Complexes of Sulfuric Acid with Hydrogen Chloride, Water, Nitric Acid, Chlorine Nitrate, and Hydrogen Peroxide: An ab Initio Investigation

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The formation of binary complexes of sulfuric acid with hydrogen chloride, water, nitric acid, chlorine nitrate, and hydrogen peroxide has been investigated by means of ab initio calculations at the Hartree−Fock and MP2 levels of theory. The hydrogen bonds for the complexes with water, hydrogen peroxide, and nitric acid are found to be strong, whereas hydrogen chloride and chlorine nitrate form only weak complexes. For the first time, structural data for binary complexes of sulfuric acid with hydrogen chloride, nitric acid, chlorine nitrate, and hydrogen peroxide have been obtained. The geometry of the calculated sulfuric acid/water complex with the highest stability is in good agreement with the available data in the literature. The stability of the sulfuric acid complexes with hydrogen peroxide and nitric acid are indications that these gases may also take part in the nucleation process of stratospheric sulfuric acid aerosol.

Introduction

The interest in the properties of gaseous H_2SO_4 is mostly due to its role in aerosol formation in both the troposphere and the stratosphere. Sulfuric acid aerosol particles have been recognized to scatter incoming solar radiation back into space.[1] In the cold stratosphere at high latitudes, sulfuric acid aerosol may play an important role for the heterogeneous chlorine activation. The heterogeneous reaction of hydrogen chloride with chlorine nitrate has been shown in the laboratory[2,3] to readily occur on many types of materials including sulfuric acid aerosol at low temperatures. Ravishankara and Hanson[4] even concluded that the heterogeneous reaction on supercooled sulfuric acid droplets near the ice frost point could occur more efficiently than on polar stratospheric cloud particles. In addition, it has been demonstrated that sulfuric acid aerosols can take up large amounts of nitric acid when cooled to temperatures near the frost point.[5−7]

The atmospheric vapor-phase production mechanism of sulfuric acid involves SO_3, which quickly interacts with H_2O in the gas phase or on the surface of aerosols, perhaps via an $H_2O{\cdot}SO_3$ adduct, to form H_2SO_4.[8−10] In the troposphere, due to its large affinity toward water, H_2SO_4 is thought to exist as hydrates ($H_2SO_4{\cdot}(H_2O)_n$) or as a condensed-phase aerosol.[11] In the stratosphere, where the ambient water vapor fraction is only 4−5 ppmv, small amounts may also exist in the free molecular form.

The formation of sulfuric acid aerosol is believed to occur via homogeneous or ion-induced nucleation of sulfuric acid and water vapor. Some additional trace gases may be involved in the nucleation process.[12] The quantitative and qualitative aspects of this nucleation process are not yet well understood. To date, there exist only a few molecular studies on the nucleation processes described above. A Hartree−Fock ab initio study was performed for the sulfuric acid monohydrate.[13] This study assumed rigid monomers and optimized only the intermolecular distances. In addition, two studies[14,15] were carried out using a classical Monte Carlo simulation to investigate sulfuric acid water clusters of different sizes. Recently, Arstila et al.[16] reported a density functional study of sulfuric acid hydrates containing one to three water molecules. They were able to show that the proton-transfer reaction is unlikely to occur for the mono- and dihydrate, while for the trihydrate the energy barrier is quite low. In a further density functional study, Bandy and Ianni[17] concluded that clusters of $H_2SO_4{\cdot}(H_2O)_n$ for $n = 3−7$ are able to form a H_3O^+ and a HSO_4^- ion.

Experimental characterizations of complexes formed by sulfuric acid with trace gases are still very rare. To date, only a matrix isolation study of sulfuric acid/water complexes,[18] as well as one for sulfuric acid/carbon monoxide complexes, has been carried out.[19] However, the reported spectra are complicated due to the simultaneous presence of SO_3, H_2SO_4, water, and sulfuric acid/water complexes of different sizes. So far, there are no experimental data available regarding the structure of sulfuric acid complexes.

The purpose of our computations is to investigate the stabilities of sulfuric acid complexes with various trace gas species that are relevant to atmospheric chemistry. As was mentioned before, only a few molecular studies of the nucleation processes of sulfuric acid with water have been reported so far.[12−17] Furthermore, to date, there exist no investigations of nucleation processes that involve additional trace gases. Our calculations may give an insight into the primary fundamental steps of the nucleation processes at the molecular level. The photochemical behavior as well as the reactivity of the complexes of sulfuric acid with trace gases may differ significantly for one or another of the monomeric trace gas molecules. This results in the possibility of an enhanced halogen activation even at the molecular level. From this behavior, we may extrapolate whether the respective trace gases are able to form stable bonds with the surface of sulfuric acid aerosol and whether these surface-bonded molecules will have an increased reactivity. As a result of the large size of these complexes, they were investigated at the SCF and MP2 levels only.

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TABLE 1: Bond Lengths and Angles of Sulfuric Acid in Comparison to Data Available in Literature

	this work						
	HF 6-311++G (2D,2P)	MP2 6-311++G (2D,2P)	HF	MP2 6-31G**	Arstila et al.[16] (BLYP)	Hofmann et al.[8] (MP2 6-31G*)	Kuczkowski et al.[25] (exptl)[a]
S═O distance	1.39	1.43	1.41	1.44	1.46	1.44	1.422
S−O distance	1.55	1.60	1.57	1.62	1.64	1.62	1.574
OH distance	0.95	0.97	0.95	0.97	0.99	0.98	0.97
O═S═O angle	123.4	124.8	123.5	125.0	123.7	125.0	123.3
O−S−O angle	102.1	101.8	101.8	101.6	101.4	101.7	101.3
S−O−H angle	110.7	107.6	110.8	107.7	108.5	108	108.5

[a] Determined from microwave spectra of gaseous H_2SO_4 molecules.

Computational Details

The geometries of monomers and complexes have been optimized at the Hartree−Fock and MP2 levels using the 6-31G** and 6-311++G(2D,2P) basis sets. The energies of the complexes calculated with the 6-31G** basis set had to be corrected for the basis set superposition error (BSSE) using the counterpoise correction[20] (largest value for H_2SO_4/H_2O was 5.8 kJ/mol), while this was negligible (<1kJ mol^{-1}) with the larger basis set. In addition, we calculated the analytic Hessian matrix at the SCF level (numeric at MP2 6-31G**) in order to determine the harmonic frequencies and zero-point energies. The corrections for the zero-point energies (ZPE) and the Gibbs free energies (ΔG) were calculated using the harmonic frequencies at the MP2 6-31G** level. All calculations were performed with the GAMESS program[21] on workstations and a Cray T3e parallel computer.

The application of large basis sets was necessary in order to get good results at the Hartree−Fock level. Since electron correlation contributes strongly to the intermolecular hydrogen bonds, we applied Møller−Plesset perturbation theory of second order (MP2) to the wave function. Although the MP2 level of theory only accounts for about 80% of the electron correlation energy, the remaining error is usually insignificant for the determination of molecular geometries. The stabilization energies of the complexes might have a certain error that should, however, be small compared to the differences in the results between the Hartree−Fock and MP2 energies.

Test Calculations. Since there are no experimental data available for sulfuric acid complexes, we tested the accuracy of our calculations on a single sulfuric acid molecule for which experimental geometries and thermodynamic data are available. Table 1 shows the calculated geometric parameters in comparison to data available in the literature, which show a good overall agreement. Despite the good agreement of the SCF with the MP2 values for the sulfuric acid monomer, the differences in the intermolecular distances of the complexes are larger. This is due to the fact that the SCF calculation neglects the electron correlation which is essential to discribe intermolecular bonds accurately. Therefore, the complexes are expected to be described better at the MP2 level. The thermodynamic data derived from the MP2/6-31G** harmonic frequencies are also in excellent agreement with data available in the literature (Table 2). These data are used to calculate the Gibbs free energy of the complexes at stratospheric conditions.

Results

Equilibrium structures of the complexes are presented in Figures 1−5. The corresponding stabilization energies are listed in Table 3. As a result of complexation, the bonds of the oxygen atoms to the sulfur are no longer equivalent and the sulfuric acid molecule has lost its C_2 symmetry. The formation of all of the complexes is exothermic at low temperatures. However, the calculated Gibbs free energies indicate that some of them may not be stable under stratospheric conditions. To calculate stabilization energies of the complexes with a high accuracy, higher correlated methods than MP2, like CISD(T), have to be applied. These calculations are, at least now, not applicable for sulfuric acid complexes containing more than 300 basis functions. In addition, these correlated methods are usually not size consistent. However, since the sulfuric acid complexes are not

TABLE 2: Thermodynamic Data for H_2SO_4 at $T = 298.15$ K

	this work[a]	Hofmann et al.[8]	Chase et al.[26] (exp)
$C_p°$ (J mol^{-1} K^{-1})	83.3	82.8	83.7
$S°$ (J mol^{-1} K^{-1})	298.5	297.9	298.8
ZPE (kJ mol^{-1})	103.3	102.5	

[a] Derived from MP2/6-31G** harmonic frequencies.

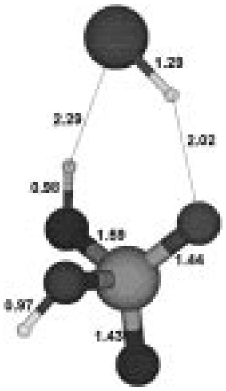

Figure 1. Complex of sulfuric acid with hydrogen chloride. The numbers indicate the respective bond lengths in angstroms from the MP2 calculation with the 6-311++G(2D,2P) basis set.

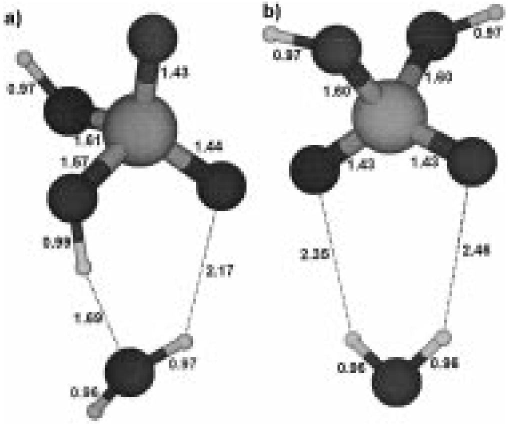

Figure 2. Optimized geometries of stable sulfuric acid monohydrate complexes. The numbers indicate the respective bond lengths in angstroms from the MP2 calculation with the 6-311++G(2D,2P) basis set.

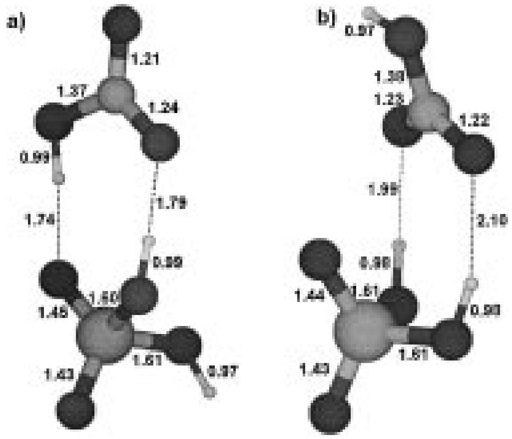

Figure 3. Optimized geometries of stable sulfuric acid/nitric acid 1:1 complexes. The numbers indicate the respective bond lengths in angstroms from the MP2 calculation with the 6-31G** basis set.

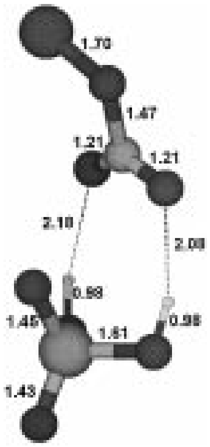

Figure 4. Optimized geometry of the stable sulfuric acid/chlorine nitrate complex. The numbers indicate the respective bond lengths in angstroms from the MP2 calculation with the 6-31G** basis set.

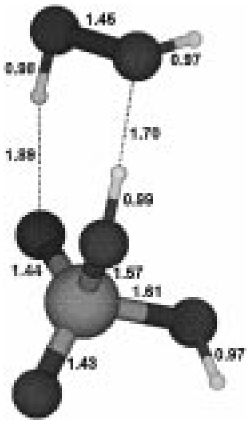

Figure 5. Optimized geometry of the stable sulfuric acid/hydrogen peroxide complex. The numbers indicate the respective bond lengths in angstroms from the MP2 calculation with the 6-311++G(2D,2P) basis set.

expected to have low lying excited states, the stabilization energies calculated at the MP2 level should have errors that are not larger than a few kilojoules per mole.

H_2SO_4·HCl. One stable configuration (Figure 1) was found for the complex formed by sulfuric acid with hydrogen chloride. There is a weak interaction between the chlorine atom and a hydrogen atom of sulfuric acid as well as a weak interaction of the hydrogen atom of hydrogen chloride with a double-bonded oxygen of sulfuric acid. As can be seen in Table 3, the inclusion of the electron correlation is quite important for this complex. The SCF stabilization energy is only about half of the one calculated by MP2. While the intramolecular distances change only insignificantly between the SCF and MP2 calculations, the intermolecular distances are more than 0.2 Å longer at the SCF level. In comparison, all bond distances change less than 0.01 Å from MP2 6-31G** to MP2 6-311++G(2D,2P). The reduction in the force constant of the hydrogen chloride in the complex compared with those of the free molecules results in a frequency shift of about −3.5% (Table 4), while the shift of the hydrogen-bonded OH group of sulfuric acid is about −2.8%. The respective bond lengths are slightly increased by 0.01 and 0.006 Å. The calculated value of the Gibbs free energy at 195 K (Table 3) indicates that this complex should be stable under cold stratospheric conditions. However, at 230 K, the Gibbs free energy is already positive, and therefore, the complex should appear only in the cold stratosphere.

H_2SO_4·H_2O. There are two stable complexes of sulfuric acid with water molecules (Figure 2). Both geometries are optimized without any constraints. This is in good agreement with the results of Givan et al.[18] who recorded infrared spectra of H_2SO_4/H_2O/SO_3 mixtures in argon matrixes. They assumed one complex has an open and one a ring structure. The calculated stabilization energies and Gibbs free energies (Table 3) show that both complexes should be stable under matrix isolation conditons close to 15 K. However, only complex a is stable under stratospheric conditions, while complex b has a positive Gibbs free energy even under very cold stratospheric conditions. Arstila et al.[16] also found two stable configurations of the sulfuric acid monohydrate with their density functional (BL-YP)[22,23] approach. While the geometry of the most stable complex has a strong hydrogen bond and is in agreement with complex a, their optimized structure of the less stable complex b shows some differences from complex a. The stabilization energy of complex a at the SCF level is −40.6 kJ/mol comparable to the −38 kJ/mol that Arstila et al.[16] determined with the density functional approach. Inclusion of electron correlation through the MP2 approach stabilizes this complex to −52.1 kJ/mol. Table 4 shows that complexation of sulfuric acid with water shifts the frequency of the bonded OH group in sulfuric acid by −16.2% (Table 4), which is the strongest decrease in the frequency in all complexes. The increase in the respective bond length of 0.026 Å is also the strongest found in the complexes studied here. Arstila et al. found a stabilization energy of only −2 kJ/mol for the weaker complex, whereas complex b shows a stabilization energy of −11.1 kJ/mol, which increases by inclusion of electron correlation trough MP2 to −15.2 kJ/mol. The geometry of the weaker H_2SO_4·H_2O complex calculated by Arstila et al. shows only the interaction of one hydrogen atom from water with sulfuric acid, while complex b shows that both hydrogen atoms have a very weak interaction with sulfuric acid. The calculation of the force constant matrix shows that the OH stretching frequencies of the water molecule from complex b show only shifts of a few wavenumbers in comparison to the monomer. The intramolecular bond lengths of complex b are the same as those in the monomers within the accuracy of the calculation.

H_2SO_4·HNO_3. Like for water, two stable complexes of sulfuric acid with nitric acid (Figure 3) have been found. Complex a with −48.8 kJ/mol is again significantly more stable than complex b with −29.7 kJ/mol, although the energy difference is not as large as that in the case of water. Further, both complexes have a negative value of the Gibbs free energy

TABLE 3: Stabilization Energies, ZPE Corrections, and Gibbs Free Energies of Sulfuric Acid Complexes with Respect to Their Monomers (All Values Are in kJ/mol^{-1}.)

species	HF 6-311++G (2D,2P)	MP2 6-311++G (2D,2P)	HF[a] 6-31G**	MP2[a] 6-31G**	ZPE[b] correction	Δ*G*[b] (195 K)	Δ*G*[b] (230 K)
H_2SO_4·HCl	−15.7	−29.0	−17.0	−27.4	5.8	−2.1	1.7
H_2SO_4·H_2O (a)	−40.6	−52.1	−49.5	−62.7	10.9	−30.7	−26.4
H_2SO_4·H_2O (b)	−11.1	−15.2	−15.1	−19.7	5.6	6.9	11.0
H_2SO_4·HNO_3 (a)	−46.1	−48.8[c]	−55.0	−58.0	5.7	−32.3	−28.8
H_2SO_4·HNO_3 (b)	−21.7	−29.7[c]	−29.3	−38.8	5.3	−12.9	−9.4
H_2SO_4·$ClNO_3$	−16.4	−17.4[c]	−22.3	−25.3	4.4	5.1	9.6
H_2SO_4·H_2O_2	−40.8	−55.1	−47.3	−60.1	8.3	−25.3	-20.0

[a] Corrected for the BSSE (see text). [b] Calculated using MP2−6-31G** harmonic frequencies. [c] Single-point calculations at the optimized MP2 6-31G** geometry.

TABLE 4: Relative and Absolute Frequency Shift of the Hydrogen-Bonded OH Group of Sulfuric Acid and of the XH (X = O, Cl) Group of the Trace Gas in Comparison to the Free Molecule Calculated at MP2 6-31G**

species	$\nu_{complex}/\nu_{H_2SO_4}$	$\nu_{complex} - \nu_{H_2SO_4}$ (cm^{-1})	$\nu_{complex}/\nu_{trace\ gas}$	$\nu_{complex} - \nu_{trace\ gas}$ (cm^{-1})
H_2SO_4·HCl	0.972	−106.3	0.965	−110.3
H_2SO_4·H_2O (a)	0.838	−620.4	0.984	−207.1
H_2SO_4·H_2O (b)			0.996	−16.6
H_2SO_4·HNO_3 (a)	0.934	−252.0	0.917	−313.3
H_2SO_4·HNO_3 (b)	0.976	−92.4		
H_2SO_4·$ClNO_3$	0.986	−54.6		
H_2SO_4·H_2O_2	0.862	−528.8	0.967	−124.4

under stratospheric conditions. In addition, the influence of the electron correlation to the complexation is much smaller since the stabilization energy differences between the SCF and MP2 levels are much smaller than those in the case of the water complex. The intermolecular bond distances of complex a indicate that there are two hydrogen bonds of comparable strength, which are much stronger than both intermolecular bonds of complex b. The frequency shift of the hydrogen-bonded OH groups of sulfuric acid and nitric acid amount to −6.6% and −8.3%, respectively (Table 4), for complex a, whereas in complex b, the frequency shift is only −2.4% for the bonded OH groups of sulfuric acid. The changes in the respective bond lengths are 0.013, 0.015, and 0.004 Å.

H_2SO_4·$ClNO_3$. Only one stable complex of sulfuric acid with chlorine nitrate (Figure 4) has been found whose structure corresponds to the sulfuric acid/nitric acid complex b. As a result of the higher electronegativity of chlorine in comparison to hydrogen, the electron density at the two oxygen atoms, which are involved in the formation of the hydrogen bonds, is slightly lower than in nitric acid. Therefore, the hydrogen bridges are not as strong as in the respective complex with nitric acid. The bond energy calculated at the highest available level of theory is only −17.4 kJ/mol. However, the Gibbs free energy of this complex is positive, even under cold stratospheric conditions. Like in the case of the HNO_3 complex, there is only a small energy change between the SCF and MP2 calculation, indicating a small influence of the electron correlation to the intermolecular bonding. The small changes in the intramolecular force constants result in a frequency change of only −1.4% (Table 4) and an increase in the bond length of 0.003 Å of the hydrogen-bridged OH bonds in comparison to free sulfuric acid. A chlorine nitrate complex similar to complex a with nitric acid is not stable due to the larger radius and higher electronegativity of the chlorine atom. The potentials of the molecules in this configuration are repulsive, and all attempts for a geometry optimization starting at this configuration resulted in a complete dissociation of the complex.

H_2SO_4·H_2O_2. H_2O_2 forms a very stable complex with sulfuric acid, which has two hydrogen bonds (Figure 5). With −55.1 kJ/mol hydrogen peroxide forms a sulfuric acid complex with the highest stabilization energy due to the formation of two strong hydrogen bonds. The value of the Gibbs free energy shows that this complex should be stable under all stratospheric conditions. The hydrogen bond from the OH group of the sulfuric acid to one of the oxygen atoms of the hydrogen peroxide is slightly weaker than the one formed by sulfuric acid to water (complex a). The bond length increases by 0.02 Å, and the frequency shifts by −13.8%. In addition, there is a strong hydrogen bond from one OH group of hydrogen peroxide to an oxygen atom of sulfuric acid. This bond increases due to complexation by 0.01 Å, and the frequency shifts by −3.3%.

Discussion

We have calculated the geometries and energetics of 1:1 complexes of sulfuric acid with hydrogen chloride, water, nitric acid, chlorine nitrate, and hydrogen peroxide at the molecular level. It is important to note that the results cannot be applied to the bulk material, since the three-dimensional arrangement of the molecules usually results in a different structure and different stabilities. In addition, at concentrations and temperatures relevant to the stratosphere, there are practically no undissociated H_2SO_4 molecules available inside an aerosol droplet. However, it can be expected that similar complexes will form on sulfuric acid aerosol surfaces, where it is unlikely that all of the sulfuric acid molecules are dissociated. The strong interactions of water, hydrogen peroxide, and nitric acid with sulfuric acid are a clear indication that these compounds will form stable complexes at the molecular level. This is also reflected in the high Henry's law constants of these molecules.[24] The Gibbs free energies of these complexes indicate that they should be stable against dissociation in the stratosphere. Therefore, these molecules are able to stick on aerosol surfaces. However, since the three-dimensional arrangement in the bulk material is usually significantly different, these calculations do not allow us to predict whether the surface-bonded molecules are able to dissolve into the bulk material of the aerosol, which would be necessary for an uptake of larger quantities of these trace gases. The relatively weak bonding energies of hydrogen chloride and chlorine nitrate with sulfuric acid molecules are on the other hand a clear indication that the probability for them to stick on sulfuric acid surfaces, and therefore the probability for heterogeneous activation on the aerosol surface, is quite low. The calculated Gibbs free energies show that the sulfuric acid/chlorine nitrate complex should not be stable under stratospheric conditions. For the sulfuric acid/hydrogen chloride complex, the calculated Gibbs free energy is negative only at temperatures found in the cold stratosphere. This is in good agreement with the observed stratospheric chlorine activation in the cold arctic stratosphere and an indication that the chlorine activation may take place on sulfuric acid aerosol as well as on PSC surfaces under these conditions.

Conclusion

We were able to calculate the geometries and energetics of complexes from sulfuric acid with various atmospherically relevant trace-gas molecules. Although only small bimolecular complexes have been considered, we gained useful insight on the interactions between sulfuric acid and these trace-gas molecules. The knowledge about these interactions is important to clarify the formation of the stratospheric sulfuric acid aerosol as well as the reactions that can occur on it. It could be shown that nitric acid, water, and hydrogen peroxide form comparably strong complexes with sulfuric acid at the molecular level. Although the results cannot be used for the bulk material, they can be considered at a first approximation to describe the interactions on the sulfuric acid aerosol surfaces, where undissociated sulfuric acid molecules may be available besides the ionic species. Furthermore, the calculations show that sulfuric acid may play an active part in the chlorine activation under cold stratospheric conditions.

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