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Recent progress in understanding the dynamics of peroxy radical interactions and their impact on atmospheric new-particle formation

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Oxidation of volatile organic compounds (VOC's) such as alpha-pinene in the atmosphere leads to the formation of relatively long-lived peroxy radicals (RO_2). These in turn undergo bimolecular self- and cross-reactions. The Kurtén research group has been making progress in understanding these reactions using computational and theoretical methods over the past few years. Our overall view is that the rate-determining step in these reactions is the formation of tetroxide intermediates (RO_4R'), which then undergo further reactions. Most importantly for understanding atmospheric aerosols, one of these reactions involves the formation of ROOR' species, which play an important role as accretion sites for new-particle formation, especially when they undergo further oxidation reactions to become highly oxidized organic molecules (HOM's) [1]. Recent joint experimental-modelling work has also demonstrated the formation of ROR' ether and ester products [2]. The reactions leading to ROOR' and ROR' formation are challenging to describe since they must include changes in the spin state(s) of the molecules involved, requiring the inclusion of intersystem crossing (ISC).

In this talk, I focus on some recent work, extending from energetics and transition state theory [3,4] to use a range of levels of theory combined with molecular dynamics to learn more about the mechanisms of these challenging reactions [5,6]. These range from ab initio multi-reference methods with large orbital active spaces, and including ISC, to CASSCF methods, semi-empirical methods, and even force-field based methods. Although force-field models cannot describe the formation of RO_4R', they are surprisingly accurate for describing the lifetime of pre-reactive complexes. A phenomenological model for the complex lifetime correlates well with experimental bimolecular reaction rates of peroxy radicals [6]. Force-field methods can efficiently simulate thousands of collisions between large alpha-pinene-derived peroxy radicals. Extrapolation from the smaller peroxy radicals to the larger atmospherically relevant systems promises to usefully guide future experiments.

[1] Rissanen (2021), *JPC-A* 125, 9027-9039.
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[3] Valiev et al. (2020), *PCCP* 22, 22314-22323.
[4] Salo et al. (2022), *JPC-A* 126, 4046-4056.
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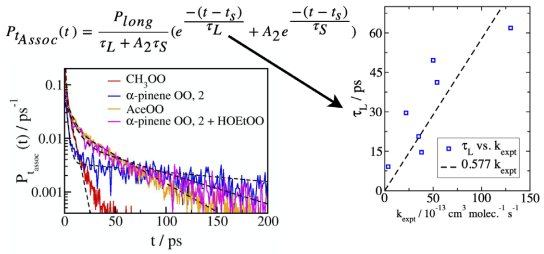
[6] Daub et al. (2022), *ACS Earth & Space Chemistry* 6, 2446-2452.



Complex lifetime $\tau_L \propto$ Reaction rate k