
Electron Transfer Processes Between Hydroquinone and Hausmannite (Mn_3O_4)

K.-H. Kung and M. B. McBride

Department of Agronomy, Cornell University Ithaca, New York 14853

Abstract: A kinetic study of the oxidation of hydroquinone by aqueous suspensions of hausmannite at pH 6 was conducted using an on-line analysis system. Electron transfer between hydroquinone and the oxide was monitored by ultraviolet and electron spin resonance spectroscopy to measure the loss of hydroquinone and the appearance of oxidation products. Although hydroquinone oxidized on the surface of the oxide and the oxide surface was altered after the reduction, hydroquinone and its oxidation products did not adsorb strongly on the surface. At a high concentration of hydroquinone, p-benzosemiquinone free radicals persisted in aqueous solution and were oxidized by dissolved O_2 . Calculations based on the thermodynamic stabilities of the oxide and the organic species involved show that the formation of p-benzosemiquinone radical by Mn reduction is feasible. The presence of the radicals indicates that the oxidation of hydroquinone by the oxide proceeded by a one-electron transfer process. At high organic/oxide ratios, an increase in the amount of hausmannite dissolved with increasing hydroquinone concentration suggests that the reduction of the oxide by the organic was not limited to the surface layer of the oxide. At a high concentration of hydroquinone, polymers were detected in solution, suggesting that radical-mediated reactions played a role in the polymerization process. A reaction scheme is proposed to explain the effect of the Mn oxide to hydroquinone ratio on the consumption of O_2 and the appearance of quinone, p-benzosemiquinone, and polymers in solution.

Key Words: Electron spin resonance • Electron transfer • Hausmannite • Hydroquinone • Manganese • Oxidation

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