

OXIDATION OF DIHYDROXYBENZENES IN AERATED AQUEOUS SUSPENSIONS OF BIRNESSITE

M. B. MCBRIDE

Department of Agronomy, Cornell University, Ithaca, New York 14853

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.

INTRODUCTION

Manganese oxides are particularly efficient in accepting electrons from phenolic compounds to form semiquinones and quinones (Ono *et al.*, 1977; Stone and Morgan, 1984; Kung and McBride, 1988). Reaction models generally assume the coordination of the phenolic group to a surface Mn atom, followed by the transfer of an electron. In soils, this process may be important in solubilizing Mn^{2+} , but whether Mn^{2+} actually appears in solution or not is determined by the degree of subsequent reoxidation of this Mn^{2+} to insoluble forms by O_2 . Recently, McBride (1987) showed that O_2 consumption in dihydroxybenzene-Mn oxide suspensions is significant if buffers are not used to maintain the $pH < 7$; however, the factors which determine the relative extent to which O_2 supersedes the Mn oxide as the ultimate electron acceptor in phenol oxidation were not established. The study reported here is a more detailed investigation of the conditions under which O_2 becomes an electron acceptor in the oxidation of 1,2- and 1,4-dihydroxybenzene (1,2-DHB and 1,4-DHB) in the absence of buffers by birnessite, a Mn oxide reported to occur in soils. Radical intermediates, detected spectroscopically, were monitored during the reaction, as were inorganic cations of interest (Mn^{2+} , H^+).

MATERIALS AND METHODS

Birnessite in the K^+ -saturated form was synthesized by the HCl-KMnO₄ procedure of McKenzie (1970). The oxide was vacuum-filtered and repeatedly washed with distilled water to ensure the removal of excess reagents, then freeze-dried. This oxide had a zero point of charge (ZPC) of 3.6, based on the pH at which KCl

additions to the oxide in suspension had no effect on pH. The surface area of the material, determined after outgassing at 120°C for 1 hr, was 25.7 m²/g by B.E.T. analysis of N₂ absorption at 77 K. Transmission electron microscopy revealed the individual particles to be sub-micrometer size and spheroidal. Considering the size of these particles, it is evident that little or no internal surface of the layered mineral was measured by the N₂ adsorption method. Powder X-ray diffraction of this product showed only one broad peak, which was identified as the 7.3-Å spacing characteristic of poorly crystallized birnessite (McKenzie, 1977).

As is common for birnessite, the infrared spectra (obtained in KBr pellets on a dispersive spectrometer) were poorly developed, the main features being: (1) strong absorption between 3000 and 3600 cm⁻¹ attributed to OH-stretch vibrations, (2) background absorption increasing continuously from 1800 to 4000 cm⁻¹, possibly due to a charge-transfer band caused by electron exchange between neighboring Mn atoms, (3) an absorption at 1630 cm⁻¹ attributed to the OH-bend vibration of adsorbed water; and (4) strong multiple absorption bands in the 400–650-cm⁻¹ region caused by lattice vibrations and characteristic of layered Mn oxide structures (Potter and Rossman, 1979; Farmer, 1974). A fairly narrow band was observed at 920 cm⁻¹, but this band does not appear to be a feature characteristic of birnessite (Potter and Rossman, 1979). The 920-cm⁻¹ band may be a feature of the hydrated surface (possibly an OH bend), inasmuch as it diminishes if the oxide is heated to 100°C.

Oxygen uptake by birnessite in the presence of 1,2-DHB and 1,4-DHB was measured in a sealed glass cell using a polarographic electrode to detect dissolved O_2 . The solution phase consisted of 20 ml of distilled water

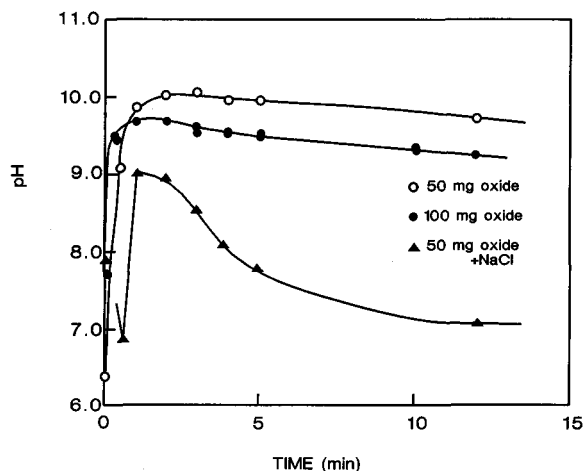


Figure 1. Effect of reaction time on the pH of birnessite-1,4-dihydroxybenzene suspensions.

(or 15 ml of water plus 5 ml of 1 M NaCl in selected experiments) and 5 ml of 0.01 M 1,2-DHB or 1,4-DHB. In some experiments, the 20 ml of distilled water was replaced by 20 ml of 0.05 M Na borate buffer (pH = 9.4). On addition of the birnessite powder (quantities ranging from 25 to 200 mg) to the solution, the cell was sealed to exclude air, and the level of dissolved O_2 was monitored. To observe the effect upon O_2 consumption, reagents such as KH_2PO_4 were injected by syringe into the cell in 1-ml quantities of concentrated aqueous solution, minimizing the introduction of dissolved O_2 . In some experiments, these reagents were pre-purged with N_2 gas to reduce O_2 entry into the cell even further. Without this purging process, 1 ml of injected reagent immediately increased the O_2 saturation of the suspensions by about 3%, provided that chemical reaction had depleted the O_2 in solution to

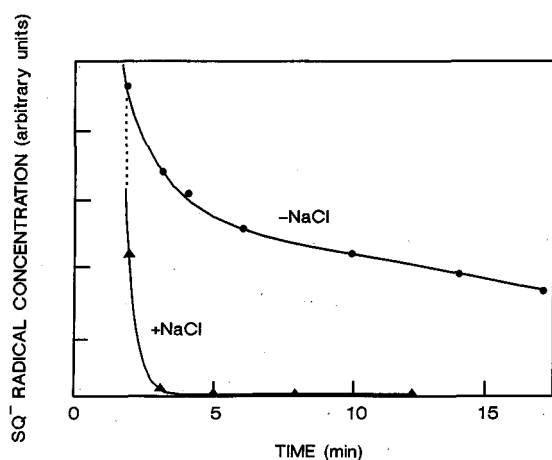


Figure 2. Effect of reaction time on the soluble p-benzosemiquinone (SQ^-) concentration in birnessite (100 mg)-1,4-dihydroxybenzene suspensions, with and without NaCl present.

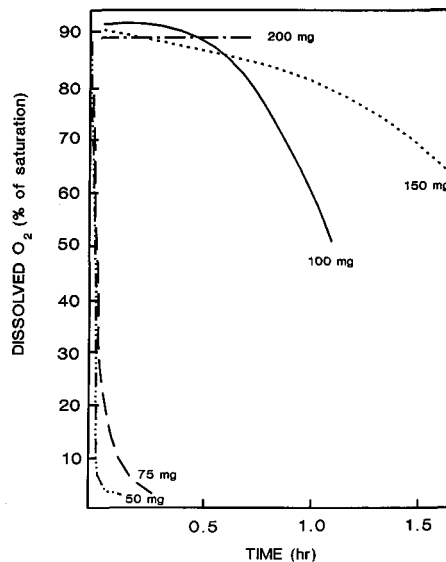


Figure 3. Molecular oxygen-uptake curves for variable quantities of birnessite reacted with 1,4-dihydroxybenzene.

only a small percentage of saturation. At higher initial O_2 -saturation levels, injected solutions produced proportionately smaller increases in the O_2 saturation. Care was taken to avoid the introduction of air bubbles during the injection of reagents.

The pH of K^+ -birnessite suspensions during reaction with the phenols was recorded in separate experiments using glass pH and reference electrodes. Reagent and oxide concentrations were identical to those employed in the O_2 -uptake studies. The suspensions were vigorously stirred after combining the oxides with the phenol solutions, and the pH was continuously monitored. These systems were open to air, unlike those sealed for the O_2 -uptake studies.

The K^+ -birnessite suspensions were also continuously monitored during reaction with the phenols for dissolved Mn^{2+} by circulating them through a quartz flat cell mounted in the cavity of a Varian E-104 electron spin resonance (ESR) spectrometer.

RESULTS

1,4-Dihydroxybenzene (1,4-DHB) oxidation

No Mn^{2+} was released into aqueous solution (as detected by ESR) upon reacting 1,4-DHB with birnessite, with or without NaCl (1 M) in solution. This lack of Mn dissolution is attributable to the very high pH generated by the electron transfer reaction within the first few seconds, as depicted in Figure 1.

The presence of NaCl caused an immediate pH decrease if birnessite was reacted with 1,4-DHB, but the pH subsequently rose rapidly and then decreased again (Figure 1). This complex behavior suggests at least two simultaneous processes that affected pH. Without phenols present, the addition of NaCl to the K^+ -bir-

nessite produced an acidic pH, which was evidently due to exchangeable H^+ on the negatively charged surfaces (data not shown). Thus, exchange of H^+ by Na^+ probably caused the rapid initial decrease in pH (Figure 1). The subsequent pH rise must then have been due to the slower electron-exchange reaction between 1,4-DHB and the oxide. Finally, the slow pH decrease, most noticeable with NaCl present, may represent the autocatalytic re-oxidation of Mn reduced by 1,4-DHB. With NaCl present in solution, many of the protons generated by oxidation were evidently displaced into solution, accounting for the much lower final pHs.

The *p*-benzosemiquinone (SQ^-) radical appeared immediately in the solution on combining 1,4-DHB and birnessite. It was detected by its distinctive ESR signal (multiplet with 1:4:6:4:1 intensity ratio). As shown in Figure 2, the radical signal initially diminished rapidly, then more slowly with time. With NaCl present, the radical signal was initially very intense, but decreased to almost undetectable levels within minutes. This pattern of radical persistence can be correlated with pH (Figure 1), inasmuch as a high pH is conducive to radical stability. The addition of NaCl to the 1,4-DHB-oxide system lowered the pH, shortening the lifetime of the SQ^- radicals in solution.

The O_2 consumption by the 1,4-DHB-birnessite system depended on the ratio of organic to oxide. Large quantities of oxide relative to 1,4-DHB removed little O_2 from solution, but small quantities removed much more, as is evident from the O_2 uptake curves of Figure 3. This result is not a consequence of the somewhat different pHs in these systems, because controlling the pH at 9.4 using borate buffer produced the same general effect. That is, as the oxide added initially to the buffered 1,4-DHB solutions was decreased from 200 mg to 50 mg, O_2 consumption diminished in much the same manner as is described by Figure 3 for the unbuffered systems. With no oxide present, O_2 consumption was extremely rapid, and was complete within a few minutes, a consequence of the rapid oxidation of 1,4-DHB by O_2 at pH 9.4. Clearly, if present in sufficient quantity, the Mn oxide reduced or even prevented O_2 uptake at pH 9.4, despite the favorability of the oxidation of 1,4-DHB by O_2 . Therefore, the oxide must have successfully competed with O_2 for reaction with 1,4-DHB, oxidizing the phenol to quinone.

1,2-Dihydroxybenzene (1,2-DHB) oxidation

The oxidation of 1,2-DHB by birnessite in the absence of a buffer had similar characteristics to 1,4-DHB oxidation, in that (1) no Mn^{2+} released to solution; (2) the reaction was accompanied by a rapid increase in pH; (3) lower oxide/phenol ratios produced a more rapid uptake of O_2 ; and (4) radicals (*o*-benzosemiquinone) appeared early in the reaction, and then diminished. The pH leveled off, however, at a lower value (8.8–9.0) during the oxidation of 1,2-DHB than during

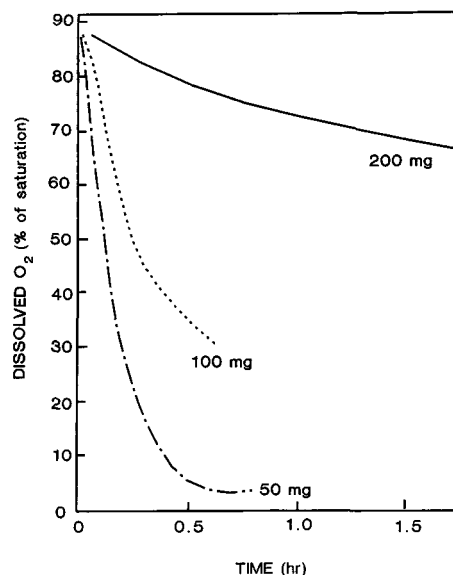


Figure 4. Molecular oxygen-uptake curves for variable quantities of birnessite reacted with 1,2-dihydroxybenzene.

the oxidation of 1,4-DHB. In addition, the uptake of O_2 as a function of oxide level, shown in Figure 4, appeared less sensitive to the oxide/phenol ratio than was indicated for 1,4-DHB. In particular, 1,2-DHB caused more rapid O_2 consumption than 1,4-DHB at high oxide levels but less at low levels. This observation may account for the fact that previous experiments had shown less O_2 uptake by Mn oxides in unbuffered media during 1,2-DHB oxidation when compared with 1,4-DHB oxidation (McBride, 1987). Although these earlier experiments were conducted with oxide/phenol ratios comparable to those used here, a more crystalline and less reactive oxide was used so that the oxide/phenol ratio was effectively lower. A comparison of Figures 3 and 4 shows that a low oxide/phenol ratio favors more rapid rates of O_2 consumption by 1,4-DHB than by 1,2-DHB.

The data in Figure 5 reveal that the oxide/phenol ratio determined the persistence of the unstable *o*-benzosemiquinone radical, detected in solution by ESR as a 9-line spectrum (Figure 6a). This radical had a very short lifetime at the high oxide levels, but disappeared much less rapidly at lower oxide levels.

Unlike 1,4-DHB oxidation by Mn oxide, which involved two separate electron transfers to form the semiquinone and then the quinone monomer (Kung and McBride, 1988), a more complex oxidation process was observed with 1,2-DHB. Figure 6 reveals that, as the 9-line ESR spectrum of *o*-benzosemiquinone diminished in intensity, it was replaced by a new spectrum which appeared to consist of four lines of nearly equal intensity. As shown on an expanded scale in Figure 7, this spectrum actually consists of eight resolved lines. The only reasonable interpretation of this spectrum is

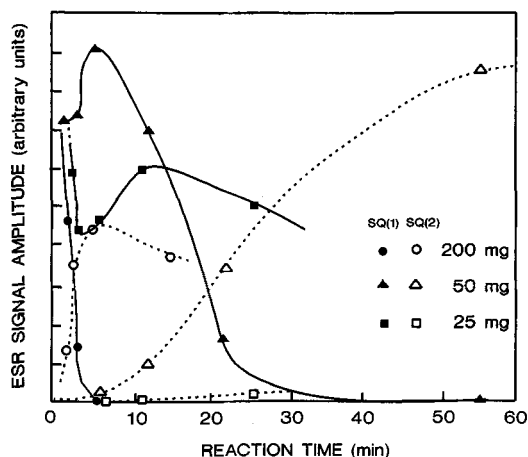
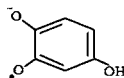


Figure 5. Effect of reaction time and birnessite level on concentration of semiquinone radical produced by reaction with 1,2-dihydroxybenzene. The o-benzosemiquinone (SQ(1)) and secondary semiquinone (SQ(2)) product concentrations are denoted by solid and broken lines, respectively.

that it was produced by a radical having three magnetically non-equivalent protons, in contrast to the o-benzosemiquinone radical, which possesses two pairs of non-equivalent ring protons. This interpretation implies that a ring-substitution reaction occurred. The new radical species may be an hydroxylated semiquinone, e.g.,



To prove that the Mn oxide had a role in the formation of this radical, aqueous 1,2-DHB was oxidized by air at pH ≥ 9 in the absence of oxide. No secondary radical species appeared after the disappearance of the o-benzosemiquinone.

Effects of reagents on O_2 oxidation of 1,2-DHB and 1,4-DHB

Injection of acidifying reagents into the birnessite-phenol systems during active O_2 uptake immediately terminated O_2 consumption. For example, 1 ml of KH_2PO_4 (0.1 g/ml) or K-acetate buffer (pH = 5.4) introduced during the reaction stopped O_2 consumption, although the previously reported release of O_2 into solution upon KH_2PO_4 addition to Mn oxide (McBride, 1987) was not observed. Pre-acidification of the birnessite-1,4-DHB suspension or introduction of KH_2PO_4 prior to the reaction similarly prevented the uptake of O_2 . In each of these experiments, the pH remained in the acidic range during the oxidation of the phenols.

Even neutral salts such as NaCl greatly decreased the rate of O_2 consumption in the birnessite-1,4-DHB system, but this low consumption rate is attributable to the ability of electrolytes to lower the pH by exchanging H^+ from the surface (see Figure 1).

It is important to stress that, although O_2 uptake was minimized by maintaining acidic solution conditions, vigorous (and sometimes complete) oxidation of the phenols by birnessite still occurred, as was visually evident from the darkening of the oxide, and confirmed by the release of Mn^{2+} and quinones into solution. Oxidation of these phenols and concomitant Mn^{2+} dissolution under buffered acidic conditions will be reported at a later date.

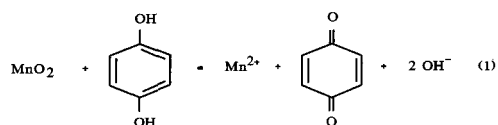
Because oxyanions such as phosphate have been reported to interact specifically with Mn oxide surfaces, thereby competing with the organic substrate for surface coordination sites (Stone and Morgan, 1987), an attempt was made to separate the obvious effect of pH on O_2 consumption from the effect of anion competition. By introducing 1 ml of Na_2HPO_4 solution (0.1 g/ml) during active O_2 uptake by borate-buffered birnessite-1,4-DHB suspensions, O_2 consumption was stopped. Thus, phosphate had an effect on the reaction beyond any indirect effect created by a pH change.

Further confirmation of the important effect of phosphate on reactivity was provided by briefly mixing 50-mg of birnessite with 0.1 M KH_2PO_4 , then washing out the unadsorbed phosphate with water. The O_2 -uptake curves of this phosphated oxide and that of the untreated oxide upon reaction with 1,4-DHB are compared in Figure 8. The delayed consumption of O_2 suggests a slowed electron transfer between the oxide and 1,4-DHB, which then failed to produce immediately the alkaline conditions favorable to O_2 consumption; however, the mechanism for this suppression of reaction is not known.

Infrared spectroscopy revealed that the birnessite spectrum was not substantially altered beyond 600 cm^{-1} as a result of phosphate treatment, but absorption between 400 and 600 cm^{-1} was greatly reduced by this treatment. Because these low-energy vibrations were attributed to the layered structure of birnessite by Potter and Rossman (1979), phosphate may actually have modified the mineral structure. Further study of phosphate-Mn oxide interactions are clearly needed.

DISCUSSION

The rapid pH increase noted when the birnessite was combined with the dihydroxybenzenes can be attributed to an electron transfer reaction of the type:



Thus, dissolution of the Mn oxide upon chemical reduction was responsible for the generation of OH^- . Subsequent dissolution of Mn^{2+} was prevented by the high pH, because of re-adsorption on the oxide or precipitation:



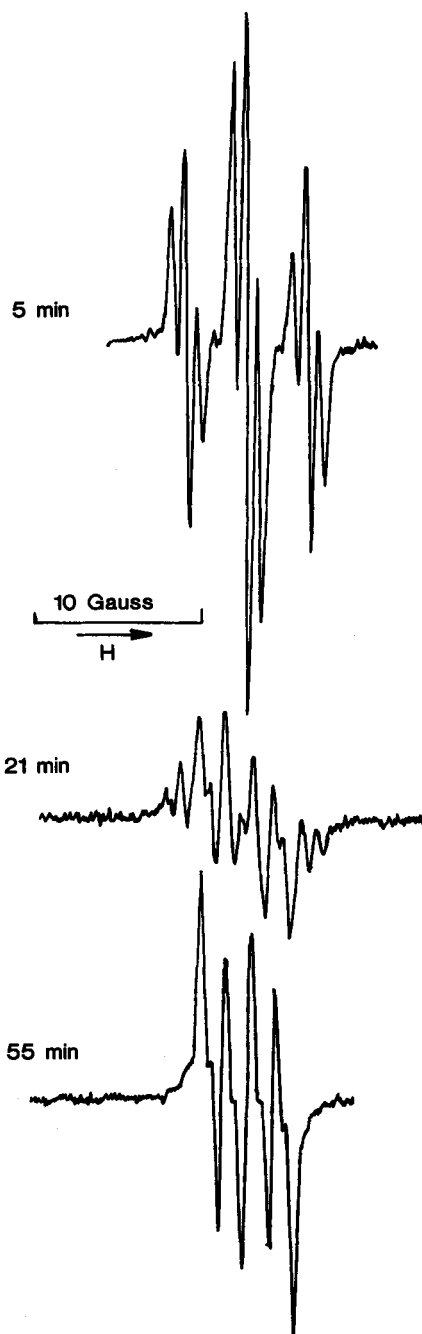


Figure 6. Electron spin resonance spectra of radicals generated by the reaction of 50 mg birnessite with 1,2-dihydroxybenzene after several time intervals.

The fact that the pH reached a plateau at or below pH 10 suggests that reaction (2), the hydrolysis and precipitation of Mn^{2+} , buffered the pH in the system. The gradual pH decrease after the initial rise could be a consequence of reaction (2) or the slow reoxidation of adsorbed Mn^{2+} by O_2 :

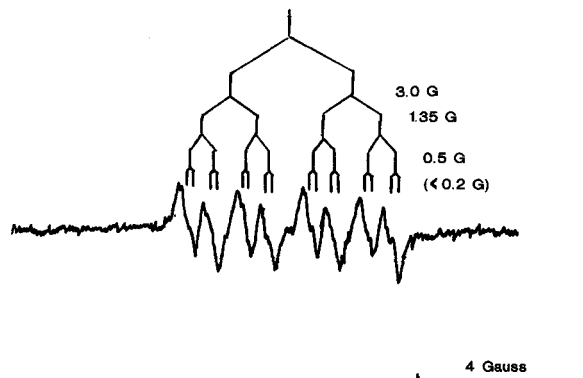
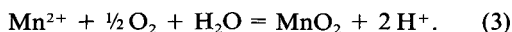


Figure 7. Fully resolved presentation and reconstruction of the electron spin resonance spectrum shown in Figure 6 (55 min), revealing hyperfine splitting caused by three non-equivalent ring protons (3.0, 1.35, and 0.5 gauss (G) hyperfine splitting values). Further weak splitting (<0.2 gauss), possibly by the proton of a ring-OH group, is incompletely resolved.

Clearly, reactions (2) and (3) can not have been wholly responsible for the failure of Mn^{2+} to appear in solution, because they would have consumed all of the alkalinity produced by reaction (1). Presumably, some of the reduced Mn was not precipitated or reoxidized, but was retained in the structure or on exchange sites.

The above reaction description appears adequate to explain the results if the manganese oxide was present in relative excess. Under these conditions, little or no O_2 was consumed initially in the reaction process. Nevertheless, an initially slow but accelerating consumption of O_2 was often observed (see Figure 3), suggesting that autocatalytic oxidation of surface Mn^{2+} may have consumed O_2 under these circumstances.

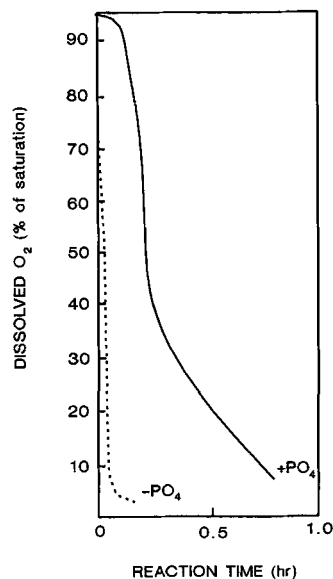
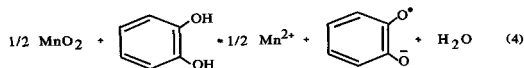
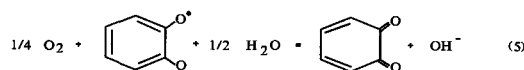


Figure 8. Molecular oxygen uptake curves of birnessite (50 mg), with and without phosphate pre-treatment, upon reaction with 1,4-dihydroxybenzene.

A quite different explanation appears necessary when the manganese oxide was not present in excess. Under these conditions, the semiquinone radical intermediates appeared immediately and persisted for some time in solution, an indication that a single electron transfer reaction of the type (shown here for 1,2-DHB),



had become important relative to reaction (1). The extremely rapid simultaneous consumption of O₂ in these same reaction systems suggests that radicals were rapidly oxidized by O₂, e.g.,



The pattern of behavior described by these experiments is consistent with the argument that the two-step oxidation of dihydroxybenzenes (to the semiquinone and then to the quinone) was driven to completion by a surplus of surface oxidation sites, whereas a deficit of sites resulted in the temporary accumulation of radicals. The radical concentration slowly diminished in solution once the rate of radical oxidation by O₂ exceeded the rate of production at the surface. Consequently, radical persistence in solution was associated with high rates of O₂ uptake and must have resulted from a continued significant rate of radical generation by the Mn oxide. The semiquinone radicals, particularly o-semiquinone, possess inherently short lifetimes in aerated aqueous solution, suggesting a rapid turnover of radicals in order to maintain a detectable concentration and consume measurable quantities of dissolved O₂ over time.

The abrupt increase in O₂-uptake rate at oxide levels < 100 mg (see Figure 3) suggests a limited capacity for oxidation by the Mn oxide surface, equivalent to about 0.5 mmole 1,4-DHB/g. Assuming that the surface Mn of birnessite has an oxidation state near 4+, one mole of surface Mn can theoretically oxidize one mole of 1,4-DHB to p-benzoquinone, and the birnessite must possess about 0.5 mmole reactive Mn/g, or about 10¹⁹ reactive Mn atoms/m² of surface, similar to the value reported by Ono *et al.* (1977) and Dollimore and Tonge (1967). This is equivalent to 12 Mn atoms/100 Å², greater than the expected density of 6–7 surface metal atoms based on structural models, and implies that the organic oxidation reaction exhausted the oxidative capacity of the surface, necessitating the role of O₂ as a secondary electron acceptor. If surface Mn atoms of the oxide were initially in the 3+ oxidation state, as suggested by a recent study (Murray *et al.*, 1985), the estimate of reactive surface Mn would have to be doubled.

Chemical buffers were generally avoided in this study because of the potential effect of these reagents on the surface reaction between the phenols and Mn oxide.

Although the pH approached a nearly constant alkaline value in less than one minute of reaction time (see Figure 1), the varying pH did complicate the interpretation of the reaction process. The experiments using borate buffer, however, established that the O₂-uptake rates were similarly dependent on Mn oxide level regardless of whether the pH was controlled at 9.4 or allowed to drift to high pH during reaction. Thus, the pH rise which resulted from reductive dissolution of the Mn oxide enabled O₂ uptake, yet the relative quantity of oxide present determined the extent of O₂ involvement in the reaction.

Reagents which acted as acid buffers (e.g., KH₂PO₄) prevented O₂ uptake, probably because organic radicals failed to accumulate and consume O₂ or because Mn autooxidation was not favorable under acidic conditions. Thus, reaction (1) was favored under these acidic conditions.

In comparing the birnessite-1,2-DHB and birnessite-1,4-DHB reaction systems (see Figures 3 and 4), low oxide levels produced greater O₂-uptake rates in the 1,4-DHB system than in the 1,2-DHB system. It may be that at these low oxide levels, which were favorable to the production of semiquinone radicals, the p-benzo-semiquinone radical was released to solution more readily than the o-benzo-semiquinone and was subsequently oxidized more rapidly by O₂. Unpublished work by the author and F. J. Sikora has shown that the benzo-semiquinone radical complexes readily with metals and may form a surface complex with Mn oxides. Conversely, at high oxide levels in the reaction systems, few semiquinone radicals were released to solution, and O₂ consumption may be largely attributed to autocatalyzed Mn reoxidation.

ACKNOWLEDGMENTS

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