Heterogeneous Oxidation of SO_2 in Sulfate Production during Nitrate Photolysis at 300 nm: Effect of pH, Relative Humidity, Irradiation Intensity, and the Presence of Organic Compounds

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Heterogeneous oxidation of SO_2 is one of the promising mechanisms to account for high loading of sulfate during severe haze periods in China. Our earlier work reported the SO_2 oxidation by OH and NO_2 produced during nitrate photolysis (*Environ. Sci. Technol. Lett.* 2019, 6, 86−91). Here, we extend that work to examine sulfate production during nitrate photolysis at 300-nm irradiation, which can additionally generate NO_2^- or HNO_2, N(III). Flow cell/in-situ Raman experiments showed that the reactive uptake coefficient of SO_2 can be expressed as $1.64 \times p_{NO3^-}$, the nitrate photolysis rate in the range of $(1.0 - 8.0) \times 10^{-5}$ M s^{-1}. Our kinetic model predicts that N(III) is the main contributor to the SO_2 oxidation, followed by NO_2 contribution. Furthermore, the addition of OH scavengers (e.g., glyoxal, or oxalic acid) does not suppress the sulfate production, because of the reduced N(III)-consuming reactions, and the high particle pH sustained by their presence. Our calculations illustrate that, under characteristic haze conditions, nitrate photolysis mechanism can produce sulfate at ~1 μg m^{-3} h^{-1} at pH = 4−6 and $p_{NO3^-} = 10^{-5}$ M s^{-1}. The present study highlights the importance of nitrate photolysis in heterogeneous oxidation of SO_2 by reactive nitrogen (NO_2^-/HNO_2 and NO_2) under atmospherically relevant actinic irradiation.

Keywords: Sulfate, Nitrate photolysis, Oxidation