of the hydration of sulfur oxides, J. Phys. Chem. A 105 (2001) 5137-5145.

[19] M. Torrent-Sucarrat, J. S. Francisco, J. M. Anglada, Sulfuric acid as autocatalyst in the formation of sulfuric acid, J. Am. Chem. Soc. 134 (2012) 20632-20644.

[20] M. K. Hazra, J. S. Francisco, A. Sinha, Hydrolysis of glyoxal in water-restricted environments: formation of organic aerosol precursors through formic acid catalysis, J. Phys. Chem. A 118 (2014) 4095-4105.

[21] D. Suelzle, M. Verhoeven, J. K. Terlouw, H. Schwarz, Generation and characterization of sulfurous acid (H₂SO₃) and of its radical cation as stable species in the gas phase, Angew. Chem., Int. Ed. Engl., 27 (1988) 1533-1534.

- [22] A. E. Voegele, C. S. Tautermann, T. Loerting, A. Hallbrucker, E. Mayer, K.R. Liedl, About the stability of sulfurous acid (H_2SO_3) and its dimer, *Chem.-Eur. J.* 8 (2002) 5644-5651.
- [23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. et al., Gaussian 09, revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.
- [24] T. Kurten, M. R. Sundberg, H. Vehkamäki, M. Noppel, J. Blomqvist, M. Kulmala, Ab initio and density functional theory reinvestigation of gas-phase sulfuric acid monohydrate and ammonium hydrogen sulfate, *J. Phys. Chem. A*, 110 (2006) 7178-7188.
- [25] B. Long, Z.-w. Long, Y.-b. Wang, X.-f. Tan, Y.-h. Han, C.-y. Long, S.-j. Qin, W.-j. Zhang, Formic Acid Catalyzed Gas-Phase Reaction of H_2O with SO_3 and the Reverse Reaction: A Theoretical Study, *Chemphyschem*, 13 (2012) 323-329.
- [26] W. Zhang, B. Du, Z. Qin, Catalytic Effect of Water, Formic Acid, or Sulfuric Acid on the Reaction of Formaldehyde with OH Radicals, *J. Phys. Chem. A*, 118 (2014) 4797-4807.
- [27] D. E. Husar, B. Temelso, A. L. Ashworth, G. C. Shields, Hydration of the Bisulfate Ion: Atmospheric Implications, *J. Phys. Chem. A*, 116 (2012) 5151-5163.
- [28] R. J. Buszek, M. Torrent-Sucarrat, J.M. Anglada, J.S. Francisco, Effects of a Single Water Molecule on the $\text{OH}+\text{H}_2\text{O}_2$ Reaction, *J. Phys. Chem. A*, 116 (2012) 5821-5829.
- [29] K. E. Riley, P. Hobza, Assessment of the MP2 method, along with several basis sets, for the computation of interaction energies of biologically relevant hydrogen bonded and

dispersion bound complexes, *J. Phys. Chem. A*, 111 (2007) 8257-8263.

[30] S. Canneaux, F. Bohr, E. Henon, KiSThelP: A program to predict thermodynamic properties and rate constants from quantum chemistry results, *J. Comput. Chem.* 35 (2014) 82-93.

[31] W. Zhang, B. Du, Z. Qin, Catalytic effect of water, formic acid, or sulfuric acid on the reaction of formaldehyde with OH radicals, *J. Phys. Chem. A* 118 (2014) 4797-4807.

[32] B. Du, W. Zhang, Kinetics and mechanism of the water-assisted reaction of NCO with CH₃OH: A quantum chemical study, *Comput. Theor. Chem.* 1044 (2014) 55-61.

[33] R. J. Buszek, J. R. Barker, J. S. Francisco, Water effect on the OH plus HCl reaction, *J. Phys. Chem. A* 116 (2012) 4712-4719.

[34] H. A. Rypkema, A. Sinha, J. S. Francisco, Carboxylic acid catalyzed hydration of acetaldehyde, *J. Phys. Chem. A* 119 (2015) 4581-4588.

[35] K. A. Holbrook, M.J. Pilling, S.H. Robertson, P.J. Robinson, *Unimolecular Reactions*, second ed., Wiley, New York, 1996.

[36] E. Wigner, Calculation of the rate of elementary association reactions, *J. Chem. Phys.* 5 (1937) 720-725.

Figure Captions

Figure 1. Schematic potential energy surface for the $\text{SO}_2 + \text{H}_2\text{O}$, and $\text{SO}_2 + 2\text{H}_2\text{O}$ reactions. The corresponding geometries have been obtained at B3LYP/cc-pV(T+d)Z and MP2/cc-pV(T+d)Z (in brackets) level of theory. The energy profile has been calculated at the CCSD(T)/CBS//B3LYP /cc-pV(T+d)Z +ZPE level of theory (bond distances in angstrom, angles in degree).

Figure 2. Schematic potential energy surface for the $\text{SO}_2 + \text{H}_2\text{O} + \text{H}_2\text{SO}_3$ reaction. The corresponding geometries have been obtained at B3LYP/cc-pV(T+d)Z and MP2/cc-pV(T+d)Z (in brackets) level of theory. The energy profile has been calculated at the CCSD(T)/CBS// B3LYP /cc-pV(T+d)Z +ZPE level of theory (bond distances in angstrom, angles in degree).

Figure 3. Structures of reactant complexes $\text{SO}_2\text{-H}_2\text{O}$, $\text{SO}_2\text{-(H}_2\text{O)}_2$ and $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$ obtained at B3LYP /cc-pV(T+d)Z level of theory (bond distances in angstrom, angles in degree).

Figure 4. NBO overlaps of donor-acceptor interactions in complexes $\text{SO}_2\text{-H}_2\text{O}$, $\text{SO}_2\text{-(H}_2\text{O)}_2$ and $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_3$, respectively ($0.05e/\text{\AA}^3$ isosurface from B3LYP /cc-pV(T+d)Z model chemistry). The second-order stabilization energies are given.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Table 1. Values of the equilibrium constant (K_{eq} , in molecules cm^{-3}), collision rate (k_1 , in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), unimolecular rate constant (k_{uni} , s^{-1}), and overall rate constant (k_{tot} , in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reactions of $\text{SO}_2\text{-H}_2\text{O} + \text{H}_2\text{O}$, $\text{SO}_2 + (\text{H}_2\text{O})_2$, $\text{SO}_2\text{-H}_2\text{O} + \text{H}_2\text{SO}_3$ and $\text{SO}_2 + \text{H}_2\text{SO}_3\text{-H}_2\text{O}$ at the temperatures $T = 200\text{-}320 \text{ K}$.

Reaction		T(K)							
		200	220	240	260	280	298	300	320
$\text{SO}_2\text{-H}_2\text{O} + \text{H}_2\text{O}$	K_{eq}	2.16×10^{-18}	4.41×10^{-19}	1.18×10^{-19}	3.94×10^{-20}	1.55×10^{-20}	7.51×10^{-21}	6.79×10^{-21}	3.50×10^{-21}
	k_{uni}	4.66×10^{-8}	1.90×10^{-6}	4.06×10^{-5}	5.32×10^{-4}	4.75×10^{-3}	2.63×10^{-2}	3.14×10^{-2}	1.62×10^{-1}
	k_{tot}	1.01×10^{-25}	8.35×10^{-25}	4.80×10^{-24}	2.09×10^{-23}	7.36×10^{-23}	1.97×10^{-22}	2.19×10^{-22}	5.67×10^{-22}
$\text{SO}_2 + (\text{H}_2\text{O})_2$	K_{eq}	1.75×10^{-18}	3.93×10^{-19}	1.15×10^{-19}	4.13×10^{-20}	1.74×10^{-20}	8.90×10^{-21}	8.31×10^{-21}	4.41×10^{-21}
	k_{uni}	4.66×10^{-8}	1.90×10^{-6}	4.06×10^{-5}	5.32×10^{-4}	4.75×10^{-3}	2.63×10^{-2}	3.14×10^{-2}	1.62×10^{-1}
	k_{tot}	8.17×10^{-26}	7.45×10^{-25}	4.66×10^{-24}	2.19×10^{-23}	8.26×10^{-23}	2.34×10^{-22}	2.61×10^{-22}	7.15×10^{-22}
$\text{SO}_2\text{-H}_2\text{O} + \text{H}_2\text{SO}_3$	K_{eq}	9.75×10^{-12}	3.56×10^{-13}	2.28×10^{-14}	2.25×10^{-15}	3.12×10^{-16}	6.66×10^{-17}	5.68×10^{-17}	1.29×10^{-17}
	k_1	3.41×10^{-10}	3.57×10^{-10}	3.73×10^{-10}	3.89×10^{-10}	4.03×10^{-10}	4.16×10^{-10}	4.17×10^{-10}	4.31×10^{-10}
	k_{-1}	3.50×10^1	1.00×10^3	1.64×10^4	1.72×10^5	1.29×10^6	6.24×10^6	7.35×10^6	3.34×10^7
	k_{uni}	5.33×10^5	1.56×10^6	3.75×10^6	7.79×10^6	1.44×10^7	2.32×10^7	2.44×10^7	3.84×10^7
	k_{tot}	3.41×10^{-10}	3.57×10^{-10}	3.72×10^{-10}	3.8×10^{-10}	3.7×10^{-10}	3.28×10^{-10}	3.21×10^{-10}	2.3×10^{-10}
$\text{SO}_2 + \text{H}_2\text{SO}_3\text{-H}_2\text{O}$	K_{eq}	2.65×10^{-21}	4.64×10^{-22}	1.10×10^{-22}	3.30×10^{-23}	1.19×10^{-23}	5.36×10^{-24}	4.94×10^{-24}	2.32×10^{-24}
	k_1	4.10×10^{-10}	4.3×10^{-10}	4.49×10^{-10}	4.68×10^{-10}	4.85×10^{-10}	5.01×10^{-10}	5.02×10^{-10}	5.19×10^{-10}
	k_{-1}	1.55×10^{11}	9.27×10^{11}	4.08×10^{12}	1.42×10^{13}	4.09×10^{13}	9.33×10^{13}	1.02×10^{14}	2.24×10^{14}
	k_{uni}	5.33×10^5	1.56×10^6	3.75×10^6	7.79×10^6	1.44×10^7	2.32×10^7	2.44×10^7	3.84×10^7
	k_{tot}	1.41×10^{-15}	7.22×10^{-16}	4.13×10^{-16}	2.57×10^{-16}	1.71×10^{-16}	1.25×10^{-16}	1.21×10^{-16}	8.89×10^{-17}