INVESTIGATING ATMOSPHERIC OXIDATION WITH MOLECULAR DYNAMICS IMAGING AND SPECTROSCOPY

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Volatile organic compounds (VOCs) in the Earth's atmosphere constitute trace gas species emitted primarily from the biosphere, and are the subject of inquiry for a variety of air quality and climate studies. Reactions intiated (primarily) by the hydroxyl radical (OH) lead to a myriad of oxygenated species (OVOCs), which in turn are prone to further oxidation. Investigations of the role that VOC oxidation plays in tropospheric chemistry have brought to light two troubling scenarios: (1) VOCs are responsible in part for the production of two EPA-regulated pollutants—tropospheric ozone and organic aerosol—and (2) the mechanistic details of VOC oxidation remain convoluted and poorly understood. The latter issue hampers the implementation of near-explicit atmospheric simulations, and large discrepancies in OH reactivity exist between measurements and models at present. Such discrepancies underscore the need for a more thorough description of VOC oxidation.

Time-of-flight measurements and ion-imaging techniques are viable options for resolving some of the mechanistic and energetic details of VOC oxidation. Molecular beam studies have the advantage of foregoing unwanted bimolecular reactions, allowing for the characterization of specific processes which must typically compete with the complex manifold of VOC oxidation pathways. The focus of this work is on the unimolecular channels of organic peroxy radical intermediates, which are necessarily generated during VOC oxidation. Such intermediates may isomerize and decompose into distinct chemical channels, enabling the unambiguous detection of each pathway. For instance, a $(1+1')$ resonance enhanced multiphoton ionization (REMPI) scheme may be employed to detect carbon monoxide generated from a particular unimolecular process. A number of more subtle mechanistic details may be explored as well. By varying the mean free path of the peroxy radicals in a flow tube, the role of collisional quenching in these unimolecular channels can be assessed. Reactive species may also be introduced to explore the competition between bimolecular and unimolecular pathways. Vibrational modes may also be excited by an IR laser, providing insight about the role of vibrational mediation in VOC oxidation.