Impact of aerosol composition on the oxidation of bisulfite during the reactive uptake of nitrogen dioxide on aqueous aerosols

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Multiphase chemistry plays a vital role in global atmosphere. The importance of multiphase chemistry in the lower troposphere has been recently underscored by the severe haze-fog pollution episodes experienced over China megacities. A key finding is that despite reduced photochemistry under the haze, the oxidation of sulfur dioxide (SO_2) into sulfate aerosol remains unabated in the presence of low levels of ozone. The main oxidant under such conditions is the nitrogen dioxide (NO_2) emitted by motor vehicles and other combustion sources. The dark conversion of bisulfite (HSO_3^-) into bisulfate (HSO_4^-) by NO_2 has been ascribed to a heterogeneous process taking place on the neutral aerosol prevalent in Northern China. Previous studies in our laboratory, however, have shown that anions catalyze the disproportionation of NO_2 into NO_2^- + NO_3^-.This suggests that coexisting anions in aerosol and aerosol acidity could impact the heterogeneous oxidation of bisulfite during the gaseous NO_2 uptake on aqueous aerosols.

This work explores the contribution of aerosol composition to the oxidation of HSO_3^- during the reactive uptake of NO_2 on the surface of aqueous solutions. The aqueous aerosol surface is generated by microjets containing chloride ion (Cl^-) or formic acid (HCOOH) as proxies of ambient inorganic and organic components. The surface is instantaneously exposed to NO_2(g) followed by in situ anion analysis via online electrospray ionization mass spectrometry. The heterogeneous reaction occurs in ~1nm interfacial layers of the aqueous aerosol under NO_2 exposures similar to atmospheric conditions. The competition between the disproportionation process controlled by aerosol anion compositions, and the oxidation of bisulfite will be followed by the HSO_4^-/NO_3^- ratio. We will review other significant pathways for the oxidation of bisulfite under atmospherically relevant condition. This work addresses how the reactive uptake of gaseous pollutants affects the aerosol composition, thereby contributing to understand the mechanisms underlying urban pollution in haze-fog episodes.

Keywords: Haze-fog pollution, nitrogen dioxide, sulfate, sulfur dioxide, China megacities

