

Measurement of the Thermodynamics of the Hydrated Dimer and Trimer of Sulfuric Acid

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We report measurements of the equilibrium constants, K_p , for the water mediated clustering of two and three sulfuric acid molecules for atmospheric temperatures and relative humidities. Limits for K_p for the formation of the sulfuric acid tetramer and higher clusters as well as the kinetics of small sulfuric acid cluster growth are also presented. These results put strong constraints on the rate of nucleation in the atmosphere via the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ neutral mechanism. We show that the neutral nucleation of H_2SO_4 and H_2O is slower than ion-induced nucleation of H_2SO_4 and H_2O for most conditions found in the middle and upper troposphere. These laboratory-based upper limits to the nucleation rates are also much lower than the predictions of the liquid drop model/classical nucleation theory.

Introduction

Particles in the atmosphere (“aerosol”) influence the formation of clouds,^{1–3} impact the Earth’s climate, and are detrimental to health and visibility. The formation of small particles by co-condensation of supersaturated gas molecules (hereafter referred to as “nucleation”) is poorly understood, yet its significance as a source of atmospheric aerosol and a central role for sulfuric acid vapor has been widely recognized.^{4,5} While nucleation in the atmosphere has been the subject of theoretical and experimental study for many decades,⁶ uncertainties in the mechanism and predicted atmospheric nucleation rates are large, due to a limited knowledge of the thermodynamics of the relevant molecular clusters⁷ of sulfuric acid.

The thermodynamic model most widely applied to atmospheric nucleation employs the capillarity/liquid drop approximation^{6,8,9} that treats the small clusters as spherical drops with a surface tension and density the same as those of the bulk liquid. Predictions from this model have long provided guidance for experimental investigators, yet the model has serious deficiencies,^{6,7} and it has been unable to quantitatively explain many atmospheric nucleation observations.^{4,5,10} However, classical theory predicts that the neutral $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ mechanism^{8,9} is an efficient source of new particles in the free troposphere where ammonia is low,¹² possibly in accordance with observations.^{11,15} Nonetheless, the role of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ nucleation in Earth’s atmosphere is highly uncertain. Recent studies using a model based on laboratory ion cluster thermodynamics^{15,16} have shown that ion-induced nucleation (IIN) of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ is also consistent with measured ultrafine particle concentrations (<3 nm diameter) in the free troposphere. The inability of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ binary classical theory to reproduce the nucleation observed in the lower troposphere has led to suggestions that nucleation of NH_3 with H_2SO_4 and H_2O may be important.^{10,13,14} A

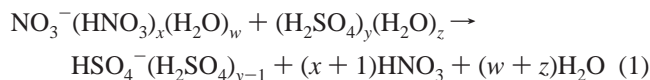
quantitative understanding of the relative contributions of neutral and ion-induced nucleation is important for evaluating anthropogenic and natural influences on particle formation and ultimately climate. If IIN is found to be a significant source of new particles, it would provide a link between cosmic rays, the primary source of atmospheric ions, and climate.¹⁷

The primary step in nucleation of the neutral $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system is the reaction of two hydrated sulfuric acid molecules, to form a “dimer” containing two H_2SO_4 molecules and associated water molecules (throughout, dimer, trimer, etc., refer to H_2SO_4 content.) It is expected that the dimer and trimer are the least stable clusters and knowledge of their thermodynamics can put strong constraints on the formation rate of higher clusters (and thus the nucleation rate), particularly for conditions where the critical cluster is small, such as the low temperatures of the free troposphere.

Here, we report laboratory measurements of the initial steps of nucleation in the neutral $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system and derive thermodynamic information for the sulfuric acid dimer and trimer. We use this information to put limits on the atmospheric nucleation rate for the neutral $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ mechanism.

Experimental Methods

$(\text{H}_2\text{SO}_4)_x(\text{H}_2\text{O})_y$ clusters were formed in the laboratory by mixing two flows of nitrogen gas, one saturated with H_2SO_4 vapor and a second containing water vapor. The mixed vapor and gas entered a flow reactor held at a fixed temperature between 230 and 255 K. Sulfuric acid clusters were detected by reaction with nitric acid–nitrate ion clusters:



where the arrow also indicates the removal of H_2O and HNO_3 ligands that occurs upon ion sampling. Full details of the experimental apparatus and procedures have been presented

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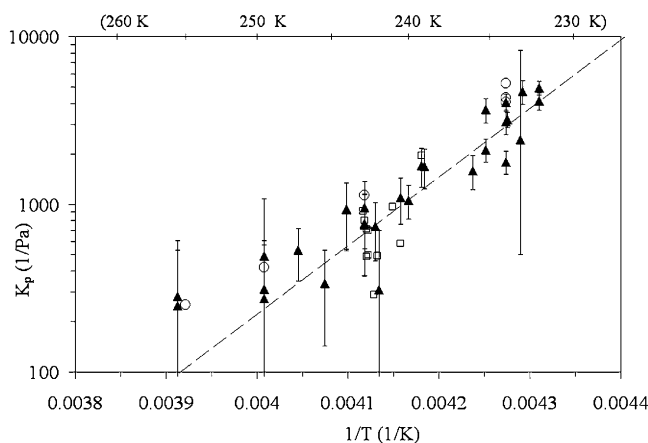


Figure 1. Measured equilibrium constant for the H_2SO_4 dimer plotted versus inverse temperature. The triangles are for $\text{RH} = 20 \pm 6\%$, the circles are for $\text{RH} = 48 \pm 10\%$, and the squares are for $\text{RH} = 6 \pm 2\%$. $[\text{H}_2\text{SO}_4]$ was between 4×10^8 and $1.5 \times 10^9 \text{ cm}^{-3}$ except for one measurement at 233 K where it was $1.4 \times 10^8 \text{ cm}^{-3}$. These data points and those for $K_p < 500 \text{ Pa}^{-1}$ are very uncertain (note the large error bars: sources of uncertainty are detailed in the Supporting Information). Error bars for the 48 and 6% RH data are not shown but are comparable to those for the 20% RH data. The line is a weighted, least-squares fit to the 20% RH data according to eq 3. Note that within the scatter this fit can also describe the 6 and 48% RH data. The data indicate that K_p varies with $\text{RH}^{0.5}$; the exponent 0.5 has an uncertainty of $\pm 100\%$.

previously.^{18,19} Presented in the Supporting Information are a schematic of the apparatus, typical experimental parameters, significant changes to the apparatus, a new procedure for acquiring the neutral dimer concentrations from the ion signals, measurements of the gas temperature, fluid dynamics simulations, and a cluster growth/evaporation model.

Results

The measured equilibrium constants, K_p , for the water mediated dimerization reaction are plotted versus $1/T$ in Figure 1. The measured cluster ion signals contain information on the H_2SO_4 content of the neutral clusters,¹⁸ and the K_p value we report is an average over the ambient water distributions for the monomer and dimer (an approach analogous to the H_2O quasi-equilibrium approach⁹)

$$K_p = \frac{\sum_i P_{2,i}}{(\sum_i P_{1,i})^2} \quad (2)$$

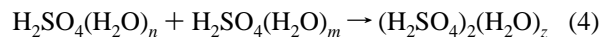
where $P_{1,i}$ and $P_{2,i}$ are the partial pressure of the i th hydrate of the monomer and dimer, respectively. Because the distributions represented by the sums likely vary with relative humidity (RH, wrt supercooled water²⁰), the data in Figure 1 are segregated into three RH bins of 48 ± 10 , 20 ± 6 , and $6 \pm 2\%$.

A weighted least-squares fit (3) of the 20% RH data is shown as the dashed line in Figure 1, giving

$$K_p (\text{Pa}^{-1}) = \exp[(9210 \pm 930)/T - (31.4 \pm 3.9)] \quad (3)$$

Noting that $K_p^\circ = \exp[(-\Delta H^\circ + T\Delta S^\circ)/RT]$ (standard state of 1 atm) yields $\Delta H^\circ = -18.3 \pm 1.8 \text{ kcal/mol}$ and $\Delta S^\circ = -39.5 \pm 7.8 \text{ cal/mol K}$ for the water mediated dimerization of H_2SO_4 (the error bars are the standard error of the coefficients.) Ab initio work²¹ predicts stabilization of the hydrated dimer by ion pair formation, giving ΔH° and ΔS° of $-20.3 \pm 2.5 \text{ kcal/mol}$

and $-46 \pm 5 \text{ cal/mol K}$, respectively, for the reaction



for $n = 1-4$, $m = 0$ or 1, and $z = n + m \leq 4$. An ab initio study²⁶ that does not report the formation of ion pairs gives an enthalpy change for formation of the dimer of -13 kcal/mol and also predicts essentially no hydration (less than 1%) of the dimer and monomer for the present conditions. Comparison of our experimental results with these two theoretical approaches suggests that (i) extensive hydration and (ii) formation of ion pairs (i.e., deprotonation of at least one H_2SO_4) is important for the dimer.

Discussion

The measured equilibrium constants for the water mediated dimer formation depend only weakly on RH, perhaps $\text{RH}^{0.5}$. This result was not anticipated because measurements²² and theoretical studies²³⁻²⁵ indicate significant hydration for the monomer (e.g., one and two waters for RH values of 10 and 50%,²² respectively, at 295 K) as well as for the dimer.²¹ A likely explanation for the weak RH dependence is that the distribution of water on the dimer is a weak function of RH for the present conditions. This is qualitatively consistent with the ab initio results²¹ that predict the distribution peaks at $z = 5$ and 6 over the range of RH and T studied here. Quantitatively, however, a complete analysis based on population-weighted decomposition rates for the hydrated dimer (i.e., the reverse of (4)) predicts a strong RH dependence of K_p due to a shifting fraction of the dimer hydrate distribution to lesser (greater) hydrates that decompose very quickly (slowly). However, increasing the stability to loss of H_2O of the small dimer hydrates ($z = 1-3$) by 0.5 kcal/mol and decreasing the stability of the well-hydrated dimers ($z = 4, 5$, and 6) by 2.5–3.5 kcal/mol, with regard to decomposition to monomers, yields a predicted K_p value that has little RH dependency and is well within the scatter of our measurements. Note that the thermodynamics²¹ of (4) for the $z \geq 4$ dimers is based on structures where both H_2SO_4 molecules are deprotonated; this shift in character of the calculations possibly allows for more uncertainty in the predicted energetics.

For the conditions of this work, the dimer is essentially in equilibrium with the monomer. The largest conversion of monomer to dimer was observed at 233 K and $[\text{H}_2\text{SO}_4] = 1.3 \times 10^9 \text{ cm}^{-3}$ where 2.4% of the monomer was converted to dimer (i.e., [dimer] was 1.2% of [monomer]), giving a predicted equilibration lifetime of 0.1 s, dominated by the decomposition of the dimer (using our measured K_p and assuming $10^{-10} \text{ cm}^3/\text{s}$ for the forward rate coefficient.) At $T < 250 \text{ K}$ and $[\text{H}_2\text{SO}_4] \geq 8 \times 10^8 \text{ cm}^{-3}$, significant concentrations ($> 2 \times 10^5 \text{ cm}^{-3}$) of higher clusters are observed. Figure 2 shows mass spectra for $\text{RH} = 7, 22$, and 56% and $[\text{H}_2\text{SO}_4]$ between 0.9 and $1.0 \times 10^9 \text{ cm}^{-3}$ at $T = 242 \text{ K}$.

Comparison of the cluster distributions with predictions from the growth model (also shown in Figure 2) yields limits on the thermodynamics and growth kinetics for the larger clusters. These values are listed in Table 1. These results show that the dimer is the least stable cluster with respect to evaporation of H_2SO_4 , and for $\text{RH} \geq 20\%$ and $[\text{H}_2\text{SO}_4] > 5 \times 10^8 \text{ cm}^{-3}$, the growth rates of the trimer, at $T \leq 240 \text{ K}$, and the larger clusters are faster than their evaporation rates. Because evaporation of the larger clusters ($y \geq 4$) is not important over the range of the present experimental conditions, their concentrations reflect steady-state conditions, and only upper limits to ΔG° can be

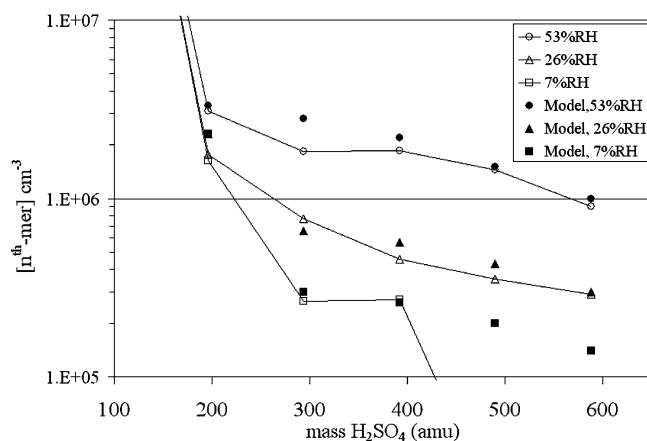


Figure 2. Number density of H_2SO_4 clusters plotted versus H_2SO_4 content at three different RH values at 240.5–243 K with $[\text{H}_2\text{SO}_4]$ between 0.9 and $1.0 \times 10^9 \text{ cm}^{-3}$. For typical conditions, the detection limit was $\sim 10^5 \text{ cm}^{-3}$ and corrections for known mass discrimination effects (e.g., Figure 2 of ref 18) were applied. The marked dependence of [cluster] on RH for similar $[\text{H}_2\text{SO}_4]$ indicates that the abundance of the larger clusters was largely limited by evaporation of the trimer whose abundance is a strong function of the extent of hydration (i.e., growth of the larger clusters was not limited by the addition of monomers.)

TABLE 1: Thermodynamics and Growth Kinetics of the Water Mediated Clusters Containing y Sulfuric Acid Molecules

$(\text{H}_2\text{SO}_4)_y(\text{H}_2\text{O})_z$ ^a	ΔG° , ^b 242 K (kcal/mol)	k_f^c ($10^{-10} \text{ cm}^3/\text{s}$)
$y = 2$, dimer	-8.7 , ^{d,e} -8.9 ^f	1.7
$y = 3$, trimer	-10.7 , ^d -11.2 , ^e < -11 ^f	1.8
$y = 4$, tetramer	< -12	2.0
$y = 5$, pentamer	< -12	2.2
$y = 6$, hexamer	< -12	2.4

^a Summation over z for each species and similarly for the monomer.

^b Free energy of formation of the hydrated y th-mer from the hydrated monomer and $(y - 1)$ th-mer. ^c Forward rate coefficient for formation of the y th-mer estimated from the cluster growth model (see the Supporting Information.) ^d 7% RH. ^e 26% RH. ^f 53% RH.

given. For some measurements, trimer evaporation is also negligible, the dimer is the “critical cluster” and nucleation is limited by dimer evaporation, and [trimer] can be far from its equilibrium value.

At $T > 240 \text{ K}$ and $[\text{H}_2\text{SO}_4] \leq 1.5 \times 10^9 \text{ cm}^{-3}$, the evaporation of the trimer overcomes growth, and the cluster distributions actually yield the K_p value for the trimer, $K_{p,3}$. We observed a strong RH effect on $K_{p,3}$: it increases by a factor of ~ 5 for an increase in RH of 6 to 20%. This RH sensitivity is consistent with the results of nucleation measurements^{27–30} that show the nucleation rate increases strongly with RH at room temperature. Shown in Figure 3 are $K_{p,3}$ values for the trimer calculated from a portion of the measurements. The measurements are consistent with $\Delta H^\circ = -22 \text{ kcal/mol}$ and $\Delta S^\circ = -45.5 \text{ cal/mol K}$ for the 20% RH data, and $K_{p,3}$ varies with $\text{RH}^{1.5}$. The uncertainties in K_p and $K_{p,3}$ are estimated to be $+100/-50\%$ and $+200/-67\%$, respectively, at 242 K. These are equivalent to ± 0.3 and $\pm 0.5 \text{ kcal/mol}$ uncertainty in ΔG° , respectively, and with the $\pm 8 \text{ cal/mol K}$ uncertainty in ΔS° , the uncertainties in K_p and $K_{p,3}$ increase from factors of 2 and 3, respectively, at 242 K to factors of 4 and 7, respectively, at 200 K.

In Figure 4, we present upper limits to the rate of nucleation for two $[\text{H}_2\text{SO}_4]$ characteristic of the atmosphere. Also shown in the figure are laboratory-based, predicted IIN rates¹⁶ and predictions from classical binary theory.⁸ The IIN rates are

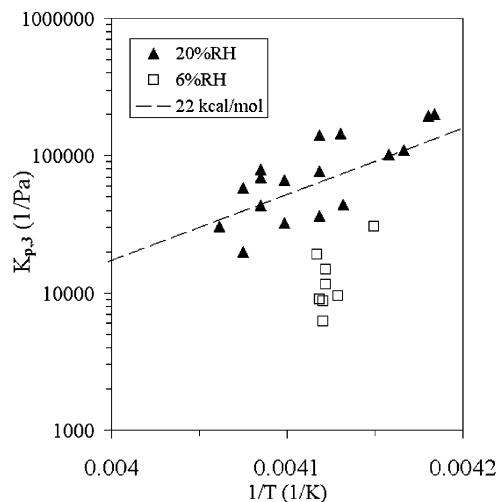


Figure 3. $K_{p,3}$ for the trimer versus inverse temperature where $K_{p,3} = [\text{trimer}]/[\text{dimer}][\text{H}_2\text{SO}_4]/kT = \Sigma P_{3,i}/\Sigma P_{2,i}\Sigma P_{1,i}$. We report measurements in a limited range of temperature (238–246 K) and RH (6–27%). Measured [trimer] at lower temperatures and higher RH were suppressed below equilibrium levels by growth to higher clusters and at higher temperatures a small amount of an impurity species was present at 293 amu and [dimer] is low and becomes highly uncertain.

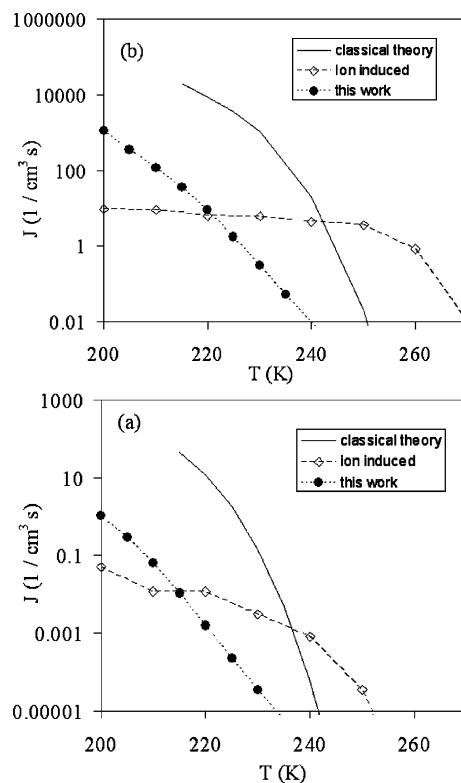


Figure 4. Net steady-state flux between the dimer and trimer at 50% RH as a function of temperature for $[\text{monomer}] = 10^6$ (a) and 10^7 cm^{-3} (b). This laboratory-based rate is an upper limit to the rate of nucleation via the neutral binary mechanism. It is given by the growth rate of the dimer via addition of H_2SO_4 minus the evaporation rate of the trimer (from steady-state [trimer] calculated assuming negligible decomposition of the tetramer.) $K_{p,3}$ for the trimer at 50% RH is given by the fit to the data at 20% RH in Figure 3 and assuming a $\text{RH}^{1.5}$ dependency. Laboratory-based IIN nucleation rates¹⁶ and predictions⁸ from classical theory for the neutral binary mechanism are also shown.

greater than the laboratory-based neutral rates at $T > 215 \text{ K}$, suggesting a dominant role for IIN under these conditions. For temperatures near 215 K, such as the conditions where substantial nucleation is observed,^{11,15} the present results suggest

comparable contributions from IIN and the neutral mechanism, while, at temperatures of <210 K, the neutral mechanism may dominate. Hence, IIN is likely the dominant H₂SO₄/H₂O mechanism for most conditions of the free troposphere. Ammonia can increase the abundance of molecular clusters of sulfuric acid,¹⁹ and it will facilitate nucleation.³⁰ However, it is not known if [NH₃] levels of a few pptv, predicted for the free troposphere,¹² are high enough to significantly influence nucleation in this region.

The laboratory-based upper limits from this work are 10⁻³–10⁻⁴ times the classical theory predictions for all conditions. The most recent classical theories^{8,9} agree within an order of magnitude with laboratory measurements near room temperature,^{27–30} where the critical cluster contains eight or more H₂SO₄ molecules. The much larger discrepancy here is likely due to the small size of the critical cluster where the energetics given by the liquid drop approximation are expected to be most in error.

The present work highlights the importance of measuring the energetics of small clusters to understanding and predicting atmospheric nucleation. It also indicates a significant and perhaps dominant role for IIN in the free troposphere.

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Supporting Information Available: Details of the experimental apparatus and analytical procedures, results of computational fluid dynamics simulations, and a description of the cluster growth model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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