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Photochemistry of Nitrous Acid and Nitrite Ion

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PHOTOCHEMISTRY OF NITROUS ACID AND NITRITE ION

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In a study of aquatic nitrogen chemistry, Zafiriou and True reported decomposition of and hydroxyl radical (OH) formation from nitrite ion (NO₂⁻) in seawater upon absorption of solar radiation. NO₂⁻ exists in an acid-base equilibrium with nitrous acid (HONO) [NO₂⁻ + $H_2O = HONO + OH^-$]. A comparison study of HONO and NO₂-photochemistry was undertaken to evaluate the importance of the preceding equilibrium.

Aqueous HONO and aqueous NO₂- were each photolyzed with 365 nm radiation. Benzene, toluene, benzoic acid, and terephthalic acid were each used as OH-scavengers (there have been no previous reports of using the latter two compounds as OH-scavengers). In the case of HONO, it was determined by ultraviolet/visible (UV/vis.) light spectroscopy that the scavenger compound was hydroxylated by OH resulting from HONO photochemical decomposition and subsequently nitrosated by HONO. In the case of NO₂-, no hydroxylated aromatic compound was detected, and no decrease in NO₂- concentration was observed. It was concluded that, at 365 nm, HONO yields OH upon photolytic decomposition and NO₂- does not photolytically decompose to yield OH. Kinetic information for both thermal and photochemical decomposition of HONO was obtained.

The proposed mechanism for OH-scavenging by benzene was examined under varying pH conditions. H_2O_2 , a known OH producer, was photolyzed in the presence of benzene. UV/vis. spectroscopy indicated that one or more hydroxylated aromatic products formed, supporting the proposed OH-scavenging mechanism.