An advanced modeling study on the impacts and atmospheric implications of multiphase dimethyl sulfide chemistry

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Oceans dominate emissions of dimethyl sulfide (DMS), the major natural sulfur source. DMS is important for the formation of non-sea salt sulfate (nss-SO_4^{2-}) aerosols and secondary particulate matter over oceans and thus, significantly influence global climate. The mechanism of DMS oxidation has accordingly been investigated in several different model studies in the past. However, these studies had restricted oxidation mechanisms that mostly underrepresented important aqueous-phase chemical processes. These neglected but highly effective processes strongly impact direct product yields of DMS oxidation, thereby affecting the climatic influence of aerosols. To address these shortfalls, an extensive multiphase DMS chemistry mechanism, the Chemical Aqueous Phase Radical Mechanism DMS Module 1.0, was developed and used in detailed model investigations of multiphase DMS chemistry in the marine boundary layer. The performed model studies confirmed the importance of aqueous-phase chemistry for the fate of DMS and its oxidation products. Aqueous-phase processes significantly reduce the yield of sulfur dioxide and increase that of methyl sulfonic acid (MSA), which is needed to close the gap between modeled and measured MSA concentrations. Finally, the simulations imply that multiphase DMS oxidation produces equal amounts of MSA and sulfate, a result that has significant implications for nss-SO_4^{2-} aerosol formation, cloud condensation nuclei concentration, and cloud albedo over oceans. Our findings show the deficiencies of parameterizations currently used in higher-scale models, which only treat gas-phase chemistry. Overall, this study shows that treatment of DMS chemistry in both gas and aqueous phases is essential to improve the accuracy of model predictions.

marine multiphase chemistry | dimethyl sulfide | multiphase modeling | CAPRAM | marine aerosols

Gaseous sulfuric acid (H_2SO_4) and aqueous sulfate (HSO_4^- , SO_4^{2-}) contribute to the formation of new aerosol particles as well as secondary particulate matter and are, thus, important for human health and the Earth's climate (1). Globally, anthropogenic sulfur emissions in the form of sulfur dioxide (SO_2) dominate atmospheric production of gaseous H_2SO_4 and particle-phase sulfate. However, the main natural source of sulfur is the oxidation of dimethyl sulfide (DMS) emitted by oceans (2), which is the most important precursor for non-sea salt sulfate (nss-SO_4^{2-}) aerosols over the open ocean (3). Sulfate aerosols strongly influence the climate both by direct negative radiative forcing (4) and as a dominant source of cloud condensation nuclei (CCN) over the open ocean (5). Because oceans cover about 70% of Earth's surface (6) and have generally low albedo, DMS oxidation plays a major role in influencing the natural radiative forcing of sulfate aerosols as well as cloud properties (3).

Investigations of the effect of DMS oxidation on natural sulfate aerosol concentrations and cloud and aerosol properties require an accurate, reduced DMS oxidation scheme in chemical transport models (CTMs) and global climate models (GCMs). Current parameterizations use fixed yields of SO_2 and methyl sulfonic acid (MSA) to calculate new nss-SO_4^{2-} aerosol formation (7–13). In the

gas phase, SO_2 can be oxidized to gaseous H_2SO_4 , which may condense on existing particles or contribute to new particle formation in low-condensation sink environments. Other loss processes for SO_2 include dry deposition or aqueous-phase reactions. MSA mainly condenses on existing particles contributing to aerosol particle mass, and it is mainly removed by dry and wet deposition. The applied parameterizations usually consider only gas-phase reactions and should be treated with caution, because the mechanism of DMS oxidation to SO_2 and MSA is not completely understood (14). Various model studies have found significantly varying yields of DMS oxidation products (15). For example, the study by von Glasow and Crutzen (5) applied different mechanistic assumptions and calculated conversion efficiencies of DMS into SO_2 of between 0.14 and 0.95 in the marine boundary layer (MBL). Predictions of sulfate aerosol formation caused by DMS oxidation and their climate impact calculated by CTMs and GCMs are, therefore, highly uncertain. The formation of other stable DMS oxidation products, mainly MSA, lowers the SO_2 yield and constitutes the main source of uncertainty to aerosol formation, because MSA production predominantly leads to growth of existing particles and suppresses new particle formation (16). Recent studies suggest that MSA can significantly assist cluster formation between H_2SO_4 and amines and thereby, contribute to new particle formation, although it is a less potent clustering agent than H_2SO_4 (17, 18). Hence, a

Significance

Climate models indicate the importance of dimethyl sulfide (DMS) oxidation in new aerosol particle formation and the activation of cloud condensation nuclei over oceans. These effects contribute to strong natural negative radiative forcing and substantially influence the Earth's climate. However, the DMS oxidation pathway is not well-represented, because earlier model studies only parameterized gas-phase DMS oxidation and neglected multiphase chemistry. Here, we performed the most comprehensive current mechanistic studies on multiphase DMS oxidation. The studies imply that neglecting multiphase chemistry leads to significant overestimation of SO_2 production and subsequent new particle formation. These findings show that an advanced treatment of multiphase DMS chemistry is necessary to improve marine atmospheric chemistry and climate model predictions.

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Fig. 1. Depiction of mean multiphase source and sink fluxes (in 10^2 molecules $\text{cm}^{-3} \text{s}^{-1}$) of the full scenario run throughout the whole model. The temperature is 280 K during noncloud conditions and 276.5 K in clouds. Only oxidation fluxes exceeding 5% of the total flux are included. The blue area highlights aqueous-phase reactions, and stable compounds are shaded yellow. The width and color of arrows indicate the magnitude of the mass flux, and dashed arrows represent phase transfer processes. Numbers above and below the arrows give the mean fluxes, and chemical species at the beginning of the small curved arrows below and above the thicker arrows describe the main reactants.

78% of DMS (in all phases) is oxidized in the aqueous phase by ozone (O_3) to DMSO (*SI Appendix, Multiphase Chemistry of DMS and Its Oxidation Products*, and Figs. S4 and S5). This reaction contributes 7% to multiphase DMS oxidation over the whole model run. Although consistent with the previous simulations by von Glasow and Crutzen (5), this finding is unexpected, because less than 0.01% of DMS partitions to the aqueous phase (Fig. 2). The contribution is explained by the very fast kinetics of the O_3 reaction, so that a large flux is established because of the reactive uptake of DMS. During in-cloud periods, the overall rate of DMS degradation decreases, with the result that the gas-phase DMS concentration increases slightly.

In conclusion, this study has shown that halogens contribute significantly to DMS oxidation and that, during cloud periods, the aqueous-phase oxidation of DMS by O_3 is dominant, whereas the overall degradation decreases. An overview of the fractional contributions of different oxidants in the DM1.0 to DMS oxidation in the gas and aqueous phases is given in *SI Appendix, Table S13* along with fractional contributions to the oxidation of DMSO, methyl

sulfenic acid (MSIA), and MSA. For the sake of completeness, the modeled evolution of the concentration–time profiles of DMS, DMSO, MSIA, and MSA along with comparisons with field measurements and mass flux analyses are discussed in detail in *SI Appendix, Multiphase Chemistry of DMS and Its Oxidation Products*.

Processing of the Main DMS Oxidation Products. The additional conversion of DMS oxidation products must also be considered to determine the effect of the overall DMS oxidation on natural radiative forcing and thus, Earth's climate. In this section, we first consider the additional processing of H-abstraction products and then, examine the reactions of DMS products of the addition pathway (Fig. 1).

The main product of the H-abstraction pathway is SO_2 , whereas only small amounts of MSA and SO_3 are formed. Furthermore, accumulation of reservoir gases, especially *S*-methyl thioformate (CH_3SCHO), may reduce the conversion of DMS to SO_2 because of CH_3SCHO deposition to the ocean. In principle, the understanding is that SO_2 forms gaseous H_2SO_4 from OH oxidation.

Fig. 2. Partitioning of DMS, DMSO, DMSO₂, MSIA, and MSA into the aqueous phase of deliquesced particles and cloud droplets throughout the second model day. The y axis is logarithmic. Gray shaded bars denote the night periods, and blue bars denote the cloud periods.

However, our results indicate that the thermal decay of $\text{CH}_3\text{SO}_3^\bullet$ into SO_3 represents the main contributor to gaseous H_2SO_4 over the open ocean. Gaseous $\text{CH}_3\text{SO}_3^\bullet$ is predominantly formed from gaseous $\text{CH}_3\text{SO}_2^\bullet$, which is mainly generated by the isomerization of gaseous $\text{CH}_3\text{S}(\text{OO}^\bullet)$ (Fig. 1). In the atmosphere, SO_3 reacts rapidly with water vapor to form gaseous H_2SO_4 . In total, 94% of the gaseous H_2SO_4 is formed because of thermal decay of $\text{CH}_3\text{SO}_3^\bullet$. Consequently, the isomerization of gaseous $\text{CH}_3\text{S}(\text{OO}^\bullet)$ is very important in determining gaseous concentrations of H_2SO_4 (additional details are in [SI Appendix](#)). However, only 4% of DMS is converted into gaseous SO_3 , whereas 24% of DMS is converted into SO_2 (Table 2). The strongly reduced importance of SO_2 to gaseous H_2SO_4 formation results from the presence of noon clouds, which enhance uptake processes and significantly reduce both the OH and SO_2 concentrations, thereby suppressing gaseous production of H_2SO_4 . Daytime clouds, therefore, greatly reduce the significance of SO_2 as an intermediate species in the formation of gaseous H_2SO_4 . Still, even in the woCloud run, in which no clouds are implemented, 80% of H_2SO_4 is formed via the thermal decomposition of $\text{CH}_3\text{SO}_3^\bullet$. This result suggests that, other than the gas-phase oxidation of SO_2 , the thermal decomposition of $\text{CH}_3\text{SO}_3^\bullet$ is a main contributor to new particle formation in the MBL in the presence of clouds. Hence, the thermal decomposition of $\text{CH}_3\text{SO}_3^\bullet$ may explain the gap between modeled and measured gaseous H_2SO_4 concentrations in coastal regions as it has been proposed before (23).

DMSO, formed via the oxidation of DMS by OH and BrO, is a key intermediate of the addition pathway. The subsequent oxidation of DMSO strongly alters new aerosol formation in the MBL (5), because it reduces the yield of SO₂ from DMS oxidation by forming additional stable oxidation products, like dimethyl sulfone (DMSO₂) and MSA. DMSO is mostly oxidized by OH to MSIA in both the gas and aqueous phases. Oxidation by halogens is of minor importance. Fig. 2 presents the partitioning of DMSO, DMSO₂, MSIA, and MSA in deliquesced particles and cloud droplets. About 1% and 2% of DMSO and DMSO₂, respectively, partition into deliquesced particles. Because of the less effective partitioning of DMSO into aerosols (Fig. 2) compared with the more oxidized products MSIA and MSA, the aqueous-phase oxidation mainly occurs in cloud droplets. It is also noteworthy that, although the production of DMSO is suppressed in cloud droplets, its oxidation is increased (*SI Appendix, Fig. S7 and Table S13*). This effect is explained by the partitioning of DMSO. With the onset of cloud formation, DMSO and DMSO₂ partition almost completely into cloud droplets because of their high Henry's Law coefficients (14).

The simulation results imply that DMSO₂ formed through the OH-addition pathway or DMSO oxidation is only a minor product of DMS oxidation in a marine environment. Therefore, DMSO₂ oxidation is not further considered in this study.

MSIA is the major DMSO oxidation product, and about 10–40% of MSIA partitions into marine aerosols. MSIA has a diurnal profile, showing stronger partitioning at night (gray shaded bars in Fig. 2). The high solubility and formation in the aqueous phase increase the importance of aqueous-phase chemistry for the MSIA fate. MSIA is almost completely degraded during daytime in the aqueous phase. Oxidation is decreased during night, explaining the diurnal partitioning profile in Fig. 2. The main oxidants are dissolved O_3 , OH, and Cl_2^- . The strongest sink flux is the reaction of MSIA and dissociated methyl sulfinic acid (MSI^-) with O_3 (42%) to form MSA. The DM1.0 is the first mechanism that has implemented these reactions. Cl_2^- and OH react mainly with MSI^- . These two oxidations have to be differentiated between oxidation in deliquesced particles and cloud droplets. The oxidation by Cl_2^- is dominant in deliquesced particles, whereas oxidation by OH dominates in cloud droplets (*SI Appendix, Table S13*). These results are clearly different from the assumption in the work by Zhu et al. (21), in which the cloud droplet Cl_2^- concentration was kept constant. The total contributions of Cl_2^- and OH to aqueous-phase MSIA oxidation are 10% and 19%, respectively. As explained in *SI Appendix, Model and Mechanism Description*, both reactions occur via an electron transfer reaction leading to high amounts of $CH_3SO_2(O_2^*)$, which reacts further with MSI^- to form dissolved MSA and $CH_3SO_3^*$ (31). $CH_3SO_3^*$ mainly decomposes to CH_3 and SO_3 , but small reaction fluxes with MSI^- occur, also forming MSA. As a result, the oxidation of MSI^- by Cl_2^- and OH leads to a net destruction of at least two MSIA molecules. Overall, the reactions of MSI^- with $CH_3SO_2(O_2^*)$ and $CH_3SO_3^*$ account for 29% of MSIA depletion. Because of these reactions, MSI^- oxidation by Cl_2^- and OH produces dissolved MSA and SO_3 in nearly equal amounts and oxidizes more MSIA/ MSI^- than the O_3 reactions.

In total, 58% of the modeled MSA is produced by the aqueous-phase reactions of MSIA/MSI⁻ with O₃, and 40% is caused by the aqueous-phase reactions of MSI⁻ with its oxidation products. In contrast, the gas-phase formation only accounts for 2% of MSA. However, the gas-phase MSA as well as gaseous H₂SO₄ production depend strongly on the rate constant of the thermal decay of CH₃SO₃^{*}, which is very uncertain (details are in *SI Appendix, Model and Mechanism Description*). Hence, additional laboratory investigations of this thermal decay are warranted. MSA remains almost entirely in the aqueous phase throughout the whole model run (Fig. 2). Our results, therefore, indicate that only aqueous-phase oxidation of MSA is important. Because of its high stability, only 2% of MSA is oxidized further by Cl₂⁻ and dissolved OH. Hence, MSA sinks do not compete with its production, and MSA accumulates in the aerosol phase. Because the tropospheric lifetime of marine aerosols is between 1 and 7 d (32), wet and dry deposition are likely the dominant tropospheric sinks of MSA.

Overall, modeling of DMS oxidation shows that the H-abstraction pathway in the gas phase leads predominantly to SO_2 and that the thermal decay of gaseous CH_3SO_3^* is the main contributor to gaseous H_2SO_4 formation, whereas the addition pathway leads to MSA involving multiphase processes. Furthermore, DMS oxidation leads to MSA and sulfate production in nearly equal amounts. The large fraction of MSA formed through aqueous-phase processes is different from parameterizations of the DMS addition pathway currently applied in GCMs mostly implemented after the work by Chin et al. (8).

SO₂ and MSA Yields and Atmospheric Implications. The contribution of DMS oxidation to natural radiative forcing is strongly influenced by the yields of SO₂ and MSA. Fig. 1 shows the importance of both gas- and aqueous-phase reactions in determining product yields. Multiphase chemistry causes a shift in the product distribution of DMS chemistry from SO₂ toward MSA. This result highlights the deficiencies of current parameterizations in climate models. Apart from multiphase chemistry in general, the results presented in Fig. 1

the DM1.0. In total, 10,212 species and 21,928 reactions were included. The simulations started on June 19 at 45° N and ran for 108 h with an assumed temperature of 280 K. In the model scenario, an air parcel is moved along a predefined trajectory starting at 850 hPa. The scenario includes eight cloud passages, which are achieved by lifting the air parcel from 850 to 800 hPa for about 2 h at noon and midnight, respectively. Because of the adiabatic cooling as the air parcel rises, the temperature falls to about 276.5 K. The in-cloud residence time of about 2 h was chosen based on the calculations by Pruppacher and Jaenicke (35). Noon and midnight clouds were chosen to study differences in nighttime and daytime clouds on multiphase chemistry.

Mechanism Development. Based on the gas-phase reactions considered in the MCMv3.2, an extended multiphase DMS chemistry mechanism, the DM1.0, has been developed in this work. For this purpose, an extensive aqueous-phase chemistry mechanism was designed using the most recent kinetic and mechanistic data.

The gas-phase reaction scheme in the DM1.0 is largely based on the DMS gas-phase oxidation mechanism of the MCMv3.2. The MCMv3.2 contains one of the most detailed gas-phase DMS oxidation mechanisms and is able to reproduce experimental findings (36). However, the MCMv3.2 does not contain DMS reactions with halogen species and is also missing some reactions that are potentially important in the marine environment (e.g., reactions with the hydroperoxyl radical). These reactions can be critical for the multiphase chemistry in the MBL (5). The chemical scheme in the MCMv3.2 was extended

by 23 reactions of reactive halogen compounds and 14 reactions of non-halogen compounds. Overall, the gas-phase mechanism scheme of the DM1.0 contains 103 reactions, including nine photolysis processes.

The SPACCIM calculates phase transfer processes according to the approach by Schwartz (37) by considering the gas-phase diffusion coefficient D_g , the mass accommodation coefficient α , and the Henry's Law coefficient H_A . These parameters were implemented in the DM1.0 for uptake of DMS, DMSO, DMSO₂, MSIA, and MSA.

The aqueous-phase mechanism of the DM1.0 contains many more intermediate steps and reaction pathways of DMS, DMSO, DMSO₂, MSIA, and MSA than any other DMS aqueous-phase mechanism. Rate constants for these reactions were chosen from recent measurements. No literature data were available for some types of reactions (such as oxygen addition at carbon-centered radicals), and they were estimated according to the treatment of this reaction kind in the CAPRAM (38). Overall, the aqueous-phase mechanism of the DM1.0 contains 49 reactions and five dissociations and represents the most detailed aqueous-phase DMS chemistry mechanism to date.

Briefly, the module described explicitly the tropospheric oxidation of DMS and its oxidation products by several oxidants (mainly OH, NO₃, Cl, ClO, Br, BrO, Cl₂[•], and SO₄[•]) in the gas and aqueous phases. For additional information, the reader is referred to [SI Appendix, Model and Mechanism Description](#).

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