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ELECTRON TRANSFER PROCESSES BETWEEN HYDROQUINONE AND HAUSMANNITE (Mn_3O_4)

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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.

INTRODUCTION

Reduction of insoluble manganese(IV, III) oxide to Mn^{2+} cations will affect the mobility of manganese in soil and its availability to plants. This reduction can be achieved by certain simple organic compounds in aqueous solution (Stone and Morgan, 1984b). Among the organics, phenolic compounds and their derivatives appear to be especially proficient in this regard. In soils, phenolic compounds may originate from (1) the biological metabolism of plants, (2) the microbial breakdown of plant residues and humic substances, and (3) pesticides and/or their degradation products.

The ability of clay minerals and oxides to promote the oxidative polymerization of some simple phenolic compounds has been demonstrated (Kyuma and Kawaguchi, 1964; Kumada and Kato, 1970; Wang *et al.*, 1978, 1983; Shindo and Huang, 1982, 1984, 1985). Among the metal oxides, the manganese(IV) oxides are the most efficient (Larson and Hufnal, 1980). Ono *et al.* (1977) studied the rate of radical formation on MnO_2 at high pH (pH 9) and proposed a mechanism which involved an abstraction of protons from hydroquinone before electron transfer. From studying the release of Mn^{2+} into solution, Stone and Morgan (1984a) demonstrated that the reduction of Mn oxide by hydroquinone is a first order reaction with respect to oxide loading and must occur on the oxide surface; i.e., phenols must form a surface complex prior to electron transfer.

Radicals are known to persist in humic substances and can be detected by electron spin resonance (Rex, 1960). Steelink (1964) and his co-workers (Tollin *et al.*, 1963) determined the free radical species to be an ortho- or para-type of semiquinone, which coexisted with quinhydrone and quinone moieties. Senesi and Schnitzer (1977) showed that fulvic acid contains two types of free radicals: a permanent type that can persist over a long period of time, and a transient type that has a relatively short life time. The latter type of radical can be generated in fulvic acid by chemical reduction, irradiation, and increasing pH. Schnitzer (1982) further implied that the synthesis of humic acid from simple phenols and phenolic acids is a one-electron transfer process and that the rate-determining step is the formation of semiquinone radicals, which can be stabilized in alkaline solution. Therefore, semiquinone generated abiotically by Mn oxide may play a role in the synthesis of humic substances from simple phenolics.

In this paper, the oxidation of hydroquinone in aqueous suspensions of hausmannite at pH 6 is described. A flowing system was used which was developed to monitor continuously the electron transfer through the rate of manganese dissolution, hydroquinone oxidation, and free radical formation.

MATERIALS AND METHODS

Manganese oxide was prepared at alkaline pH by air oxidation as described by McBride (1987). The oxide

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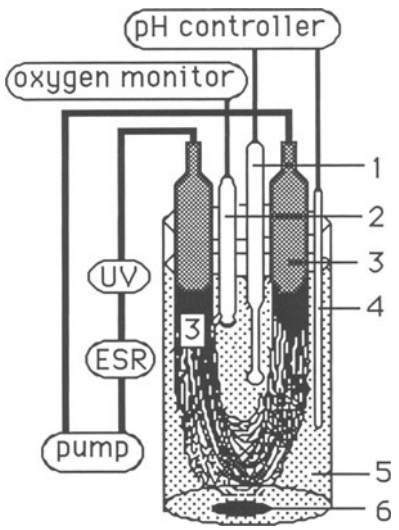


Figure 1. Diagram of closed continuous-flow system used to monitor reaction between hausmannite (Mn_3O_4) and hydroquinone: 1, pH electrode; 2, O_2 probe; 3, fiber bundle; 4, acid and/or base inlet; 5, suspension of the oxide and organics; 6, magnetic stir bar.

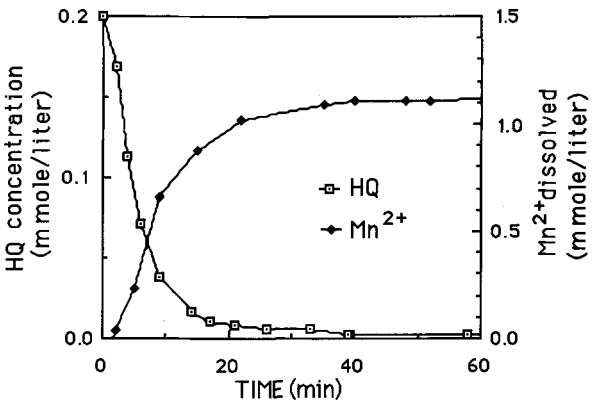


Figure 2. Change in solution concentration of hydroquinone (HQ) and Mn^{2+} due to the oxidation reaction. Initial concentrations were 2×10^{-4} M hydroquinone and 600 mg of hausmannite (Mn_3O_4) at pH 6.

was acidified to pH 6 and freeze-dried prior to use. X-ray powder diffraction (XRD) showed the oxide to be hausmannite (Mn_3O_4) with diagnostic d-values of 4.90, 3.08, 2.87, 2.76, 2.48, 2.36, and 2.03 Å. The infrared spectrum (IR) of the mineral, however, revealed sharp absorption bands at 1155, 1120, and 1080 cm^{-1}, indicative of structural OH vibrations, possibly from manganite and/or groutite (MnOOH). The bulk and surface structures of the oxide may possibly be different, caused by the preparative acidification step which generated surface Mn–OH groups by disproportionation: $Mn_3O_4 + 2H^+ \rightarrow 2\ MnOOH + Mn^{2+}$. In support of this hypothesis, Murray et al. (1985) demonstrated that hausmannite (Mn_3O_4) spontaneously converts to manganite (γ-MnOOH) through the intermediate feitknechtite (β-MnOOH) by aging, and the oxide surface during this transformation is dominated by Mn(III).

Hydroquinone and other chemicals were analytical grade, commercially available reagents and were used without further purification. The water was distilled and deionized. All the experiments were carried out at 22 ± 1°C.

A closed flowing system (shown in Figure 1) was developed to study the kinetics of the reaction. The 220-ml cylindrical reaction container was made of polyester (or glass). A rubber stopper was used to cover the container and to hold the desired probes. The suspension within the container was mixed by a magnetic stir bar. To permit spectrophotometric analysis of the solution phase without interference from the oxide particles, a bundle of hollow fibers (having a molecular weight cut-off of 6000) was used as a semipermeable membrane to separate the aqueous solution from the oxide suspension within the reaction chamber. Aqueous solution within the fiber bundles was continuously circulated by a Masterflex peristaltic pump through Nalgene tubing, and a flat, flow-type electron-spin-resonance (ESR) cell and a micro-flow-type ultraviolet (UV) cell were connected in line with the pump to allow on-line analysis of the solutions by ESR and UV spectrometry. The working volume of the fibers was 8 ml, and the flow rate within the fibers was about 80 ml/min. The total volume of the on-line system was about 20 ml. From preliminary experiments, the time required for diffusion to equalize solute concentration across the fiber membrane was 3–6 min.

To conduct an oxidation experiment, pre-weighed dry oxide was added to the desired concentration of hydroquinone solution, and the pH of the solution was adjusted to 6. A pH controller (Type 45AR, Chemtrix) maintained constant pH by addition of 0.05 N NaOH or HCl during reaction. A polarographic oxygen electrode (Model 53 Oxygen monitor, Yellow Springs Instrument Company) was used to monitor the amount of molecular oxygen consumed during the reaction. Simultaneously, dissolved Mn^{2+} and organic free radicals were detected by an ESR spectrometer (Varian E-104) at X-band frequency. Relative Mn^{2+} signal amplitudes were converted to concentrations using aqueous $MnCl_2$ solutions as standards. For organic free radicals, spectra were recorded at low microwave power (5 mW) to avoid saturation effects. Hydroquinone and quinone concentrations were continuously monitored from the absorption intensities at 288 and 245 nm, respectively, using a UV spectrophotometer (Perkin-Elmer model 200). Baseline (using the absorbance at 320 nm) adjustment was applied to the final calculation of concentration to eliminate the interfering absorbance of polymers in solution.

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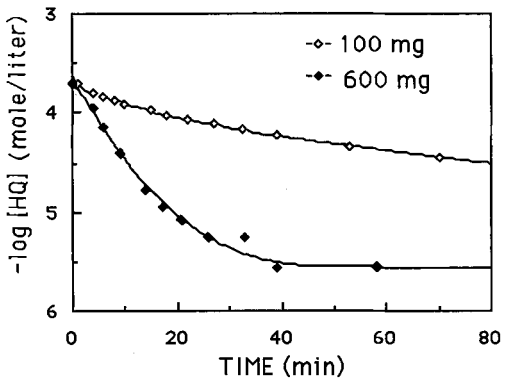


Figure 3. Loss of hydroquinone from solution at pH 6 due to oxidation at 100 and 600 mg hausmannite (Mn_3O_4) loadings. Initial hydroquinone concentration = 2×10^{-4} M.

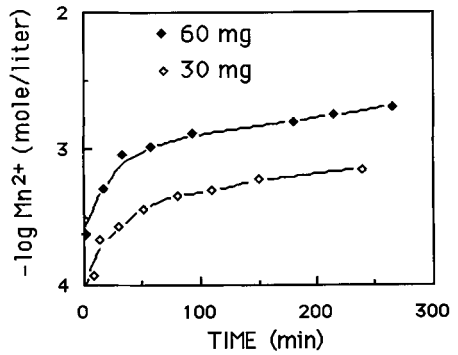


Figure 4. Mn^{2+} appearance in solution at pH 6 with time at 30 and 60 mg hausmannite (Mn_3O_4) loadings. Initial hydroquinone concentration = 2×10^{-2} M.

At the end of the experiment, the oxides were separated from the suspension by centrifugation and freeze-dried. Pressed KBr pellets containing these powder samples were then analyzed by infrared spectrophotometry (Perkin-Elmer model 281).

RESULTS AND DISCUSSION

Kinetics of the electron transfer

Electron transfer from hydroquinone to the oxide was clearly indicated by the release of Mn^{2+} accompanying the loss of hydroquinone from solution (Figure 2). This observation indicated that electron(s) extracted from hydroquinone reduced surface manganese, releasing Mn^{2+} into solution. The p-benzoquinone concentration could not be quantified because the quinone absorption at 245 nm exceeded the usable absorbance range of the spectrometer. This is a result of the high yield of the reaction and the large molar absorptivity of the monomeric quinone. As hydroquinone oxidized, large amounts of the oxidation product, p-benzoquinone, were identified in the solution. As the oxidation of hydroquinone approached completion, the concentration of soluble Mn^{2+} reached a maximum. For example, in the reaction shown in Figure 2, a 2×10^{-4} M hydroquinone solution was initially combined with 600 mg of the Mn oxide. Equilibrium was reached within 1 hr. No organic radical and few organic polymers were detected during the entire reaction.

For the same concentration of hydroquinone and a smaller amount of added oxide, a slower rate of oxidation was measured. For example, in Figure 3, the loss of hydroquinone from solution for the same initial hydroquinone concentration (2×10^{-4} M) and two different loadings of the Mn oxide is shown. The slower oxidation of hydroquinone in the presence of a lower concentration of the oxide suggests that organics were first complexed to the oxide surface before electron transfer took place (Stone and Morgan, 1984a). At higher concentrations of the oxide, more surface was available for hydroquinone complexation and a faster oxidation rate was noted. The results also show that for a given initial concentration of hydroquinone, a higher oxide concentration not only increased the dissolution *rate* of Mn^{2+}, but also increased *total* Mn^{2+} dissolved into the solution (Figure 4). Conversely, for higher initial hydroquinone concentrations, the final concentration of dissolved Mn^{2+} increased, as shown in Figure 5. These results indicate that rate as well as extent of formation of soluble manganese depended on both the quantity of the oxide present and the hydroquinone concentration. No clear maximum of Mn^{2+} dissolution within the reaction periods, however, was apparent at high hydroquinone concentration. Lack of a consistent value of Mn^{2+} dissolved per unit surface area of oxide at different hydroquinone concentrations implies that the reduction of the Mn oxide was not limited to the surface layer of Mn atoms; i.e., the reaction released Mn^{2+} beyond that initially exposed at the surface as long as excess hydroquinone was available. The variability of the amount of Mn^{2+} dissolved per unit surface area, however, could also have been due to (1) the spontaneous release of Mn^{2+} during the disproportionation of the structural Mn^{3+} and the de-

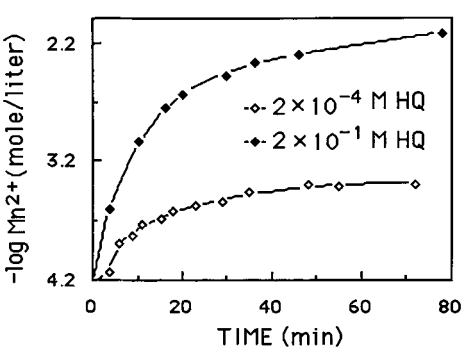


Figure 5. Rate of Mn^{2+} dissolution at pH 6 at two initial hydroquinone concentrations. Initial hausmannite (Mn_3O_4) loading was 100 mg.

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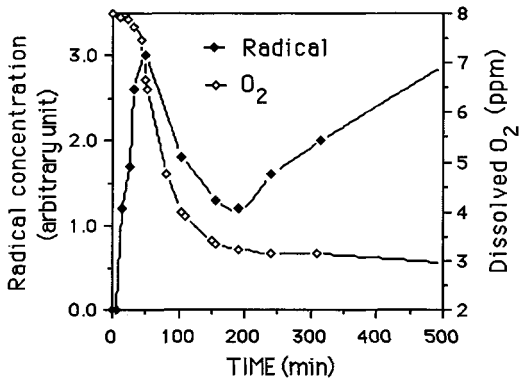


Figure 6. Concentration of p-benzosemiquinone radical (arbitrary units) and dissolved O_2 in solution as a function of time.

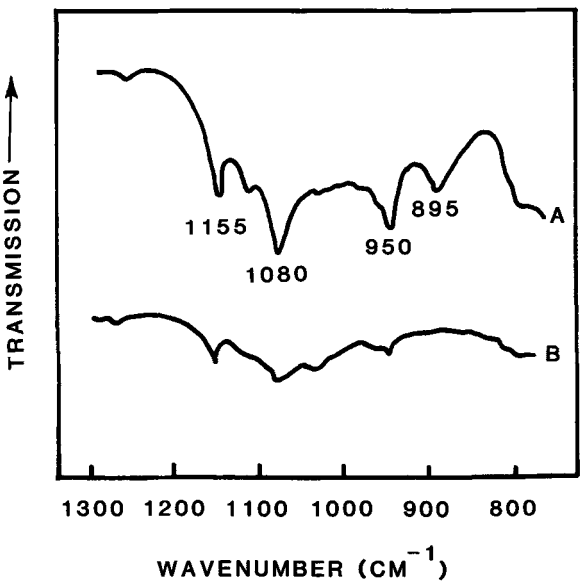


Figure 7. Infrared spectrum of hausmannite (Mn_3O_4) before (A) and after (B) the oxidation of hydroquinone at pH 6.

composition of hausmannite to MnO_2 and/or MnOOH (Bricker, 1965; Murray *et al.*, 1985), (2) variable retention of reduced Mn by the oxide structure, and (3) the involvement of O_2 in the reaction process (*vide infra*).

p-Benzosemiquinone anion radical

ESR spectroscopy detected, during the electron transfer process, a quintet of hyperfine lines arising from four equivalent protons (hyperfine coupling constant = 2.4 G, g value = 2.005), confirmed to be the p-benzosemiquinone anion radical spectrum (Wertz and Vivo, 1955; Fukuzumi *et al.*, 1975). From studies of the generation of the free radicals at various initial ratios of organic and oxide, radical formation apparently depended not only on the hydroquinone concentration, but also on the amount of oxide present, agreeing with the studies of Fukuzumi *et al.* (1975) and Ono *et al.* (1977) at pH 9, in which the formation rate of radicals was found to be first order with respect to both phenol concentration and the amount of the Mn oxide.

The presence of semiquinone radicals confirmed that the reduction of hausmannite involved a one-electron transfer process. Surprisingly, this anion radical, which is stable in aqueous solution only at high pH, persisted in the oxide suspensions at pH 6. The radical became more abundant at relatively high concentrations of hydroquinone. For example, for 0.16 mmole hydroquinone/mg of oxide, the concentration of radical initially increased, but then decreased simultaneously with the consumption of dissolved O_2 (Figure 6). Once oxygen was depleted, the concentration of the free radical gradually increased again. Evidently, the rapidly generated semiquinone anion radical was slowly oxidized by dissolved O_2 in the solution. Furthermore, at even higher relative hydroquinone concentration (0.5 mmole hydroquinone/mg of oxide), dissolved O_2 was apparently consumed as soon as the oxidation of hydroquinone began (i.e., without a short period of delay characteristic for the lower hydroquinone concentrations of Figure 6), and the concentration of free radical increased dramatically (data not shown). These results imply that if the manganese oxide was overwhelmed by the reducing capacity of the hydroquinone, O_2 acted as a secondary, less-preferred electron acceptor to surface manganese. Also, oxide suspensions containing high concentrations of hydroquinone possessed insufficient oxidizing capacity to oxidize hydroquinone to quinone completely, resulting in the accumulation of the semiquinone radicals. The persistence of these radicals in solution despite their chemical instability suggests a near steady-state condition in which the oxide generated radicals at a rate comparable to their rate of oxidation by O_2.

Infrared studies

Although an inner-sphere electron transfer reaction requires the formation of a surface complex (Stone and Morgan, 1984b), no significant amount of organic was detected on the oxide surface by IR spectroscopy after the reaction (Figure 7). Evidently, hydroquinone and its oxidation products did not strongly adsorb on the oxide surface at pH 6. This observation is consistent with the result that hydroquinone and catechol failed to adsorb on the hausmannite at levels detectable by Fourier-transform IR spectroscopy (McBride, 1987). Lack of adsorption of the semiquinone anion radical and/or its oxidative polymers on the hausmannite may have been due to electrostatic repulsion between the oxide and the organics (Mn oxides have low zero points of charge and are negatively charged at pH 6) or the low specific surface area (about 20 m^2/g) of the oxide.

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The IR spectra also showed bands due to structural Mn–OH to be diminished by the reaction with hydroquinone (Figure 7). Possibly, these OH groups were largely at the surface and were converted to H_2O during Mn reduction [see Eq. (1)], or organics interacted with surface OH groups, weakening or broadening these bands. Because little evidence of adsorption was found, the second explanation seems less likely. Nevertheless, the surface-promoted oxidation of hydroquinone suggests that a surface complex did form, even if it was transitory. High-charge metal cations (e.g., Fe^{3+}) have a significant capacity to complex with phenolic groups at pH 6 (McBride, 1987), and surface Mn^{3+} may similarly coordinate to one of the phenolic groups in hydroquinone.

Thermodynamic studies

The process of hydroquinone oxidation is described as follows (Laird, 1979), where HQ is hydroquinone, $SQ^{\cdot-}$ is the semiquinone anion radical, and Q is quinone:

$$H \xrightarrow{2H^+} HQ^{2-} \xrightarrow[-1.23\ V]{e^-} SQ^{\cdot-} \xrightarrow[-0.54\ V]{e^-} Q$$

The one-electron reduction potentials of quinone in aprotic solvent, measured polarographically from the half-wave potential (vs. saturated calomel electrode) were 0.54 and 1.23 V (Peover, 1962). The equilibrium constants for hausmannite and manganite (Bolt and Bruggenwert, 1976) are shown as follow [Eqs. (1, 2)]:

$$Mn_3O_4 + 8H^+ + 2e^- \longrightarrow 3Mn^{2+} + 4H_2O$$
$$\log K = 61.1 \quad (1)$$

$$\gamma\text{-MnOOH} + 3H^+ + e^- \longrightarrow Mn^{2+} + 2H_2O$$
$$\log K = 24.6 \quad (2)$$

The appearance of semiquinone anion radical indicates that the reduction of the hausmannite was a one-electron transfer process. A reasonable reaction sequence is that hydroquinone first approached the oxide and formed a surface complex. Protons were then extracted by the oxide from both hydroquinone and water while an electron was transferred [as shown in Eq. (3)]. Thus, the hydroquinone dianion was oxidized to the semiquinone anion radical, and the Mn_3O_4 was reduced to Mn^{2+}. Once the radicals were produced, the competition for further reaction began, i.e., semiquinone competed with hydroquinone for further oxidation by the Mn_3O_4 [Eqs. (3, 4)]. Equilibrium constants shown for the following equations were calculated from the standard redox potentials of the respective half-cell reactions.

$$Mn_3O_4 + 2HQ + 4H^+ \longrightarrow 3Mn^{2+} + 2SQ^{\cdot-} + 4H_2O$$
$$K_{eq} = 4.22 \times 10^{27} \quad (3)$$

$$2SQ^{\cdot-} + Mn_3O_4 + 8H^+ \longrightarrow 3Mn^{2+} + 2Q + 4H_2O$$
$$K_{eq} = 9.04 \times 10^{50} \quad (4)$$

These K_{eq} values can not be generally applied in a quantitative manner, because the oxide used in this study may not have the surface structure of Mn_3O_4; some evidence exists that a manganite-like layer was present on the surface, consistent with the view that Mn(III) tends to be the favored oxidation state at the surface (Murray *et al.*, 1985). Thus, a more comprehensive representation of the experiments should include the following reactions:

$$\gamma\text{-MnOOH} + HQ + H^+ \longrightarrow Mn^{2+} + SQ^{\cdot-} + 2H_2O$$
$$K_{eq} = 7.27 \times 10^7 \quad (5)$$

$$SQ^{\cdot-} + \gamma\text{-MnOOH} + 3H^+ \longrightarrow Mn^{2+} + Q + 2H_2O$$
$$K_{eq} = 3.36 \times 10^{19} \quad (6)$$

The greater the standard redox potential, the larger the equilibrium constant and the stronger the thermodynamic driving force of the reaction. The effective redox potential, however, depends also on the concentration of reagents and products. At the beginning of the reaction, the concentration of hydroquinone was much greater than that of semiquinone and Eq. (5) was dominant. Once hydroquinone had been largely consumed, the radical further oxidized to quinone as soon as it was generated on the oxide surface [Eq. (6)]. If the hydroquinone concentration remained high, however, the semiquinone radical concentration may have increased as the reaction proceeded [Eq. (5)] and some radicals were released from the oxide surface into aqueous solution before further oxidation occurred [Eq. (6)]. These semiquinone radicals were then oxidized by dissolved O_2:

$$SQ^{\cdot-} + \tfrac{1}{4}O_2 + H^+ \longrightarrow \tfrac{1}{2}H_2O + Q \quad (7)$$
$$K_{eq} = 5.28 \times 10^{15}$$

or were directly coupled to form polymeric compounds (which were detected by upward shifts in the baseline of the UV spectra). Thus, Eqs. (5) and (6) explain why radicals were not detected in solution at low hydroquinone/oxide ratios, because the excess of surface MnOOH groups allowed the radical to be oxidized at the surface [Eq. (6)] immediately upon its generation [Eq. (5)]. Conversely, for relatively high hydroquinone/oxide ratios, radicals accumulated in solution and were gradually oxidized by O_2, because Eq. (6) was rendered

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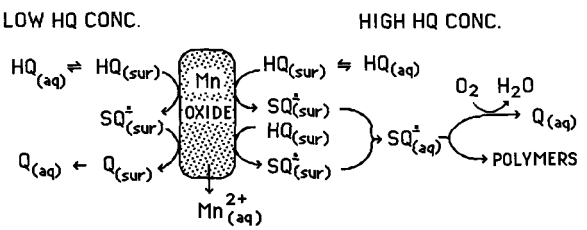
unfavorable by the limited quantity of oxidizing surface groups.

Polymers in solution

In aqueous solution, both visual evidence of the browning caused by the high-intensity absorption of conjugated chromophoric groups and upward shifts in the UV-visible spectral baselines indicated that higher hydroquinone concentrations produced more polymers. Inasmuch as the existence of free radicals was correlated to hydroquinone concentration, free radical coupling mechanisms were probably involved in the polymerization. The products of these polymerization reactions were not further studied; however, their UV-visible absorption profiles appeared to be similar to those of phenolic polymers (Shindo and Huang, 1982, 1984, 1985).

Reaction scheme

Based upon the observations of the effect of hydroquinone concentration on the consumption of O_2, and appearance of different organic products, a surface reaction scheme is proposed in the diagram below:



This diagram denotes species formed at the surface (sur), and species in the solution phase (aq).

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