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Significance of Ammonia in Growth of Atmospheric Nanoclusters

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We apply accurate quantum chemistry methods to study the thermochemistry of molecular clusters containing ammonia, water, and sulfuric acid and investigate initial reaction steps in atmospheric nucleation by calculating free energies for the related reactions. The results indicate that ammonia is a key reactant enhancing the growth of small water−sulfuric acid clusters in atmospheric conditions. The role of ammonia becomes significant when the nanoclusters contain more than one or two sulfuric acid molecules. This implies a lower limit of 1:3 for the NH_3/H_2SO_4 mole ratio of atmospheric sulfuric acid−water−ammonia clusters.

Introduction

Aerosol particles affect global radiation balance and human health.[1,2] Particle formation is observed frequently in the Earth's atmosphere,[3,4] but the first reaction mechanisms forming the particles have remained elusive. As the newly nucleated particles contain less than 100 molecules, these nanostructures are below the experimental detection limit. Therefore, theoretical methods are required to obtain information on the initial stages of particle formation. Experimental studies have indicated that particle formation via nucleation involves sulfuric acid and water molecules. Furthermore, a strong nucleation-enhancing effect of ammonia has been observed.[5] The stability of ammonia-containing atmospheric sulfuric acid−water clusters has been studied using the classical liquid drop model and equilibrium thermodynamics.[6] Previously, the role of ammonia in hydrates of sulfuric acids has been computationally studied by applying density functional theory (DFT, using the B3LYP exchange-correlation functional) or MP2 perturbation theory to clusters containing one sulfuric acid molecule. These attempts[7,8] failed to explain the observed enhancing effect of ammonia on water−sulfuric acid particle formation. Our PW91/DNP study[9] on clusters containing two sulfuric acid molecules, one ammonia, and up to seven water molecules demonstrated that the effect of ammonia on some cluster size classes is significant, but the predicted overall fraction of ammonia-containing two-acid clusters in the atmosphere was still small due to mass balance effects. Nadykto and Yu[10] investigated two-acid clusters with up to two water molecules and up to one ammonia molecule using the PW91 density functional with the large 6-311++G-(3df,3pd) basis set. They also concluded that the effect of ammonia increases with the number of acid molecules. We have recently reported results from RI-MP2/aug-cc-pV(T+d)Z computations on two-acid clusters containing multiple ammonia molecules but no water.[11] The calculations indicate that the NH_3/H_2SO_4 mole ratio of small sulfuric acid−water−ammonia clusters in the atmosphere is not likely to be larger than 1:1, with a value of 1:2 being more probable in most conditions.

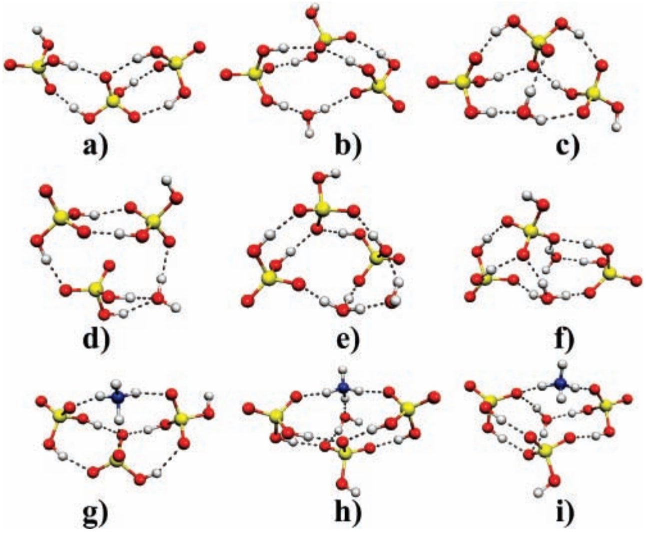

Figure 1. The most stable clusters: (a) $(H_2SO_4)_3$, (b) $(H_2SO_4)_3{\cdot}H_2O$(i), (c) $(H_2SO_4)_3{\cdot}H_2O$(ii), (d) $(H_2SO_4)_3{\cdot}H_2O$(iii), (e) $(H_2SO_4)_3{\cdot}(H_2O)_2$(i), (f) $(H_2SO_4)_3{\cdot}(H_2O)_2$(ii), (g) $(H_2SO_4)_3{\cdot}NH_3$, (h) $(H_2SO_4)_3{\cdot}NH_3{\cdot}H_2O$(i), and (i) $(H_2SO_4)_3{\cdot}NH_3{\cdot}H_2O$(ii). White = hydrogen, red = oxygen, yellow = sulfur, and blue = nitrogen.

The aim of this study is to complement earlier results on smaller cluster types by estimating a lower limit to the NH_3/H_2SO_4 mole ratio of sulfuric acid−water−ammonia clusters in atmospheric conditions. We investigate the effect of adding a third sulfuric acid molecule to the clusters using a more advanced density functional method together with RI-MP2 (resolution of identity second-order Møller−Plesset) perturbation theory. We systematically perform electronic structure and vibrational frequency calculations for all sulfuric acid−water−ammonia cluster stoichiometries up to $(H_2SO_4)_3{\cdot}NH_3{\cdot}H_2O$.

Computational Details

The interactions in sulfuric acid−water−ammonia clusters are dominated by hydrogen bonds. In many previous quantum

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TABLE 1: Gibbs Free Energies for Complexation (Relative to Free Molecules with a Pressure of 1 atm) in Units of kcal mol^{-1} are Listed at Temperatures of 298, 265, and 242 K as a Function of the Number of Sulfuric Acid Molecules ($x = 1, 2, 3$) in the Clusters

$T = 298$ K	$(H_2SO_4)_x$	$(H_2SO_4)_x \cdot H_2O$	$(H_2SO_4)_x \cdot (H_2O)_2$	$(H_2SO_4)_x \cdot NH_3$	$(H_2SO_4)_x \cdot NH_3 \cdot H_2O$
$x = 1$	0	−2.6	−4.6	−7.3	−8.6
$x = 2$	−8.3	−11.2	−13.8	−22.3	−26.2
$x = 3$	−12.9	−12.5	−20.6	−29.9	−36.2

$T = 265$ K	$(H_2SO_4)_x$	$(H_2SO_4)_x \cdot H_2O$	$(H_2SO_4)_x \cdot (H_2O)_2$	$(H_2SO_4)_x \cdot NH_3$	$(H_2SO_4)_x \cdot NH_3 \cdot H_2O$
$x = 1$	0	−3.6	−6.6	−8.2	−10.6
$x = 2$	−9.3	−13.5	−17.1	−24.7	−29.6
$x = 3$	−15.4	−16.2	−25.3	−33.8	−41.0

$T = 242$ K	$(H_2SO_4)_x$	$(H_2SO_4)_x \cdot H_2O$	$(H_2SO_4)_x \cdot (H_2O)_2$	$(H_2SO_4)_x \cdot NH_3$	$(H_2SO_4)_x \cdot NH_3 \cdot H_2O$
$x = 1$	0	−4.3	−8.0	−8.9	−12.0
$x = 2$	−10.1	−15.1	−19.4	−26.4	−32.0
$x = 3$	−17.1	−18.8	−28.6	−36.4	−44.3

chemistry studies on these systems, the B3LYP functional is employed for the treatment of exchange-correlation of the electrons. However, comparison to experiments[12] and previous studies[10,13] demonstrate that B3LYP does not give a proper description for the electronic structure of hydrogen bonds. To better take into account the noncovalent interactions, we employ the newer generation hybrid-meta-GGA functional MPW1B95[14] together with the augmented correlation consistent basis set of valence double-ζ quality[15] aug-cc-pV(D+d)Z for the structure optimization and vibrational frequency calculations. The MPW1B95 functional has shown[16] high-accuracy performance, for example, for van der Waals complexes. The final electronic energies are calculated using the RI-MP2 method[17,18] and the larger triple-ζ aug-cc-pV(T+d)Z basis set.[15] In our recent high-level study on small neutral and charged sulfuric acid−water clusters,[19] we have demonstrated that at the RI-MP2 level, increasing the basis set size beyond aug-cc-pV(T+d)Z has only a small effect on the intermolecular binding (complexation) energies. For example, for the $H_2SO_4 \cdot H_2O$ cluster, the difference between aug-cc-pV(T+d)Z and aug-cc-pV(5+d)Z complexation energies was less than 0.3 kcal/mol. It should be noted that the commonly used counterpoise (CP) correction seems to significantly exaggerate basis set related errors for large basis sets containing multiple diffuse basis functions.[19,20] The auxiliary basis sets needed for the RI expansion are given by Weigend et al.[21] We use the Gaussian 03 program suite[22] for the DFT calculations and the Turbomole v.5.8. program suite[23,24] for the RI-MP2 calculations. In the DFT calculations, the convergence with respect to the electronic energy in the self-consistent field (SCF) step, maximum force and root-mean-square (rms) force are the Gaussian default limits (10^{-6}, 4.5×10^{-4}, and 3×10^{-4} au, respectively). Test calculations on the sulfuric acid dimer using tighter optimization criteria (1.5×10^{-5} and 1×10^{-5} au with respect to the maximum and rms force, respectively) and an ultrafine integration grid indicate that the effect of tighter optimization criteria on the free energy for complexation is less than 5%. For the RI-MP2 calculations, the SCF convergence limit is 10^{-7} au. For all stoichiometries, several cluster configurations are studied, but only the most stable structures are discussed here. Initial guess structures are obtained by a combination of comparisons to earlier studies,[8−10,25,26] chemical intuition and—for the largest three-acid clusters—limited conformational searches using Car−Parrinello molecular dynamics with the CPMD code[27] and semiempirical Monte Carlo sampling with the Spartan 02 program.[28] Vibrational frequency calculations are used to verify that all structures correspond to minima on the potential energy surface.

TABLE 2: Free Energies for Complexation (ΔG) at Two Sets of Atmospheric Conditions, Relative to Free Molecules, in Units of kcal mol^{-1}, for Different Size Sulfuric Acid−Ammonia−Water Clusters[a]

cluster	atmospheric ΔG_1	atmospheric ΔG_2
Clusters with One Sulfuric Acid:		
$H_2SO_4 \cdot NH_3$	16.61	17.77
$H_2SO_4 \cdot H_2O$	13.22	14.84
$H_2SO_4 \cdot NH_3 \cdot H_2O$	17.53	18.74
$H_2SO_4 \cdot (H_2O)_2$	13.59	15.26
Clusters with Multiple Sulfuric Acids:		
$(H_2SO_4)_2$	16.89	20.83
$(H_2SO_4)_2 \cdot NH_3$	12.61	16.37
$(H_2SO_4)_2 \cdot H_2O$	15.95	20.06
$(H_2SO_4)_2 \cdot NH_3 \cdot H_2O$	11.05	14.84
$(H_2SO_4)_2 \cdot (H_2O)_2$	15.64	19.80
$(H_2SO_4)_3$	23.39	29.89
$(H_2SO_4)_3 \cdot NH_3$	16.04	22.40
$(H_2SO_4)_3 \cdot H_2O$	25.74	32.45
$(H_2SO_4)_3 \cdot NH_3 \cdot H_2O$	12.26	18.59
$(H_2SO_4)_3 \cdot (H_2O)_2$	19.99	26.74

[a] ΔG_1 corresponds to $T = 242$ K, $P_{AM} = 14$ ppt $= 4.246 \times 10^8$ cm^{-3}, $P_{SA} = 2.000 \times 10^7$ cm^{-3}, and $P_W = 6.812 \times 10^{15}$ cm^{-3} (RH = 50%); ΔG_2 corresponds to $T = 265$ K, $P_{AM} = 1000$ ppt $= 2.769 \times 10^{10}$ cm^{-3}, $P_{SA} = 1.000 \times 10^7$ cm^{-3}, and $P_W = 4.524 \times 10^{16}$ cm^{-3} (RH = 50%).

Results and Discussion

The most stable clusters with three acids are presented in Figure 1. The structures are drawn using the MOLEKEL 4.3 visualization package.[29] The corresponding electronic energies, enthalpies, and entropies are presented in the Supporting Information along with the coordinates for all studied cluster structures. The Supporting Information also contains data for $(H_2SO_4)_2 \cdot (NH_3)_2$ and $(H_2SO_4)_2 \cdot (NH_3)_3$ clusters. Comparison of these structures to those presented in ref 11 demonstrates that the MPW1B95/aug-cc-pV(D+d)Z and RI-MP2/aug-cc-pV-(D+d)Z methods yield relatively similar minimum geometries. Thermal contributions to the enthalpies and entropies are computed using the rigid rotor and harmonic oscillator approximations. For some stoichiometries, two or more isomers are very close to each other with respect to the free energy. In these cases, data for all of them are presented. Lower-case roman numerals are used to distinguish between the different isomers.

Table 1 lists the obtained Gibbs free energies for complexation (ΔG; calculated with respect to free molecules) at three temperatures (298, 265, and 242 K) and monomer pressures of 1 atm as a function of the number of sulfuric acid molecules in the cluster ($x = 1, 2, 3$). As can be seen from Table 1, the presence of ammonia is favored thermodynamically: the free

TABLE 3: Calculated Reaction Free Energies, in Units of kcal mol^{-1}, for the Addition of One Sulfuric Acid at $T = 242$, 265, and 298 K and Monomer Pressures of 1 atm

reaction	ΔG (242 K)	ΔG (265 K)	ΔG (298 K)
$H_2SO_4 + H_2SO_4 \leftrightarrow (H_2SO_4)_2$	−10.09	−9.34	−8.28
$H_2SO_4 + H_2SO_4{\cdot}NH_3 \leftrightarrow (H_2SO_4)_2{\cdot}NH_3$	−17.49	−16.49	−15.04
$H_2SO_4 + H_2SO_4{\cdot}H_2O \leftrightarrow (H_2SO_4)_2{\cdot}H_2O$	−10.75	−9.87	−8.60
$H_2SO_4 + H_2SO_4{\cdot}H_2O{\cdot}NH_3 \leftrightarrow (H_2SO_4)_2{\cdot}H_2O{\cdot}NH_3$	−19.97	−18.99	−17.59
$H_2SO_4 + H_2SO_4{\cdot}(H_2O)_2 \leftrightarrow (H_2SO_4)_2{\cdot}(H_2O)_2$	−11.44	−10.55	−9.27
$H_2SO_4 + (H_2SO_4)_2 \leftrightarrow (H_2SO_4)_3$	−6.98	−6.03	−4.64
$H_2SO_4 + (H_2SO_4)_2{\cdot}NH_3 \leftrightarrow (H_2SO_4)_3{\cdot}NH_3$	−10.06	−9.05	−7.61
$H_2SO_4 + (H_2SO_4)_2{\cdot}H_2O \leftrightarrow (H_2SO_4)_3{\cdot}H_2O$	−3.70	−2.70	−1.25
$H_2SO_4 + (H_2SO_4)_2{\cdot}H_2O{\cdot}NH_3 \leftrightarrow (H_2SO_4)_3{\cdot}H_2O{\cdot}NH_3$	−12.28	−11.33	−9.98
$H_2SO_4 + (H_2SO_4)_2{\cdot}(H_2O)_2 \leftrightarrow (H_2SO_4)_3{\cdot}(H_2O)_2$	−9.14	−8.15	−6.75

energy for complexation is less negative in clusters without ammonia and prominently decreases when NH_3 is introduced to the system. In Table 1, we can also notice that the free energy for complexation is lowered significantly more due to the presence of ammonia when the number of sulfuric acids increases from one to three.

The free energies for complexation at standard conditions listed in Table 1 do not directly explain the nucleation-enhancing effect of ammonia in the atmosphere. The cluster size distribution depends also on the relative atmospheric concentrations of each molecular species in the atmosphere through the law of mass action. This is the reason for the low concentration of ammonia found in the fully hydrated two-acid cluster size distribution:[9] since the ambient concentrations of ammonia are much lower than those of water, ammonia is out-competed by water even though it is more strongly bound to the clusters. We calculate the free energies for complexation at two representative atmospheric conditions: low temperature with a low ammonia concentration, and higher temperature with a high ammonia concentration. The free energies at ambient pressures (or concentrations) $\Delta G(P_{SA}, P_{AM}, P_W)$ are related to the standard free energies for complexation $\Delta G(P_0 = 1\text{ atm})$ in terms of the partial pressures as follows:

$$\Delta G(P_{SA}, P_{AM}, P_W) = \Delta G(P_0) + n_{SA}RT\ln\left[\frac{P_0}{P_{SA}}\right] + n_{AM}RT\ln\left[\frac{P_0}{P_{AM}}\right] + n_W RT\ln\left[\frac{P_0}{P_W}\right]$$

where n_X is the number of molecules of type X in the cluster and the subscripts SA, AM, and W stand for sulfuric acid, ammonia, and water, respectively. Table 2 lists the two representative atmospheric free energies for complexation (ΔG_1 and ΔG_2) for all calculated cluster sizes. We observe that all atmospheric ΔG values are positive (see Table 2), but for the molecular clusters which contain both multiple sulfuric acids and ammonia, they are clearly lower than for the clusters containing no ammonia. For example, ΔG_1 for the $(H_2SO_4)_3{\cdot}H_2O$ cluster without ammonia is 25.7 kcal mol^{-1}, whereas for the corresponding cluster with ammonia $(H_2SO_4)_3{\cdot}NH_3{\cdot}H_2O$ it is 12.3 kcal mol^{-1}. The implication is that ammonia makes it more likely for the clusters to grow, i.e., the nucleation barrier for clusters containing ammonia is lower, which is in agreement with the nucleation experiments.[5,12] For the two-acid clusters, the difference in ambient ΔG values for ammonia-containing and ammonia-free clusters of the same molecularity is around 4−5 kcal mol^{-1}. In our previous study,[9] we found that ΔG differences of this size are cancelled out when the full effects of hydration are modeled, as adding water molecules tends to weaken the acid−ammonia binding. (See ref 11 for a detailed discussion.) For the three-acid clusters, the corresponding ΔG difference is 8−10 kcal/mol, which is large enough not to be cancelled out by the addition of more water molecules. Thus, further hydration will probably not change the qualitative conclusion that the presence of ammonia significantly enhances the formation of the three-acid clusters. This implies a lower limit of 1:3 for the NH_3/H_2SO_4 mole ratio of atmospheric sulfuric acid−water−ammonia clusters.

To understand the thermochemistry further, we also calculate the reaction free energies for the addition of one sulfuric acid molecule to the clusters. The reaction free energies at three different temperatures are listed in Table 3. All values correspond to reactions between the most stable cluster types at each temperature. The free energy for the acid addition reaction is significantly lower for the ammonia-containing clusters than for the ammonia-free clusters. This indicates strongly that cluster growth by addition of sulfuric acid molecules proceeds primarily via the ammonia-containing clusters.

Hanson and Lovejoy[30] have reported experimental values for these reaction energies, but our theoretical values cannot be directly compared with them. The reason for this is that the experimental values are averaged over the hydrate distributions for the participating species. Even at the lowest RH conditions (7%) reported in the measurements, the peak of the hydrate distribution, e.g., for the dimer, is located at five or six water molecules.[25,30] Furthermore, since the average number of water molecules bound to an acid *n*-mer may be different than the sum of the average number of water molecules bound to a monomer and a ($n - 1$)-mer, the measured free energies may contain contributions from extra water molecules as well. Thus, the main contribution to the experimental value, for example, for the free energy of the dimer-to-trimer growth reaction, comes from reactions of the type $(H_2SO_4)_2{\cdot}(H_2O)_{5\cdots6} + H_2SO_4 \pm y(H_2O) \leftrightarrow (H_2SO_4)_3{\cdot}(H_2O)_{(5\cdots6\pm y)}$, the energetics of which cannot be calculated from the data set of our study. Nevertheless, our calculated free energies (at 242 K) for the reactions for the unhydrated clusters $(H_2SO_4) + (H_2SO_4) \leftrightarrow (H_2SO_4)_2$ and $(H_2SO_4) + (H_2SO_4)_2 \leftrightarrow (H_2SO_4)_3$ (−10.1 and −7.0 kcal mol^{-1}, respectively) are in relatively good agreement with the experimental values for the hydrated clusters (−8.7 and −10.7 kcal mol^{-1}, respectively). The differences between the computed and measured values are almost certainly explained by the effects of hydration, which can easily shift acid addition energies by 2−3 kcal mol^{-1}, as can be seen from Table 3 (or the results of our previous study[9]).

Previous quantum chemistry studies have found that one- and two-acid cluster distributions are dominated by ammonia-free clusters with multiple water molecules. This has been thought to be in disagreement with the experimental observations of the important role of ammonia in nucleation. However, our three-acid data shows that this need not be the case. Even if the relative fractions of ammonia-containing clusters in the one- and two-acid cluster distributions are small, it is possible that these clusters are responsible for the growth of the clusters into observable sizes.

Conclusions

The influence of multiple sulfuric acid molecules in sulfuric acid−water−ammonia clusters in atmospheric conditions is studied computationally. Quantum chemical calculations at the RI-MP2/aug-cc-pV(T+d)Z//MPW1B95/aug-cc-pV(D+d)Z level demonstrate that the binding of ammonia to the clusters is significantly increased by the addition of acid molecules. Calculations on larger clusters indicate that ammonia is a key reactant that enables small sulfuric acid−water clusters to grow. The significant role of ammonia becomes apparent only in clusters containing multiple sulfuric acid molecules, where the difference between the binding energies of ammonia and water is large enough to overcome the mass balance effect of their concentration ratio in the atmosphere.

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Supporting Information Available: The electronic energies, enthalpies, entropies, and Cartesian coordinates for all cluster structures discussed here and data for $(H_2SO_4)_2 \cdot (NH_3)_2$ and $(H_2SO_4)_2 \cdot (NH_3)_3$ clusters to facilitate comparison with earlier studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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