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Reactive oxygen species production from secondary organic aerosols: the importance of singlet oxygen

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Organic aerosols have an atmospheric lifetime of approximately one week. During this time, these aerosols will be subjected to atmospheric processing including exposure to sunlight. Photochemistry of organic aerosols produces reactive oxygen species (ROS) in-situ capable of transforming their chemical and physical properties, with implications for air quality and climate. In surface aquatic environments rich in organic matter, singlet oxygen $^1O_2$) concentrations are typically 1000 times higher than OH radical concentrations. On the other hand, $^1O_2$ has recently been quantified in atmospherically relevant systems, namely in fog waters and in road dust. Although $^1O_2$ is a selective oxidant, we wondered whether it would also be present within secondary organic aerosol (SOA) and whether its steady-state concentrations were elevated enough to impact the degradation of key organic aerosol tracers. To address these knowledge gaps, we generated secondary organic aerosols from key anthropogenic precursors such as toluene, naphthalene, dimethylnathphalene and biphenyl in a laboratory smog chamber. We then extracted the collected SOA filters and submitted the soluble extracts to atmospherically-relevant photochemical conditions. Using furfuryl alcohol as a probe for $^1O_2$, we determined steady-state concentrations of this oxidant and calculated $1O_2$ quantum yields for each SOA sample. Subsequent quantification of OH radicals and peroxides allow for the comparison of degradation rates between ROS specie. We find that for molecules found in SOA such as amino acids (histidine, tryptophan, methionine), organo-nitrogen compounds (imidazole, indole, niclosamide) and phenolic compounds (hydroquinone, resorcinol) have a shortened lifetime by more than half when $^1O_2$ reactivity is taken into consideration. In all, this study presents the first measurements of $^1O_2$ and OH radical quantum yields in aqueous extracts of laboratory-generated secondary organic aerosols and our findings highlight the importance of $^1O_2$ as an in-situ oxidant within organic aerosols. Thus, we recommend that $^1O_2$ rate coefficients with key atmospheric pollutants be the focus of further aerosol kinetic research.