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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 ( $\text{NO}_2^-$ ) in seawater upon absorption of solar radiation.  $\text{NO}_2^-$  exists in an acid-base equilibrium with nitrous acid (HONO) [ $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HONO} + \text{OH}^-$ ]. A comparison study of HONO and  $\text{NO}_2^-$  photochemistry was undertaken to evaluate the importance of the preceding equilibrium.

Aqueous HONO and aqueous  $\text{NO}_2^-$  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  $\text{NO}_2^-$ , no hydroxylated aromatic compound was detected, and no decrease in  $\text{NO}_2^-$  concentration was observed. It was concluded that, at 365 nm, HONO yields OH upon photolytic decomposition and  $\text{NO}_2^-$  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.  $\text{H}_2\text{O}_2$ , 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.