OXIDATION OF 1,2- AND 1,4-DIHYDROXYBENZENE BY BIRNESSITE IN ACIDIC AQUEOUS SUSPENSION

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Abstract—The rate and extent of oxidation of dihydroxybenzenes (DHB) to quinones in acetate-buffered suspensions of synthetic birnessite were studied using Mn dissolution to monitor reaction progress. Concentration of free Mn^{2+} in the aqueous phase was continuously monitored by electron spin resonance, and ultraviolet-visible (UV-VIS) spectroscopy was utilized to quantify dihydroxybenzene and quinone concentrations. Although dissolution of the oxide and release of Mn^{2+} to solution generally accompanied phenol oxidation, a threshold oxidation level had to be exceeded before Mn^{2+} appeared in solution. Once this threshold was surpassed, the mole quantity of Mn^{2+} dissolved equaled the mole quantity of organic oxidized for 1,4-DHB, but exceeded the quantity of organic oxidized for 1,2-DHB. Thus, the latter phenol was more efficient in dissolving the oxide. Soluble phosphate suppressed Mn^{2+} release without influencing the degree of organic oxidation, suggesting that phosphate chemically interacted with reduced Mn to hinder its dissolution. UV spectra provided tentative evidence for the transitory existence of Mn^{3+}-1,4-DHB complexes in the solution phase.

Infrared spectra of the birnessite after reaction with 1,4-DHB indicated some new features, which may have been a result of the reduction of surface Mn atoms to the 3+ oxidation state. These features were not present after reaction with 1,2-DHB, confirming that the latter phenol efficiently dissolved the oxide to release Mn^{2+}. Although the initial Mn dissolution was very rapid and was attributed to a surface reaction, further slow Mn release accompanied by more complete oxidation of the phenols suggests a process limited by the rate of dissolution of the solid.

Key Words—Birnessite, Dihydroxybenzene, Electron spin resonance, Manganese, Oxidation, Phenol, Ultraviolet-visible spectroscopy.

INTRODUCTION

Soil manganese oxides are potentially important sources of soluble Mn for plants, but because of the low solubility of Mn^{3+} and Mn^{4+}, chemical reduction to Mn^{2+} is necessary to enable significant concentrations of Mn to exist in soil solution. Many organic compounds can solubilize Mn by reduction, including diphenolics, salicylic acid, pyruvic acid, oxalic acid, and fulvic acid (Stone and Morgan, 1984a, 1984b). Organics, such as malate (Jauregui and Reisenauer, 1982) and glutamate (Traina and Doner, 1985a), are oxidatively decomposed during the reduction of Mn oxides. Even monophenolic compounds, particularly those containing electron-donating substituent groups on the aromatic ring, can be oxidized by Mn oxides, releasing Mn^{2+} (Lehmann *et al.,* 1987; Stone, 1987). Although the reductant molecules in soils may be exuded from roots or microorganisms, the Mn dissolution reaction itself is abiotic.

The present study was designed to investigate the reduction of Mn in birnessite by dihydroxybenzenes (DHB) at a controlled acidic pH, a situation which may be encountered in acid soils in which the buffer capacity of the soil prevents the reaction itself from changing the pH. In the absence of buffer, the birnessite-DHB reaction raises the solution pH markedly (McBride, 1989). The effect of various factors on extent of reaction and the amount of Mn^{2+} solubilized was deter-

mined in the present study, including the nature of the reductant (o-dihydroxy vs. p-dihydroxy benzenes), reductant/oxide ratio, and the presence of phosphate.

MATERIALS AND METHODS

Birnessite in the K-saturated form was synthesized according to the procedure of McKenzie (1970), washed repeatedly with water to remove excess reagents, and freeze-dried. The properties of this poorly crystalline form of birnessite are summarized elsewhere (McBride, 1989).

A weighed quantity (usually 100 mg) of the birnessite powder was placed in a beaker with 20 ml of K-acetate buffer (pH = 5.4, 0.2 M) and 5 ml of distilled water. If other reagents were introduced, the 5 ml of water was replaced by 5 ml of the reagent (e.g., 10^{-2} M KH_2PO_4). The experiment was initiated by adding 5 ml of 10^{-2} M 1,2-DHB or 1,4-DHB to the beaker while stirring vigorously with a magnetic stir bar. The concentration of Mn^{2+} in the aqueous phase was then monitored by circulating the suspension through a flat quartz cell mounted in the cavity of a Varian E-104 electron spin resonance (ESR) spectrometer and periodically measuring the Mn^{2+} signal intensity. Aqueous $MnCl_2$ standards were used to convert the Mn^{2+} ESR signal amplitudes to molar concentrations. The use of ESR allowed analysis of free soluble Mn^{2+} in less than 1 min of the reaction's inception. Analysis by more con-

ventional methods would have required a separation step (e.g., filtration), increasing the difficulty of obtaining estimates of reaction progress in the first seconds of reaction. Furthermore ESR measured free Mn^{2+} only, with no interference from Mn in colloidal form or other oxidation states.

Preliminary experiments with the K-birnessite in K-acetate buffer at pH = 5.4 revealed that no detectable Mn^{2+} was released into the aqueous phase until the DHB was added to the suspension. Thus, unlike hausmannite (Kung and McBride, 1988), this Mn oxide appeared stable in acidic solution. In addition, continuous stirring of the suspension was necessary, because a lack of stirring often caused DHB-induced Mn^{2+} dissolution, even if it did not occur in identical systems with stirring. This effect is attributed to inhomogeneous reduction of unstirred oxide suspensions, in which substantial reduction and subsequent dissolution occurred at exposed surfaces, whereas other surfaces not exposed to the DHB were not reduced. Once Mn^{2+} was released to solution, preliminary experiments showed that it could be readsorbed by a further addition of birnessite, emphasizing the importance of the quantity of oxide in controlling Mn^{2+} release.

None of these buffered reactions occurred with a significant consumption of O_2 over the time scale of the experiment (measured by polarographic electrode in sealed solutions) or a detectable generation of semiquinone radicals (measured by ESR). The acidic pH evidently prevented the accumulation of radicals and the associated consumption of O_2 (McBride, 1989).

Further experiments were conducted using ESR to detect the rapid release of Mn^{2+} from K-birnessite as the concentration of DHB was increased in small increments. After combining 20 ml of K-acetate buffer and 5 ml of H_2O with 25 mg of K-birnessite in a beaker, the system was stirred continuously as small aliquots of 10^{-2} M 1,2-DHB or 1,4-DHB were added. After each addition (0.2–0.5 ml), ESR showed Mn^{2+} release to be complete within about 5 min, and a further addition of DHB was made. This experiment allowed cumulative Mn^{2+} release to be plotted as a function of reductant added, but it did not provide an estimate of the fraction of reductant actually oxidized.

Complementary experiments were conducted with different quantities of 1,2-DHB or 1,4-DHB and a constant amount of birnessite to compare directly the quantity of organic oxidized with the amount of Mn dissolved over a range of birnessite/DHB ratios. In these experiments, 20 ml of K-acetate buffer and 25 mg of K-birnessite were combined with 1.0, 2.0, 4.0, 8.0, and 16.0 ml of 10^{-2} M 1,2-DHB or 1,4-DHB, and sufficient distilled water was added to bring the total volume to 36 ml. After shaking for 5 min, the suspensions were centrifuged and the supernatants collected for analysis. Total soluble Mn was determined by atomic absorption spectrophotometry (AA); soluble free Mn^{2+} was determined by ESR. For 1.4-DHB, the soluble phenol and its oxidation product (p-benzoquinone) were estimated by their UV absorbances at 288 and 242 nm, respectively. For 1,2-DHB, the soluble phenol in the supernatant was determined by absorbance at 274 nm, but the quinone concentration could not be measured because the oxidation products did not have the simple UV-visible spectrum expected for the o-benzoquinone monomer (λ = 385 nm). Instead, a broad peak centered at 408 nm and a significant background absorbance were evident, suggesting the formation of polymeric quinones.

Following these analyses, the centrifuged birnessite samples that had been reduced by DHB were freeze-dried and analyzed by dispersive infrared (IR) spectroscopy in KBr pellets.

RESULTS AND DISCUSSION

ESR detection of Mn dissolution

Release of Mn^{2+} into buffered aqueous solutions (pH = 5.4) upon reaction of birnessite with both 1,2-DHB and 1,4-DHB was initially rapid, as shown in Figures 1 and 2, but approached an apparent maximum within several minutes. In the 1,4-DHB reaction, the Mn^{2+} concentration tended to decrease gradually after the initial reaction (Figure 1), whereas a gradual increase in soluble Mn^{2+} was evident after the initial rapid reaction with 1,2-DHB (Figure 2). The slow decrease in the Mn^{2+} concentration may reflect a re-adsorption process, inasmuch as birnessite has been shown to adsorb Mn^{2+} specifically (Traina and Doner, 1985b). On the other hand, the slow Mn^{2+} increase observed with 1,2-DHB could reflect a more aggressive dissolution of the oxide by 1,2-DHB than by 1,4-DHB. This difference in behavior may indicate that 1,2-DHB was able to complex with Mn^{3+} or Mn^{4+} in the solid. The stability constant of the Mn^{2+}-1,2-DHB complex was not sufficiently great to allow the complex to form at low pH.

Despite identical reaction conditions, 1,2-DHB induced a greater initial release of Mn^{2+} from the oxide than did 1,4-DHB, a fact which may be related to the chelating potential of 1,2-DHB and its possible coordination to surface Mn^{3+} or Mn^{4+} ions. Such a coordination process would be conducive to subsequent electron transfer.

Several variables influenced the quantity of Mn^{2+} dissolved. For example, increasing the amount of birnessite from 25 to 100 mg at a constant 1,4-DHB level resulted in no Mn^{2+} dissolution (see Figure 1). Evidently, a certain threshold of Mn reduction by 1,4-DHB had to be attained before *any* Mn^{2+} appeared in solution. This behavior is in marked contrast to the observation by Stone and Morgan (1984a), that increasing the Mn oxide loading in suspension caused 1,4-DHB to dissolve increasing amounts of Mn^{2+} according to the rate law:
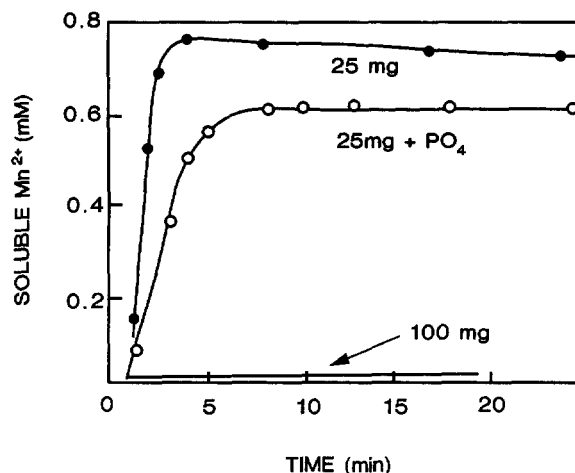
Figure 1.   1,4-dihydroxybenzene-induced dissolution of free Mn^{2+} from birnessite (25 mg and 100 mg) detected by electron spin resonance. Effect of soluble phosphate on dissolution is also shown.

Figure 2.   1,2-dihydroxybenzene-induced dissolution of free Mn^{2+} from birnessite as detected by electron spin resonance. Effect of soluble phosphate on dissolution is shown.

$$d[Mn^{2+}]/dt = k[1,4\text{-DHB}] ([MnO_x]_o - [Mn^{2+}]),$$

where $[MnO_x]_o$ is the initial amount of Mn oxide. Several differences in their experiment probably account for the discrepancy in behavior. First, their study of the effect of suspension loading on Mn^{2+} dissolution was done with a large excess of reductant (1,4-DHB). Consequently, Mn^{2+} dissolution continued over the time of the experiment. In the present study, Mn dissolution was essentially complete within the first few minutes, and most of the 1,4-DHB was oxidized (*vide infra*). The lower extent of reduction of surface Mn achieved in the present study was probably conducive to Mn^{2+} retention in the structure or on exchange sites. Secondly, the oxides employed in the two studies had very different points of zero charge, suggesting that the oxide used in the present study possessed greater surface negative charge and a greater capability to readsorb Mn^{2+} that was dissolved by chemical reduction of the surface.

Soluble phosphate also affected Mn^{2+} release, as 5 ml of 10^{-2} M KH_2PO_4 in the K-acetate buffer reduced both the initial rate of Mn^{2+} dissolution by 1,2-DHB and 1,4-DHB and the total quantity of Mn^{2+} released (Figures 1 and 2). Inasmuch as phosphate suppressed Mn^{2+} release by both phenols, the mechanism of suppression probably did not involve competition between phosphate and the phenols for surface coordination sites. If such competition existed, phosphate should have suppressed the 1,4-DHB reaction much more effectively than the 1,2-DHB reaction, because 1,4-DHB can only weakly coordinate with metals and could easily be displaced from oxide surface sites by phosphate. Unfortunately, the presence of the K-acetate buffer complicated this analysis, as acetate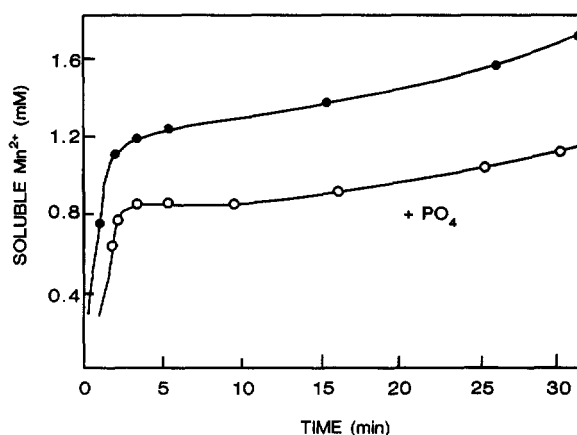 itself may act as a competing ligand in the absence of phosphate. Nevertheless, Stone (1987) noted that acetate had a negligible effect on the rate of Mn oxide reduction by phenols.

The inhibition of Mn^{2+} dissolution by phosphate, first observed by Stone and Morgan (1984a), may actually have been caused by the formation of solid Mn^{2+}-phosphate phases, such as $MnHPO_4$, rather than by ligand competition. Calculations of ion-activity products in solution showed that the solubility product of $MnHPO_4$ was initially exceeded in the present experiments. Despite the fact that Mn oxides appear to adsorb little phosphate (Stone and Morgan, 1984a), a Mn^{2+}-phosphate solid phase probably suppressed the release of Mn^{2+} generated by reduction. In support of this hypothesis, additional experiments using even higher concentrations of KH_2PO_4 failed to reveal a pronounced effect of phosphate on the yield of p-benzoquinone from the birnessite-1,4-DHB reaction. Furthermore, adding KH_2PO_4 to the solutions *after* release of Mn^{2+} from birnessite-1,4-DHB systems caused an immediate decrease in free soluble Mn^{2+} (detected by ESR), consistent with an ion pairing or a precipitation reaction. Thus, phosphate had little effect on the initial electron transfer reaction between 1,4-DHB and the oxide. Retardation of Mn^{2+} release must therefore be attributed to a secondary reaction between dissolved Mn^{2+} and the phosphate, not to competition of phosphate with the organic for binding sites on the oxide as proposed by Stone and Morgan (1984a).

Based upon the measured quantity of 1,4-DHB and 1,2-DHB removed from solution during reaction, the fraction of these phenols oxidized to quinones was calculated to be 0.90 and 0.76, respectively (for the experimental conditions used to generate the data in Figures 1 and 2). This difference may reflect the different reduction potentials of 1,2-benzoquinone (0.78 V) and 1,4-benzoquinone (0.699 V), indicating that 1,2-DHB is more difficult to oxidize than 1,4-DHB. The mole
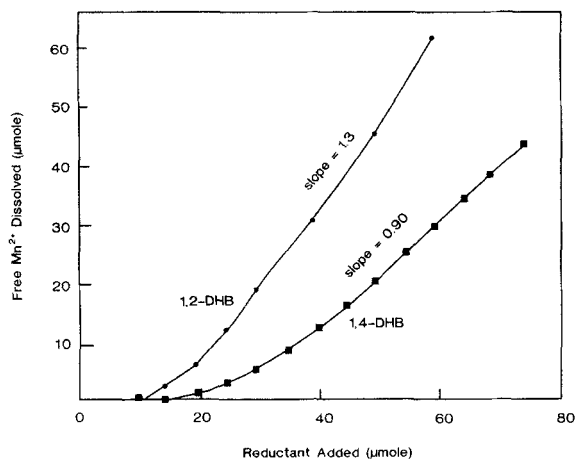
Figure 3. Dissolution of free Mn^{2+} from birnessite by incremental addition of dihydroxybenzenes to buffered birnessite suspensions, detected by electron spin resonance.

Table 1. Stoichiometry in the reaction of 1,4-dihydroxybenzene (DHB) with birnessite in K-acetate buffer.[1]

1,4-DHB			p-Quinone produced (μmole)	Quinone + unoxidized phenol (μmole)	Mn dissolved (μmole)
Added (μmole)	Remaining (μmole)	Oxidized (%)			
10	0.78	92.2	9.35	10.1	2.66
20	1.9	90.5	19.5	21.4	10.0
40	4.1	89.8	38.3	42.4	28.5
80	8.9	88.9	74.3	83.2	64.4
160	63.5	60.3	93.5	157	83.9

[1] 25 mg birnessite used at pH = 5.4.

The Mn^{2+}-release data of Figure 3, determined by ESR, did not measure *total* Mn dissolved, because soluble Mn^{2+} complexed with ligands is not generally detectable by ESR (McBride, 1982). Because a concentrated acetate buffer was used in these experiments, Mn-acetate complexes were expected in solution, undetected by ESR. In particular, for the pH and acetate concentrations used, calculations from the known stability constant of Mn-acetate predicted that the free Mn^{2+} ion should comprise 61% of total soluble Mn^{2+}. Analyses of the solution phase after reaction of several concentrations of the phenols with birnessite confirmed that between 60 and 70% of the soluble Mn as determined by AA was ESR-detectable. Also, ESR indicated that 62% of Mn^{2+} added to a blank sample (K-acetate buffer without the oxide) was ESR-detectable and therefore uncomplexed. Thus, within experimental error, acetate complexation accounts for the difference between free Mn^{2+} (detected by ESR) and total soluble Mn. As a consequence, the curves of Figure 3 represent only 60–70% of the total Mn dissolved by titration.

Measurement of total Mn dissolution and oxidation products

Because ESR detection of Mn^{2+} did not measure total soluble Mn, birnessite-phenol reactions were conducted in which the quantity of dissolved Mn was measured by AA. In these experiments, the quantity of phenol oxidized was simultaneously determined by UV-VIS spectrophotometry. The results of these experiments for 1,4-DHB (Table 1) reveal the following points: (1) Oxidation of 1,4-DHB was a nearly constant percentage (90%) of that added, except at the highest level of 1,4-DHB. (2) Total Mn dissolved was small relative to the quantity of phenol oxidized at low 1,4-DHB levels, but increased at higher levels, becoming linearly proportional to the amount of 1,4-DHB oxidized. (3) The sum (in moles) of p-benzoquinone released to solution and 1,4-DHB unreacted equaled the molar quantity of 1,4-DHB initially added to the oxide, proving that neither reactant nor product adsorbed at experimentally detectable levels on the oxide.
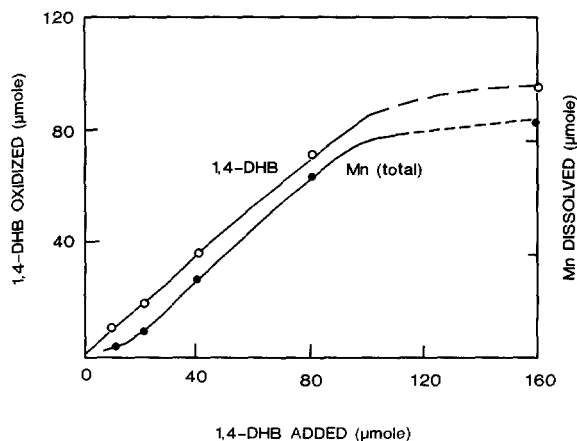
Figure 4 depicts the dependence of total Mn dis-

ratio of Mn^{2+} released to phenol oxidized, however, was 0.71 for 1,4-DHB and 1.2 for 1,2-DHB under these same reaction conditions. Clearly, 1,4-DHB caused less Mn dissolution than expected from the reaction stoichiometry. Inasmuch as the average valence of structural Mn in birnessite is slightly less than 4+, the expected mole ratio of Mn^{2+} released to 1,4-DHB oxidized is slightly greater than unity. Thus, reduced Mn was probably retained in the oxide if 1,4-DHB was the reductant. Either incomplete dissociation of the reduced surface Mn atoms or immediate readsorption of dissolved Mn^{2+} at other surface sites could have produced the deficit of Mn^{2+} release. Other studies of birnessite reduction have similarly shown a deficit in Mn^{2+} dissolution attributed to surface retention (Traina and Doner, 1985a).

The importance of oxide/reductant ratio in determining the release of Mn^{2+} into solution is quite evident on comparing the behavior of 100 mg and 25 mg of birnessite at a constant 1,4-DHB level (Figure 1). The effect of this ratio was further quantified by directly measuring Mn^{2+} dissolved (using ESR) as 1,2-DHB and 1,4-DHB were added to the birnessite suspension in small increments. Figure 3 shows these "titrations" of the oxide with phenols and reveals that a threshold level of phenol reductant had to be added before any Mn^{2+} was released to solution. Once this threshold had been exceeded, the ratio of Mn^{2+} dissolved to reductant added increased and then stabilized at a constant value. On a mole basis, however, this ratio was larger for 1,2-DHB (1.3) than for 1,4-DHB (0.9), again revealing the greater efficiency of Mn dissolution by 1,2-DHB. At reductant levels higher than those plotted in Figure 3, the mole ratio (i.e., slope) diminished, a likely consequence of the limited quantity of oxide, much of which dissolved at high reductant levels.

Figure 4.   1,4-dihydroxybenzene oxidized and total Mn dissolved as a function of amount of 1,4-dihydroxybenzene added to 25 mg of birnessite.
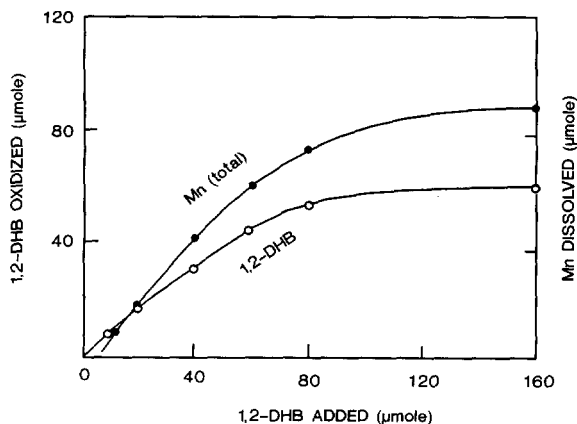

Figure 5.   Amount of 1,2-dihydroxybenzene oxidized and total Mn dissolved as a function of amount of 1,2-dihydroxybenzene added to 25 mg of birnessite.

solved and 1,4-DHB oxidized on the quantity of 1,4-DHB added. The birnessite appears to have maintained a constant deficit of Mn^{2+} released relative to phenol oxidized of about 8 μmole, which may have represented the capacity of the surface to undergo reduction without dissolution. Based on the surface area of the oxide, this value was equal to about 8 Mn atoms/100 Å^2, roughly equal to the expected surface density of Mn atoms (McBride, 1989). This retention of reduced Mn was not exchangeable, inasmuch as the addition of high concentrations of neutral salts during the reaction between 1,4-DHB and birnessite failed to release any additional Mn^{2+}. Therefore, the average oxidation state of Mn in the oxide must have changed at low 1,4-DHB addition levels. Further reduction of the oxide by greater 1,4-DHB additions produced equimolar release of soluble Mn^{2+} (see Figure 4), so that the average oxidation state of Mn in the solid did not change further.

The results for 1,2-DHB oxidation by birnessite (25 mg) at several 1,2-DHB addition levels are reported in Table 2. Because of polymerization reactions, the oxidation products were complex, and quinone pro-

duction could not be quantified. A broad absorption maximum at 408 nm was evident for the solution, increasing in intensity at higher 1,2-DHB levels. A comparison of Table 1 and Table 2 reveals the following differences between 1,2-DHB and 1,4-DHB oxidation by birnessite: (1) 1,2-DHB oxidation was less complete than 1,4-DHB oxidation, possibly because the former is thermodynamically more stable (see above discussion). (2) Dissolved Mn equaled or exceeded oxidized 1,2-DHB on a mole basis, unlike Mn dissolution by 1,4-DHB, suggesting little capacity of birnessite to retain reduced Mn in the presence of 1,2-DHB.

Figure 5 compares Mn dissolution with 1,2-DHB oxidized, revealing that the ratio of Mn-dissolved to 1,2-DHB oxidized was about 1.36. This mole excess of Mn release may have been a function of the oxidation state of Mn in the oxide, which for a synthetic birnessite has been reported to be 3.57+ (Golden *et al.*, 1987). For that oxidation state, 1.27 moles of Mn^{2+} could be released for each mole of 1,2-DHB oxidized, assuming no ability of the oxide to retain the reduced metal. The value of 1.36 moles reported here is therefore reasonable, but may indicate an oxidation state of Mn slightly less than 3.57+ in the birnessite used for this study.

Evidence for soluble complexed Mn^{3+}

One result of the UV-VIS spectroscopic analysis of buffered 1,4-DHB solutions that had reacted with birnessite is difficult to explain, namely, the consistent bathochromic shift of the 1,4-DHB absorbance, normally at 286 nm, to 295 nm. The shift, as shown in Figure 6a, was observed at all except the highest level of 1,4-DHB added to the birnessite (see Table 1), but it was temporary, inasmuch as the absorbance of the solutions separated from the oxides shifted back to 286 nm within a day (Figure 6b). As the band shifted back to 286 nm, it weakened, and a broad absorption in the

Table 2.   Stoichiometry in the reaction of 1,2-dihydroxybenzene (DHB) with birnessite in K-acetate buffer.[1]

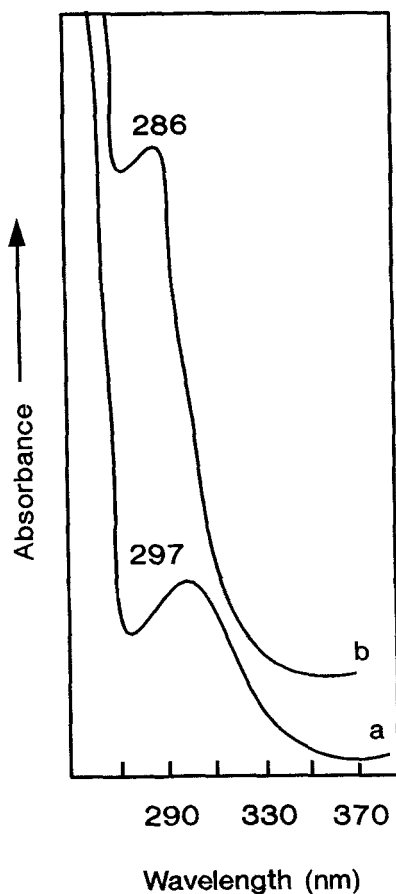| | 1,2-DHB | | |
Added (μmole)	Remaining (μmole)	Oxidized (%)	Mn dissolved (μmole)
10	1.6	84	8.5
20	3.8	81	18.3
40	9.8	76	42.9
60	16.3	73	61.6
80	22.8	72	75.3
160	97.8	39	90.4

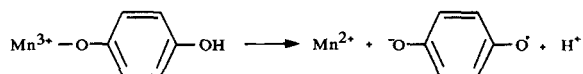[1] 25 mg birnessite used at pH = 5.4.

Figure 6. Ultraviolet spectrum of (a) the separated aqueous phase immediately after reaction of 40 μmole of 1,4-dihydroxybenzene with 25 mg of birnessite, and (b) the separated aqueous phase after 1 day of exposure to air.

$$Mn^{3+}-O\!-\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-OH \longrightarrow Mn^{2+} + \ ^-O\!-\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-O^{\cdot} + H^+$$

These radicals may then have polymerized.

As described above, analysis of the solutions by ESR after the birnessite and 1,4-DHB had reacted had already shown that soluble Mn was largely (or totally) in the form of free Mn^{2+} and Mn^{2+}-acetate complexes. The bathochromic shift of 1,4-DHB, however, was observed only in solutions having high soluble Mn/1,4-DHB mole ratios (See Table 1). thus, a small fraction of the dissolved Mn could have been in the 3+ oxidation state, complexed with a large fraction of the 1,4-DHB, and may not have been detected by the analysis of Mn speciation using ESR. Nevertheless, the existence of Mn^{3+} in the aqueous birnessite-1,4-DHB reaction systems could not be directly confirmed. The fact that no evidence for Mn^{3+} was noted in the 1,2-DHB reaction with oxide, despite the ability of 1,2-DHB to chelate strongly with M^{3+} ions, may indicate that electron transfer between this phenol and Mn^{3+} was sufficiently facile to reduce the metal immediately.

Evidence for surface vs. dissolution reaction

The incomplete oxidation of the phenols by birnessite, evident from the data of Tables 1 and 2, is unexpected in one respect, because calculations using known oxidation potentials of Mn oxides predict complete oxidation of 1,2-DHB and 1,4-DHB to quinones. An estimate of reactive surface sites on this oxide using reasonable densities of surface metal ions (Stone and Morgan, 1984a), is less than 10 μmole/25 mg, which is below the lowest level of reductant used in these experiments (see Tables 1 and 2). Thus, the oxidation capacity of the oxide surface layer was probably exceeded, resulting in incomplete oxidation. If a much longer reaction time of 18 hr was used, however, UV-VIS spectroscopy indicated more complete oxidation of 1,4-DHB and more evidence of quinone polymers in solution, having an ill-defined absorbance maximum near 470 nm. Evidently, slow oxidation and polymerization continued after the initially rapid electron transfer process, driven by the thermodynamic favorability of the reaction, but possibly hindered by slow diffusion processes once the surface layer's oxidative capacity had been exhausted. It may be that a chemically reduced surface layer built up, hindering further contact between reductant and oxidizing sites.

Evidence for Mn oxide alteration using IR

The reaction between 1,4-DHB and birnessite had some effects on the IR spectrum of the oxide (Figure 7). The most significant effects of reaction with increasing levels of buffered 1,4-DHB were (1) an increase in intensity of bands at 1560, 1414, and 1346 cm^{-1}, (2) several weak bands appearing in the 1000–1200-cm^{-1} region, and (3) a decrease in intensity of
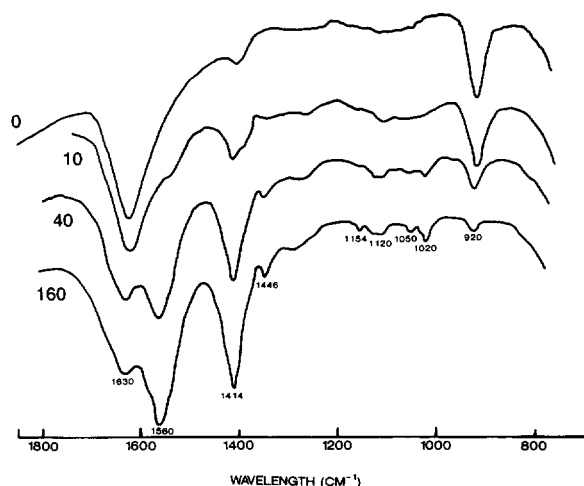
visible region intensified and shifted from about 425 to 435 nm. Reaction between 1,4-DHB and a different Mn oxide, hausmannite, failed to produce this bathochromic shift of 1,4-DHB, although oxidation of 1,4-DHB was confirmed by the appearance of 1,4-benzoquinone in solution.

Bathochromic shifts in π–π^* transitions of aromatic molecules can be caused by complexation with metals, but soluble Mn^{2+} does not shift the 1,4-DHB spectrum in solutions buffered at pH 5.4 (unpublished data). Thus, a metal capable of complexing 1,4-DHB may have been present in solution. Mn^{3+} is unstable in aqueous solution as the free ion, but it can be stabilized by complexing anions (Cotton and Wilkinson, 1980). The acetate utilized in the present experiments may have retarded its decomposition. Thus, the gradual loss of the bathochromic shift, accompanied by apparent polymerization of organics, suggests that Mn^{3+}-1,4-DHB complexes existed temporarily in solution, but decomposed to form radicals:

Figure 7.   Infrared spectra of dried birnessite samples after reaction between 0, 10, 40, and 160 μmole of 1,4-dihydroxybenzene and 25 mg of the oxide.

the oxide band at 920 cm^{-1}. The 1560-, 1414-, and 1346-cm^{-1} bands are attributed to acetate in the unwashed oxide (Alcock *et al.*, 1976), and were largely eliminated by a single water wash of the oxide. Whether the acetate was weakly adsorbed or physically entrained was difficult to determine, but comparable bands at 1560 and 1420 cm^{-1} have been reported for acetate adsorbed on alumina (Hayashi *et al.*, 1969). The fact that they strengthened with increasing 1,4-DHB additions may be an indication of increased surface positive charge of the chemically reduced surface (greater ZPC), resulting from retention of reduced Mn in the structure. The surface may have adsorbed anions (i.e., acetate) electrostatically to neutralize the newly developed surface charge.

The weak bands at 1020, 1050, 1120, and 1154 cm^{-1}, although not reported for birnessites (Potter and Rossman, 1979), are at similar positions to OH-bend vibrations in manganite and groutite (McBride, 1987; van der Marel and Beutelspacher, 1976). Their appearance in proportion to the extent of reduction of birnessite suggests a reaction in which the surface Mn is converted to the reduced (3+) state. A change in oxidation state implies that dissolution of the oxide by 1,4-DHB was incomplete and further supports the suggestion from the Mn^{2+}-release data (see Figure 4, for example) that reduced Mn was retained in the structure.

The final observation from the IR spectra was the reduced intensity of the band at 920 cm^{-1} induced by reaction with 1,4-DHB (Figure 7). Although birnessite is not reported to absorb at this spectral position (Potter and Rossman, 1979), certain Mn oxides have bands at about 920 cm^{-1} (van der Marel and Beutelspacher, 1976). The band does not appear to have been assigned,

but it may be a bend vibration of a surface Mn^{4+}-OH group, which would diminish as Mn^{4+} is reduced to Mn^{3+}.

The IR spectra of birnessite after reaction with 1,2-DHB are not reported here, but differed from the spectra in Figure 7 in two respects. First, at comparable phenol addition-levels, 1,2-DHB caused much greater weakening of the band at 920 cm^{-1}. Second, bands in the 1000–1200-cm^{-1} region were not found. Consistent with the efficient dissolution of Mn by 1,2-DHB (see Figure 5), these results point to the complete removal of reduced Mn from the solid, leaving no evidence of a partially reduced surface layer.

SUMMARY AND CONCLUSIONS

The stoichiometry of Mn dissolution as a result of the reduction of birnessite by dihydroxybenzenes was a function of the reductant/oxide ratio and the position of substitution of the phenolic groups on the reductant. Retention of reduced Mn in the solid phase was particularly evident for the reaction with 1,4-DHB, in which Mn dissolution was less than that theoretically expected from the amount of reductant oxidized. In contrast, 1,2-DHB dissolved Mn more efficiently, releasing Mn^{2+} in the expected quantities relative to the amount of reductant oxidized. For both isomers of DHB, a threshold concentration of reductant had to be exceeded before any Mn^{2+} appeared in solution, but this concentration was higher for 1,4-DHB. IR spectroscopy suggested that reduced Mn (probably Mn^{3+}) was retained in the structure following reduction by 1,4-DHB but not after reduction by 1,2-DHB.

In all these electron transfer reactions, buffered at pH 5.4, radical products were not detected; rather, oxidation of the phenols generated quinones directly. Neither 1,4-DHB nor its oxidation product, p-benzoquinone, was adsorbed by the birnessite at detectable levels. Whether adsorption occurred in the 1,2-DHB reaction system could not be determined, because the complex soluble oxidation products formed in this system could not be quantified on a mole basis.

Phosphate influenced the DHB-birnessite reaction by reducing the rate of Mn^{2+} dissolution. This effect appeared to be the result of a secondary reaction, the precipitation of Mn^{2+}-phosphate phases, because phosphate did not notably reduce the amount of reductant oxidized to quinones.

Oxidation of the phenols was incomplete at all levels of addition to birnessite, a result which suggests a type of surface reaction in which the capacity of the oxide to oxidize phenols rapidly is limited by the surface area available for reaction. Nevertheless, the capacity to oxidize these phenols increased at higher levels of added phenols, greatly exceeding the oxidative capacity of the surface layer itself. This behavior is similar to that reported for hausmannite (Kung and McBride, 1988), in which surface area determined the *initial* reaction

rate and extent of oxidation, but oxidation continued at a slower rate beyond that expected from the surface-localized process. The slower process may be limited by the rate of dissolution of the surface layer to expose new reactive sites.

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