

Sulfur Chemistry in the Marine Atmosphere and Its Influence on Aerosol Formation and Growth

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Long Term Goals

Our long-term research goal is to understand how aerosols are produced and grow in the marine atmosphere with special emphasis on processes in the boundary and buffer layers. Specifically we want to understand in detail how dimethyl sulfide emitted by the oceans is oxidized in the marine atmosphere and how the products produced are involved in the formation and growth of atmospheric particles. We want to understand the importance of new particles formed in the free troposphere and brought into the boundary and buffer layers by subsidence. Finally we want to determine the influence of anthropogenic sulfur compounds, mainly sulfur dioxide, on the growth and formation of atmospheric particles especially in the near-shore environment.

Objective

Our first objective was to develop a comprehensive photochemical model of the chemistry of dimethyl sulfide and its oxidation products. Our second objective was to determine the impact of this chemistry on the formation and growth of new particles in the boundary and buffer layers. A third objective was to evaluate the importance of anthropogenic and volcanic sources of sulfur compounds, particularly SO₂, on the formation and growth of atmospheric particles. A final and fourth objective was the evaluation of the importance of new particles formed from oxidized SO₂ in the free troposphere that are brought into the boundary and buffer layers by subsidence.

Approach

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In collaboration with Dr. D.D. Davis and coworkers at Georgia Tech., a detailed photochemical model of the chemistry of dimethyl sulfide in the equatorial marine boundary layer would be developed. This model would be based on a detailed photochemical model developed by Dr. Davis that contained a limited set of sulfur species. The sulfur chemistry added would be based on laboratory kinetics data where available. Rate constants would be estimated from either thermodynamics data or from high level ab initio molecular orbital studies when laboratory kinetic data were not available. Field data from our Christmas Island Campaign (Bandy et al., 1996) would be used to evaluate the model and to investigate the range of unrestrained parameters in the model.

The processes leading to the formation and growth of new atmospheric particles would be studied. Specifically we would use high level ab initio or density functional molecular orbital theory to study the small clusters of sulfuric acid and water that are known to be the first steps in the formation of new particles. These data would be used to evaluate the importance of these hydrates in the formation of new particles. The same methods would be used to study the influence of ammonia on the formation and growth of atmospheric particles.

Work Completed

A detailed photochemical model of the chemistry of the oxidation of DMS was developed and tested. As part of this development a detailed ab initio study of many potential intermediates was carried out. The structures and energetics of $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ $n=0-7$ were obtained using density functional theory at the B3LYP/ 6-311++G(2d,2p)// B3LYP/ 6-311++G(2d,2p) level of theory. The results are shown in figures 1 and 2. The structures and energetics of $(\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O})_2$ were obtained using density function theory at the B3LYP/ 6-311+G(2d,p)// B3LYP/ 6-311+G(2d,p) level of theory.

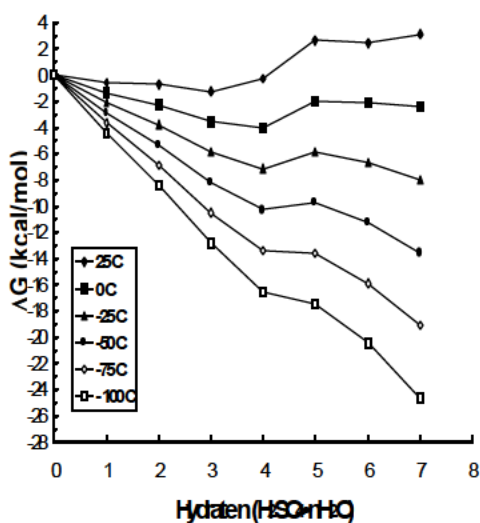


Figure 1. Cumulative free energy of hydration for $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$.

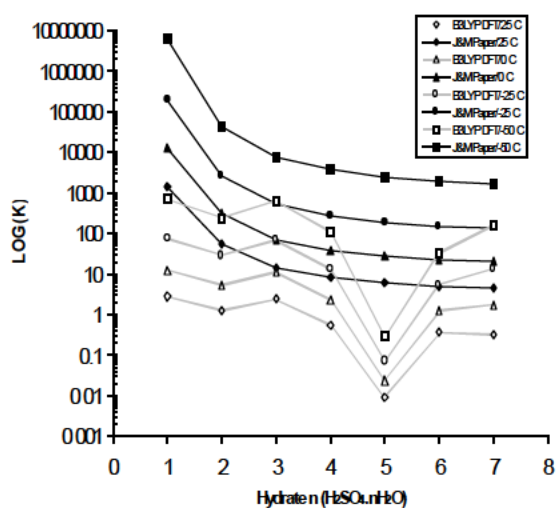


Figure 2. Equilibrium constants for $\text{H}_2\text{SO}_4 \cdot (n-1)\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$. J&M Paper refers to the equilibrium constants calculated by Jaeger-Voirol and Mirabel.[Jaeger-Voirol, 1989 #10]

Results

The photochemical model developed (Chen et al., submitted for publication fall 1997) yielded a diurnal variation for SO₂, and DMS which were virtually identical to the experimental data of Christmas Island (Bandy et al., 1996). Diurnal variations for dimethyl sulfoxide (DMSO) and (DMSO₂) did not agree as well with experiment. A DMS surface flux estimated from the model was 3.2×10^{13} molecules m⁻² s⁻¹ agreed well with that estimated by Bandy et. al., 3.4×10^{13} molecules m⁻² s⁻¹, using mass balance methods. A diurnal variation for H₂SO₄ and OH generated by the model agreed well with measurements made at Christmas Island in the NASA PEM Tropics B program in August, 1996. This leaves little doubt that H₂SO₄ is a major product of DMS oxidation. Finally the rate of loss of SO₂ to the ocean was found to have a deposition velocity of 0.7 cm s⁻¹ which is slightly higher than obtained by Bandy et al. using mass balance.

The structures of H₂SO₄•nH₂O clusters (n=1-7) obtained by density functional methods are much different than the structures of the corresponding bulk phases of the same composition. The H₂SO₄•nH₂O clusters studied are bound together by hydrogen bonds, some of which are extremely strong. Only the n=7 cluster contained a H₃O⁺ ion. This result should be compared to the bulk phase structures where H₂SO₄ and two H₂O's have been converted to two H₃O⁺ ions and a free SO₄⁻ ion. Clearly it is inappropriate to use the properties of the bulk solutions to estimate the properties of small H₂SO₄•nH₂O clusters.

That full ionization has not occurred at n=7 indicates that in the formation of larger clusters, the free energy of this ionization process is still available for increasing the size of the particle. Complete ionization occurs when the quantity of dielectric becomes sufficient to stabilize the ion pairs produced. At this stage the particle may grow by adding H₂SO₄. Finally, there is a contribution to the so-called surface free energy by the fact that in larger clusters, ions may be stable in the bulk parts of the particle but not near the surface. As the surface of the particle is approached, the amount of dielectric available to stabilize the ions rapidly decreases and a hydrogen bonded molecular complex of H₂SO₄ and H₂O results. It is likely that most of the H₂O and H₂SO₄ near the surface of such particles are hydrogen bonded molecular complexes.

Impact

A photochemical model of the chemistry of DMS has been developed which can predict the rate of formation H₂SO₄. This is important because H₂SO₄ is the most important species in the formation and growth of atmospheric particles. Given the flux of SO₂ into the system from other sources such as anthropogenic and volcanic sources we can predict the rate at which the species most important in new particle production and growth is generated. We have shown that the properties of small clusters cannot be estimated from the properties of the bulk system as is done in most commonly used versions of homogeneous nucleation theory (Jaeger-Voirol, P. Mirabel, 1988). Using formation constants for H₂SO₄•nH₂O obtained in this study, we found that the formation

of hydrates reduces the nucleation rate predicted by homogeneous nucleation theory by only a factor of 0.5. This is in contrast to a factor of about 10^{-5} estimated by Jaecker-Voirol and Mirabel. Finally, this work suggests that homogeneous nucleation theory may be inappropriate for estimating the rates of formation of new particles in the $\text{H}_2\text{SO}_4\text{-nH}_2\text{O}$ system. Not only are the cluster properties hard to estimate, the system may not come to equilibrium as required by homogeneous nucleation theory. A kinetic model including each elementary reaction in the process of forming new particles is the proper next step. Using reaction rate constants obtained in this program estimated using density function theory can form the basis for such a model and is a goal for future work.

Transitions

Visibility in the marine atmosphere is an important issue for the Navy. Optical target acquisition, ordinance guidance and navigation are all affected by visibility. Our results are a good first step in developing a model that is based on good fundamental science. Most of the gas phase work is now complete. What are needed is a model for the formation of new particles that is based on fundamental science and an improved model for the growth of these new and preexisting particles.

References

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