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Comparison of the Reactivity of Hydroxyl Radicals Produced from H₂O₂ and HONO

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The reactivity of hydroxyl radicals formed thermally and photochemically under varying conditions was studied. Hydroxyl radicals produced by thermal and photochemical reactions of aqueous H$_2$O$_2$ were compared with ·OH photochemically produced from HONO. In these systems, the aqueous reaction solutions were saturated with benzene which is a known scavenger for ·OH.

1) A significant effect of pH on the ·OH production was observed during photolysis of H$_2$O$_2$. The concentration of reaction products were doubled when solution pH varied from 13 to 2.

2) Additionally, the role of dissolved gases was found to be important. An oxygen purged solution of H$_2$O$_2$ yielded four times as much photolysis product as a similar non-purged solution.

3) Catalytic formation of ·OH from H$_2$O$_2$ was also studied using CuSO$_4$ catalyst. This system seem the most efficient with a total of 77% of the dissolved benzene converted into phenol.

4) The photochemistry of HONO/NO$_2^-$ system is the subject of a parallel study. Hydroxyl radicals formed by the photolysis of this system are scavenged by benzene. Products formed include para-nitrosophenol (PNP) and phenol.

Analytical techniques for isolating and quantifying phenol from H$_2$O$_2$ reactions were also designed to identify PNP. Reaction products were analyzed using UV/Vis spectroscopy. However, possible HONO photolysis products had nearly overlapping absorbances. Therefore, both the HPLC with a C$_{18}$ column and GC were also used. Neither of these instruments were useful in analyzing the products sufficiently. Presently, product analysis using a silica gel column on the HPLC is in progress.