
Oxidation of Dihydroxybenzenes in Aerated Aqueous Suspensions of Birnessite

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Abstract: The oxidation of 1,2- and 1,4-dihydroxybenzenes (1,2-DHB and 1,4-DHB) by unbuffered aerated suspensions of synthetic birnessite was studied by continuously monitoring the H^+ , Mn^{2+} dissolved O_2 , and organic radical concentration of the aqueous phase during the reaction. The reaction rapidly generated a very high pH, attributed to oxide dissolution, and the alkaline conditions prevented Mn^{2+} release into solution over the entire reaction period. Semiquinone radical anions accumulated early in the reaction and then diminished. A secondary radical product appeared in solution during the reaction of the oxide with 1,2-DHB, and was tentatively identified as an hydroxylated semiquinone. The oxide/DHB ratio controlled the maximum concentration and persistence of these radicals in solution as well as the degree to which O_2 was consumed as an electron donor. In general, low oxide/DHB ratios promoted O_2 uptake by the system, consistent with the subordinate role of O_2 as a competing electron acceptor in the presence of excess Mn oxide. Soluble phosphate suppressed O_2 consumption, but the mechanism by which it interacted with the reaction system was not determined.

Key Words: Birnessite • Dihydroxybenzene • Electron spin resonance • Manganese • Oxidation

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