

## 2.085 Role of Sulfate Radical Anion Chemistry in Heterogeneous OH Oxidation of Organosulfates.

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Abstract:

Organosulfates are important organosulfur compounds present in atmospheric particles, but it remains largely unclear how they chemically transform in the atmosphere. To gain a fundamental understanding of how organosulfates evolve, this work investigates the heterogeneous OH radical-initiated oxidation of sodium methyl sulfate ( $\text{CH}_3\text{SO}_4\text{Na}$ ) particles, the smallest organosulfate detected in atmospheric particles, using an aerosol flow tube reactor at a high relative humidity of 85 %. Aerosol mass spectra measured by an atmospheric pressure ionization source (Direct Analysis in Real Time, DART) coupled with a high-resolution mass spectrometer showed that neither functionalization nor fragmentation products are detected. Instead, the ion signal intensity of the bisulfate ion ( $\text{HSO}_4^-$ ) increases significantly after oxidation. We postulate that sodium methyl sulfate tends to fragment into a formaldehyde and a sulfate radical anion ( $\text{SO}_4^{\bullet-}$ ) upon OH oxidation. The formaldehyde is likely partitioned back to the gas phase. The sulfate radical anion can abstract a hydrogen atom from neighboring sodium methyl sulfate to form the bisulfate ion. Overall, we firstly demonstrate that the heterogeneous OH oxidation of an organosulfate can lead to the formation of sulfate radical anion and produce inorganic sulfate. Fragmentation processes and sulfate radical anion chemistry play a key role in determining the compositional evolution of sodium methyl sulfate during heterogeneous OH oxidation.