INTRODUCTION

Atmospheric nucleation rates have been shown to be dependent on sulphuric acid (H$_2$SO$_4$) concentration (Weber et al. 1996, Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2009). However, laboratory experiments on H$_2$SO$_4$-nucleation have failed to reproduce ambient observations (e.g. Wyslouzil et al., 1991; Viisanen et al, 1997; Ball et al, 1999; Young et al 2008). Very recently Sipilä et al. (2010) showed that the disagreement between ambient data and laboratory studies is most probably related to improper experimental design and that sulphuric acid nucleation in ultra clean laboratory conditions can indeed explain atmospheric nucleation rates. If H$_2$SO$_4$ is responsible for the nucleation the first step should be formation of (hydrated) H$_2$SO$_4$-dimer which can and have been measured by means of chemical ionization mass spectrometry (CI-MS, Eisele and Hanson, 2000; Hanson and Eisele, 2002; Hanson and Lovejoy, 2006; Zhao et al., 2010).

Eisele and Hanson (2000) measured clustering dynamics of H$_2$SO$_4$ and H$_2$O at T~240 K and RH of 20-63%. They concluded that the critical cluster in their experiments contained 4 sulfuric acid molecules. Hanson and Eisele, 2002, on the other hand, illustrated the potential stabilization of the sulfuric acid clusters with ammonia. Their results were indicative of the importance of sulfuric acid dimer associated with ammonia to the new particle formation pathway in the atmosphere. Hanson and Lovejoy (2006) measured thermodynamics of hydrated dimer and trimer of H$_2$SO$_4$ in temperature range of 238 to 246 K and in relative humidity varying from 6 to 27% and empirically determined temperature dependent equilibrium constants for dimer – monomer ratios.

Main challenge in measuring the neutral clusters is related to the fact that clustering in the CI-MS drift tube by ion-induced mechanism is faster than the neutral mechanism and can cover the signal from neutral clusters. Therefore, the application of the cluster mass spectrometry to field
studies with low H$_2$SO$_4$ concentrations is not straightforward and first reports from the atmosphere appeared only very recently (Zhao et al., 2010). They found appearance of H$_2$SO$_4$ clusters during nucleation event up to pentamer. Consistently with Sipilä et al. (2010) the researchers (Zhao et al., 2010) concluded that H$_2$SO$_4$ is driving the nucleation, but they also speculated that clusters are most probably stabilized by a third body.

In this study we investigated the formation of H$_2$SO$_4$ dimers in clean (9.0) air containing H$_2$SO$_4$ and H$_2$O in atmospherically relevant temperature of 293K and relative humidity of 22% using a CI-MS for measuring the concentrations of H$_2$SO$_4$ and H$_2$SO$_4$• H$_2$SO$_4$ formed inside a Leibniz-institute for Tropospheric Research laminar flow tube (IfT-LFT).

EXPERIMENTAL

Our experiments were performed in Leibniz-Institute for Tropospheric Research laminar flow tube (IfT-LFT). A detailed description of IfT-LFT and the experimental setup can be found elsewhere (Sipilä et al., 2010). These experiments were conducted at temperature of 293K and at relative humidity of 22%. Due to geometrical reasons the applicable residence time in IfT-LFT – CI-MS combination ranges from 32 to 115 seconds.

Two methods to produce H$_2$SO$_4$ were used. First, the H$_2$SO$_4$ was produced by flushing a small stream of clean gas through the saturator containing pure H$_2$SO$_4$ kept at 288 K. Saturated flow was then mixed with humidified carrier gas in the entrance of the IfT-LFT. Second, the H$_2$SO$_4$ was produced in-situ in the IfT-LFT via the reaction of OH-radicals with SO$_2$. Concentrations of H$_2$SO$_4$ and H$_2$SO$_4$• H$_2$SO$_4$ were measured with a CI-MS (Petäjä et al., 2009).

RESULTS AND CONCLUSIONS

Contradictory to Hanson and Lovejoy (2006) in our experiments no steady state between formation and evaporation of dimers was achieved. In the present study significantly (~7 orders of magnitude) higher signals from dimers were observed than could be assumed from extrapolation of the empirical equilibrium constants (Hanson and Lovejoy, 2006) to our temperature of 293K. The dimer signal detected in our experiment showed a clear dependency on residence time and sulphuric acid monomer concentration.

Our experimental setup differs from that used in some of the earlier studies (Eisele and Hanson, 2000; Hanson and Eisele, 2002; Hanson and Lovejoy, 2006; Zhao et al., 2010), where reaction time between NO$_3^-$ ions and H$_2$SO$_4$ clusters in the CI-MS charger was altered. Instead we kept the reaction time in the charger constant and performed the experiments with different residence times in the flow tube. This approach allowed us to distinguish between the signals from originally neutral and subsequently charged dimers, and signals from dimers formed by ion-induced mechanism via attachment of H$_2$SO$_4$ molecule to artificially charged HSO$_4^-$ ion. The ion induced mechanism should be only dependent on [H$_2$SO$_4$] entering the instrument, whereas the neutral pathway for dimer formation should be dependent on the residence time in the IfT-LFT.
However, the observation of neutral dimers by our method is only possible if the residence times are shorter than the time required for reaching the steady state between the forward and backward reaction of dimer formation.

The first estimation suggested that the formation rate of dimers is close to kinetic limit. A more detailed analysis suggested that the evaporation rate of dimers was in the range of 0.01-0.001 s\(^{-1}\). The estimation is based on the measurements where sulphuric acid was produced continuously via \(\text{OH} + \text{SO}_2\) reaction. The simulations to estimate evaporation rates were performed using a Dynamical Atmospheric Cluster Model (Kulmala, 2010, Atm. Res, in press). A more detailed kinetic modelling as well as quantum chemical calculations will be performed in the future to link our results to atmospheric new particle formation.

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