Formation Kinetics of Isoprene Epoxydiol-Derived Secondary Organic Aerosol Are Altered Near the Sulfate/Bisulfate pKa

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Abstract

Low-pH aerosols comprise a large fraction of atmospheric fine particulate matter. The effects of pH on secondary organic aerosol (SOA) formation are not well understood, in part because of the difficulty of accurately measuring aerosol pH. Of particular interest are the atmospherically-abundant isoprene epoxydiols (IEPOX), which undergo acid-driven reactions to form SOA. Models have assumed no upper limit for IEPOX-SOA formation rates as acidity increases. However, recent work has shown that organosulfate formation from IEPOX slows as the equilibrium of inorganic sulfate ($Sulf_{inorg}$) shifts from sulfate (SO_4^{2-}) towards bisulfate (HSO_4^-), which is a weaker nucleophile. We performed a series of trans-ß-IEPOX uptake experiments with ammonium sulfate seed solutions acidified to between pH 0 and 3, and modelled time-resolved methyltetrol (MT) and methyltetrol sulfate (MTS) formation and $Sulf_{inorg}$ consumption (k_{MT} = 0.018 M^{-2} s^{-1}, k_{MTS} = 0.28 M^{-2} s^{-1}). We found an inflection point between pH 1 and 1.4, below which MT formation dominates and above which MTS formation dominates, consistent with a changing balance of protonated and deprotonated $Sulf_{inorg}$. Modelled MT and MTS formation fit the experimental data well both above and below the inflection point except at pH 1.4, where it significantly underpredicted the data at low initial IEPOX/$Sulf_{inorg}$ ratios. This indicates multi-phase chemical dynamics beyond those represented in our model, leading to very efficient IEPOX-SOA formation at pH 1.4. Further investigation is warranted into the connection of IEPOX-SOA formation with initial IEPOX/$Sulf_{inorg}$ ratio and aerosol pH.