Enhanced Sulfate Production During Nitrate Photolysis in the Presence of Halide Ions in Atmospheric Particles

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Heterogeneous oxidation of SO_2 is an effective production pathway of sulfate in the atmosphere. We recently reported a novel pathway for the heterogeneous oxidation of SO_2 by in-particle oxidants (OH, NO_2 and NO_2^-/HONO) produced from particulate nitrate photolysis (Environ. Sci. Technol. 2019, 53, 8757–8766). Particulate nitrate is often found to coexist with chloride and other halide ions, especially in aged sea-salt aerosols and combustion aerosols. Reactive uptake experiments of SO_2 with UV-irradiated nitrate particles showed that sulfate production rates were enhanced by a factor of 1.4, 1.3 and 2.0 in the presence of Cl^-, Br^- and I^-, respectively, compared to those in the absence of halide ions. The larger sulfate production was attributed to enhanced nitrate photolysis promoted by the increased incomplete solvation of nitrate at the air-particle interface due to the presence of surface-active halide ions. Modeling results based on the experimental data show that the nitrate photolysis rate constants increase by a factor of 2.0, 1.7, and 2.1 in the presence of Cl^-, Br^- and I^-, respectively. The present study demonstrates that the presence of halide ions enhances sulfate production produced during particulate nitrate photolysis and provides insights into the enhanced formation of in-particle oxidants that may increase atmospheric oxidative capacity.

Keywords: Enhanced nitrate photolysis, Halide ions, Sulfate production, Heterogeneous photochemistry