ORGANIC ANION ADSORPTION ON ALUMINUM HYDROXIDES: SPIN PROBE STUDIES

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Abstract—The nature of organo-phosphate and carboxylate bonding in aqueous suspensions of noncrystalline alumina, boehmite, and gibbsite has been studied using the anionic nitroxide spin probes 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxyl and 4-hydroxy-2,2,6,6-tetramethyl-piperidinooxyl dihydrogen phosphate. Analysis of the electron spin resonance (ESR) spectra of these molecules revealed that adsorption of both molecules occurred rapidly on the high surface area alumina and boehmite, whereas only the organophosphate adsorbed on gibbsite. A loss in rotational motion of the molecules accompanied adsorption, with the greater degree of motional restriction observed for the carboxylate attributed to steric restrictions to rotation about the surface-bound C–COO⁻ bond axis. The ease of displacement of adsorbed carboxylate from surface binding sites by weakly adsorbing anions (Cl⁻, ClO₄⁻) compared to organophosphate suggests that the carboxylate adsorbed by ligand exchange of a single surface OH, whereas the organophosphate probably formed a bidentate bond. The carboxylate bound on noncrystalline alumina showed evidence of nonspecific electrostatic adsorption in addition to ligand exchange of surface OH. This weak bonding was indicated by a moderate loss in rotational motion and ease of exchangeability.

Key Words—Adsorption, Aluminum hydroxide, Boehmite, Carboxylate, Electron spin resonance, Gibbsite, Organophosphate.

INTRODUCTION

Anion adsorption on iron and aluminum oxides has interested soil chemists because of the ability of these oxides to "fix" certain agronomically important anions, most notably phosphate. A review of anion adsorption by Parfitt (1978) outlined three basic mechanisms of adsorption: (1) nonspecific electrostatic interaction between surface M-OH₂⁺ groups and the anion (e.g., NO₃⁻); (2) ligand exchange of a single surface OH⁻ group by the anion (e.g., F⁻); and (3) ligand exchange of two surface groups by the anion to form a binuclear bridging complex (e.g., PO₄³⁻).

Organic anions also adsorb on oxides, although individual mechanisms have not often been determined clearly. Whereas monocarboxylic acids, such as benzoic acid (Parfitt *et al.*, 1977a; Parfitt *et al.*, 1977b) and 2,4-dichlorophenoxyacetic acid (Watson *et al.*, 1973) are relatively weakly and reversibly adsorbed on hydrous oxides, dicarboxylic acids (e.g., oxalic acid) are strongly adsorbed (Parfitt *et al.*, 1977a). The most likely mechanism for monocarboxylic acid adsorption seems to be ligand exchange of a single surface OH, but the COO⁻ groups of dicarboxylic acids, such as oxalate, probably displace two adjacent surface hydroxyls to form a binuclear complex (Parfitt *et al.*, 1977a; Parfitt and Russell, 1977).

Organophosphates, such as adenosine triphosphate (ATP), adsorb on layer silicate clays in small amounts (Graf and Lagaly, 1980), with the mechanism probably involving ligand exchange of OH groups by phosphate on crystallite edges or oxide impurities.

The use of anionic organic spin probes to study the adsorption process on oxides by electron spin resonance (ESR) can provide information on surface-organic interaction not obtainable by other methods. The technique is sensitive, permitting adsorption of small quantities of organic anion to be studied, and allows fully wet systems to be analyzed. The spin probe technique has been demonstrated for the fatty acid-alumina reaction, confirming that adsorption occurs by bonding of the carboxylated end of the molecule to the surface (McBride, 1980). The present spin probe study was undertaken to determine bonding mechanisms of organophosphate and carboxylate anions on crystalline and noncrystalline hydrous aluminum oxides.

MATERIALS AND METHODS

Adsorption experiments were conducted on boehmite, gibbsite, and noncrystalline alumina, characterized by methods described previously (McBride, 1982). The surface areas of the alumina, boehmite, and gibbsite are 111, 147, and 6.7 m²/g, respectively, as determined by the N₂-B.E.T. method. The reactive hydroxyl contents of the minerals are 2775, 64, and 48 mmole/100 g, respectively, as measured by the fluoride-reaction method described by Perrott *et al.* (1976). The very high hydroxyl value obtained for noncrystalline alumina reflects the partial dissolution of this material in NaF.

Nitroxide spin probes with anionic functional groups, 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxyl (TEMPO-COOH) and 4-hydroxy-2,2,6,6-tetramethyl-piperidinooxyl dihydrogen phosphate (TEMPO-H₂PO₄),

having the chemical structures shown below were obtained from Syva Research Chemicals.

TFMPO–COOH   **TEMPO–H₂PO₄**
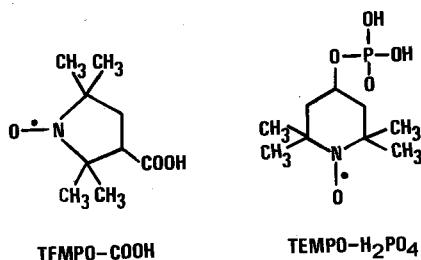
They were dissolved in distilled water to prepare $\sim 5 \times 10^{-4}$ M TEMPO-COOH and $\sim 4 \times 10^{-4}$ M TEMPO-H₂PO₄ solutions. The solutions were kept refrigerated, although the TEMPO-H₂PO₄ solution apparently hydrolyzed over time, releasing orthophosphate. Earlier suggestions (McBride, 1980) that TEMPO-H₂PO₄ did not adsorb on oxides appear to be in error. Although the nitroxide portion of the molecule was not adsorbed after hydrolysis, the phosphate *was* adsorbed. Thus, ESR could be used to verify adsorption of the phosphate only if hydrolysis had not occurred. All experiments using TEMPO-H₂PO₄ were conducted rapidly with freshly prepared probe solutions to minimize hydrolysis in this study.

Adsorption experiments were conducted by adding 2 ml (in most experiments) of aqueous probe solution to 50, 100, or 200 mg of solid. The quantity of solid was varied depending upon the level of adsorption expected from preliminary studies. In some cases, varying amounts of probe solution were added to a constant quantity of solid to obtain adsorption isotherms. The pH and length of equilibration time were also adjusted to observe the effect on adsorption.

ESR spectra were obtained by centrifuging the equilibrated suspensions and analyzing the wet solids in capillary tubes on a Varian E-104 (X-band) spectrometer. In some experiments the solids were rinsed free of non-adsorbed probe by repeated water washing prior to ESR analysis. Supernatants were quantitatively analyzed for spin probe content by ESR using standard spin probe solutions when adsorption isotherms were to be determined. The ESR spectra of all solids were determined at room temperature, but selected samples were chosen for analysis at higher and lower temperatures controlled by the Varian E-257 variable temperature accessory.

RESULTS AND DISCUSSION

Spin probes in aqueous solution

The spectrum of TEMPO-COOH in solution at room temperature (Figure 1A) consists of three equally intense hyperfine lines with a hyperfine splitting of 13.7 gauss and a g-value of 2.0051. The spectrum of aqueous TEMPO-H₂PO₄ is very similar. Because the electron
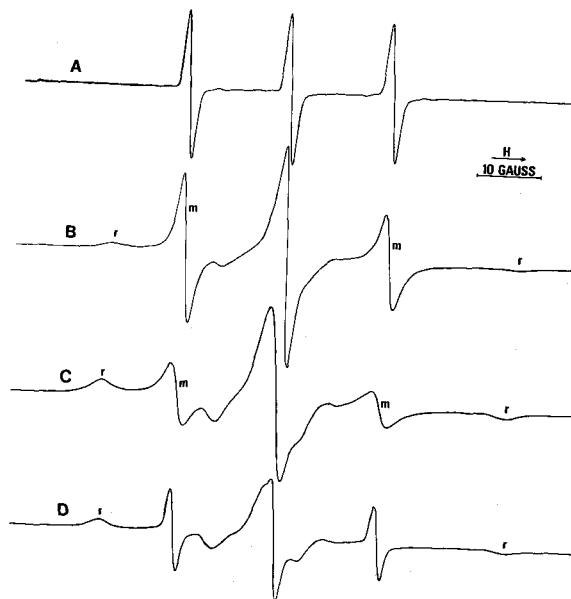

Figure 1. Room temperature ESR spectrum of aqueous 5×10^{-4} M TEMPO-COOH (A) and spectra of aqueous suspensions of TEMPO-COOH (2 ml of 5×10^{-4} M) equilibrated with noncrystalline alumina (50 mg), after 2-hr reaction time and removal of excess probe (B), after 500-hr reaction time and removal of excess probe (C), and after 20-min equilibration of the suspension described in C with 1 M NaClO₄ (D). The letters "m" and "r" mark the outer resonance peaks of the "mobile" and "rigid" fractions of adsorbed TEMPO-COOH, respectively.

spin-nuclear spin dipolar interaction is anisotropic, the spectrum is symmetrical only when rapid molecular rotation averages the dipolar interaction to zero. The isotropic spectrum of Figure 1A arises from rapid molecular tumbling. The rotational correlation time, τ_R (i.e., the approximate time for molecular reorientation), of TEMPO-COOH in aqueous solution at room temperature, calculated from the ESR spectrum by the method applicable to rapid rotation (McBride, 1980; Nordio, 1976), is 3.9×10^{-11} sec.

TEMPO-COOH on aluminum hydroxides

Two forms of TEMPO-COOH adsorbed on oxides were observed in this study. One is relatively mobile ($\tau_R \sim 10^{-9}$ sec), with a spectrum recognized by unequal peak heights of the three hyperfine lines arising from incomplete rotational averaging of spectral anisotropies. However, rapid exchange between adsorption sites and solution prevents the separation of the isotropic spectrum of nonadsorbed probe from this spectrum, and the observed spectrum is a weighted average, dependent upon the fraction of time that the probe spends in solution and in the adsorbed state. Although water washing could not remove the adsorbed mobile probe from the oxides, it did remove most of the excess probe in solution, thereby leaving a greater fraction of the
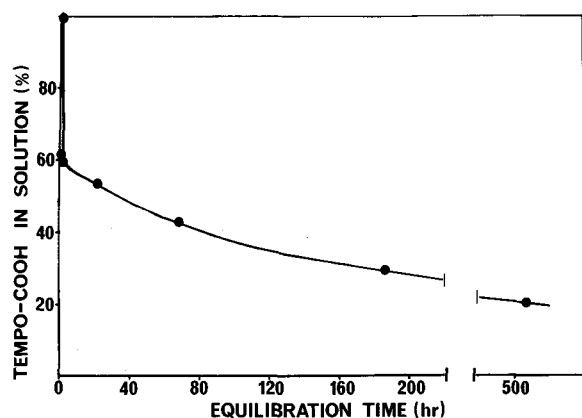
Figure 2. Time dependence of the adsorption of TEMPO-COOH (2 ml of 5×10^{-4} M) from solution by noncrystalline alumina (50 mg).

TEMPO-COOH in the adsorbed state. The result of washing is a shift of the "average" spectrum toward a less isotropic line shape with a longer calculated τ_R. This type of spectrum, representing mobile (but largely adsorbed) probe molecules, is labelled by the letter "m." Calculated τ_R values for this form of probe are not absolute in the sense that repeated water washing did not remove *all* of the free probe in the solution phase.

The second type of adsorbed TEMPO-COOH is identified by low-field and high-field resonances arising from rigid or near-rigid probe molecules which, by chance, have their z-axes parallel to the applied magnetic field of the spectrometer. While the central portion of the rigid-limit spectrum may be obscured by spectra of mobile probes, the low-field and high-field extrema are easily observed. This type of spectrum is characteristic of motionally restricted spin probes with $\tau_R \geq 10^{-8}$ sec, and is labelled by the letter "r." Because rigidly-bound probes cannot exchange rapidly enough with mobile probes (adsorbed or in solution) to produce time-averaged spectra, discrete rigid-limit spectra are often superimposed on spectra of mobile probes.

Noncrystalline alumina. The initial adsorption of TEMPO-COOH on noncrystalline alumina was quite rapid, as indicated by the quick loss of ESR signal from aqueous solution upon addition of the solid (Figure 2). However, slow adsorption continued for several weeks after the initial rapid process. The ESR spectra of the wet alumina after a few hours (Figure 1B) and after a 500-hr equilibration (Figure 1C) indicate that most of the rapidly adsorbed TEMPO-COOH is bound in a mobile form (m), whereas slow adsorption is associated with a more rigidly bound fraction (r). The estimated correlation time of the mobile adsorbed TEMPO-COOH is 0.80×10^{-9} sec, obtained from the spectrum of alumina washed free of excess probe in solution. This value is about 20 times longer than τ_R for nonadsorbed

aqueous probe. From the Arrhenius equation, it can be estimated that the rotational activation energy, E_a, is increased by about 50% due to adsorption on the surface. This result suggests a relatively weak bonding mechanism for the more mobile adsorbed probe, possibly electrostatic attraction to surface $Al-OH_2^+$ groups. Since the adsorption was carried out at a pH between 4 and 5, a significant quantity of positive surface charge should have been present.

A weak rigid-limit spectrum (extrema denoted by "r" in Figure 1B), slowly grew in intensity with time (Figure 1C). This spectrum is most likely associated with the slow adsorption process depicted in Figure 2, and represents strongly restricted TEMPO-COOH ($\tau_R \sim 10^{-8}$ sec). Addition of ClO_4^- ions to the alumina converted the spectrum of mobile adsorbed TEMPO-COOH to an isotropic solution spectrum, whereas the rigid-limit spectrum was less affected (Figure 1D).

The results indicate the presence of three types of TEMPO-COOH in the aqueous alumina suspensions: (1) nonadsorbed probe in solution; (2) loosely bound probe, probably held electrostatically and readily exchanged from the surface by nonspecifically adsorbing anions such as ClO_4^-; and (3) rigidly bound probe, most likely adsorbed by ligand exchange of surface OH and not readily displaced from the surface by nonspecifically adsorbing anions.

Further experiments with competing anions showed that ClO_4^- displaced much of the rigidly bound probe over several hours. However, Cl^- displaced both loosely and rigidly bound TEMPO-COOH instantaneously. Chloride adsorbs more strongly on oxides than NO_3^- or ClO_4^-, and may adsorb in small amounts by ligand exchange (Parfitt, 1978). The ease of exchange of the rigidly adsorbed probe by Cl^- suggests that the COOH group, unlike phosphate, does not form a bidentate complex with the surface.

Increased temperature produced small increases in mobility of the two forms of bound probe, as revealed by slight spectral changes. The τ_R of mobile adsorbed TEMPO-COOH decreased from 0.8×10^{-9} sec at 20°C to 0.63×10^{-9} sec at 60°C. The effect of decreased temperature was to eliminate most of the mobile probe ("m") near $-20°C$ with an increase in intensity of the rigid probe ("r") spectrum. At $-50°C$, all of the mobile probe had disappeared, leaving only a rigid-limit spectrum. The value of A'_{zz}, the rigid-limit z-axis hyperfine splitting (McBride, 1979), was measured as 32.1, 36.0, and 37.6 gauss at 20°C, $-20°C$, and $-50°C$, respectively. The increase in A'_{zz} is indicative of greater motional restriction as the temperature was lowered. This loss in mobility was reversible.

Gibbsite and boehmite. Adsorption experiments using gibbsite showed no evidence of adsorbed TEMPO-COOH, probably due to the low surface area and small amount of reactive surface OH groups. Boehmite ad-
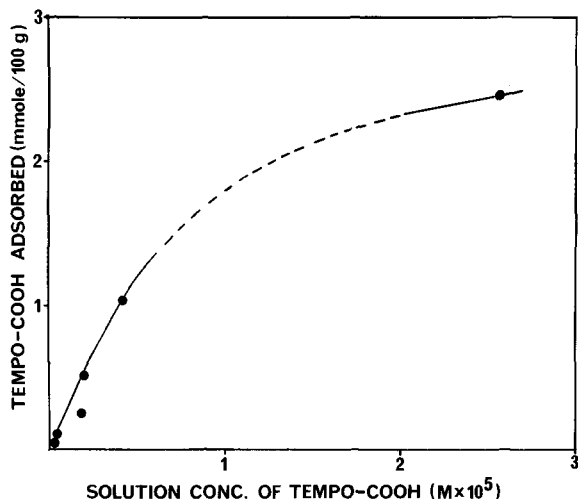
Figure 3.   Adsorption isotherm of TEMPO-COOH on boehmite, 100 mg boehmite equilibrated with 10 ml of aqueous solution for 1 day.

Figure 4.   ESR spectrum of TEMPO-COOH in boehmite suspension prepared by reacting 100 mg boehmite with 2 ml of 5×10^{-4} M TEMPO-COOH and water washing to remove excess probe (A), and the same sample after addition of 1 M NaClO$_4$ (B). The letters "r" and "s" mark resonance positions of the rigidly bound and free solution probe, respectively.

sorbed several millimoles per 100 g of TEMPO-COOH, as shown by the adsorption isotherm of Figure 3. However, several differences in adsorption were observed for the boehmite compared to noncrystalline alumina. The slow adsorption process of alumina (Figure 2) was not evident with boehmite. Adsorption was essentially complete within 0.5 hr or less, suggesting that at least part of the slow reaction in the noncrystalline alumina was due to diffusion into micropores. In addition, adsorbed TEMPO-COOH on boehmite was immobilized, as shown by the dominant rigid-limit spectrum (Figure 4A). The solution-phase free probe (denoted by "s") could be eliminated by several rapid water rinses of the boehmite. Unlike noncrystalline alumina, boehmite had no mobile adsorbed TEMPO-COOH. Whereas ClO$_4^-$ ions displaced a fraction of the rigidly-bound TEMPO-COOH into solution (Figure 4B), citric acid readily displaced *all* of the adsorbed probe. The results are consistent with the concept of TEMPO-COOH bonding by ligand exchange on boehmite, with little or no electrostatic (nonspecific) bonding.

Neither adsorption level nor adsorption pH significantly altered the spectrum of TEMPO-COOH on boehmite; the value of A$'_{zz}$ remained at 32.4 gauss as the pH was varied between 3.5 and 7 and as the quantity of adsorbed probe ranged from 0.05 to 2.4 mmole/100 g as the level of added TEMPO-COOH was increased. Evidently, neither pH nor quantity of adsorption sites occupied had any substantial effect on the bonding mechanism. The TEMPO-COOH was restricted to a similar degree on the boehmite as the rigid form of probe on alumina as shown by the similarity of the A$'_{zz}$ values on these two materials. The effect of pH on adsorption is shown in Figure 5. Adsorption decreased at pH values above 5, a result consistent with the observation
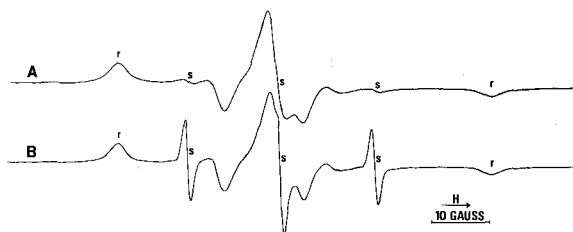
that maximum adsorption of organic acids on oxides occurs at a pH nearly equal to the pK$_a$ of the acid (Watson *et al.*, 1973).

Increased temperature caused the mobility of the boehmite-bound probe to increase slightly as reflected by a decrease in the A$'_{zz}$ value. Bound probe also desorbed at higher temperature, as indicated by a loss in intensity of the rigid-limit spectrum relative to the solution spectrum. Evidently, the adsorption reaction is exothermic. Estimates of τ_R for the rigidly bound probe were made at several temperatures using the approximation that $\tau_R = b(1 - S)^{-1}$ (Freed, 1976) where b is a constant and S is the ratio of A$'_{zz}$ to the limiting value of A$_{zz}$ (37.5 gauss) at very low temperature ($-180°$C) when motional averaging of spectral parameters is negligible. These estimates of τ_R were 8.0, 7.0, 6.4, and 5.7×10^{-9} sec at 20°, 40°, 60°, and 80°C, respectively. The weak dependence of motional reorientation of the bound TEMPO-COOH on temperature is quite different from that observed for probes motionally restricted in solvents, where an energy barrier to reorientation created by the surrounding solvent molecules can be overcome at high temperature. The motion of bound nitroxide in biological systems, like that of adsorbed nitroxide in this study, has been demonstrated to be insensitive to temperature (Sachs and Latorre, 1974).

TEMPO-H$_2$PO$_4$ on aluminum hydroxides

All of the materials rapidly adsorbed TEMPO-H$_2$PO$_4$ at detectable levels. The spectra of the adsorbed probe (Figure 6) are characteristic of probes undergoing incipient slow motion. Estimates of τ_R from these spectra using the method applicable to rapid rotation gives values on the order of 4×10^{-9} sec at room temperature; these estimates may be somewhat inaccurate because the method requires that τ_R be less than 5×10^{-9} sec (Smith, 1972) and the motion be isotropic. Nevertheless, the adsorbed TEMPO-H$_2$PO$_4$ is bound more rigidly than the mobile fraction of TEMPO-COOH on alumina, but less rigidly than the near rigid-limit fraction of TEMPO-COOH. Because phosphate is known
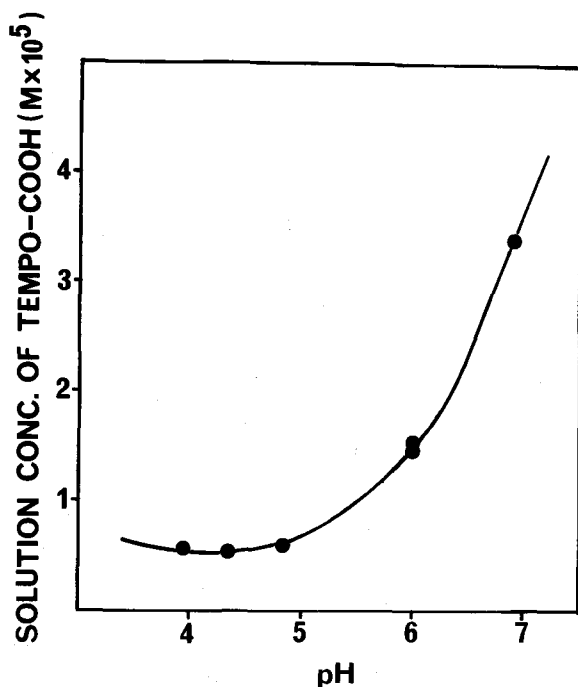
Figure 5. Relationship between pH and concentration of TEMPO-COOH in solution phase after 1 day equilibration of 10^{-4} M probe solution (10 ml) with 100 mg boehmite.

Figure 6. ESR spectra of TEMPO-H₂PO₄ in suspensions of noncrystalline alumina (A), boehmite (B), and gibbsite (C) after reaction of 4×10^{-4} M TEMPO-H₂PO₄ (2 ml) with 50 mg sample for 2 hr and removal of excess probe by water washing.

to adsorb more strongly than carboxylates, probably via a binuclear bridging bond, the relatively mobile nature of adsorbed TEMPO-H₂PO₄ compared with the rigidly adsorbed TEMPO-COOH may seem surprising. For example, the spectrum of TEMPO-COOH adsorbed on boehmite (Figure 4A) is much nearer rigid-limit than the spectrum of TEMPO-H₂PO₄ on boehmite (Figure 6B). However, molecular models of the two probes reveal that TEMPO-COOH bound to the surface via the COO⁻ group has a very limited ability to twist or rotate through the C–COO⁻ bond because of steric restrictions created by the methyl groups. In contrast, TEMPO-H₂PO₄, even though it may be anchored to the surface by two bonds to adjacent surface Al atoms, has the ability to rotate relatively freely through the C–O–P–O linkage to the surface. The rapid thermal motions of the N–O group at the unbound end of the molecule partially average spectral anisotropies and cause the ESR spectrum to deviate from rigid limit.

Evidence that TEMPO-H₂PO₄ bonded more strongly to the surfaces than TEMPO-COOH is observed from anion competition studies. Perchlorate (ClO₄⁻) did not displace bound TEMPO-H₂PO₄ from boehmite, whereas Cl⁻ was only slightly more effective, in contrast with the results for TEMPO-COOH, where Cl⁻ and ClO₄⁻ displaced much of the rigidly adsorbed probe. Addition of aqueous Ca(HPO₄)₂ solution to gibbsite, boehmite, and noncrystalline alumina displaced a portion of the bound TEMPO-H₂PO₄ into solution, as shown by a rap-
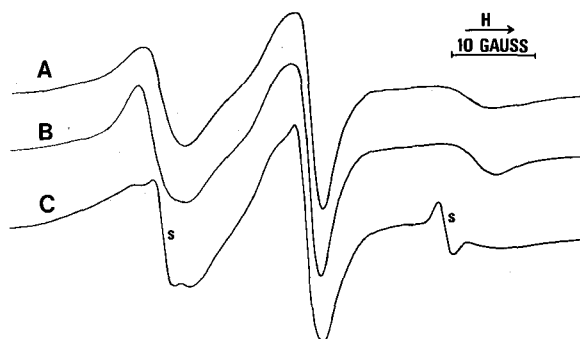
id loss in the spectrum of bound probe and the appearance of the solution spectrum. The stronger bonding of TEMPO-H₂PO₄ on the surfaces when compared with TEMPO-COOH and the ability of inorganic phosphate to compete with TEMPO-H₂PO₄ are probably a result of the ability of phosphate to form a bidentate surface bond.

The spectrum of adsorbed TEMPO-H₂PO₄ on gibbsite was accompanied by a spectrum of solution probe (denoted by "s" in Figure 6C). Repeated washing of the gibbsite did not eliminate this solution spectrum, suggesting that washing induced desorption from adsorption sites. The fact that inorganic phosphate completely desorbed all of the TEMPO-H₂PO₄ from gibbsite supports the concept that the molecule was bound weakly on gibbsite. Any adsorption must have occurred at particle edges, because the OH groups on the (001) face of gibbsite do not react with anions (Parfitt, 1978). Levels of addition of TEMPO-H₂PO₄ to the minerals were between 10 and 20 mmole/100 g. Although noncrystalline alumina and boehmite readily "fixed" this amount of organophosphate, gibbsite did not. If F⁻-displaceable OH⁻ is used as a measure of phosphate fixation sites, this gibbsite should have adsorbed no more than 24 mmole phosphate/100 g. Thus, the apparently weak adsorption on gibbsite may have arisen because most or all of the potential phosphate fixation sites were occupied by TEMPO-H₂PO₄. The boehmite sample adsorbed both TEMPO-H₂PO₄ and TEMPO-COOH readily, despite having only slightly more reactive OH⁻ groups (as measured by F⁻ displacement) than gibbsite. The boehmite, although crystalline, possessed a high surface area and large quantity (per unit weight) of surface groups capable of adsorbing organic anions.

The mobility of bound TEMPO-H₂PO₄ on boehmite and noncrystalline alumina was relatively insensitive to temperature, much like the behavior of adsorbed TEMPO-COOH. Estimated values of τ_R for adsorbed TEMPO-H₂PO₄ decreased from 4.0×10^{-9} to 3.0×10^{-9} sec

as the temperature was increased from 20° to 80°C. The direct phosphate-surface bond, preventing random molecular rotation, was probably responsible for this result.

SUMMARY

The bonding of the organophosphate on aluminum hydroxide is stronger than bonding of the carboxylate. The degree of motional restriction of the organic anions on the fully hydrated surfaces suggests that boehmite adsorbs the carboxylic acid largely by ligand exchange, while noncrystalline alumina adsorbs the molecule by both ligand exchange and nonspecific electrostatic processes. The disordered surface of alumina is expected to have a high concentration of OH^- groups coordinated to only one Al atom. These OH^- groups readily protonate at low pH, generating positive charge which retains anions by electrostatic attraction. Evidently, much less positive charge develops on the boehmite than on the alumina used, despite the similar surface areas of the two materials. The marked difference in reactivity with fluoride anion demonstrates that the noncrystalline alumina had many more reactive OH groups than boehmite.

Although high surface-area gibbsite has been shown in other studies to adsorb monocarboxylic acids weakly, no evidence of retention of the carboxylic acid probe by gibbsite after water washing was observed in this study. The very low surface area of the gibbsite sample used may have been responsible. However, organophosphate probe was adsorbed in small amounts by the gibbsite.

ACKNOWLEDGMENT

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Резюме—Исследовались свойства органо-фосфатных и карбоксилатовых связей в водных растворах некристаллических глиноземов, бемита и гиббсита, используя анионные азотоокисные спиновые зонды 3-карбокси-2,2,5,5-тетраметил-1-пиролидинолоксиль и 4-гидрокси-2,2,6,6-тетраметил-пиперидинооксиль двухводородного фосфата. Анализ спектров этих молекул путем электронного спинового резонанса (ЭСР) показал, что адсорбция обоих молекул происходила быстро на глиноземах и бемите с большой площадью поверхности, тогда как только органофосфат адсорбировался на гиббсите. Потеря ротационного движения молекул сопутствовала адсорбции с большим ограничением движения наблюдаемого для карбоксилатов, приписанного стерическому затруднению роиации около оси связи C–COO⁻. Свобода перемещения адсорбированного карбоксилата из поверхностных мест слабо адсорбирующими анионами (Cl⁻, ClO₄⁻) по сравнению с органофосфатами предлагает, что карбоксилат адсорбировался путем лигандного обмена одноповерхносных ионов OH, тогда как органофосфаты, вероятно, образовывали двухзубчатую связь. Карбоксилат, связанный на некристаллическом глиноземе, указывал на признаки неособенной электростатической адсорбции в дополнение к лигандному обмену поверхностных OH. Умеренная потеря ротационного движения и свобода обменной способности указывали на слабость этой связи. [E.C.]

Resümee—Es wurde die Art der Organophosphat- bzw. Organocarboxylatbindung von nicht kristallisierten Aluminiumoxid, Boehmit, und Gibbsit in wässrigen Lösungen untersucht, wobei die anionischen Nitrox-idspinsonden 3-carboxy-2,2,5,5-tetramethylen-1-pyrolidinyloxyl- und 4-hydroxy-2,2,6,6-tetramethylen-pi-peridinooxyl-Dihydrogenphosphat verwendet wurden. Die Auswertung der Elektronenspinresonanz (ESR)-Spektren dieser Moleküle zeigte, daß die Adsorption beider Moleküle an den äußeren Oberflächen von Aluminiumoxid und Boehmit schnell ging, während an Gibbsit nur das Organophosphat adsorbiert wurde. Mit der Adsorption war ein Verlust der Rotationsbewegung des Moleküls verbunden, wobei der größere Anteil der Bewegungsverminderung, der bei Carboxylat beobachtet wurde, sterischen Behinderungen der Rotation um die an die Oberfläche gebundene C-COO⁻-Bindungsachse zugeschrieben wurde. Die Leich-tigkeit, mit der adsorbierte Carboxylate von den Oberflächenplätzen durch schwach adsorbierende An-ionen (Cl⁻, ClO₄⁻) im Vergleich zu Organophosphat verdrängt werden, deutet darauf hin, daß das Car-boxylat durch Ligandenaustausch eines einzigen Oberflächen-(OH) adsorbiert ist, während das Organo-phosphat wahrscheinlich eine zweizähnige Bindung bildet. Die Bindung von Carboxylat an nicht kristal-lisiertes Aluminiumoxid zeigt Hinweise auf nicht spezifische elektrostatische Adsorption zusätzlich zum Ligandenaustausch von Oberflächen-(OH). Diese schwache Bindung zeigt sich durch einen geringen Ver-lust der Rotationsbewegungen und in der leichten Austauschbarkeit. [U.W.]

Résumé—On a étudié la nature des liaisons organo-phosphate et carboxylate dans des suspensions aqueuses d'alumine, de boéhmite et de gibbsite non-cristallines, en utilisant les probes nitroxides de spin anioniques phosphate dihydrogène 3-carboxy-2,2,5,5-tétraméthyl-l-pyrrolidinyloxyl et 4-hydroxy-2,2,6,6-tétramé-thyl-pipéridinooxyl. L'analyse des spectres de resonance à spin d'électrons de ces molécules a révélé que l'adsorption des 2 molécules s'est rapidement produite sur la haute aire de surface de l'alumine et de la boéhmite, tandis que seul l'organophosphate a été adsorbé sur la gibbsite. Une perte de motion rotationelle des molécules a accompagné l'adsorption, le degré le plus élevé de restriction de mouvement observé pour le carboxylate étant attribué aux restrictions stériques à la rotation autour de l'axe liant C–COO⁻ lié à la surface. La facilité de déplacement de carboxylate adsorbé de sites de surface liants par des anions ad-sorbant facilement (Cl⁻, ClO₄⁻), comparée à l'organophosphate suggère que le carboxylate a adsorbé par l'échange ligand d'un seul OH de surface, tandis que l'organophosphate a probablement formé un lien bidentate. Le carboxylate lié sur l'alumine non-cristalline a montré l'évidence d'adsorption électrostatique non-spécifique en plus de l'échange ligand d'OH de surface. Cette liaison faible était indiquée par une perte modérée de motion rotationelle et la facilité d'échange. [D.J.]