



Photochemical enhancement of the reaction between ozone and chlorophyll at the air-water interface

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The kinetics of the heterogeneous reaction between gas-phase ozone and chlorophyll present at the air-water interface are altered in the presence of actinic radiation. Glancing-angle laser-induced fluorescence measurements of the surface concentration of chlorophyll were used to study the kinetics of this reaction, which display a Langmuir-Hinshelwood mechanism under all dark conditions, but in salt solutions of high enough pH there is a large enhancement in the rate and a change to a linear dependence on ozone concentration when the solution is illuminated with actinic light. The wavelength dependence of this enhancement was studied, using a series of long-pass filters. Only when the illumination was restricted to wavelengths above ~ 800 nm did the mechanism revert to that seen in darkness. The excitation spectrum of chlorophyll on the water surface is somewhat different with low vs. high pH substrates; in salt solutions a transient absorption feature is observed upon chlorophyll illumination. These results suggest a strong role for photo-redox surface chemistry in the atmosphere, with bio-organic compounds as sensitizing agents.