Heterogeneous Oxidation of SO\textsubscript{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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Importance of heterogeneous oxidation of SO\textsubscript{2} into sulfate
- Heterogeneous oxidation of SO\textsubscript{2} into sulfate as important sulfate production pathways
- Increasing role of nitrate in particulate matter in China
- In this paper, we propose a novel pathway for sulfate production during photolysis of particulate nitrate\textsuperscript{2,3}

In-situ aerosol flow cell coupled with Raman spectrometer
- Particle sample: ammonium nitrate (AN)
- Irradiation: 300 nm LED
- Photon flux: \(1.5 \times 10^{11}\) photons cm\textsuperscript{-2} s\textsuperscript{-1}
- SO\textsubscript{2} (g): 7.7 ppm
- RH: 80%
- Reaction time: up to 1 day

Proposed mechanism for heterogeneous oxidation of SO\textsubscript{2} into sulfate during nitrate photolysis
- In-particle oxidants produced from nitrate photolysis at \(>290\) nm irradiation: OH, NO\textsubscript{3}, and NO\textsubscript{2}; HNO\textsubscript{3}
- 4 pathways for oxidation of dissolved SO\textsubscript{2} by: (1) NO\textsubscript{3}, (2) OH, (3) NO\textsubscript{2}, HNO\textsubscript{3}, (N(III)), (4) H\textsubscript{2}O\textsubscript{2}
- Organics react with OH to produce O\textsubscript{3}/HO\textsubscript{2}
- Self reaction of O(3)/HO\textsubscript{2} for H\textsubscript{2}O\textsubscript{2} production

Evidence for sulfate production during nitrate photolysis
- (i) Dark experiment (AN + SO\textsubscript{2}) in air and (ii) AN photolysis without SO\textsubscript{2} (AN + UV in air): no sulfate production
- NaCl photolysis with SO\textsubscript{2} (NaCl + UV + SO\textsubscript{2} in air): significantly low sulfate production
- AN photolysis with SO\textsubscript{2} in air (AN + UV + SO\textsubscript{2} in air) and N\textsubscript{2} (AN + UV + SO\textsubscript{2} in N\textsubscript{2}): sulfate production
- AN photolysis with SO\textsubscript{2} and delay irradiation (AN + delay UV in air): significant sulfate production during irradiation

Effect of initial particle pH, RH, and irradiation intensity on reactive uptake coefficient of SO\textsubscript{2} for sulfate production, \(\gamma_{\text{SO}_2}\)
- Insensitive to initial particle pH: rapid pH drop during sulfate production
- Less sensitive to RH
- Strong correlation with irradiation intensity (photon flux)
- High sensitivity of \(\gamma_{\text{SO}_2}\) with nitrate photolysis rate, \(p_{\text{NO}_3}\) (M s\textsuperscript{-1}):
  \[\gamma_{\text{SO}_2} \sim 1.64 + p_{\text{NO}_3}\]

Effect of organic compounds on sulfate production
- Higher sulfate production for SN + Gly in air than SN in air: contribution of H\textsubscript{2}O\textsubscript{2} to SN pathway and higher particle pH during reactions (3.5 for SN + Gly and 1.5 for SN)
- Comparable sulfate production of AN + Oxlac in air and N\textsubscript{2} with pure AN
- Lower sulfate production for AN + NaBC: no O\textsubscript{3}/HO\textsubscript{2} (i.e., H\textsubscript{2}O\textsubscript{2}) production

Kinetic modeling: atmospheric implications
- Dominance of N(III) pathway
- Contribution of H\textsubscript{2}O\textsubscript{2} pathway for SN + Gly
- Minor contributions of OH and NO\textsubscript{3} pathways

Evidence for sulfate production rates during nitrate photolysis
- Enhanced sulfate production rates during nitrate photolysis in the presence of chloride ions at [Cl\textsubscript{\text{-}}] [NO\textsubscript{3}\text{-}] \(\leq 0.2\)
- Enhanced sulfate production rates in the presence of Br\textsubscript{\text{-}} or I due to increased nitrate photolysis rate constant, \(k_{\text{NO}_3}\)

Summary
1. Significant sulfate production (\(p_{\text{NO}_3}\) of \(10^{-1}\)) during nitrate photolysis: \(\gamma_{\text{SO}_2} \approx 1.64 + p_{\text{NO}_3}\)
2. No inhibiting effect of the presence of organics on sulfate production during nitrate photolysis

Ongoing work
1. Halide-induced enhancement of nitrate photolysis
2. Effect of nitrate photolysis on formation of secondary organic aerosol

References:
3. Zhang et al., to be submitted.