Investigating the Formation of H_2SO_4 from ion-induced Oxidation of SO_2

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Atmospheric aerosols are very important in human life. They participate in the formation of cloud, acting as cloud condensation nuclei. Aerosols particles are either emitted directly to the atmosphere or produced by nucleation of gas-phase species. It is therefore fundamental to understand the formation of aerosols in order to predict climate. However, the mechanism of nucleation is not fully relatively understood.

Sulphuric acid (H_2SO_4) has been identified as an important precursor for the formation of atmospheric particles (Kulmala *et al* (2006)). It interacts strongly with bases, water, and various organics in the atmosphere and forms stable molecular clusters. Understanding the mechanism of nucleation is closely related to understanding the atmospheric production of H_2SO_4. H_2SO_4 is mostly from SO_2 oxidation by OH radical, catalysed by UV light. Recently, to complement the UV-induced mechanism, a new synthesis mechanism involving ions was found (Enghoff *et al* (2008)).

It was found that SO_2 reacts rapidly with e.g. O_2^-, O_3^-, and CO_3^- (Möhler *et al (*1992)) to form atmospherically relevant ions. Due to the low oxidation state of its sulfur atom, SO_2 is seemingly an important species in the production of ions relevant to aerosol science. Thereby, we have investigated the oxidation reaction of SO_2 by SO_4^-, detected in the atmosphere at relatively high concentration by Ehn *et al* (2010).

We used a density functional theory calculation to determine structures and formation energies of relevant species for our reactions. The reaction rates were determined using the transition state theory and all the calculations were performed at T=298.15 K and p= 1atm.

Results

Upon collision between SO_2 and SO_4^-, a $SO_2.SO_4^-$ cluster is formed and an oxidation subsequently occurs inside the cluster. The stable oxidation intermediate, $SO_3SO_3^-$, is formed with ca. 8 kcal/mol Gibbs free energy gain This means that the formation of $SO_3SO_3^-$ is a likely process at standard conditions. The energy gained by forming $SO_3SO_3^-$ might induce its decomposition into SO_3 and SO_3^-, but the decomposition reaction is endothermic by ca. 18 kcal/mol (Fig. 1). However, $SO_3SO_3^-$ is a long-lived species and may collide with abundant atmospheric species like O_2. The set of reactions

$$SO_4^-(H_2O)_{0\text{-}1} + SO_2 \rightarrow SO_3SO_3^-(H_2O)_{0\text{-}1}, \quad (R1)$$
$$SO_3SO_3^-(H_2O)_{0\text{-}1} + O_2 \rightarrow SO_5^-(H_2O)_{0\text{-}1} + SO_3, \quad (R2)$$

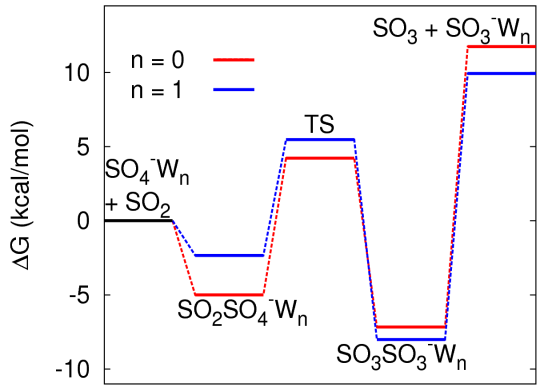

Figure 1. Free energy surface of SO_2 reaction with SO_4^-. The reaction forms a stable intermediate, $SO_3SO_3^-$, likely stable towards decomposition to SO_3 and SO_3^-. "TS" denotes transition state.

follows, where O_2 molecule induces evaporation of SO_3, while stabilizing SO_3^- as SO_5^-. The dehydrated products of reaction R2 is formed with ΔG=1.5 kcal/mol. The presence of water destabilizes the products by ca 3 kcal/mol. SO_3 easily hydrates in the atmosphere and is detected as H_2SO_4, while SO_5^-, detected in the atmosphere by Enh *et al* (2010) has been part of a complete study by Bork et al (2012).

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