

Kinetics of the multiphase formation of oxidized organic aerosol

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Atmospheric organic aerosol (OA) tends to be substantially higher in mass loading and carbon oxidation state than OA produced in laboratory studies, suggesting major gaps in our understanding of the chemistry underlying OA formation and/or evolution. In recent years a number of pathways have been put forth as possible mechanisms for the generation of large amounts of highly oxidized OA. However, assessing the viability of these schemes as key atmospheric OA sources is difficult, in part because their kinetics tend to be poorly constrained. This prevents comparisons between laboratory data and ambient observations, namely the observed formation timescales of oxidized OA (on the order of one day in the atmosphere). Here we present a series of laboratory studies of the formation of oxidized organic aerosol, focusing not only on the reaction products (as described by the abundance and average oxidation state of particulate organic carbon), but also on the rate at which these products are formed. Oxidative “aging” of secondary organic aerosol mixtures (in which gas-phase reaction products are exposed to sustained concentrations of hydroxyl radicals) is found to lead to increases in both particle mass and degree of oxidation, but over timescales substantially longer than a day. Heterogeneous oxidation of particulate organics is similarly found to be too slow to account for observations of oxidized OA formation, consistent with results from a number of other studies. Multiphase chemistry – the oxidation of species within liquid (organic or aqueous) droplets – has been suggested as an alternative mechanism for the efficient formation of highly oxidized OA. However this process can also be quite slow under atmospheric conditions, because the organics must first partition into the condensed phase prior to being oxidized. Therefore both oxidation and gas-particle partitioning govern the kinetics of these reactions; consideration of both together may suggest important channels for the rapid formation of highly oxidized, low-volatility organics.