

## COORDINATION COMPLEXES OF *p*-HYDROXYBENZOATE ON Fe OXIDES

KING-HSI KUNG AND MURRAY B. MCBRIDE

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

**Abstract**—Adsorption of *p*-hydroxybenzoate anion on synthetic Fe oxides, hydroxides, and oxyhydroxides (hereafter referred to as oxides) was measured at pH 5.5, and the organic-oxide interaction was characterized using diffuse-reflectance Fourier-transform infrared (DRIFT) spectroscopy. Surface complexes with ferrihydrite, hematite, goethite, and noncrystalline Fe oxide were investigated. Infrared (IR) spectra of the oxides after separation from *p*-hydroxybenzoate solutions showed the organic to be coordinated by an inner-sphere mechanism to the oxide surface through the carboxylate group. Bidentate binding of the carboxylate was identified to be the dominant type of complexation on the oxides. Although the IR study suggested that goethite formed the strongest surface iron-carboxylate bond, the total amount of organic adsorbed was the least on this oxide. This result suggested that bond energy was less important than adsorption site density in determining the amount of organic anion adsorption. Increasing ionic strength had little effect on adsorption by the noncrystalline Fe oxide, but dramatically decreased adsorption on hematite and goethite. This difference might have been due to anion competition for binding sites. At pH 5.5, the amount of organic adsorbed per unit weight of oxides (in 0.05 M NaClO<sub>4</sub>) followed the order: ferrihydrite > noncrystalline Fe oxide > hematite > goethite. Adsorption per unit of surface area however, followed the order: ferrihydrite > hematite > noncrystalline Fe oxide > goethite. The hematite adsorption reaction appeared to be driven by entropy, inasmuch as the reaction was endothermic. The difference among the oxides in surface reactivity toward *p*-hydroxybenzoate is hypothesized to have been caused by differences in both quantity and structural arrangement of reactive sites on the oxide surface.

**Key Words**—Adsorption, Ferrihydrite, Goethite, Hematite, Infrared spectroscopy, Iron oxides, *p*-Hydroxybenzoate.

### INTRODUCTION

*p*-Hydroxybenzoic acid has been recognized for many years as one of the most common simple phenolic acids in soil (Walters, 1917; Whitehead, 1964). The persistence of this organic compound in soil solution may suppress the growth of some crops. For example, in a hydroponic study, *p*-hydroxybenzoate was found to inhibit the growth of wheat, corn, and soybean seedlings (Wang *et al.*, 1967). In the natural environment, *p*-hydroxybenzoic acid originates from microbial synthesis, root exudation, leachate from plant leaves, and lignin decomposition (Reddy *et al.*, 1977; Stevenson, 1967). In soil solution, the concentration of the acid varies, usually falling in the range 10<sup>-4</sup> to 10<sup>-6</sup> M (Wang *et al.*, 1967; Whitehead, 1964; Stevenson and Ardakani, 1972; Whitehead *et al.*, 1982). *p*-Hydroxybenzoic acid is believed to be inactivated in soil by adsorption, because the water-extractable concentration from plant roots is much greater than the concentration extracted from soils (Whitehead *et al.*, 1982). The adsorption process may therefore suppress phytotoxicity of this organic acid.

Oxides, hydroxides, and oxyhydroxides (collectively referred to hereafter as oxides) of Fe and other metals have been reported to be effective sorbents for organic anions in soil. Appelt *et al.* (1975) found the adsorption of selected phenolic acids in volcanic ash-derived soil

to be highly pH-dependent. Inasmuch as the removal of organic matter did not affect the adsorption and chloride anion did not compete strongly with phenolic acid adsorption, they suggested that the adsorption process is a ligand-exchange reaction involving noncrystalline mineral components, which are abundant in volcanic soils. Huang *et al.* (1977) further determined that noncrystalline Al and Fe oxides retained much more phenolic acids than did phyllosilicates, and that the removal of these noncrystalline materials from soil significantly decreased the adsorption of phenolic acids. In view of the fact that oxides can control the solubility of low molecular weight organic acids in soils, a detailed understanding of the mechanism of bonding of phenolic acids on oxides is necessary to a complete description of soil geochemical processes.

In the present work, the capability of different synthetic Fe oxides to adsorb *p*-hydroxybenzoate was studied. Ferrihydrite, hematite, goethite, and noncrystalline Fe oxide were chosen as adsorbents because they are the most common Fe oxides found in soils. All the adsorption isotherms were obtained at pH 5.5 in 0.05 M NaClO<sub>4</sub> background electrolyte, similar to the pH and ionic strength of soil solutions. In addition, the effect of varying ionic strength on adsorption was assessed using a range of NaClO<sub>4</sub> concentrations. The binding mechanism of the organic compound onto dif-

ferent synthetic Fe oxides was deduced from infrared spectroscopic studies of the organic-oxide complex.

## MATERIALS AND METHODS

*p*-Hydroxybenzoic acid and the other chemicals used were analytical grade, and water was distilled, deionized, and filtered through a 0.2- $\mu\text{m}$  Millipore filter. All experiments were conducted at  $22 \pm 1^\circ\text{C}$ , unless noted otherwise.

### *Iron oxide preparation and characterization*

Noncrystalline  $\text{Fe}(\text{OH})_3$  was prepared by rapid hydrolysis of ferric sulfate with concentrated KOH. The suspension was mixed and aged for 72 hr at room temperature. The dark-brown solid precipitate was washed repeatedly with water prior to freeze-drying. This material proved to be amorphous to X-rays. The Mössbauer spectrum at room temperature showed the characteristic doublet of poorly crystalline or noncrystalline Fe oxides (Bowen and Weed, 1984). Surface area calculated from  $\text{N}_2$  adsorption by the three-point BET method was  $208 \text{ m}^2/\text{g}$ .

The ferrihydrite preparation involved the hydrolysis of ferric salt at low pH for 12 hr, followed by raising the pH with dilute NaOH, and finally aging the mixture for 10 days at  $80^\circ\text{C}$ . The precipitate was dialyzed against distilled water for two weeks and freeze-dried. X-ray powder diffraction (XRD) indicated a poorly crystalline product containing ferrihydrite and some oxyhydroxide phases. The room-temperature Mössbauer spectrum also showed a doublet characteristic of poorly crystalline Fe oxides. The surface area, calculated by the BET method, was  $154 \text{ m}^2/\text{g}$ .

Hematite was prepared by a method similar to that described by Kung and McBride (1988b). Two separate preparations (labeled A and B) were used in this study. From XRD, one product was identified as a highly crystalline, pure hematite (A); the other was identified as a less crystalline hematite (B). Room-temperature Mössbauer spectra of both products revealed six-line spectra arising from the magnetic hyperfine interaction characteristic of hematite. The surface areas of the freeze-dried hematites were  $39.2$  (A) and  $77.1$  (B)  $\text{m}^2/\text{g}$ .

Two separate batches of goethite (labeled A and B) were prepared by reacting 0.2 M ferric chloride with sufficient NaOH to produce a pH of  $\sim 5$  and then aging the precipitate at  $60^\circ\text{--}70^\circ\text{C}$  for several days. The solids were water-washed and freeze-dried. IR spectra showed intense absorption peaks at  $790$  and  $895 \text{ cm}^{-1}$ , characteristic of goethite. Mössbauer spectra at room temperature showed the sextet arising from the characteristic magnetic hyperfine interaction of crystalline goethite. XRD confirmed the powders to be pure goethite. Surface areas for these goethites, calculated using the BET method, were  $89.4$  (A) and  $111$  (B)  $\text{m}^2/\text{g}$ .

### *Infrared spectroscopy*

The organic-oxide complex was studied by diffuse-reflectance infrared Fourier-transform (DRIFT) spectroscopy using dry powders (neat) mounted on a diffuse reflectance accessory. Two FTIR spectrometers (IBM, Model IR-48 and Perkin-Elmer, Model 1720-X) were used for this purpose. The samples were prepared by equilibrating the oxides at pH 6 with 2 mM aqueous solutions of the organic in 0.05 M  $\text{NaClO}_4$  as background electrolyte. After 18 hr of shaking, the solid product was separated from the solution by centrifugation, washed twice with 0.05 M  $\text{NaClO}_4$  at the same pH, and finally freeze-dried. Reference oxides were prepared by an identical treatment in which the organic compound was excluded from the equilibrating solution. The DRIFT spectra were obtained by ratioing the organic-oxide spectrum against the reference oxide spectrum, a process which minimized IR bands arising from the oxide itself. Alkali halide disks or plates were not used because interaction of the sample with the halide salt was expected to produce spectral changes of the carboxylate groups due to anion exchange or high pressure (Deacon and Phillips, 1980). In fact, preliminary spectra revealed that this "salt effect" did indeed alter the positions of the carboxylate adsorption bands.

### *Adsorption isotherms*

Pre-weighed 100-mg quantities of oxide were shaken in capped polycarbonate centrifuge tubes for 18 hr with 25 ml of the desired concentration of *p*-hydroxybenzoic acid solution that had been preadjusted to pH 5.5 by dilute NaOH or  $\text{HClO}_4$ . In all experiments, 0.05 M  $\text{NaClO}_4$  was used to maintain the total ionic strength at an essentially constant value. No adsorption onto the tube or cap was detected. Preliminary studies from an on-line ultraviolet (UV) analysis technique similar to that reported by Kung and McBride (1988a) showed the adsorption to be complete within 20 min. Thus, some additional adsorption experiments were conducted with only 2 hr of shaking. After mild shaking of the tubes for the chosen time period, the suspensions were centrifuged and/or filtered, and the clear supernatant was diluted, if necessary, for absorbance measurement by UV spectrometry at 245.5 nm (Perkin-Elmer Lambda 4C spectrophotometer). This measured absorbance was found to be proportional to the concentration of the organic remaining in the solution phase, based upon the linearity of standard curves for prepared *p*-hydroxybenzoic acid solutions. The amount of the organic adsorbed was then calculated from the difference between the initial and final concentration in the equilibrated solutions.

The effect of ionic strength on adsorption was studied by a method similar to that described for the adsorption isotherm studies (see above), but using 200 mg of

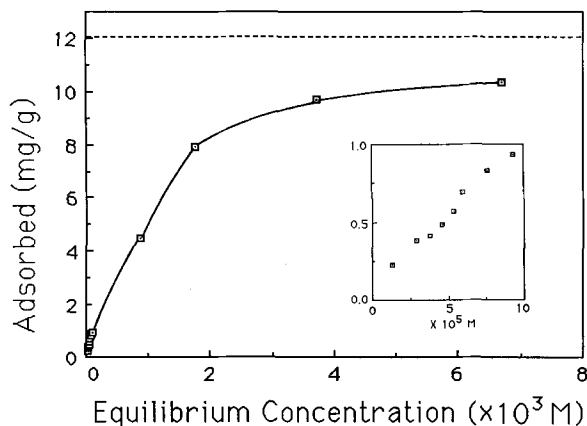


Figure 1. Adsorption of *p*-hydroxybenzoate from aqueous solution at pH 5.5 with 0.05 M NaClO<sub>4</sub> by hematite A (reaction time = 18 hr). Inset is an expansion showing low concentration region. The maximum calculated adsorption value is shown as dashed line.

oxide at an initial organic concentration of  $1 \times 10^{-4}$  M at pH 5.5.

Adsorption of the organic at different temperatures was measured in an on-line analysis system similar to that reported by Kung and McBride (1988a). In a temperature-controlled reaction chamber, the aqueous phase was separated from the oxide suspension by a bundle of hollow fibers, allowing the aqueous solution to be monitored directly by UV spectroscopy to quantify the adsorption of the organic.

Potential inorganic-anion adsorption capacity was estimated from phosphate-adsorption isotherms. In this experiment, 200-mg quantities of oxide were equilibrated for 2 hr with sodium phosphate (initial concentrations of 2, 4, 6, 8, and  $10 \times 10^{-3}$  M) at initial pH of 5.5, using 0.05 M sodium nitrate as the background electrolyte. The final concentration of phosphate was measured by ion chromatography (Dionex Model 2000i). NaClO<sub>4</sub> was not chosen here as the background electrolyte, because the perchlorate anion is difficult to elute from the anion chromatographic column.

## RESULTS AND DISCUSSION

### Adsorption isotherms

The isotherm for *p*-hydroxybenzoic acid adsorption on hematite A at pH 5.5 is depicted in Figure 1. One hundred milligrams of oxide was equilibrated with low ( $2\text{--}12 \times 10^{-5}$  M) and high ( $1\text{--}7 \times 10^{-3}$  M) concentrations of *p*-hydroxybenzoic acid for 18 hr. The inset in the figure shows the adsorption isotherm at the lower range of concentrations. The total isotherm can be fit satisfactorily to the Langmuir adsorption equation. The maximum calculated adsorption value, based on the fitted Langmuir equation, is shown by the dashed line in Figure 1. The essentially linear adsorption curve at low equilibrium concentration is consistent with the

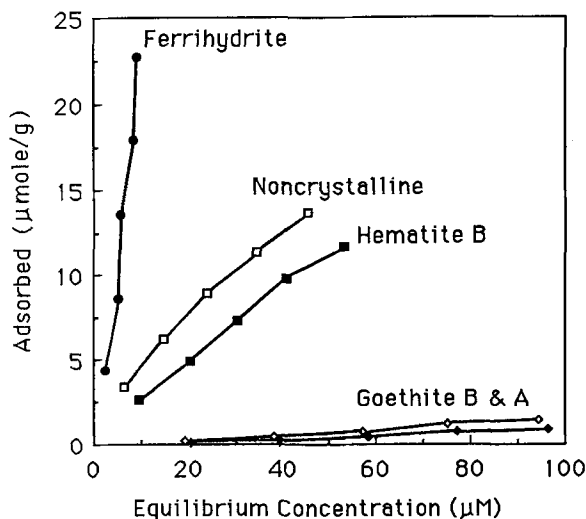


Figure 2. Isotherms for *p*-hydroxybenzoate adsorption onto different Fe oxides at pH 5.5 in 0.05 M NaClO<sub>4</sub> (reaction time = 2 hr). Surface areas of these oxides are 154 (ferrihydrite), 208 (noncrystalline), 39.2 (hematite A), 77.1 (hematite B), 89.4 (goethite A), and 111 (goethite B) m<sup>2</sup>/g.

Langmuir adsorption model for low adsorption-site coverage.

Figure 2 shows the adsorption isotherms of *p*-hydroxybenzoic acid on the various Fe oxides at the lower concentration range ( $2\text{--}10 \times 10^{-5}$  M). On a weight basis, ferrihydrite was the most adsorptive oxide, whereas the goethite samples were the least adsorptive. The slopes of the essentially linear adsorption isotherms were 2.63, 0.265, 0.215, 0.012, and 0.018 for ferrihydrite, noncrystalline Fe oxide, hematite B, goethite A, and goethite B, respectively. The linearity of the isotherms suggested a low degree of coverage of the surface reactive sites by the organic in the presence of excess ClO<sub>4</sub><sup>-</sup> anion. The different surface reactivities of the oxides evident in Figure 2 could arise from different adsorption mechanisms as well as from different reactive site densities on the oxide surfaces. Inasmuch as the oxides displayed a wide range of surface areas, a direct comparison of surface reactivity could be more accurately made once adsorption was normalized on a unit surface area basis. For this reason, the data in Figure 2 were replotted in Figure 3 as adsorption per unit surface area. From Figure 3, the surface density of adsorption appears to follow the order: ferrihydrite > hematite > noncrystalline Fe oxide >> goethite. A greater adsorption suggests a higher density of reactive sites and/or a more energetic adsorption process. The oxides differ in crystal structure, and therefore the difference in adsorption may have been caused by differences in the type as well as in the quantity of binding sites (*vide infra*).

The relatively low slope of the adsorption curve of the noncrystalline Fe oxide was unexpected because this material was presumed to have a high density of

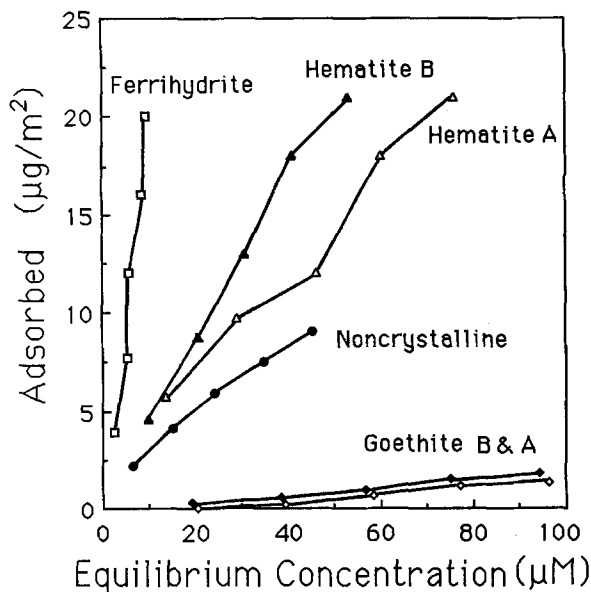


Figure 3. Isotherms for *p*-hydroxybenzoate adsorption onto different Fe oxides, calculated on a unit surface area basis. Data taken from Figures 1 and 2. See Figure 2 legend for oxide surface areas.

reactive surface sites due to the disorganized nature of the structure. Apparently, sulfate introduced in the synthesis of this material occupied some of the ligand exchange sites (Musié *et al.*, 1982) and inhibited adsorption of the organic. Although hematite adsorbed more *p*-hydroxybenzoate than did noncrystalline Fe oxide at low ionic strength, this tendency was reversed at a high ionic strength. Thus, the noncrystalline Fe oxide apparently had a high density of surface sites, but their reactivity at low ionic strength was limited by adsorbed sulfate.

To compare the organic and inorganic anion-bonding capacities of the oxides, the adsorption of phosphate on hematite B, goethite B, and noncrystalline Fe oxide was determined. For these oxides, phosphate adsorption followed L- and/or H-type isotherms, which were fitted to the Langmuir equation. The Langmuir adsorption maximum was 217, 275, and 996  $\mu\text{mole/g}$  for goethite, hematite, and noncrystalline Fe oxide, respectively. Singly coordinated surface-hydroxyl groups and Lewis acid sites are believed to be the reactive sites for anion complexation on Fe oxides (Parfitt, 1978). Phosphate adsorption is commonly employed to estimate the total quantity of these sites.

*p*-Hydroxybenzoic acid adsorption followed the same general trend as phosphate adsorption on the different oxides; however, fewer than one third of the phosphate-reactive sites of hematite, for example, were occupied by organic anion. These data suggest that the organic anion was adsorbed on only some of the potentially reactive sites. Much more phosphate than *p*-hydroxybenzoate was retained on the noncrystalline

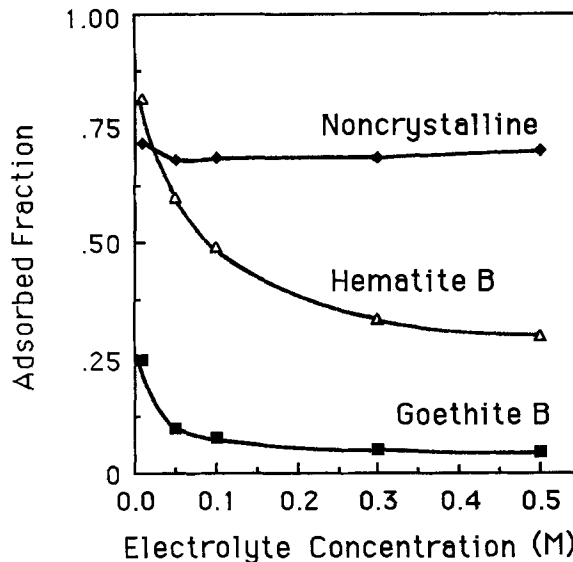


Figure 4. Fraction of *p*-hydroxybenzoate adsorbed as function of ionic strength for hematite B, goethite B, and noncrystalline Fe hydroxide. See Figure 2 legend for oxide surface areas.

Fe oxide, again reflecting the presence of adsorbed sulfate on the oxide, which was apparently much more readily displaced by phosphate than by *p*-hydroxybenzoate. Furthermore, phosphate "sorption" may also involve precipitation reactions, thereby leading to an overestimation of reaction sites.

#### Effect of ionic strength

The effect of ionic strength on the adsorption of *p*-hydroxybenzoic acid was studied by varying the  $\text{NaClO}_4$  concentration. Figure 4 shows the result of a 50-fold change in ionic concentration (0.01 to 0.5 M) on adsorption from an initial concentration of  $1 \times 10^{-4}$  M *p*-hydroxybenzoic acid by three different oxides: hematite B, noncrystalline Fe oxide, and goethite B. Changing the ionic strength had little effect on the adsorption of *p*-hydroxybenzoic acid by noncrystalline Fe oxide, possibly reflecting the dominance of sulfate as a competing anion. In contrast, adsorption on hematite and goethite was strongly influenced by the change of ionic strength. For constant surface-potential materials such as Fe oxides at pHs of less than the zero point of charge, an increase in ionic strength will increase the surface positive charge (Bloesch *et al.*, 1987). The decreased adsorption, however, probably resulted from competition by the perchlorate anion for sites that adsorbed the organic anion. This competition was undoubtedly very weak, but the very high perchlorate/benzoate mole ratios in solution presumably reversed the favored organic anion adsorption. Similarly, Parfitt *et al.* (1977) showed that increased ionic strength reduced the adsorption of oxalate on goethite, even though the oxalate anion formed a binuclear surface complex.

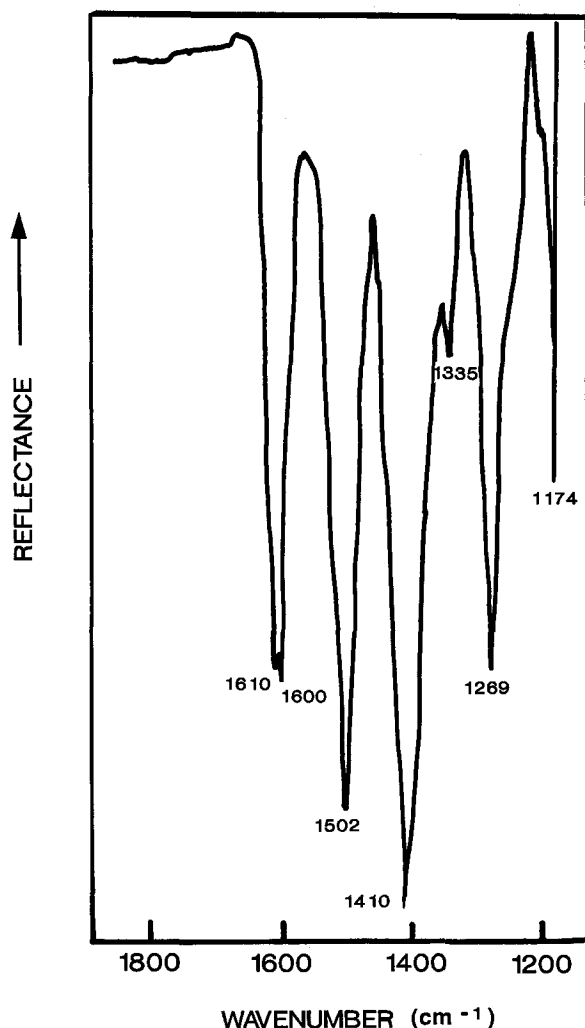


Figure 5. Diffuse-reflectance Fourier-transform infrared spectrum of *p*-hydroxybenzoate adsorbed on ferrihydrite.

Besides increasing competition, the higher ionic strength should have decreased the chemical activity of the organic anion in solution (Stumm and Morgan, 1981), thereby suppressing adsorption.

#### DRIFT study of the oxide-organic complex

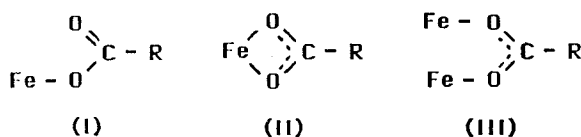
The DRIFT spectrum of *p*-hydroxybenzoate adsorbed on ferrihydrite is shown in Figure 5. The carboxylic C=O stretching vibration for the free acid, located at  $1677\text{ cm}^{-1}$ , is replaced by bands near  $1410$

and  $1500\text{ cm}^{-1}$  when the molecule is adsorbed. These bands correspond to the symmetric and asymmetric stretching vibrations, respectively, of the carboxylate anion. Bands at  $1600$  and  $1500\text{ cm}^{-1}$  are aromatic-ring stretching vibrations; the latter is partially obscured by the carboxylate vibration. A band at  $\sim 1170\text{ cm}^{-1}$  has been assigned to a ring C-H vibration. The band at  $\sim 1270\text{ cm}^{-1}$  is probably a phenolic-OH vibration.

The positions of the more prominent IR bands observed after adsorption of the organic on the various synthetic oxides under the same experimental conditions are listed in Table 1. For comparison, the free anion form of *p*-hydroxybenzoate ( $\text{Na}^+$  salt) was also prepared and analyzed in powder (neat) form by DRIFT.

The spectral shifts of the ring C-C-stretch vibration suggest that the vibrational energy of the ring was changed by adsorption, meaning that a shift of the  $\pi$ -electron density was caused by complexation of the organic with surface  $\text{Fe}^{3+}$ . More notably, adsorption induced a marked decrease in the wavenumber of both the symmetric and asymmetric stretching vibrations of the carboxylate anion, a result expected for metal complexation to carboxylate (Nakamoto, 1968). This wavenumber decrease was accompanied by relatively little change in the energy of the phenolic C-OH-stretching vibration, confirming that the organic was chemisorbed on the Fe oxide surface via the carboxylate group. Intensification of the carboxylate symmetric vibration relative to the asymmetric vibration upon adsorption may be further indication of an inner-sphere metal-carboxylate bond.

The carboxylate ion can coordinate to metals to form a unidentate (I), bidentate (II), or bridging (III) complex (Collman *et al.*, 1987).



A simplified relationship based on the separation ( $\Delta$ ) between the carboxylic symmetrical and asymmetrical stretching vibrations is commonly used to identify the mode of complexation (Deacon and Phillips, 1980; Nakamoto, 1986). In general, for unidentate (I) coordination,  $\Delta$  is larger than that in the free ion. Conversely,  $\Delta$  in bidentate (II) coordination is smaller than

Table 1. Infrared absorption bands ( $\text{cm}^{-1}$ ) of free and adsorbed *p*-hydroxybenzoate.

	Phenolic C-OH, ring C-H	Sym. COO-	Asym. COO-	Ring C=C
Ferrihydrite	1174, 1269	1410	1502	1600, 1610
Noncrystalline	1173, 1273	1400	1499	1595, 1606
Hematite	1172, 1267	1395	1496	1598, 1605
Goethite	1171, 1275	1387	1490	1597, 1607
Free ( $\text{Na}^+$ salt)	1170, 1267	1430	1577	1610, 1620

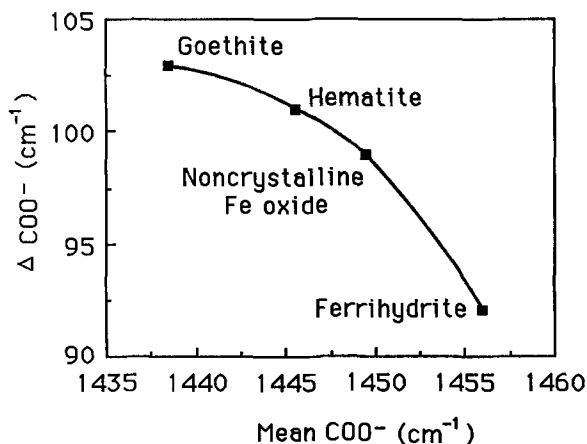


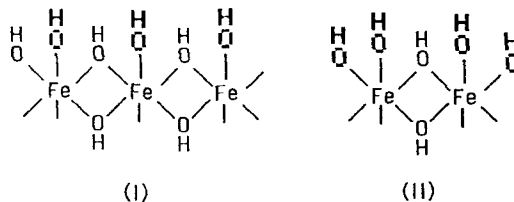
Figure 6. Relationship between separation ( $\Delta$ ) and mean value of carboxylate symmetric and asymmetric stretching vibrations for various Fe oxides.

that in the free ion. In bridging (III) complexes, however,  $\Delta$  is close to the free ion value.

For *p*-hydroxybenzoate, the separation between the symmetric and asymmetric stretching vibrations for the free ion in the sodium salt form was  $147 \text{ cm}^{-1}$ . Because the separations obtained from the DRIFT studies of adsorbed *p*-hydroxybenzoate (Table 1) were smaller than those of the free anion, the coordination of *p*-hydroxybenzoate on Fe oxides was reasoned to be dominated by the bidentate bonding arrangement. The slight increase, however, of the separation,  $\Delta$ , in the order ferrihydrite < noncrystalline Fe oxide < hematite < goethite suggested that the carboxylate group had coordinated to surface  $\text{Fe}^{3+}$  increasingly in a bridging arrangement in that order, with the greatest bridging character being in goethite.

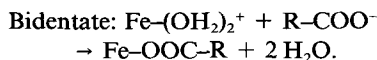
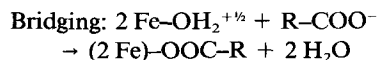
As mentioned above, chemisorption of carboxylate to surface  $\text{Fe}^{3+}$  should have weakened the carboxylate C–O bond due to the electron-withdrawing effect of  $\text{Fe}^{3+}$ , thereby explaining the observed shift of the C–O stretching vibrations to lower wavenumber upon adsorption (Table 1). The relative strength of the coordination bond can be estimated by comparing the relative magnitudes of shift of the C–O stretching frequencies (Nakamoto, 1968). For the bridging complex, this carboxylate shift should have been more dramatic, because the coordination is binuclear (involving two  $\text{Fe}^{3+}$  ions) rather than mononuclear. The relation between the symmetric-asymmetric band separation ( $\Delta$ ) and the mean energy value of these two vibrational bands, measured for the various Fe oxides, is plotted in Figure 6. In this illustration, the binding mechanism was inferred from the band separation, whereas the bond strength was inferred from the mean position. Of the oxides, goethite appeared to have the highest propensity for bridging, as suggested by its comparatively large reduction in carboxylate vibrational energy as well as the larger band separation compared with the

free organic anion. Structural models reveal that the carboxylate can form a bridging complex on the goethite surface because the singly coordinated (A-type) hydroxyls are arranged in rows along the major reactive crystal faces (e.g., (100)), with each A-type hydroxyl coordinated to a different Fe atom (Parfitt, 1978). On reactive hematite crystal faces, however, both bridging and bidentate complexation are possible, because A-type hydroxyls are arranged both in pairs to a single Fe atom and in rows. Structural diagrams of the bridging (I) and bidentate (II) surface groups are shown below, with the reactive (A-type) hydroxyls indicated by bold type.



#### General description of adsorption reaction

The ligand exchange reactions at the oxide surface are described ideally as:



The theoretical entropy change,  $\Delta S^\circ$ , associated with the replacement of two  $\text{H}_2\text{O}$  molecular by one organic anion in these reactions, based on the known value (Weast, 1982) of the standard state entropy of water and carboxylate anion (16.7 and 20 entropy units, respectively), can then be calculated. The resulting positive value of  $T\Delta S^\circ$ ,  $+4 \text{ kcal/mole}$ , reflects the increased degrees of motional freedom generated by the ligand exchange. This analysis does not consider entropy changes associated with the surface in the process of adsorption.

The standard free energy,  $\Delta G^\circ$ , of the adsorption reaction can theoretically be calculated from the equilibrium constant,  $K$ , using the thermodynamic relationship that  $\Delta G^\circ = -RT \ln K$ . The Langmuir bonding constant, estimated from the adsorption isotherms, can be equated to this equilibrium constant using certain assumptions (Parfitt, 1978). This procedure was applied to the adsorption isotherm of *p*-hydroxybenzoic acid on hematite A, and  $\Delta G^\circ$  for the adsorption was calculated to be about  $-4 \text{ kcal/mole}$ . From the equation relating free energy to enthalpy,  $\Delta H^\circ$ , and entropy,  $\Delta S^\circ$ , of the reaction,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , it becomes evident that the entropy term probably accounted for most of the free energy change associated with the adsorption process. In other words, entropy was probably

the major driving "force" in the reaction. In a similar way, catechol adsorption on Al oxides, almost certainly a surface chelation reaction (McBride and Wesselink, 1988), has similarly been shown to be entropy-driven based on the effect of temperature on the equilibrium (unpublished data obtained in this laboratory). In the present study, adsorption on goethite was found to be exothermic, based on the effect of temperature on adsorption. Inasmuch as  $\Delta H^\circ$  is expected to be small in magnitude for ligand exchange of water by carboxylate ( $H_2O$  and  $R-COO^-$  have comparable ligand field strengths on the spectrochemical series), the reversal from an endothermic reaction in hematite to an exothermic reaction in goethite may actually involve little change in the absolute value of  $\Delta H^\circ$ .

From this discussion the free energy of adsorption,  $\Delta G^\circ$ , is clearly not necessarily correlated to organic-oxide bond energy, because the binding mechanisms on the different oxides may not have been the same. In theory, the relative adsorption energies for the different adsorbates could have been obtained from the adsorption isotherms using one particular oxide, allowing the assumption of an invariant binding mechanism. Under these controlled experimental conditions, adsorption isotherms with greater slopes indicate greater adsorption energy. In the present study, the free energy of adsorption per unit weight of oxide followed the order: ferrihydrite > noncrystalline Fe oxide > hematite > goethite. This free energy, however, is made up of energy and entropy changes associated with the adsorption. The energy term depends on the bond energy of the surface complex, but both energy and entropy are likely to be sensitive to the mechanism of adsorption. Surprisingly, the bond energy inferred from spectroscopic data (see Figure 6) was inversely related to the degree of adsorption measured by the isotherms (see Figure 2); however, different entropy contributions to the adsorption free energy on different oxides may have produced this effect. The IR spectra (*vide supra*) provided some evidence for dependence of the mechanism on the structure of the oxide. Although bidentate (mononuclear) complexation of carboxylate was predominant on Fe oxides, some tendency toward bridging (binuclear) complexation was evident on goethite. Such differences in mechanism of bonding likely produced different enthalpy and entropy contributions to the total free energy of reaction.

In addition to the difference in binding mechanism, the total quantity of reactive sites on the oxide surfaces should be considered if the adsorptive properties of oxides are to be compared. For example, different mechanisms would require different numbers of surface  $Fe^{3+}$  sites, e.g., binuclear bonding occupies twice as many  $Fe^{3+}$  sites as does mononuclear bonding. Furthermore, proton adsorption, which can convert A-type hydroxyl to reactive sites ( $Fe-H_2O^{+1/2}$ ) on oxides, appears to be influenced by the distribution and

density of the structural hydroxyl at the surface (Hiemstra *et al.*, 1987). Recently, the reactivity of hematite toward phosphate has been demonstrated from structural models to depend on crystallite shape, i.e., arrangement of surface hydroxyls on crystallite faces (Barron *et al.*, 1988). Thus, the amount of adsorption is not necessarily related to bond strength of the complex, if density and/or distribution of reactive sites become variables in the adsorption process. For example, the low reactivity of goethite toward *p*-hydroxybenzoate compared with that of hematite (or the less crystalline oxides) was apparently not due to an intrinsically weak surface-carboxylate bond, but rather to the dominance of crystallite faces on goethite having low densities of carboxylate-adsorbing sites. Therefore, the difference in surface reactivity among the oxides was probably caused by differences in both quantity and arrangement of reactive sites.

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