Clays and Clay Minerals, Vol. 36, No. 4, 303–309, 1988.

ELECTRON TRANSFER PROCESSES BETWEEN HYDROQUINONE AND IRON OXIDES

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Abstract—The kinetics of hydroquinone oxidation by aqueous suspensions of pure hematite and goethite-ferrihydrite mixtures at pH 6.0, 7.4, and 9 was studied using an on-line analysis system. The electron transfer between hydroquinone and the Fe oxides was monitored by UV-visible and electron spin resonance spectroscopy. The adsorption of organics on the Fe oxide surface was detected by Fourier-transform infrared spectroscopy. For different Fe oxides, a higher surface area was correlated with a greater oxidizing ability and greater adsorption of organics, suggesting that the oxidation reaction was a surface process. A reversal of the initially rapid redox reaction was found in this system, suggesting a delayed release of Fe^{2+} into solution as the reduction of the Fe oxide proceeded. Redox potential calculations confirmed the thermodynamic favorability of the reaction reversal. A distribution of the reduced state over neighboring Fe atoms on the oxide surface probably was responsible for the initial suppression of Fe^{2+} release into the aqueous phase. Based upon these observations and detection of the semiquinone radical as an intermediate of hydroquinone oxidation, an inner-sphere one-electron transfer mechanism for the oxidation of hydroquinone at the oxide surface is proposed.

Key Words—Electron spin resonance, Electron transfer, Ferrihydrite, Goethite, Hematite, Hydroquinone, Iron.

INTRODUCTION

Studies by Scheffer *et al.* (1959), designed to model the synthesis of humic substances by iron oxides at various pHs, reported dark-colored products in solution (as measured by the optical density), as well as at the surface of the oxides. This process of "humification" was significantly stimulated by the presence of iron oxides. Since then, the oxidation and polymerization of simple phenolic acids to humic substances as promoted by soil inorganic components has been widely studied (Kyuma and Kawaguchi, 1964; Wang *et al.*, 1978, 1983; Shindo and Huang, 1982, 1984). A general review discussing the role of soil minerals in the abiotic polymerization of phenolic compounds and formation of humic substances has been recently published (Wang *et al.*, 1986). Nevertheless, most reported studies have been limited to observing the extent of the humification effect; i.e., they have concentrated on the detection and quantification of the ill-defined end products (humified polyphenols) by means of optical density, infrared spectroscopy, scanning electron microscopy, and total O_2-uptake measurements. It is apparent that more detailed research is required to elucidate the mechanism of the oxide-organic reaction.

Kung and McBride (1988) reported the kinetics of hydroquinone oxidation in an aqueous suspension of hausmannite (Mn_3O_4). Here, the oxidation reaction was apparently a surface process: the greater the surface area in suspension (with increased oxide loadings), the faster hydroquinone oxidized and the more Mn^{2+} dissolved. Kung and McBride (1988) continuously monitored the concentration of p-benzosemiquinone anion radical, a suggested precursor of humic substances, by electron spin resonance of the solution phase throughout the reaction period. This radical, which is stable only at high pH, was found to persist in the Mn oxide suspensions at pH 6. The presence of the radical suggested that the reduction of the Mn oxide involved a one-electron transfer process. In the present work, the oxidation reaction of hydroquinone by Fe oxide is reported in the expectation that Fe oxides, while less powerful oxidizing agents than Mn oxides, are more important in a practical sense because of their widespread occurrence in soils.

MATERIALS AND METHODS

The mixture of iron oxides used in this study was synthesized by a method similar to that of Fischer and Schwertmann (1972). At room temperature, 7 M ammonium hydroxide solution was added to $Fe(NO_3)_3$ solution until the NH_3 was in 30% excess of the stoichiometric requirement. After the solid precipitate was centrifuged and washed three times with water, the oxide suspension was adjusted to pH 6.0 with 6 N H_2SO_4. Then the oxide suspension (about 11 g Fe/liter) was placed in an oven at 70°C in a stoppered flask and shaken occasionally by hand. After three days incubation, the sample was centrifuged, washed repeatedly with water, and freeze-dried. The oxide sample was examined by X-ray powder diffraction (XRD), infrared spectroscopy (IR), and Mössbauer spectroscopy. From XRD the oxide was found to be a mixture of hematite

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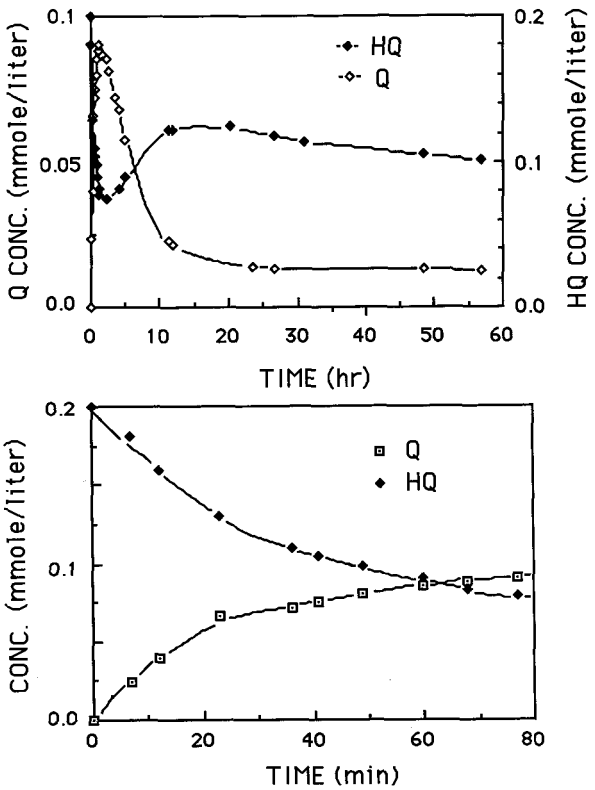


Figure 1. (a) Upper. Hydroquinone and quinone concentration vs. time. Initial concentrations were 2×10^{-4} M hydroquinone and 600 mg of goethite-ferrihydrite mixture at pH 6.0. (b) Lower. Same as a, with scale expanded to show only the first 80 min of reaction.

and goethite, with ferrihydrite and lepidocrocite impurities. Room-temperature Mössbauer spectra showed two 6-line components arising from the magnetic hyperfine interactions of hematite and goethite and a doublet attributable to ferrihydrite or microcrystalline goethite. IR spectra of the oxide in KBr pellets showed strong absorption bands at 795 and 890 cm^{-1} typical of goethite. Thus, this mixture was largely goethite-ferrihydrite, although the hematite fraction was more crystalline, having a larger particle size than the goethite. The surface area, calculated from N_2 adsorption at −196°C by the B.E.T. method, was 240 m^2/g.

Hematite was prepared by aging ferric nitrate solution (about 0.06 M with respect to Fe^{3+}) in a stoppered flask for 3 days at 90°C. The sample was transferred to dialysis tubing and dialyzed against fresh water for 3 days. The dialyzed sample was dried in an oven at 55°C and carefully crushed and mixed before analysis. Both XRD and Mössbauer spectroscopy showed this sample to be well-crystallized hematite, free from goethite impurities. Surface area by the B.E.T. method was found to be 48.5 m^2/g.

The experimental arrangement for the study of hydroquinone oxidation by Fe oxides was similar to that reported by Kung and McBride (1988) for hausmannite. As in their work, the aqueous phase was monitored by UV-visible and electron spin resonance spectroscopy to measure the loss of hydroquinone and the appearance of oxidation products. In separate experiments, the Fe^{2+} concentration was measured during the reaction. A colorimetric method (Traister and Schilt, 1976) was used to determine the ferrous concentration by chelation with 2,4-bis(5,6-diphenyl-1,2,4-triazin-3-yl)-pyridine tetrasulfonic acid tetra-sodium salt (G. Frederick Smith Chemical Company). Diffuse-reflectance Fourier-transform infrared spectrophotometry (IBM Model IR-98) was used to study the air-dry organic-oxide complex, which had been centrifuged from suspension after the experiment.

RESULTS AND DISCUSSION

Redox reaction between the oxide and hydroquinone

As shown in Figure 1, the oxidation of hydroquinone in the presence of the Fe oxide mixture (goethite-ferrihydrite) was detected as an increase of the oxidation product, p-benzoquinone, in aqueous solution and a decrease in the concentration of hydroquinone. Different Fe oxides produced different extents of hydroquinone oxidation. For example, for the same weight of oxide and concentration of hydroquinone under the same experimental conditions, the goethite-ferrihydrite mixture oxidized about twice as much hydroquinone as did pure hematite within the first 5 hr, probably because of the much higher surface area of the goethite-ferrihydrite mixture. The oxidizing ability of either the goethite-ferrihydrite mixture or the hematite, however, was much less than that of a low-surface area hausmannite. For suspensions of the hausmannite, hydroquinone was completely oxidized to monomeric quinone and/or quinone polymers within 1 hr (Kung and McBride, 1988). From O_2-consumption rates, a more vigorous catalytic oxidation of catechol and hydroquinone by Mn oxides than by Fe oxides has also been demonstrated (McBride, 1987).

Three stages of reaction during the oxidation of hydroquinone are evident from the data reported in Figure 1: First, the concentration of hydroquinone decreased to a minimum and the concentration of p-benzoquinone increased to a maximum. Second, the concentration of p-benzoquinone began to decrease, whereas that of hydroquinone increased. Last, the concentration of both hydroquinone and p-benzoquinone decreased. The first stage, replotted in Figure 1b on an expanded time scale for clarity, was probably caused by a fast redox reaction on the Fe oxide surface as Fe^{3+} accepted electrons from adsorbed hydroquinone molecules which then oxidized to quinone. As the oxidation of hydroquinone proceeded, the oxide surface must have become more and more reduced inasmuch as

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little or no O_2 was consumed by the reaction; however, this reduced state may have been distributed over the surface and shared by Fe atoms.

As the surface layer of the oxide continued to be reduced by hydroquinone, more and more Fe^{2+} was formed on the surface. Once the oxidizing capacity of the surface was depleted (i.e., the oxide surface resisted further reduction as the hydroquinone/quinone ratio diminished) quinone generation ceased. Because the consumption of O_2 was small and the Fe^{2+} in solution remained near the analytical detection limit (0.10 ppm) throughout the reaction, any Fe^{2+} released into solution must have been immediately oxidized to Fe^{3+} by the excess quinone in solution, precipitating ferric hydroxide. This reduction of quinone to hydroquinone by the delayed release of Fe^{2+} probably caused the significant *increase* of hydroquinone concentration, which was found consistently in the second stage. The decrease of the concentrations of both hydroquinone and quinone in solution (stage 3 of Figure 1a) can be attributed to the polymerization of organic monomers to polymers and/or to the adsorption of organics on the oxide surface. Assuming that polymers formed, these products were probably strongly adsorbed by the oxides. Some evidence for polymers in solution was detected as an increase in the UV-visible background absorbance. Nevertheless, this broad absorbance was much less evident than in the Mn oxide-hydroquinone systems (Kung and McBride, 1988).

Reversal of the redox reaction

The reversal of the hydroquinone oxidation reaction described above during stage 2 became thermodynamically feasible as the reaction progressed, and the quinone concentration in solution increased and the concentration of Fe^{2+} in solution exceeded that of Fe^{3+}. This fact is demonstrated by the following calculation. Using the half-reactions (1) and (2) below, where Q = quinone, HQ = hydroquinone, and E° is the reaction emf,

$$Q + 2H^+ + 2e^- \longrightarrow HQ \qquad E° = 0.699\ V \quad (1)$$

$$2Fe^{2+}_{(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + 2e^- \qquad E° = -0.77\ V \quad (2)$$

The standard-state potential E°, of the total redox reaction, Eq. (3), was calculated:

$$2Fe^{2+}_{(aq)} + Q + 2H^+ \rightleftharpoons HQ + 2Fe^{3+}_{(aq)} \qquad E° = -0.071\ V \quad (3)$$

The negative value of E° suggests the quinone reduction reaction (from quinone to hydroquinone) is not feasible at standard-state conditions. At stage 2, however, the Nernst equation can be used to calculate

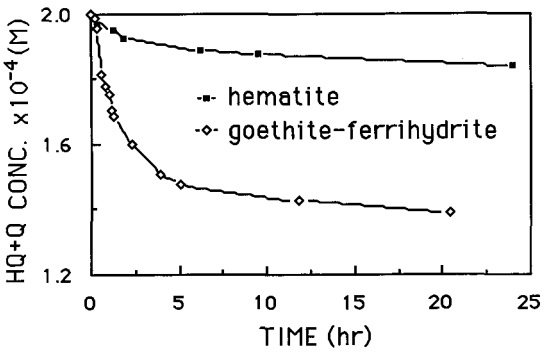


Figure 2. Total concentration of hydroquinone and quinone in solution as a function of time. Initial concentrations were 2×10^{-4} M hydroquinone and 600 mg of goethite-ferrihydrite mixture at pH 6.

the potential of the redox reaction at the actual solution concentrations. This potential, assuming that [Q] = [HQ] = 10^{-4} M, pH = 6, $[Fe^{2+}] = 10^{-6}$, $[Fe^{3+}]$ was controlled by noncrystalline $Fe(OH)_3$ solubility, 10^{-39} (Bolt and Bruggenwert, 1976), has the value:

$$\begin{aligned} E &= E° + (0.059/2)\log([Fe^{2+}][H]^2[Q])/([HQ][Fe^{3+}]^2) \\ &= -0.07 - 0.059\ pH + 0.059\log([Fe^{2+}]/[Fe^{3+}]) + 0.029\log([Q]/[HQ]) \\ &= -0.07 - 0.35 + 0.059\log((10^{-6})/(10^{-15})) \\ &= 0.11\ V \end{aligned}$$

The positive value of E indicates the thermodynamic favorability of reaction (3), i.e., the reduction of the quinone by soluble Fe^{2+}, but does not explain how the oxidation of hydroquinone initially proceeded past the equilibrium point during stage 1. Possibly, by delaying release of Fe^{2+} into solution until sufficient hydroquinone had been oxidized to generate high levels of quinone in solution, the surface raised the oxidation state of the solution to a higher level than would have been possible if all Fe species had been in solution from the beginning. Further, the delayed release of Fe^{2+} into solution was also feasible because the ratio of hydroquinone to surface Fe^{3+} was very small (*vide infra*).

Inasmuch as molecular orbital descriptions of edge-shared FeO_6 octahedra predict that weak Fe–Fe bonding can allow electron hopping between Fe^{2+} and Fe^{3+} (Sherman, 1986), the electron which transferred from hydroquinone onto the Fe oxide surface may have been distributed over Fe atoms neighboring the reduced Fe atom, thereby stabilizing the reduced state (at least temporarily) and causing the delayed Fe^{2+} release. In any event, the dissolution of Fe^{2+} must have been slower than the release of quinone from the surface in the first stage of the reaction, with the result that the solution phase reached disequilibrium toward the end of stage 1.

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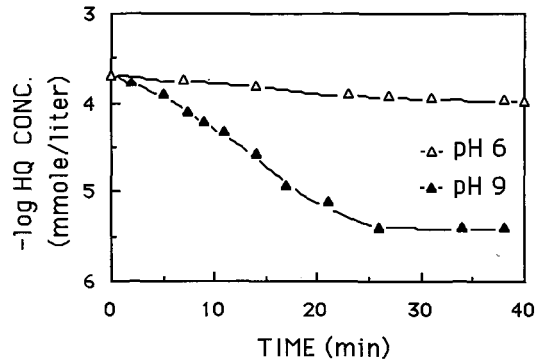


Figure 3. Change in solution concentration of hydroquinone due to oxidation at pH 6 (△) and pH 9 (●) by goethite-ferrihydrite mixture (same conditions as Figure 2).

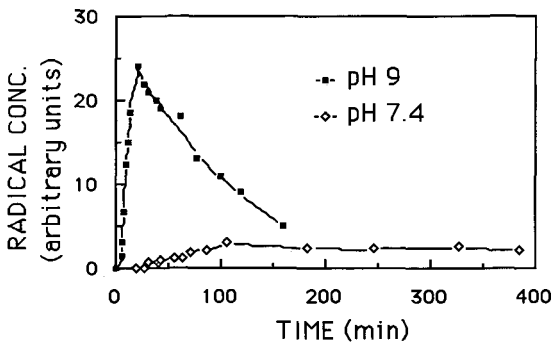


Figure 4. Concentration of p-benzosemiquinone radical (arbitrary units) as function of time at pH 7.4 and 9 in hydroquinone-mixed oxide suspension (same conditions as Figure 3).

Depletion of organic monomers from solution

The combined effect of polymerization and adsorption by the oxide depleted the total quantity of organic monomers (hydroquinone + quinone) in solution. Different Fe oxides possessing variable oxidation abilities also gave rise to different levels of monomer depletion. As shown in Figure 2, the goethite-ferrihydrite mixture produced a much higher degree of depletion than pure hematite under the same experimental conditions. For both materials, two stages of depletion were found. The inital steep part of the curve (within the first 2 hr) suggests a vigorous oxidation reaction to polymers and relatively complete adsorption of these polymers onto the surface. The second stage of depletion suggests a slow but constant reaction rate for both polymerization and adsorption. The difference in depletion among the oxide materials used was probably due at least in part to the difference in surface area, with the higher surface-area materials providing more sites for adsorption and promotion of polymerization. As indicated by Stone (1986), different oxide composition and crystal structure, as well as surface area, may influence reactivity; however, from the present experiments, whether or not hematite and goethite surfaces have different intrinsic reactivities cannot be stated.

Radical formation and the effect of pH

High pH facilitates the humification reaction. Schnitzer (1982) implied that the rate-determining step in the synthesis of humic acid from simple phenolic acids is the formation of semiquinone radicals, which can be stabilized in alkaline solution. For hausmannite systems, a radical-mediated oxidation reaction of hydroquinone was proposed (Kung and McBride, 1988). As shown in Figure 3 for the goethite-ferrihydrite mixture, the higher the pH, the greater the hydroquinone oxidation rate. Because high pH facilitated the reaction, the radical-mediated oxidation of hydroquinone is suggested. At high pH, the radical was relatively more stable than at low pH. The radical was apparently released into solution once it was generated on oxide surfaces, inasmuch as p-benzosemiquinone anion radicals were found in the Fe oxide-hydroquinone reaction at pH 7.4 and 9 (Figure 4). At pH 7.4, the hydroquinone oxidation rate was similar to that at pH 6 (shown in Figure 3), but unlike oxidation at pH 6, a detectable but small concentration of radical persisted during the entire experimental period (Figure 4). In contrast, at pH 9, the concentration of radicals increased abruptly in solution and then gradually decreased as the reaction proceeded. The accumulation of the radicals at high pH probably was due to the fast oxidation of hydroquinone, and the subsequent decrease in concentration is attributed to oxidation of the radical by dissolved O_2, a process also observed in the hausmannite system (Kung and McBride, 1988).

At the higher pH, the generation of the radical by O_2 oxidation was favorable even in the absence of Fe oxides. Therefore, the patterns of radical appearance and loss shown in Figure 4 cannot be unequivocally attributed to surface reactions involving the oxides. The Fe oxide-hydroquinone system described in Figure 4 generated no detectable semiquinone radicals at pH 6, again consistent with the behavior of aqueous hydroquinone in the absence of Fe oxides. If the hydroquinone concentration was raised to 2×10^{-2} M, however, a slow accumulation of semiquinone radicals was measured in solution at pH 6 in the presence of the same quantity of Fe oxide. This almost constant rate of radical production is plotted in Figure 5. An estimate of the number of surface Fe atoms for the 600 mg of the Fe oxide mixture used in these experiments, based upon an assumed goethite (or hematite) surface structure and the known surface area, is about 3 mmole. At the concentration of hydroquinone used in most of these studies (2×10^{-4} M) the mole ratio of hydroquinone to surface Fe^{3+} was a very small fraction (0.01–0.02). Thus, complete oxidation to quinone by surface Fe^{3+} could readily have been accomplished without reducing many of the surface Fe atoms. At 2×10^{-2}

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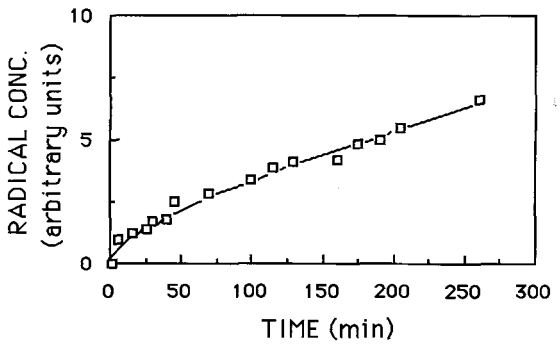


Figure 5. Formation of p-benzosemiquinone radical (arbitrary units) at pH 6 (2×10^{-2} M hydroquinone and 600 mg of goethite-ferrihydrite mixture initially present).

M hydroquinone, however, the mole ratio of hydroquinone to surface Fe^{3+} was near unity, and radical generation may have been favored by the fact that only partial oxidation of hydroquinone to quinone was possible by Fe^{3+} at the surface, unless O_2 also acted as an electron acceptor. At pH 6, direct oxidation of hydroquinone by O_2 was very slow, allowing the concentration of surface-generated radicals to gradually increase. At moderately high pH, the reduced iron generated by the electron transfer to the surface may have been reoxidized by O_2, as was suggested by McBride (1987) from the observed consumption of O_2 during the Fe oxide-hydroquinone reaction. The rate of O_2 consumption in those studies did not depend on the quantity of oxide present, which may be due to the fact that they were conducted with a large excess of surface Fe^{3+} atoms relative to hydroquinone. Thus, to have increased the excess of oxide further may not necessarily have promoted greater hydroquinone oxidation and production of Fe^{2+}.

It should be stressed that, although oxidation of hydroquinone in aqueous solution by O_2 is favored at high pH (pH 9), this may not have been true for oxidation on an iron oxide surface. The similar degree of hydroquinone oxidation at pH 6 and 7.4 suggests little effect of pH on the surface oxidation, consistent with a reaction such as:

$$HQ + 2\,Fe(OH)_3 \rightarrow 2\,Fe(OH)_2 + Q + 2\,H_2O,$$

where the equilibrium is unaffected by pH. The high rate of hydroquinone oxidation in the iron oxide suspensions at pH 9 may to a large degree be a reflection of the ease of oxidation of hydroquinone by soluble O_2 in alkaline solution.

FTIR study

The diffuse reflectance FTIR spectrum of the hematite used in the oxidation of hydroquinone at pH 7 is shown in Figure 6. In this spectrum, the absorption bands are shifted in position relative to the absorption bands of hydroquinone and quinone. The band at 1660

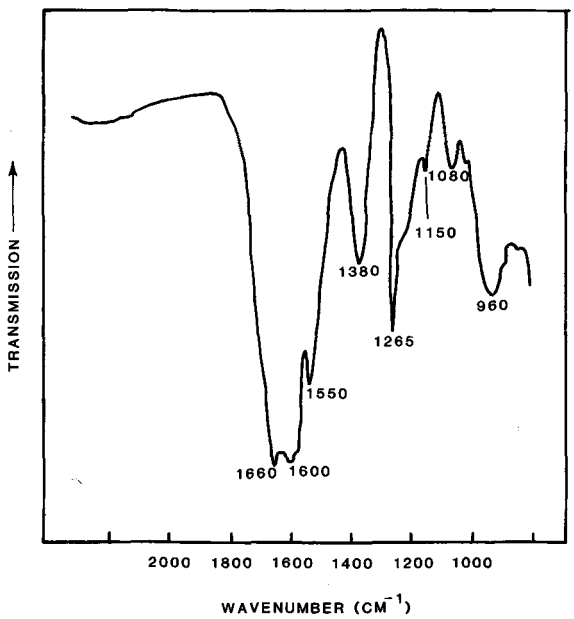


Figure 6. The diffuse-reflectance Fourier-transform infrared spectrum of hematite after oxidation of hydroquinone at pH 7, ratioed against spectrum of untreated hematite.

cm^{-1} is probably the quinone-type C=O stretch vibration. Bands at 1600 and 1550 cm^{-1} are likely the ring C=C stretching vibrations, and the band at 1380 cm^{-1} is possibly the in-plane OH deformation. The sharp band at 1265 cm^{-1} and the weak band at 1080 cm^{-1} are likely due to the C–O stretching vibrations. The 1150-cm^{-1} band is possibly the in-plane ring C–H band.

From a study of the oxidation of organics on oxide surfaces, Stone and Morgan (1987) proposed that oxidation occurred via the following reaction steps: (1) precursor surface-complex formation between the organic molecule and oxide surface site, (2) electron transfer beween the metal and organic in this surface complex, and (3) dissociation of the successor complex and release of the oxidized product into solution. From the shift of the IR spectrum of the hydroquinone on adsorption, the molecule apparently chemisorbed on the Fe oxide. For example, the aromatic-ring stretch vibrations of the adsorbed hydroquinone were shifted relative to those of the non-sorbed molecule, indicating a perturbation caused by chemisorption. Chemisorption suggests that an inner-sphere complex formed between hydroquinone and the surface oxides, which facilitated electron transfer. Because the C–O–H bands were present, hydroquinone apparently bonded to Fe at the surface via only one of the OH groups. This result is reasonable, inasmuch as both OH groups probably could not interact simultaneously with the surface because of steric reasons. The fact that hydroquinone bonds more strongly on Al oxides than does phenol

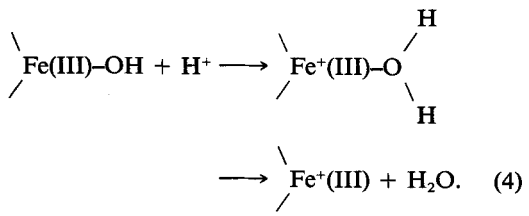
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(McBride and Wesselink, 1988) lends credence to the hypothesis that the second OH group attached to the ring increased the Lewis base properties of the molecule and resulted in stronger metal-phenol monodentate complex formation (Stone and Morgan, 1987). Alternatively, H-bonding to surface OH groups of the oxide by the second phenolic group of hydroquinone might have assisted the adsorption. Because quinone-type molecules were also detected on the surface, slow dissociation of the successor complex and incomplete release of the oxidation products into solution may have been a limiting factor for further reaction in the Fe oxide system.

Reaction mechanism

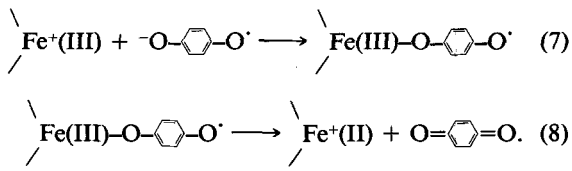
A possible mechanism of reaction consistent with the above experimental results follows.

Step 1. At the surface of Fe oxide, the surface hydroxyl group can be protonated to form Fe(III)-H_2O, a Lewis acid site, as shown below:



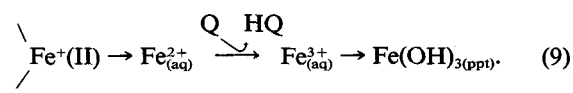
Step 2. Because surface-bonded water is a good leaving group, it can be displaced by hydroquinone through a ligand exchange process to form an inner-sphere organic-Fe(III) complex [Eq. (5)]. Electron transfer within the complex then forms structural Fe(II) (with a positive surface charge) and the semiquinone radical:

Step 3. At low hydroquinone concentration and low pH (i.e., pH 6) the radical will be oxidized by another Lewis acid site of Fe(III) to form quinone, which is then released into aqueous solution, as follows:



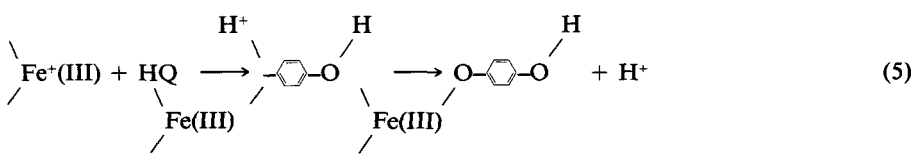
At high pH (i.e., pH 9), however, the radical is relatively stable in aqueous solution and is generated in aqueous solution by reaction of hydroquinone with O_2. At high concentration of hydroquinone, most of the reaction sites are occupied by hydroquinone [Eq. (5)], and the generation rate of radical is faster than its oxidation and/or decomposition; thus, the radical will accumulate in solution even at pH 6 if the Fe oxide is present.

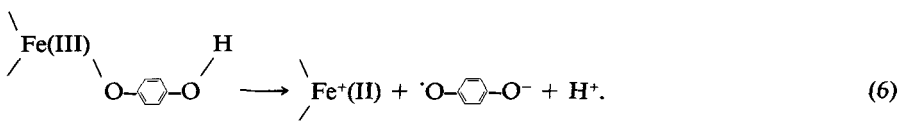
Step 4. In step 4, structural Fe(II) dissociates into solution. This aqueous Fe^{2+} will be immediately oxidized to Fe^{3+} by quinone, and will then precipitate.



ACKNOWLEDGMENTS

This research was supported by National Science Foundation Grant EAR-8512226. The authors thank Tim Wachs for obtaining the Fourier-transform infrared spectra.





https://doi.org/10.1346/CCMN.1988.0360403 Published online by Cambridge University Press

REFERENCES

Bolt, G. H. and Bruggenwert, M. G. M. (1976) *Soil Chemistry:* Elsevier, Amsterdam, 281 pp.

Fischer, W. R. and Schwertmann, U. (1972) The formation of hematite from amorphous iron(III) hydroxide: *Clays & Clay Minerals* **23,** 33–37.

Kyuma, K. and Kawaguchi, K. (1964) Oxidative changes of polyphenols as influenced by allophane: *Soil Sci. Soc. Amer. Proc.* **28,** 371–374.

Kung, K.-H. and McBride, M. B. (1988) Electron transfer processes between hausmannite (Mn_3O_4) and hydroquinone: *Clays & Clay Minerals* **36,** 297–302.

McBride, M. B. (1987) Absorption and oxidation of phenolic compounds by Fe and Mn oxides: *Soil Sci. Soc. Amer. J.* **51,** 1466–1472.

McBride, M. B. and Wesselink, B. (1988) Chemisorption of catechol on gibbsite, boehmite and amorphous alumina surfaces: *Environ. Sci. Technol.* (in press)

Sherman, D. M. (1986) Cluster molecular orbital description of the electronic structures of mixed-valence iron oxides and silicates: *Solid State Communications* **58,** 719–723.

Scheffer, F., Meyer, B., and Niederbudde, E. A. (1959) Humingbildung unter katalytischer Einwirkung natürlich vorkommender Eisenverbindungen im Modellversuch: *Z. Pflanzenernaehr. Bodenkd.* **87,** 26–44.

Schnitzer, M. (1982) *Quo Vadis* soil organic matter research?: *Whither Soil Research, Panel Disc. Paper 5, 12th Int. Cong. Soil Sci., New Delhi, India, 1982,* 67–78.

Shindo, H. and Huang, P. M. (1982) Role of Mn(IV) oxide in abiotic formation of humic substances in the environment: *Nature* **305,** 57–58.

Shindo, H. and Huang, P. M. (1984) Catalytic effects of manganese(VI), iron(III), aluminum, and silicon oxides on the formation of phenolic polymers: *Soil Sci. Soc. Amer. J.* **48,** 927–934.

Stone, A. T. (1986) Absorption of organic reductants and subsequent electron transfer on metal oxide surfaces: in *Geochemical Processes at Mineral Surface,* J. A. Davis and K. F. Hayes, eds., ACS Symposium Series 323, Amer. Chem. Soc., Washington, D.C., 446–461.

Stone, A. T. and Morgan, J. J. (1987) Reductive dissolution of metal oxides: in *Aquatic Surface Chemistry,* W. Stumm, ed., Wiley, New York, 221–254.

Traister, G. L. and Schilt, A. A. (1976) Water-soluble sulfonated chromogenic reagents of the ferroin type and determination of iron and copper in water, blood serum, and beer with the tetraammonium salt of 2,4-bis(5,6-diphenyl-1,2,4-triazin-3-yl)pyridinetetrasulfonic acid: *Anal. Chem.* **48,** 1216–1220.

Wang, T. S. S., Li, S. W., and Ferng, Y. L. (1978) Catalytic polymerization of phenolic compounds by clay minerals: *Soil Sci.* **126,** 15–21.

Wang, T. S. C., Wang, M. C., Ferng, Y. L., and Huang, P. M. (1983) Catalytic synthesis of humic substances by natural clay, silts, and soils: *Soil Sci.* **135,** 350–360.

Wang, T. S. C., Huang, P. M., Chou, C.-H., and Chen, J.-H. (1986) The role of soil minerals in the abiotic polymerization of phenolic compounds and formation of humic substances: in *Soil Minerals with Natural Organics and Microbes,* P. M. Huang and M. Schnitzer, eds., Soil Science Society of America, Madison, Wisconsin, 251–281.

(Received 14 November 1987; accepted 22 February 1988; Ms. 1739)

https://doi.org/10.1346/CCMN.1988.0360403 Published online by Cambridge University Press