

OH-initiated heterogeneous aging of highly oxidized organic aerosol

Sean H. Kessler¹, Theodora Nah^{2,3}, Kelly E. Daumit⁴, Jared D. Smith², Stephen R. Leone³, Charles E. Kolb⁵, Douglas R. Worsnop⁵, Kevin R. Wilson², Jesse H. Kroll^{1,4*}

¹Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA 02139

²Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720

³Department of Chemistry, University of California, Berkeley, CA 94720

⁴Department of Civil & Environmental Engineering, Massachusetts Institute of Technology, Cambridge MA 02139

⁵Center for Aerosol and Cloud Chemistry, Aerodyne Research Inc., Billerica MA 01821

*Corresponding author: jhkroll@mit.edu

The oxidative evolution (“aging”) of organic species in the atmosphere is thought to have a major influence on the composition and properties of organic particulate matter, but remains poorly understood, particularly for the most oxidized fraction of the aerosol. Here we measure the kinetics and products of the heterogeneous oxidation of highly oxidized organic aerosol, with an aim of better constraining atmospheric aging processes of oxidized compounds, which are found primarily in the condensed phase. Submicron particles composed of model oxidized organics—1,2,3,4-butanetetracarboxylic acid (C₈H₁₀O₈), citric acid (C₆H₈O₇), tartaric acid (C₄H₆O₆), and Suwannee River fulvic acid—were oxidized by gas-phase OH in a flow reactor, and the masses and elemental composition of the particles were monitored as a function of OH exposure. In contrast to our previous studies of less-oxidized model systems (squalane, erythritol, and levoglucosan), particle mass did not decrease significantly with heterogeneous oxidation. Carbon content of the aerosol always decreased somewhat, but this mass loss was approximately balanced by an increase in oxygen content. The estimated reactive uptake coefficients of the reactions range from 0.37 to 0.51 and indicate that such transformations occur at rates corresponding to 1-2 weeks in the atmosphere, suggesting their importance in describing the atmospheric lifecycle of organic particulate matter.