Understanding the oxidation mechanism of methanesulfinic acid by ozone in the atmosphere

Guochun Lv¹, Chenxi Zhang² & Xiaomin Sun¹

Methanesulfinic acid (MSIA) is an important intermediate in the oxidation of dimethyl sulfide (DMS) in the marine boundary layer. The oxidation of MSIA by ozone in the gas phase to form methanesulfonic acid (MSA) was investigated using theoretical calculations in this paper. Three pathways can be found for the reaction of MSIA with ozone. The highest energy barrier is 13.02 kcal mol⁻¹ in the most favorable pathway. By comparing the reaction rate of MSIA + O₃ with that of MSIA + OH, it can be concluded that the oxidation of MSIA by O₃ to form MSA is of minor significance relative to its oxidation by OH radical in the gas phase. This study can provide some information for the theoretical and experimental studies in the significantly heterogeneous and aqueous-phase oxidation of MSIA by O₃.

Dimethyl sulfide (CH₃SCH₃, DMS) emitted by oceans is the main natural source of S-containing compound¹–³. The oxidation of dimethyl sulfide is considered of great importance in the marine boundary layer, because the main oxidation products, methanesulfonic acid (MSA) and sulfuric acid, can contribute to the formation of non-sea salt sulfate (nss-SO₄²⁻) aerosol, which can act as the cloud condensation nuclei and can promote the formation of marine stratus clouds⁴–⁶. The reactions with OH radical during the day time⁵,⁷ and with NO₃ radical⁵,⁸,⁹ in the night initiate the DMS oxidation, and these reactions can be classified as adduct reactions and abstraction reactions. Numerous intermediates such as dimethyl sulfoxide (CH₃SOCH₃: DMSO), methanesulfinic acid (CH₃S(O)OH: MSIA), dimethyl sulfone (CH₃SO₂CH₃: DMSO₂) and CH₃SOₓ(x = 0 – 3) radicals can be formed through the subsequent reaction⁵,¹⁰. The branching and many intermediates indicate that the DMS oxidation mechanism is complicated. Therefore, although a number of studies have worked on this area⁵,⁶,¹⁰–¹⁹, the oxidation mechanism still cannot be understood completely.

MSIA, an important intermediate in the process of DMS oxidation, is formed through the OH radical addition to DMSO with the elimination of CH₃ radical. Using LFP-TDLAS technique, Urbanski et al.²⁰ have proved that the reaction of DMSO with OH radical can form MSIA and CH₃ radical in high yield. The same conclusion also is obtained in subsequent researches including laboratory studies and quantum chemistry calculations²¹–²⁷. Barnes et al.⁵ also concluded that the MSIA is an important DMS secondary oxidation product through OH radical oxidation of DMSO in their review paper.

In addition to the formation of MSIA, their further oxidation also needs to be focused on. The MSIA is soluble in water, and its Henry’s law coefficient is higher than that of DMSO and lower than that of MSA⁵. Thus, the reaction involving MSIA can occur in gas phase, in aqueous phase and on the surface of aqueous atmospheric media. The OH radical and O₃ are thought as the main oxidants in oxidizing the MSIA⁵,¹⁸,²⁸,²⁹. The ab initio and density functional theory (DFT) calculations are useful tools for mechanism research. Tian et al.²⁸ have used DFT method to study the reaction of OH radical with methanesulfinic acid (MSIA). They found that the association-decomposition reaction (MSIA + OH → adduct → CH₃SO + H₂O → CH₃ + SO₂ + H₂O) is more favorable than direct CH₃ radical-abstraction reaction (MSIA + OH → adduct → CH₃ + H₂SO₃ → CH₃ + SO₂ + H₂O). In another theoretical study²⁹, the author also found the two kinds of reaction mechanism, and concluded that the formation channel of CH₃ radical and H₂SO₃ should not be negligible because more than 30% of MSIA react with OH via this channel within the range of 298–600 K.

For the oxidation of MSIA by O₃, some studies have considered it. Enami et al.¹⁸ have performed the experiment to investigate the OH radical-initiated oxidation of DMSO on the air-water interface. In their work, they have concluded that the MSIA (or dissociated methanesulfinic acid) formed by the reaction OH + DMSO can further be oxidized by O₃ or OH + O₂, producing the MSA. In the modeling study of Hoffmann et al.⁶, the reaction

¹Environment Research Institute, Shandong University, Jinan, 250100, China. ²College of Biological and Environmental Engineering, Binzhou University, Binzhou, 256600, China. Correspondence and requests for materials should be addressed to X.S. (email: sxmwch@sdu.edu.cn)
of MSIA and dissociated methanesulfinic acid with O₃ leading to MSA in the aqueous phase contribute in total 42% to MSIA degradation. However, to our knowledge, the mechanism of the reaction MSIA + O₃ has not been considered by the theoretical study.

In this paper, we will investigate the reaction of MSIA with ozone using DFT method and ab initio method. To find the most favorable pathway, the reaction energy barrier in different pathways is calculated and compared. We also compared rate constants of the MSIA + O₃ reaction with that of the MSIA + OH reaction, so as to evaluate their atmospheric importance.

Results and Discussion

The reaction of MSIA with O₃ Figure 1 shows the potential energy profile for MSIA + O₃ reaction. The corresponding structures of reactants, intermediates, transition states and products are drawn in Fig. 2. The thermodynamic data for the reaction MSIA with O₃ are summarized in Supplementary Information (Table S1). For MSIA, as shown in Fig. 1 and Fig. 2, two conformers, called as MSIA-I and MSIA-II, can be found. The MSIA-I can transform into MSIA-II with a transition state (energy barrier of 1.00 kcal mol⁻¹), which is depicted in Supplementary Fig. S1. Two pathways are identified in the reaction of MSIA-I and O₃ (path 1: starting from C1-1, path 2: from C2-1 to MSA + O₂). In path 1, as MSIA-I approaches the O₃ molecule, the complex C1-1 can be
formed. The C1-1 is stabilized by 4.60 kcal mol\(^{-1}\) with respect to MAIA-I + O\(_3\). The complex C1-1 is held together by two hydrogen bonds and one van der Waals interaction. As shown in Fig. 2, the hydrogen atom of MSIA-I interacts with the two oxygen atoms of ozone to form the two hydrogen bonds, whereas sulfur atom is involved in the formation of van der Waals interaction with an oxygen atom of ozone. After the formation of the complex C1-1, the reaction proceeds via a transition state (TS1-1) with the energy barrier of 13.02 kcal mol\(^{-1}\) related to C1-1 to form the C1-2. In the complex C1-2, one oxygen atom has bonded with sulfur atom. The subsequent transformation from C1-2 to C1-3 corresponds to the hydrogen atom transfer process. The energy barrier with the transition state TS1-2 is 3.43 kcal mol\(^{-1}\). For C1-3, it is obviously more stable than C1-2 because its energy is lower 44.97 kcal mol\(^{-1}\) than that of C1-2. The result indicates that the effect of hydrogen atom transfer process is to adjust the structure so as to increase the stability of complex. The C1-3 passes through a transition state TS1-3 with energy barrier of 11.87 kcal mol\(^{-1}\) to form the complex consisting of MSA with \(^1\)O\(_3\) (C1-4), which is lie 3.74 kcal mol\(^{-1}\) below the final product (MSA + \(^1\)O\(_3\)).

In path 2, the reaction begins with the formation of complex C2-1 with the binding energy of 2.98 kcal mol\(^{-1}\). The C2-1 involves one van der Waals interaction between an oxygen atom of MSIA-I and an oxygen atom of ozone. The complex C2-2 can be formed through a transition state TS2-1 with the energy barrier of 36.89 kcal mol\(^{-1}\). Then, the C2-2 transform to the complex (C2-3) via a transition state TS2-2 with the energy barrier of 5.53 kcal mol\(^{-1}\). The TS2-2 involves the breaking of O-O bond and simultaneously the formation of O-S bond. The C2-3 is held together by one van der Waals interaction between an oxygen atom of methanesulfonic acid (MSA) and an oxygen atom of \(^1\)O\(_3\), and is expected to be stable toward break up to MSA + \(^1\)O\(_3\).

In the reaction between MSIA-I and O\(_3\), only one pathway (named as path 3) can be found. As the similar structure between MSIA-I and MSIA-II, its sequence of steps C3-1 \(\rightarrow\) TS3-1 \(\rightarrow\) C3-2, has the same feature as the sequence C2-1 \(\rightarrow\) TS2-1 \(\rightarrow\) C2-2. The binding energy of C3-1 relative to MSIA-II and ozone is 3.01 kcal mol\(^{-1}\). The barrier height in the process for path 3 is 38.44 kcal mol\(^{-1}\). After the complex (C3-2) formation, the reaction proceeds through transforming the dihedral angle O\(_3\)SO\(_2\)H\(_2\) to C2-2. The transformation process needs to go through a transition state TS3-2, and overcome the energy barrier of 0.95 kcal mol\(^{-1}\). Then the reaction goes on along the sequence of steps C2-2 \(\rightarrow\) TS2-2 \(\rightarrow\) C2-3.

To sum up, there are three pathways in the reaction of methanesulfonic acid (MSIA) with ozone. For path 2 and path 3, the initial step needs to overcome the energy barrier of around 40 kcal mol\(^{-1}\), and the energy for most of complexes and transition states is 30 kcal mol\(^{-1}\) higher than that of reactants. All barrier heights in path 1 do not exceed 14 kcal mol\(^{-1}\), and only the energy of TS1-1 is 8.42 kcal mol\(^{-1}\) higher than that of reactants. Thus, the path 1 is the most favorable reaction pathway.

**Atmospheric implications.** To evaluate the importance of the methanesulfonic acid (MSA) formation by the reaction MSIA + O\(_3\), we will compare the rate between the reaction of MSIA with ozone and the reaction of MSIA with OH radical. Considering that the channel in which the CH\(_3\) radical and H\(_2\)SO\(_3\) are formed for about 1/3 for the reaction of MSIA with OH radical, we will compare this slower reaction channel with the favorable channel (path 1) in the reaction of MSIA with ozone.

Although the channel mentioned above in the reaction MSIA + OH has been reported, we also recalculate it at the CCSD(T)/aug-cc-pV(T+d)Z//M06-2X/aug-cc-pV(T+d)Z level to perform a fully legitimate comparison at the same level of theory. Figure 3 shows the potential energy and the structure of all stationary points for MSIA + OH reaction. The thermodynamic data are tabulated in Supplementary Information (Table S2). For this channel, we found that only MSIA-I can react with OH radical to form CH\(_3\) radical and H\(_2\)SO\(_3\), which is called as path 4 in this paper. The complex (C4-1) consisting of MSIA-I and OH radical is firstly formed with the binding energy of 7.49 kcal mol\(^{-1}\) in this channel, which agrees with the value (8.14 kcal mol\(^{-1}\)) calculated by González-García \textit{et al.}\textsuperscript{29}. Then, the C4-1 can evolve via TS4-1 with the energy barrier of 3.06 kcal mol\(^{-1}\), into the complex C4-2 whose energy is 10.61 kcal mol\(^{-1}\) lower than that of reactants. Once the C4-2 is formed, it can be
After converting the mix ratio to concentration in molecules cm$^{-2}$ at 298 K. The concentration of ozone in the troposphere is a few tens of parts per billion by volume (ppbv) in mix 298 K, whereas that of path 4 is transformed from 3.87 kcal mol$^{-1}$ to H$_2$SO$_3$. The barrier height in the transforma-
tion from C4-2 to products is only 0.87 kcal mol$^{-1}$ with OH radical.

As the multiple transition states occur in path 1 and path 4, the unified statistical model 30 is applied to calcu-
late $k_{uni}$.

$$\frac{1}{k_{uni}} = \frac{1}{k_{TS1-1}} + \frac{1}{k_{TS1-2}} + \frac{1}{k_{TS1-3}}$$

$$\frac{1}{k_{uni4}} = \frac{1}{k_{TS4-1}} + \frac{1}{k_{TS4-2}}$$

The relative rate for path 1 and path 4 can be obtained as follows:

$$\frac{v_1}{v_4} = \frac{K_{eq}k_{uni1}[MSIA-I][O_3]}{K_{eq}k_{uni4}[MSIA-I][OH]} = \frac{k_1}{k_4}[O_3]/[OH]$$

The rate constant $k_1$, $k_4$, and the ratio between $k_1$ and $k_4$ within the range of 220 K to 298 K are shown in Table 1. The corresponding $K_{eq}$, $k_{TS}$ and $k_{uni}$ are put into Supplementary Information (Table S3). As shown in Table 1, the rate constant of path 1 changes from 1.22 $\times$ 10$^{-14}$ to 1.79 $\times$ 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 220 K to 298 K. It is obvious from the ratio between $k_1$ and $k_4$ that the rate constant for the reaction MSIA + O$_3$ is about 10$^{13}$–10$^{16}$ times lower than that for the reaction MSIA + OH within the range of 220 K to 298 K. The concentration of ozone in the troposphere is a few tens of parts per billion by volume (ppbv) in mix ratio$^{31}$. After converting the mix ratio to concentration in molecules cm$^{-3}$ (1 ppbv = 2.50 $\times$ 10$^{11}$ molecules cm$^{-3}$ at 1 atm and 298 K), the concentration of ozone is $~$10$^{15}$ molecules cm$^{-3}$. The concentration of OH radical is $~$10$^{16}$ molecules cm$^{-3}$ in the troposphere$^{32}$. The concentration ratio between ozone and OH radical is about 10$^{5}$. Thus, considering the rate constants and concentration, the reaction rate of MSIA with ozone is 10$^{8}$–10$^{11}$ times slower than that of MSIA with OH within the range of 220–298 K. The conclusion can be drawn that the gas-phase oxid-
ation of MSIA by ozone to form SIA is of minor importance relative to the reaction of MSIA with OH radical. The result also indicates that the oxidation of DMSO through MSIA intermediate in the gas phase mainly produce SO$_2$ (subsequently converting to H$_2$SO$_3$).

Table 1. The rate constant (cm$^3$ molecule$^{-1}$ s$^{-1}$) and rate constant ratio for the reaction of MSIA with ozone and with OH radical.

| T (K) | 220 | 240 | 260 | 280 | 298 |
|-------|-----|-----|-----|-----|-----|
| $k_1$ | $1.22 \times 10^{-14}$ | $5.88 \times 10^{-14}$ | $2.40 \times 10^{-14}$ | $7.13 \times 10^{-14}$ | $1.79 \times 10^{-11}$ |
| $k_2$ | $3.87 \times 10^{-4}$ | $1.67 \times 10^{-4}$ | $8.21 \times 10^{-4}$ | $4.51 \times 10^{-4}$ | $2.84 \times 10^{-4}$ |
| $k_1/k_2$ | $3.15 \times 10^{-9}$ | $3.33 \times 10^{-9}$ | $2.73 \times 10^{-9}$ | $1.58 \times 10^{-9}$ | $6.31 \times 10^{-13}$ |
Conclusion
The oxidation of methanesulfinic acid (CH$_3$S(O)OH: MSIA) by ozone in the atmosphere has been investigated in this paper using the quantum chemical calculations. Two conformers of MSIA and the three reaction pathways can be found. The pathway (MSIA + O$_3$ → C1 → TS1 → C1-2 → TS1-2 → C1-3 → TS1-3 → C1-4 → MSA + 1O$_3$) is the most favorable because its highest energy barrier is 13.02 kcal mol$^{-1}$, which is evidently lower than those of another two pathways. By kinetics analysis, the oxidation of MSIA by ozone is 8–11 orders of magnitude slower than that by OH radical in the range of 220–298 K. The result indicates that the oxidation of MSIA by ozone is minor important in most cases relative to its oxidation by OH radical in the gas phase. Although it has shown the unimportance of the reaction in the gas phase, the study about the gas-phase oxidation of MSIA by ozone is meaningful because it can provide some information for the theoretical and experimental studies in the significantly heterogeneous and aqueous-phase oxidation of MSIA by ozone.

Methods
All geometric structures were optimized using M06-2X method with the aug-cc-pVTZ basis set for the H, C, O atoms and aug-cc-pV(T+d)Z basis set for the S atom (for simplification, the group of basis set was called as aug-cc-pV(T+d)Z). For aug-cc-pV(T+d)Z basis set, it is to add one additional high-exponent d function to aug-cc-pVTZ so as to obtain satisfactory convergence behavior. The revised basis set has been used in many sulfur-containing systems, and it has been proved that the aug-cc-pV(T+d)Z basis set can obtain more accurate results. After optimization, the frequency calculation was performed in order to confirm the energy minimum points and transition states, and to obtain the zero point energy correction and thermal correction. The intrinsic reaction coordinate (IRC) calculation also was carried out to ensure that the transition states connected with the corresponding reactants and products. For M06-2X method, the ultrafine integration grid was chosen to enhance calculation accuracy at reasonable additional cost. Single-point energies were refined using the CCSD(T) method with aug-cc-pV(T+d)Z basis set. To estimate the extent of nondynamic correlation, the T$_1$ diagnostic (computed using CCSD(T)/aug-cc-pV(T+d)Z) was used. If the value of T$_1$ is more than 0.04, the single reference wave function is considered to be unreliable. The value of T$_1$ calculated for all species in this paper (see Supplementary Table S4) is below 0.04, indicating that the CCSD(T) method is suitable. All quantum chemistry calculations were carried out with Gaussian 09 suit of software. The geometries were drawn using the CYLview software package.

For the reaction of MSIA with O$_3$, it involves in the O$_3$ biradical character and produced 1O$_2$, which makes the optimization process more complex. It is because for biradical stationary points the unrestricted formalism needs to be considered so as to obtain the stable broken-symmetry solution. Our strategy is firstly to use the restricted M06-2X method to gain all stationary points in these pathways, then to verify the stability of the wave function using the keyword stable in Gaussian. It can be found that there are two kinds of stationary points related to the unstable wave function: one is from the beginning of pathway, which consists of O$_3$-MSIA complex and the first transition state in the pathway; another is from the end of pathway, which composes of the last transition state and produced 1O$_2$-MSA complex. For the former, the reason of wave function instability is biradical character of O$_3$. We re-optimize these points by specifying the keyword stable = opt to generate a stable initial guess. After the geometries were optimized, the stability of wave function is tested again using the keyword stable. If the instability is found, it needs to repeat the optimized process until the wave function is stable. For the letter, the wave function instability is understandable because the ground state of O$_3$ is a triple state. Since the MSIA with O$_3$ react in the singlet potential energy surface, the produced O$_3$ is singlet state. Thus, in this case, the stationary points related to wave function instability do not need to re-optimize.

For the kinetics analysis, the electronic energies based on the CCSD(T)/aug-cc-pV(T+d)Z level of theory, while the partition functions obtained from the M06-2X/aug-cc-pV(T+d)Z level of theory. The conventional transition-state theory (TST) with Wigner tunneling correction was used to calculate the rate constants. All rate constants were calculated by using the KiSThelP program.

Data Availability
The data generated or analyzed during the current study are available from the corresponding author on reasonable request.

References
1. Andreae, M. O. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. *Mar. Chem.* **30**, 1–29 (1990).
2. Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J. & Stoiber, R. E. Sulfur emissions to the atmosphere from natural sources. *J. Atmos. Chem.*** 14**, 315–337 (1992).
3. Andreae, M. O. & Crutzen, P. J. Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry. *Science* **276**, 1052 (1997).
4. Charlson, R. J., Lovelock, J. E., Andreae, M. O. & Warren, S. G. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **326**, 655 (1987).
5. Barnes, I., Hjorth, J. & Mihalopoulos, N. Dimethyl Sulfide and Dimethyl Sulfoxide and Their Oxidation in the Atmosphere. *Chem. Rev.* **106**, 940–975 (2006).
6. Hoffmann, E. H. *et al.* An advanced modeling study on the impacts and atmospheric implications of multiphase dimethyl sulfide chemistry. *Proc. Natl. Acad. Sci. USA* **113**, 11776 (2016).
7. Cooper, D. J. Estimation of hydroxyl radical concentrations in the marine atmospheric boundary layer using a reactive atmospheric tracer. *J. Atmos. Chem.* **25**, 97–113 (1996).
8. Butkovskaya, N. I. & LeBras, G. Mechanism of the NO$_3$− DMS Reaction by Discharge Flow Mass Spectrometry. *J. Phys. Chem.** **98**, 2582–2591 (1994).
9. Nakano, Y., Ishitake, T., Aloisio, S. & Kawasaki, M. Temperature and Pressure Dependence of the Rate Constants of the Reaction of NO3 Radical with CH$_3$SH and CH$_3$SH$_2$. *J. Phys. Chem. A* **110**, 7401–7405 (2006).
10. Mardyukov, A. & Schreiner, P. R. Atmospherically Relevant Radicals Derived from the Oxidation of Dimethyl Sulfide. *Acc. Chem. Res.* **51**, 475–483 (2018).
28. Tian, Y.
27. González-García, N., González-Lafont, À. & Lluch, J. M. Variational Transition-State Theory Study of the Dimethyl Sulfoxide (DMSO) and OH Reaction.

31. Cooper, O. R.
32. Stone, D., Whalley, L. K. & Heard, D. E. Tropospheric OH and HO2 radicals: field measurements and model comparisons.

19. Domin, D., Braida, B. & Bergès, J. Influence of Water on the Oxidation of Dimethyl Sulfide by the ·OH Radical.

23. Kukui, A., Borissenko, D., Laverdet, G. & Le Bras, G. Gas-Phase Reactions of OH Radicals with Dimethyl Sulfoxide and Methane Sulfinic Acid.

21. Arsene, C., Barnes, I. & Becker, H. K. FT-IR product study of the photo-oxidation of dimethyl sulfide: Temperature and O2 partial pressure dependence.

25. Resende, S. M., de Bona, J. C. & Sombrio, Pd. S. Theoretical study of the role of adducts in the atmospheric oxidation of dimethyl sulfide.

24. Wang, L. & Zhang, J. Ab initio study of reaction of dimethyl sulfoxide (DMSO) with OH radical.

26. Baptista, L., da Silva, E. C. & Arbilla, G. Theoretical investigation of the gas phase oxidation mechanism of dimethyl sulfoxide by OH radical.

40. Hratchian, H. P. & Schlegel, H. B. Accurate reaction paths using a Hessian based predictor–corrector integrator.

41. Hratchian, H. P. & Schlegel, H. B. Using Hessian Updating To Increase the Efficiency of a Hessian Based Predictor-Corrector integrator.

47. Legault, C. Y.

Acknowledgements
This work is supported by National Natural Science Foundation of China (21337001 and 21607011), Natural Science Foundation of Shandong Province (ZR2018MB043), and The Fundamental Research Funds of Shandong University (2018JC027).
Author Contributions
G.C.L., C.X.Z. and X.M.S. conceived and designed the research. G.C.L. performed the calculation and analyzed the data, and wrote the main manuscript text. C.X.Z. and X.M.S. revised the initial manuscript. All of the authors discussed the results, and contribute to the final manuscript.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-36405-0.

Competing Interests: The authors declare no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2019