

Aerosol Oxidation Speeds Up in Smoggy Air



Particulates small enough to remain suspended in the air scatter sunlight effectively, making for spectacular sunsets. However, they can have some adverse health effects, and their complex chemical interactions with other forms of pollutants—and the implications of those interactions for climate change models—are still not well understood.

Organic aerosols (nanometer-sized liquid or solid particles suspended in air) are important constituents of the troposphere, and their chemistry has large-scale impacts on climate, pollution, and health. Accurate predictions of these aerosol impacts require a robust microphysical understanding of all relevant chemical reaction mechanisms and time scales, including those involving highly reactive free-radical molecules. However, detailed modeling is complicated by the large number of possible chemical transformations that aerosols undergo in the atmosphere. To help clarify the situation, researchers from Berkeley Lab measured multiphase aerosol reaction rates using the vacuum-ultraviolet (VUV) aerosol mass spectrometer (AMS) at the Chemical Dynamics Beamline of the ALS. They discovered an unexpectedly large acceleration in aerosol oxidation in the presence of anthropogenic pollutants

commonly found in smoggy air, a result that could help bring models closer in line with observations.

Many current atmospheric-chemistry models underpredict the daily evolution of organic aerosols. While these models account for reactions between gas-phase hydroxyl radicals (OH)—the most widespread oxidizer in the troposphere—and the liquid or solid surfaces of organic aerosols, the reactions are generally considered much too slow to contribute to the observed daily changes in aerosol composition. However, these analyses are based on studies conducted under conditions of low nitrogen oxide (NO_x), which is relevant to remote regions but not urban areas, where NO_x gases are produced by fossil-fuel combustion.

In this work, heterogeneous (gas/liquid or gas/solid) reaction rates were measured in “polluted” atmospheres, i.e. in the presence of gas-phase nitric oxide (NO),

The Aerosol Factor

The average adult breathes 3000 gallons of air per day (EPA Fast Facts). In the troposphere, the lowest part of Earth’s atmosphere, that air will include aerosol particles so small they can remain suspended for weeks at a time. The EPA classifies such particles smaller than 2.5 micrometers as a health risk because they easily travel deep into the lungs, where they may accumulate and react. They have been linked to serious health problems, from decreased lung function to premature death in people with heart or lung disease.

Aerosols can also play a role in shifting the balance of Earth’s “radiation budget,” offsetting somewhat the warming effects of greenhouse gases by increasing the amount of cloud cover and reflecting energy back into space. However, because the heterogeneity of organic aerosols makes their chemistry so complex, we need much more data to truly understand how these invisible particles mix and transform in the presence of other atmospheric constituents.

Dynamic chemical rate measurements at the ALS by Richards-Henderson et al. provide new evidence for the rapid oxidation of atmospheric aerosols in urban environments. This oxidation rate is much faster than previously believed, leading to a new chain-reaction mechanism for organic aerosol oxidation that should improve climate-change models.

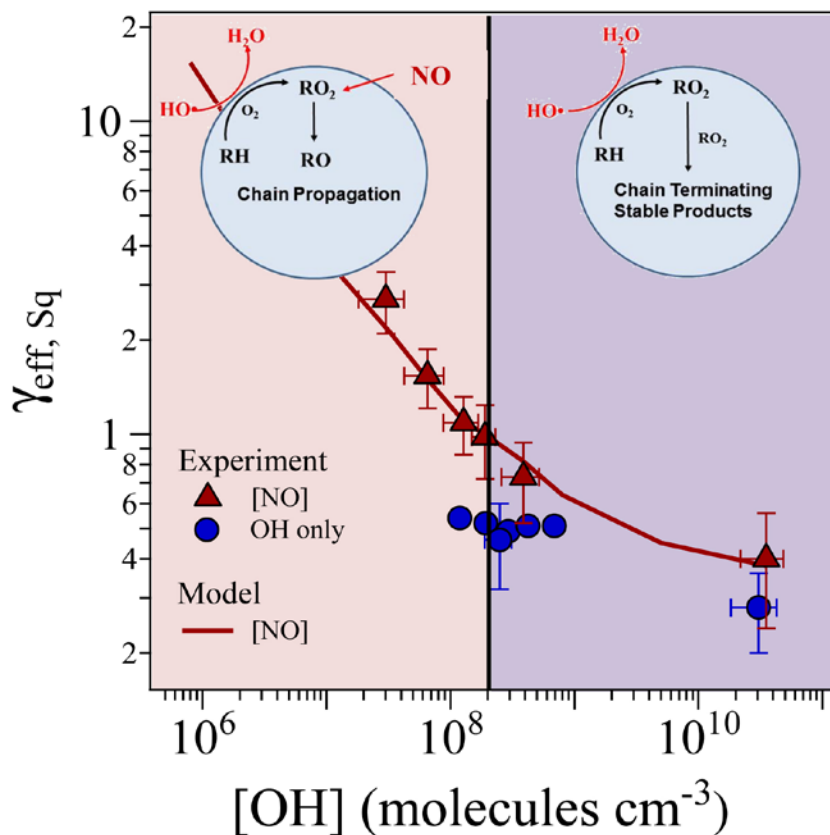
on single-component organic-aerosol proxies (both liquid or solid) in a specialized reaction chamber designed to mimic atmospheric conditions. The chemical

compositions of the proxies were measured using a VUV-photoionization aerosol mass spectrometer at ALS Beamline 9.0.2. The tunability of the VUV light allowed the photoionization energy to be tuned to the ionization threshold of each molecule, reducing the degree of molecular fragmentation (a form of noise in the spectrum) and simplifying the analysis of the spectral fingerprints of the product molecules. The rate of decay of a given proxy was used to quantify the effective uptake coefficient, γ_{eff} , which in turn revealed how fast a reaction occurred. The results show that, as the OH concentration decreases, there is a steep increase in the effective uptake of the aerosol.

Because OH quickly reacts with nearby hydrocarbons and oxygen to produce peroxy radicals (RO_2 , where R is a generic hydrocarbon-based radical), at high concentrations of OH, the concentration of RO_2 will also be relatively high. Thus, at high OH concentrations, RO_2 radicals mostly react with other RO_2 radicals, which leads to stable products that do not react any further. At much lower OH concentrations (approaching atmospheric levels), RO_2 reacts primarily with NO, which leads to sustained, free-radical chain reactions that result in oxidation rates 10–30 times faster than previously observed.

These rate measurements, covering four orders of magnitude in OH concentration, overturn the commonly held belief that gas-phase reactions dominate organic aerosol formation and aging and that heterogeneous oxidation is simply too slow (on the order of weeks) to play a significant role in the daily chemical transformations (on the order of hours) of organic aerosols in urban environments. The incorporation of this new free-radical chain-reaction mechanism into global and regional models is expected to improve aerosol mass and composition predictions.

Upcoming work will investigate the analogous role of SO_2 , also present in polluted environments, in accelerating the γ_{eff} heterogeneous oxidation rates of organic particles. Also, the researchers plan to evaluate the importance of NO in



The effective uptake as a function of hydroxyl radical concentration [OH] with a nitric oxide concentration [NO] of 84 ± 22 ppb (red triangles) and without NO (blue circles) for the liquid-phase organic-aerosol proxy, squalane (Sq). Lines are model predictions. Error bars represent ± 1 SE (standard error).

generating RO radicals in more complex aerosol systems and for more dilute aqueous solutions and semi-solids in order

to better understand the role that molecular structure and particle phase has on chain cycling reactions.

Publication about this research: N.K. Richards-Henderson, A.H. Goldstein, and K.R. Wilson, "Large Enhancement in the Heterogeneous Oxidation Rate of Organic Aerosols by Hydroxyl Radicals in the Presence of Nitric Oxide," *J. Phys. Chem. Lett.* 6, 4451 (2015).

Research conducted by: N.K. Richards-Henderson and K.R. Wilson (Berkeley Lab) and A.H. Goldstein (University of California, Berkeley).

Research funding: U.S. Department of Energy (DOE), Office of Basic Energy Sciences (BES) and Office of Science Early Career Research Program. Operation of the ALS is supported by DOE BES.

Published by the
**ADVANCED LIGHT SOURCE
COMMUNICATIONS GROUP**

