

Experimental Observation of Strongly Bound Dimers of Sulfuric Acid: Application to Nucleation in the Atmosphere

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Sulfuric acid is a key compound in atmospheric nucleation. Here we report on the observation of a close-to-collision-limited sulfuric acid dimer formation in atmospherically relevant laboratory conditions in the absence of measurable quantities of ammonia or organics. The observed dimer formation rate was clearly higher than the measured new particle formation rate at ~ 1.5 nm suggesting that the rate limiting step for the nucleation takes place after the dimerization step. The quantum chemical calculations suggested that even in the ultraclean conditions there exist (a) stabilizing compound(s) with (a) concentration(s) high enough to prevent the dimer evaporation. Such a stabilizing compound should be abundant enough in any natural environment and would therefore not limit the formation of sulfuric acid dimers in the atmosphere.

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Atmospheric nucleation rates have been shown to be dependent on sulfuric acid concentration ($[\text{H}_2\text{SO}_4]$) [1–3]. Until recently, laboratory experiments on H_2SO_4 nucleation have failed to reproduce ambient observations [4–7], but Sipilä *et al.* [8] showed that the disagreement between the ambient data and the laboratory studies is related to experimental design and that sulfuric acid nucleation in ultraclean laboratory conditions can indeed explain the atmospheric nucleation rates. If H_2SO_4 is responsible for the nucleation, the first step should be a formation of (possibly hydrated) sulfuric acid dimers which can and have been measured by means of chemical ionization mass spectrometry (CI-MS) [9–12].

In the Chemical Ionization Mass Spectrometer (CI-MS) charger a high concentration of nitrate ions (NO_3^-) is gently added to the sample air. When colliding with a NO_3^- ion, sulfuric acid molecule and dimer donate a proton to the nitrate ion. With a constant collision energy, majority are then detected in the mass spectrometer as bisulphate ion HSO_4^- and some in a form of sulfuric acid-bisulphate cluster ($\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$), respectively. The main challenge in measuring the dimer formation rate is related to the clustering of neutral and charged H_2SO_4 molecules inside the CI-MS drift tube. This ion-induced dimerization inside the instrument can veil the signal from the neutral dimers [12]. Therefore, the deployment of the cluster mass spectrometry to atmospheric H_2SO_4 concentrations is not straightforward and first reports have appeared only very recently, showing sulfuric acid clusters during gas-to-particle conversion up to a pentamer [12] or in naturally charged ions up to a tetramer [13]. Consistently with Sipilä *et al.* [8], Zhao *et al.* [12]

concluded that H_2SO_4 is driving the nucleation, but they also speculated that the clusters are most probably stabilized by a third body.

In this study we investigated the formation of H_2SO_4 dimers with a novel approach. The experiments were conducted in clean air (purity: 99.9999999%) containing atmospherically relevant concentrations of H_2SO_4 and H_2O at temperature of 293 K and relative humidity of 22%. We used a CI-MS for measuring the concentrations of H_2SO_4 monomers and dimers at the outlet of the Leibniz-institute for Tropospheric Research laminar flow tube (IfT-LFT) [8,14]. Additionally, total number concentration of particles with diameters down to 1.5 nm [8] were measured at the outlet of IfT-LFT together with commercial and tuned up particle detectors [8,15]. Sulfuric acid was produced either from a liquid sample or via $\text{OH} + \text{SO}_2$ reaction in the gas phase. The OH radicals were produced *in-situ* either from ozone photolysis or via ozonolysis of alkenes in absence of light. Within the flow tube, the generated H_2SO_4 monomers underwent collisions resulting in sulfuric acid dimer formation. In the experiments using *in-situ* produced H_2SO_4 the concentration at the outlet of the IfT-LFT was also estimated by kinetic modeling [14].

Unlike in the previous experiments [9–11], we varied the residence time (reaction time) in the flow tube while keeping the sample ionization and collision energy constant. This approach allowed us to distinguish between the signals from originally neutral dimers and the signals from dimers formed by ion-induced mechanism inside the CI-MS. The ion-induced mechanism should be only dependent on $[\text{H}_2\text{SO}_4]$ entering the instrument, whereas the neutral pathway for the dimer formation should be

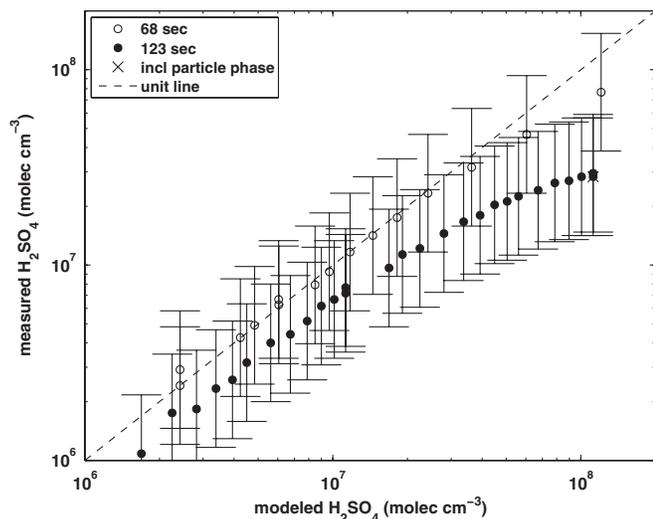


FIG. 1. The measured sulfuric acid (H_2SO_4) monomer concentration as a function of modeled 14 H_2SO_4 concentration at the end of the IFT-LFT with two different residence times. Correction for the H_2SO_4 condensing onto the particle phase is marked with a cross.

dependent on the residence time in the IFT-LFT. The observation of neutral dimers was possible since the residence times (32 to 115 sec) were shorter than the time required for reaching a steady state (400–1000 sec) between the dimer formation and evaporation reactions in our experiments.

First indication for the existence of sulfuric acid clusters below the detection limit of the particle counters was obtained in an O_3 photolysis experiment when the measured output concentration of the IFT-LFT was compared to the output concentration from a kinetic model (Fig. 1). For a low modeled H_2SO_4 concentration, the calculated and CI-MS measured concentrations, despite a small offset, were equal within the experimental error. With the increasing $[\text{H}_2\text{SO}_4]$, the CI-MS signal started to deviate from the predicted. With the highest $[\text{H}_2\text{SO}_4]$ we were able to measure also the aerosol size distribution and estimate the loss of gas phase $[\text{H}_2\text{SO}_4]$ into the particles, which could not account for the model-measurement discrepancy (Fig. 1). This indicated that there has to be a higher order loss mechanism for H_2SO_4 . It should be noted that this additional loss becomes visible only with a long enough residence time, suggesting that the loss process takes place inside the IFT-LFT and is not (at least completely) caused by any artefact in the CI-MS operation in high $[\text{H}_2\text{SO}_4]$ (Fig. 1).

Figure 2 depicts the measured dimer concentration at the output of the IFT-LFT as a function of measured sulfuric acid monomer concentration, which was either produced *in-situ* (open symbols) or generated from the liquid saturator (filled symbols). A close to a quadratic dependence of the dimer concentration on the monomer concentration is clearly visible in both sets of experiments. For a given residence time, the monomer concentrations were lower during liquid sample experiments than in the *in-situ*

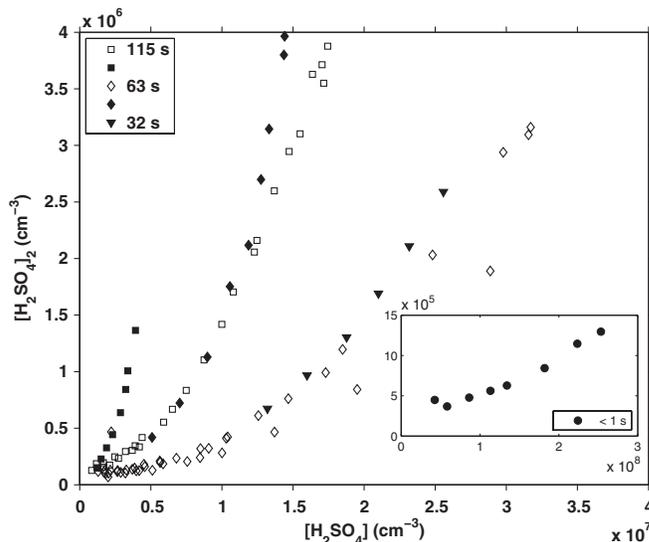


FIG. 2. The detected dimer concentration as a function of monomer concentration measured at the end of the IFT-LFT with different residence times at the flow tube. Open symbols indicate data from the O_3 -photolysis experiments, and filled symbols H_2SO_4 from the liquid saturator. The inset shows data measured immediately after the sulfuric acid saturator yielding the maximum contribution of ion-induced dimerization in the CI-MS charger. Please note the different scale in the inset.

photolysis data set. This is due to a different production profiles and losses and different reaction times [8]. The quadratic behavior, however, is expected also in case of artificial ion-induced dimer formation in the CI-MS charger. The data taken from the IFT-LFT inlet directly after the sulfuric acid saturator with a residence time of less than 1 s (Fig. 2 inset) gives the maximum contribution of the ion-induced dimer formation in the CI-MS charger, which is small compared to the dimer formation rates observed with the longer residence times. By alternating the residence time in the flow tube we have shown that the dimer signal is not only dependent on the H_2SO_4 monomer concentration, but varies also as a function of the time available for the gas kinetics in the flow tube (Fig. 2).

In the experiments where the OH radicals were produced via ozonolysis of alkenes, the residence time was kept constant. The aim was to investigate whether different organic oxidation products formed in a reaction chain starting from organics and O_3 can affect the dimer formation process, e.g., via stabilization of the dimers. If some of these compounds would stabilize the clusters, it should be evaporated from the dimer before the detection in order to result in the observed—sulphuric acid dimer signal. Independent of the organic precursor (TME: tetramethyl-ethylene, MCH: methyl-cyclohexene, limonene and α -pinene) or on the concentration of the precursor and its products, the dimer signal depended only on the monomer concentration (Fig. 3). This suggests that either the oxidation products of these organics do not assist the dimer formation, or that the unknown stabilizing compound in

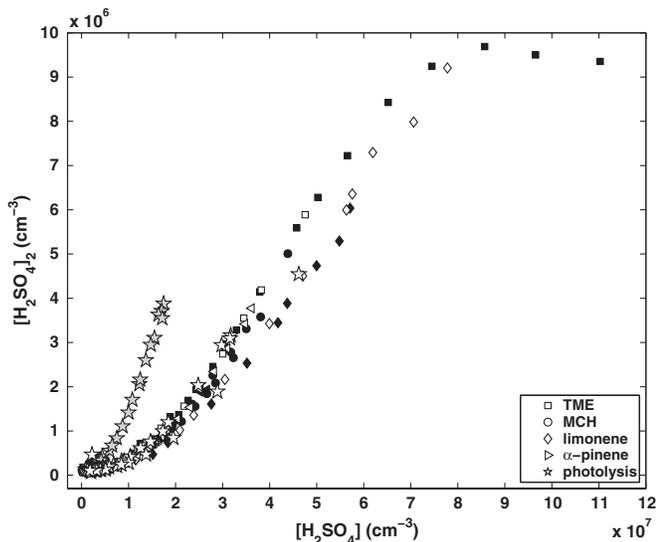


FIG. 3. The measured sulfuric acid dimer concentration as a function of the measured monomer concentration in different experiments involving a suite of organic compounds. Open symbols illustrate data where the organic precursor concentration was varied whereas the filled symbols are from experiments, where SO_2 was varied. The experiments with the organics were all performed with a residence time of 97 sec. Results from photolysis experiments (absence of organics) with a residence time of 63 or 115 sec are given for comparison as open stars (photolysis, 63 sec) and filled stars (photolysis, 115 sec). It should be noted that H_2SO_4 profiles in photolysis experiments are not identical to experiments utilizing the dark reaction for the OH production.

the system is already saturated so that an addition of any stabilizing compound does not anymore cause a measurable effect on the clustering process. With $[\text{H}_2\text{SO}_4]$ exceeding $\sim 10^8 \text{ cm}^{-3}$ the dimer signal shows saturation (Fig. 3). This possibly indicates significant formation of trimers and larger sulfuric acid clusters, which are outside of the mass range of our CI-MS.

In order to explain the observations we performed kinetic modelling with two different models [14,16]. The measured dimer formation rates in the photolysis experiment as well as those resulting from the DACM model [16] are presented in Fig. 4. The measured dimer formation rate is close to the collision rate of H_2SO_4 molecules (the uppermost line in Fig. 4). Since the detectable dimer formation rate can not be this high with the evaporation rates observed in earlier experiments [11], a presence of a stabilizing compound in the sulfuric acid dimers is presumable (see supplemental material [17]). We simulated the dimer formation rate with respect to varying concentrations of dimethylamine (DMA), being suggested as a strong stabilizing compound [18]. According to the recent calculations [19], practically all $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{DMA}$ clusters are detected as sulfuric acid dimers in CI-MS, and a significant portion of $\text{H}_2\text{SO}_4 \cdot \text{DMA}$ clusters are detected as pure H_2SO_4 molecules, both due to the evaporation of the DMA immediately after charging. Thus we used the sum of $[\text{H}_2\text{SO}_4]$ and $[\text{H}_2\text{SO}_4 \cdot \text{DMA}]$ for modelling the measured H_2SO_4 concentration.

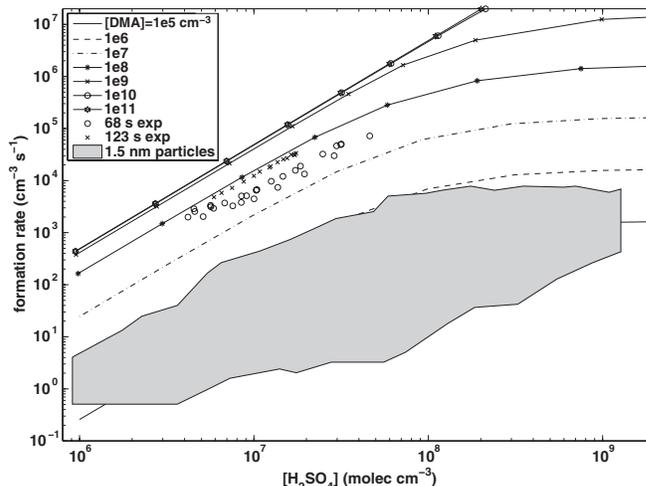


FIG. 4. The measured and modeled dimer formation rates as a function of sulfuric acid concentration. The modeled formation rates correspond to different concentration of dimethylamine (DMA). See text for more details.

The formation rate of stable dimers was modeled as the formation rate of clusters containing two H_2SO_4 molecules and one or two DMA molecules. In these simulations the preferred pathway for stable dimer formation was $\text{H}_2\text{SO}_4 \cdot \text{DMA} + \text{H}_2\text{SO}_4 \cdot (\text{DMA})$, clearly overwhelming the formation rate via pathway $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 + \text{DMA}$. (See supplemental material [17]). The modeled formation rate of sulfuric acid dimers containing DMA is very close to the collision rate of H_2SO_4 molecules and/or $\text{H}_2\text{SO}_4 \cdot \text{DMA}$ clusters at DMA concentrations equal or larger than 10^8 cm^{-3} (Fig. 4). Such a concentration of DMA, or of some other stabilizing agent, is possibly present even in our ultraclean conditions, where impurities are assumed to be smaller than 10^{10} cm^{-3} ($< 500 \text{ ppt}$). Thus, the observed formation rate of sulfuric acid dimers is very close to the modeled formation rate with $[\text{DMA}]$ of 10^8 cm^{-3} assuming that the stabilizing molecule evaporate before detection in the CI-MS.

A comparison to nucleation rates for particles with diameter larger than 1.5 nm measured in the same facility [8] reveals that the dimer formation rate is 2–4 orders of magnitude higher than the particle formation rate at 1.5 nm (Fig. 4). This suggests that there is at least one local minimum in the formation free energy profile either at or after the dimer formation and before the particles have grown above the detection limit of PHA-UCPC ($\text{dp} \geq 1.5 \text{ nm}$).

Our results suggest that the formation rate of sulfuric acid dimers associated with stabilizing molecule(s) is close to the collision rate of sulfuric acid molecules, and that the evaporation rate is substantially smaller than expected from the earlier experimental studies [11]. Extrapolating the results of [11] to our temperature suggests that there should be a steady state between the formation and the evaporation of dimers after ca 0.1 s. Also their anticipated ratio between dimer and monomer concentration is

substantially smaller than that was observed in our experiments. Our data show no steady state behavior and the ratio is different for the different H_2SO_4 concentration profiles and residence times, which are shorter than the estimated time scales needed to reach a steady state. The key differences are the different temperature range and completely different absolute water concentration, see supplementary material. Another possibility for the apparent disagreement between Hanson and Lovejoy [11] and our study is that the contaminants, unavoidably present in any gas, were different regarding their chemical nature as well as their concentrations. The contaminants could affect the experiments in several ways. They can stabilize the dimers and/or help them to grow to larger clusters. Depending on the chemical nature of the compounds, they might also prevent the charging of the stabilized dimers within the CI-MS, or they might remain in the cluster after the charging causing the detection of the cluster at a mass different from sulfuric acid dimer.

Quantum chemical calculations suggest that in our experiment a stabilizing compound was inevitably present. However, since a great care was taken in order to purify the gases and no measurable signal from any contaminants was observed [8], it is plausible that this unknown compound (s), is abundant in any natural environment and will therefore not limit the dimer formation rate.

We have shown that close-to-collision-limited formation of sulfuric acid dimers occur in ultraclean (impurities <500 ppt) environment in ambient relevant temperature of 293 K and relative humidity of 22%. We showed that the stable dimer formation takes place independent of the source of H_2SO_4 , and that adding organic precursors into the gas mixture has no effect on the dimer formation rates. Results were compared to quantum chemical calculations concerning the stability of the sulfuric acid clusters. These calculations revealed that the sulfuric acid dimer even in a hydrated form is not stable enough to explain our observations. This discrepancy suggests that some other, still unknown species, act in the system stabilizing the clusters. Promising candidates for the stabilizing substance are amines as shown theoretically by quantum chemical methods [18,20] and recently detected also experimentally in laboratory [21,22] and in ambient measurements [23,24]. Amines, or some other base molecules, would also fit in to our results, because the clusters containing two H_2SO_4 molecules and ammonia or amine molecule(s) should be detected as pure H_2SO_4 dimers in CI-MS [19]. Since we performed our experiment in ultrapure carrier gas in the absence of any measurable quantities of ammonia or organic impurities, the stabilizing agent(s) are likely to be more abundant in any natural environment and therefore, close-to-collision-limited dimerization should occur in all atmospheric conditions. Ambient observations [25] also indicate concentrations of amines in the concentration range of 10^8 – 10^9 cm^{-3} . This conclusion is similar to that given by Sipilä *et al.* [8].

The dimer formation rate exceeds the nucleation rate of 1.5 nm particles by 2–4 orders of magnitude. The result is in agreement with ambient observations. Based on that observation we conclude that the rate limiting step in nucleation process is not the formation of the sulfuric acid dimer. In atmospheric conditions, clustering of H_2SO_4 (maybe with water and some stabilizing substances) can possibly produce a pool of clusters that are later activated for growth by, e.g., sulfuric acid or supersaturated organic vapors.

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