4.005 OH-Radical Oxidation of Organic Species at the Air-Water Interface.

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Abstract:

Products and intermediates of the prompt oxidation of a variety of carboxylic acids, including cis-pinonic acid and benzoic acid, initiated by gas-phase hydroxyl radicals, ×OH(g), at the air-water interface were detected by mass spectrometry in a novel setup under various experimental conditions. Exposure of sub-millimolar reactant aqueous microjets to ~ 10 ns ×OH(g) pulses from the 266 nm laser flash photolysis of O_3(g)/O_2(g)/H_2O(g)/N_2(g) mixtures yielded an array of interfacial species, including peroxyl radicals ROO× and hydroperoxides ROOH, that were unambiguously and simultaneously identified *in situ* by mass spectrometry. Our results are consistent with a Langmuir−Hinshelwood mechanism rather than an Eley-Rideal mechanism. We propose an interface-specific oxidation mechanism for the heterogeneous reaction of amphiphilic organic species (aq) with ·OH(g). The connection between the present fundamental findings and atmospheric chemistry is discussed.