Oxidation of Gas-Phase SO_2 on the Surfaces of Acidic Micro-Droplets: Implications for Sulfate and Sulfate Radical Anion Formation in the Atmospheric Liquid Phase

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The oxidation of SO_2(g) on the interfacial layers of micro-droplet surfaces was investigated using an spray-chamber reactor coupled to an electrospray ionization mass spectrometer. Four major ions, HSO_3^-, $SO_3^{\cdot-}$, $SO_4^{\cdot-}$ and HSO_4^-, were observed as SO_2(g)/N_2(g) gas-mixture was passed through a suspended micro-droplet flow, where the residence time in the dynamic reaction zone was limited to a few hundred micro-seconds. The relatively high signal intensities of $SO_3^{\cdot-}$, $SO_4^{\cdot-}$, and HSO_4^- compared to those of HSO_3^- as observed at pH < 3 without addition of oxidants other than oxygen suggests an efficient oxidation pathway via sulfite and sulfate radical anions on droplets possibly via the direct interfacial electron transfer from HSO_3^- to O_2. The concentrations of HSO_3^- in the aqueous aerosol as a function of pH were controlled by the de-protonation of hydrated sulfur dioxide, $SO_2 \cdot H_2O$, which is also affected by the pH dependent uptake coefficient. When H_2O_2(g) was introduced into the spray chamber simultaneously with SO_2(g), HSO_3^- is rapidly oxidized to form bisulfate in the pH range of 3 to 5. Conversion to sulfate was less at pH < 3 due to relatively low HSO_3^- concentration caused by the fast interfacial reactions. The rapid oxidation of SO_2(g) on the acidic micro-droplets was estimated as 1.5×10^6 [S(IV)] (M s^{-1}) at pH $\leq$ 3. In the presence of acidic aerosols, this oxidation rate is approximately two orders of magnitude higher than the rate of oxidation with H_2O_2(g) at a typical atmospheric H_2O_2(g) concentration of 1 ppb. This finding highlights the relative importance of the acidic surfaces for SO_2 oxidation in the atmosphere. Surface chemical reactions on aquated aerosol surfaces, as observed in this study, are overlooked in most atmospheric chemistry models. These reaction pathways may contribute to the rapid production of sulfate aerosols that is often observed in regions impacted by acidic haze aerosol such as Beijing and other mega-cities around the world.