Title: The underestimated role of tert-butyl alcohol, a scavenger of •OH, in photochemical inorganic redox reactions

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Abstract

Reactive oxygen species (ROS) play important roles in natural and engineered aquatic systems by participating in various redox reactions. Among all radicals produced in natural photochemical processes, the hydroxyl radical (•OH) is one of the most reactive free radicals, contributing to the oxidative destruction of organic pollutants and the electron transfer of inorganic ions. To eliminate the role of •OH in the oxidation processes, tert-butyl alcohol (TBA) is often utilized as a scavenger of •OH because of its high reaction rate constant with •OH. It is commonly assumed that •OH can be fully scavenged by TBA, and that TBA will terminate the redox reaction. However, we found when TBA is utilized as a •OH scavenger it generates a secondary peroxyl radical (ROO•). Although ROO• is less reactive than •OH, it has an extended half-life and diffusion distance that allow ROO• to participate in more redox reactions, such as photochemical oxidation of Mn^{2+}(aq) to Mn oxide solids. In addition, the presence of TBA affected the crystalline phases, oxidation states, and morphologies of the formed Mn oxide solids. Thus, the role of •OH in aqueous redox reactions cannot be determined simply by adding •OH scavenger without considering the effect of secondary radicals on the system's oxidation.