REACTION OF BENZENE WITH Cu(II)- AND Fe(III)-EXCHANGED HECTORITES

M. P. Eastman, D. E. Patterson, and K. H. Pannell

Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968

Abstract—The reaction of benzene with exchangeable Cu(II) and Fe(III) in hectorite clay films was studied by electron paramagnetic resonance (EPR). The reaction when carried out in a sealed tube between 60° and 100°C produced a variety of organic radical products. The nature of these products depended on the concentration of water in the reaction medium and the reaction time. The free radicals were accompanied by a reduction in the oxidation state of the metal ions; this process had a zero-order dependence on the metal ion concentration. The activation energies determined from the zero-order rate constants are 67 $\pm$ 11 kJ/mole (Cu(II)) and 46 $\pm$ 6 kJ/mole (Fe(III)). The free radicals initially formed under anhydrous conditions appeared to populate sites in the interlayer region; the activation energies determined for this first order process are 57 $\pm$ 9 kJ/mole (Cu(II)) and 42 $\pm$ 3 kJ/mole (Fe(III)). These activation energies are within experimental error of those determined from the metal ion kinetics. The EPR signal due to organic radicals showed little temperature dependence; thus, exchange processes involving organic free radicals were probably not important in determining EPR lineshapes.

Key Words—Adsorption, Benzene, Copper, Electron paramagnetic resonance, Free radical, Hectorite, Iron.

INTRODUCTION

The reaction of benzene with Cu(II)- and Fe(III)-exchanged smectites was reported by Mortland *et al.* (1971), Rupert (1973), and Pinnavaia *et al.* (1974). They demonstrated that chemisorption of benzene by clay under dehydrating conditions produced two chemical species distinguishable by their color, electron paramagnetic resonance (EPR), and infrared (IR) spectra. A greenish yellow, type I species has an EPR spectrum dominated by the resonance produced by the metal ion exchanged into the clay and an IR spectrum indicative of the presence of a π-type metal-benzene complex. A burgundy type II species has a single-line EPR spectrum apparently due to organic free radicals and an IR spectrum which suggests the presence of an organic species having less aromatic character than benzene. Pinnavaia *et al.* (1974) found that the two species are reversibly interconvertible by the addition or removal of small amounts of water, with the type II species dominating under more anhydrous conditions. From EPR studies of benzene and other arene reactions in Cu(II)-exchanged montmorillonite, Rupert (1973) suggested that the reaction forming the type II species involved electron transfer from benzene to Cu(II) and that Heisenberg or chemical-exchange phenomena involving the benzene cations and/or neutral benzene molecules produced a single, exchange-narrowed EPR line. Discussions concerning what aspects of the clay environment lead to such a facile reaction between the metal ions and the benzene, what kinetics describe this reaction, and why the radical product is stable in the interlayer region of the clay were absent.

To learn more about the free radicals and free radical-forming reactions in systems containing type II species, EPR investigations were carried out on Cu(II)- and Fe(III)-exchanged hectorites. Previously the type II species had been prepared by refluxing the exchanged clay in a Dean-Stark trap or by placing the clay in a desiccator containing benzene and P_2O_5. In the present work the reaction was carried out at constant temperature in a sealed tube containing an exchanged clay film and dried benzene in an oxygen-free environment. The effects of temperature, water, and time on the reaction products and their concentration were noted, and differences between the free radicals produced under these conditions and those of previous experiments were investigated.

EXPERIMENTAL

Spray-dried hectorite from Hector, California, having a cation-exchange capacity of 100 meq/100 g was a gift from NL Industries. Calcium carbonate present in the clay was removed with a citric acid-sodium citrate buffer (pH = 5.7); interlayer iron was removed by reacting 0.5 g of the clay with 0.5 g sodium dithionite at about 50°C for 30 min. The clay was then washed with deionized water and placed in stirred 1.0 N solution of $CuCl_2$ or $FeCl_3$ for about 24 hr. Approximately 50 ml of the metal chloride solution was used per gram of clay. The exchanged hectorites were washed with distilled water and centrifuged until a negative Ag^+ test for Cl^- was obtained from the centrifugate. The treated hectorite was resuspended in deionized water, poured into polyethylene containers, and air-dried on a vibrating stage.

Sections (4 mm $\times$ 12 mm) of the film were mounted
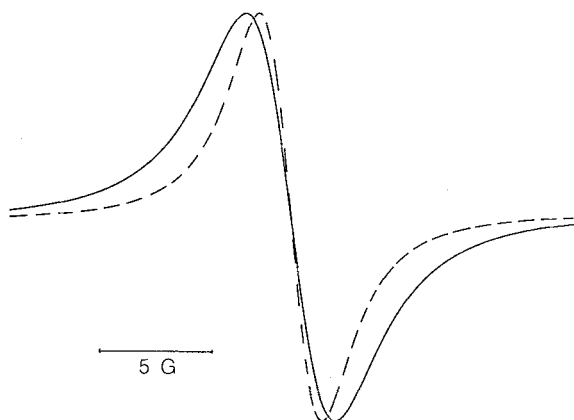
Figure 1. Organic free-radical signal produced by the reaction of Fe(III)-exchanged hectorite with benzene (——) and deuterobenzene (------).

Table 1. Spectral parameters for the free radicals produced at 85°C by the reaction of Fe(III)- and Cu(II)-exchanged hectorites with benzene and deuterobenzene.[1]

	Cu(II)-C_6H_6	Fe(III)-C_6H_6	Fe(III)-C_6D_6
g ∥	2.0024	2.0026	2.0025
g ⊥	2.0024	2.0024	2.0024
ΔH ∥	2.77 G	3.52 G	2.35 G
ΔH ⊥	2.86 G	3.79 G	2.61 G

[1] Reaction time = 1 hr.

on a quartz support with Teflon tape, placed in a 8-mm quartz tube, and attached to a vacuum line. The system was evacuated while at room temperature, and 7 ml of benzene (dried over a molecular sieve) was distilled onto the film. In some experiments small quantities of water were distilled into the sample tube. The sample tubes were then sealed and heated in a tube furnace. For the kinetic studies, the samples were heated in situ using a thin-walled quartz sample holder in conjunction with a Varian 906790-07 temperature controller. This system maintained cavity temperatures to ±1.5°C. The EPR spectrometer employed was described by Eastman *et al.* (1982).

The nitroxide radicals used, ditertiary butyl nitroxide and 4-amino-2,2,6,6-tetramethylpiperiodino-1-oxy, were supplied by Eastman Kodak Company.

The thickness of the clay films was determined by IR interferometry on a Perkin Elmer 580B infrared spectrometer using the fringe-pattern analysis technique often applied to the evaluation of infrared cell path lengths (Gordon and Ford, 1972). Thus, a film sample with a central portion cut out (1 cm²) was placed between two NaCl plates; the plates were brought in contact with the surface of the film, and the fringe pattern between 3000 and 2000 cm⁻¹ was measured. The thickness of the film, Δt, was calculated from the expression

$$\Delta t = (\text{number of fringes})/2(\nu_1 - \nu_2),$$

where ν_1 and ν_2 are, respectively, the wavenumbers at which the scan began and ended. The number of fringes were counted between ν_1 and ν_2.

EXPERIMENTAL RESULTS

EPR spectra

Freshly prepared Cu(II)- and Fe(III)-exchanged hectorite films give EPR spectra similar to those described

in the literature (Rupert, 1973; Pinnavaia *et al.*, 1974). After allowing these films to react with benzene between 65° and 100°C, the resonance due to the metal was reduced and a new single-line resonance was observed. Figure 1 shows the resonance obtained by reacting a Fe(III)-exchanged hectorite with benzene and with deuterobenzene. The reduction in linewidth which occurred when the reaction was carried out with deuterobenzene indicates the organic origin of the resonance and shows that the unpaired electron on the radical was coupled to neighboring protons. As reported by Rupert (1973) the number of organic radicals produced in this reaction is a small percentage of the metal ions that underwent reaction and no longer have a resonance. Table 1 summarizes the spectral parameters which characterize the radical resonance for the Cu(II) and Fe(III) films. In Table 1, ⊥ and ∥ refer to the perpendicular and parallel orientations of the plane of the film with respect to the direction of the applied magnetic field. The temperature dependence of the resonance due to the radical was studied using a powder sample prepared from a film of Fe(III)-exchanged hectorite. Between −105°C and +100°C, the linewidth changed by less than 5% and the lineshape was essentially unchanged.

Lineshape

Lineshape analyses indicate a nearly Lorentzian lineshape for the organic radical resonance in systems prepared from dried benzene. An analysis of the lineshape for the Fe(III)-exchanged hectorite-benzene system (Figure 2) shows the extent of non-Lorentzian character in terms of the deviations of experimentally determined points from the solid line drawn for a pure Lorentzian system. The lineshape analysis was initiated by drawing a straight line from the zero point of the first derivative of the resonance to the first point on the base line where the resonance has zero amplitude. The maximum amplitude of the resonance was measured, and the points at which the resonance was 80%, 60%, 40%, 20%, and 10% of the maximum were marked. Perpendiculars to the straight line were constructed from each of the marked points, and the distance from the zero to each of the perpendiculars was measured. These distances were converted to multiples
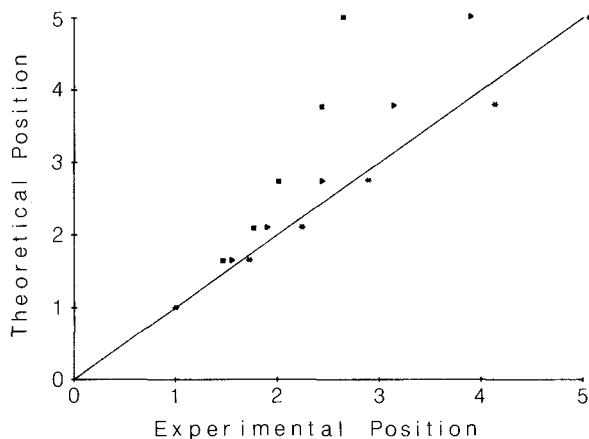
Figure 2.   Lorentzian lineshape analysis for the organic free-radical signal produced by the reaction of Fe(III)-exchanged hectorite with dried benzene (*), benzene with 3 mole % water (▶), and benzene with 6 mole % water (■).

Figure 4.   Linewidth of the organic free radical signal produced by the reaction of Fe(III)-exchanged hectorite with benzene containing controlled amounts of water.

of the linewidth and compared to the values for a Lorentzian lineshape. If the distances, at a given amplitude %, for the experimental and theoretical line were equal, the plotted points lie on the solid line in Figure 2.

The lineshape analyses for Fe(III)-exchanged hectorite-benzene systems to which controlled amount of water were added (Figure 2) show that deviations from Lorentzian character increased with the addition of water. The experimental points for the systems studied are compared in Figure 3 with the solid line drawn for a pure Gaussian lineshape. The plot was prepared using the same approach described for the Lorentzian lineshape. Figure 4 shows the effect of the added water on the linewidth observed for a Fe(III)-exchanged hectorite film mounted with the plane of the film parallel
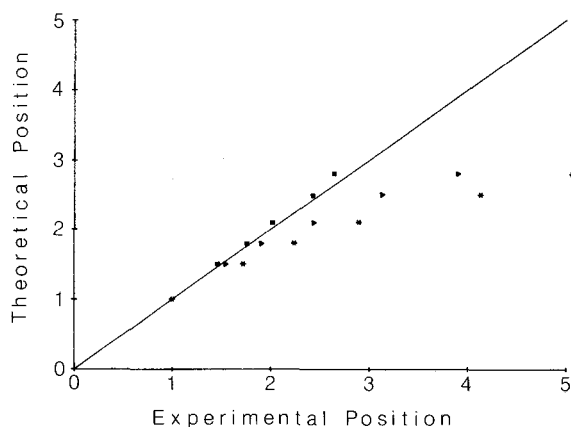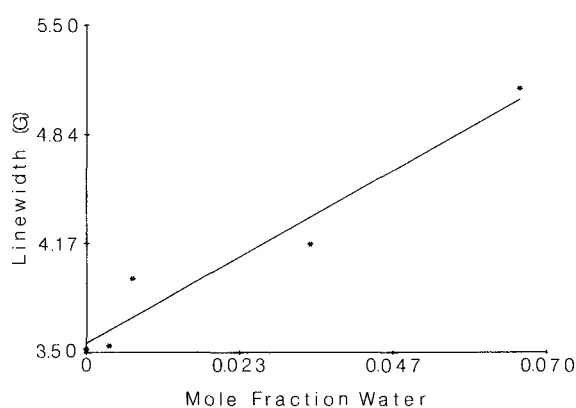

Figure 3.   Gaussian lineshape analysis for the organic free-radical signal produced by the reaction of Fe(III)-exchanged hectorite with dried benzene (*), benzene with 3 mole % water (▶), and benzene with 6 mole % water (■).

to the applied magnetic field. The results in Figures 3 and 4 indicate an increase in inhomogeneous line broadening and Gaussian character when water was added; thus, protons from the water were incorporated into the organic radical and probably reduced the extent of conjugation in that radical. The results described above for the Fe(III)-exchanged hectorite also hold for the Cu(II)-exchanged hectorite; the analyses were carried out on the Fe(III)-exchanged system because spectral interference from unreacted metal was less than for the Cu(II)-exchanged system.

Kinetics

The experimental techniques employed made it possible to measure the time evolution of the free radical signal and the metal ion signal on films as large as 4 mm × 12 mm. These films were ~6.7 × 10⁻² mm in thickness before being placed in benzene; the reaction did not alter their thickness within experimental error. Figure 5 shows the amplitude of the Cu(II) and free radical signals as a function of time for the Cu(II)-exchanged hectorite-benzene reaction. The data for Cu(II) (Figure 5) were collected only after the Cu(II) resonance showed the lineshape characteristic of a film to be fully intercalated by benzene. This precaution was necessary because the intensity of an EPR signal is directly proportional to its amplitude only in the limit of a nonvarying lineshape and linewidth (Wertz and Bolton, 1972).

The features exhibited for the free radical signal in Figure 5 have a rapid initial increase in amplitude (t < 25 min), followed by a plateau (25 < t < 60 min), and then a further increase in amplitude. The measured g values increased slightly with time; the change during the run was 0.0003. The linewidths varied ±10% from the values in Table 1. Figure 5 shows that the increase in the free radical signal was accompanied by
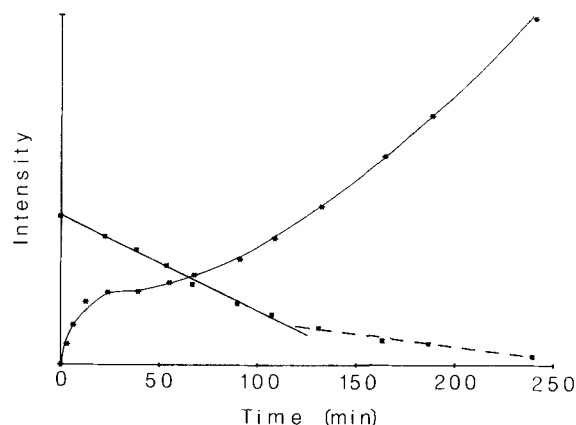
Figure 5. Amplitude of the organic free-radical signal (*) and the Cu(II) signal (■) as a function of time at 86°C for the reaction of benzene with Cu(II)-exchanged hectorite.

Figure 7. A plot of $\ln(S)o/\ln(S)t$ vs. time for the benzene-Cu(II)-hectorite system at 78°C (■) and 93°C (*).

a linear decrease in the Cu(II) signal (t < 125 min). At times >125 min, the Cu(II) signal continued to decrease, but at a slower rate. Results for Fe(III)-exchanged hectorite were similar to those in Figure 5 except that the radical-forming reactions were more rapid, and data on the intensity of the metal ion signal were more difficult to obtain due to the width of the resonance.

The data in Figure 5 show that the Cu(II) concentration can be described initially by zero-order kinetics. The kinetics describing the increase in the free radical concentration are more difficult to discern. The experimental data suggest a reaction in which free radicals are produced at specific sites within the film. The concentration of these sites can be taken as proportional to the difference between the asymptotic value of the amplitude curve (all sites filled) and the experimentally determined value of that curve measured at time t.
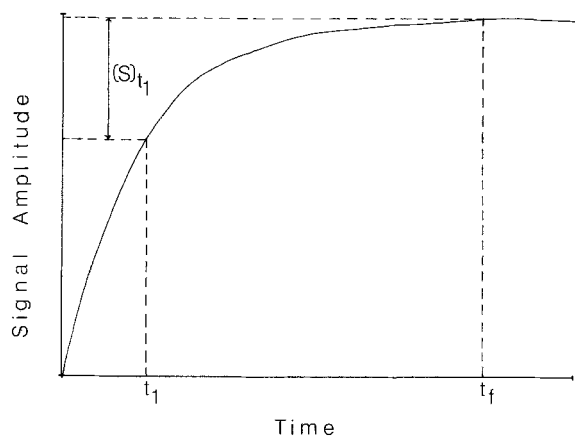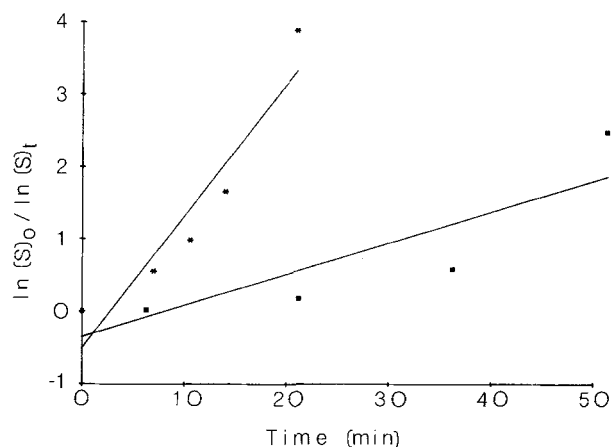
This relationship is shown schematically in Figure 6 where S represents the measured difference.

Figure 7 is a plot of $\ln(S)o/\ln(S)t$ vs. time at 78° and 93°C for the Cu(II)-exchanged hectorite system; similar plots were prepared for the Fe(III)-exchanged hectorite system at temperatures between 65° and 93°C. At temperatures significantly lower than ~65°C the reaction proceeded too slowly, and at temperatures above ~95°C, the possibility of metal ion-clay reactions is a potential problem (McBride, 1982). Films heated in the absence of benzene for several hours at 95°C showed no EPR spectral evidence of metal ion-clay reactions.

Figures 8 and 9 are Arrhenius plots for the zero-order rate constants determined from the Cu(II) and Fe(III) signals and the first-order rate constants deter-

Figure 6. Schematic plot of unreacted site concentration, (S), (in arbitrary units) as a function of time.
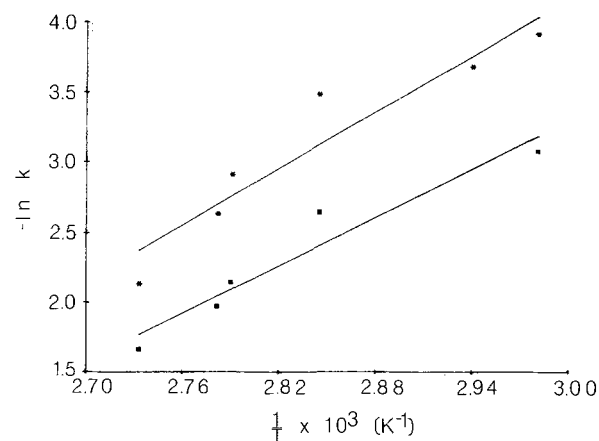

Figure 8. Arrhenius plots for the zero-order rate constant determined from the amplitude of the Cu(II) signal in the reaction of benzene with Cu(II)-exchanged hectorites (*), the first-order rate constant determined from the amplitude of the free radical signal in the reaction of benzene with Cu(II)-exchanged hectorites (■).
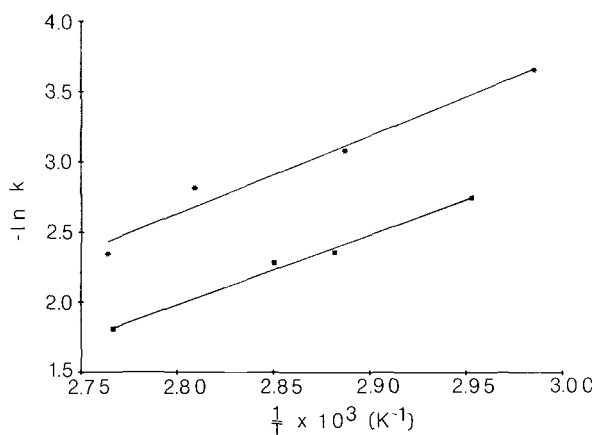
Figure 9. Arrhenius plots for the zero-order rate constant determined from the amplitude of the Fe(III) signal in the reaction of benzene with Fe(III)-exchanged hectorites (*), the first-order rate constant determined from the amplitude of the free radical signal in the reaction of benzene with Fe(III)-exchanged hectorites (■).

mined from the amplitude of the organic free radical signals. The activation energy calculated from the Cu(II) data is 67 ± 11 kJ/mole; that from the corresponding free radical data is 57 ± 9 kJ/mole. The activation energy from the Fe(III) data is 46 ± 6 kJ/mole; that from the corresponding free radical data is 42 ± 3 kJ/mole. The errors were determined from the standard deviation for the slope as calculated by least squares.

Free radical chemistry

It is important to know whether the radicals produced in the two regions of radical growth in Figure 5 are similar and whether they are related to radicals previously studied. The g-value and linewidth data suggest strong similarities. Both the Cu(II)- and Fe(III)-exchanged hectorite films reacted with benzene under the conditions described by Rupert (1973) and Pinnavaia *et al.* (1974) to produce type I and type II complexes. In contrast to these films, films prepared using the sealed-tube technique showed no tendency to change from a burgundy color on exposure to the atmosphere or to water. Examination of the free radical signal after film exposure to the atmosphere showed striking differences. Films heated in benzene for short times (<1 hr) and exposed to the atmosphere gave signals which did not decrease appreciably over a period of several months. Films heated for long periods (>5 hr) gave a signal which decreased more rapidly upon atmospheric exposure of the film than did the signal from type II radicals. All radicals in films prepared by the sealed-tube technique reacted more rapidly with nitroxide radicals than did type II radicals. This reaction was accomplished by allowing nitroxide radicals to adsorb from the vapor phase onto a reacted film. The extent

of reaction was observed as a reduction and eventual elimination of the EPR signals from the radicals in the clay. Thus, Figure 5 shows the evolution of two distinct radicals and/or radical environments.

DISCUSSION

Soma *et al.* (1983) reported resonance Raman studies of the reaction of Cu(II)- and Ru(III)-exchanged montmorillonites with benzene. They proposed the formation of poly(p-phenylene) polymer chains in the interlayer region of the clay with a portion of the aromatic groups of the polymer existing as cations in the absence of water. In their model the number of cations formed is equal to the number of metal ions reduced. Our experiments on the reaction of benzene with transition metal-exchanged hectorites suggest that this reaction formed a variety of radicals in the interlayer region. The nature of the radicals which formed appears to depend both on the availability of water and on the reaction time. The observation of orientation-dependent resonances (Table 1) with virtually no temperature dependence shows that the free radicals which formed are in rigid environments. Hydrogen (and presumably oxygen) from available water molecules were incorporated into the radical products. The observations that the number of free radicals produced was only a small fraction of the metal ions consumed in the reaction and that the color of the films after reaction in the sealed tube was independent of the radical concentration suggest the occurrence of significant non-radical chemistry. The radicals produced may be similar to those in coals; thus, the electron nuclear resonance method used by Schlick *et al.* (1978) to resolve the proton hyperfine interactions in a coal EPR signal is probably applicable here.

The kinetics of the reaction shows that the metal ions within the clay acted independently in the reaction. We postulate that the stable free radicals which formed were located at specific sites in the interlayer. Treating the kinetic data for radical formation according to this postulate yields activation energies which agree within experimental error with those for the disappearance of the metal ions. These sites may have been an environment in which stable radicals were readily formed or ones in which radicals which were present during the reaction were stabilized.

Two significant factors influenced the course of the reaction between benzene and metal ions in the interlayer region of clays. First, the benzene molecules were undoubtedly oriented in the interlayer region as can be inferred from work on the ordering of nitroxide radicals in clays (McBride, 1979). Second, the large electric fields in the interlayer region of clays favored an optimum dispersal of positive charge in this region. Farmer and Russell (1971) discussed the role of charge dispersal in lowering the electrostatic energy of various

interlayer complexes in layered silicates. In the reaction studied here, dispersal was likely accomplished in the very early stages of the reaction by two electron-exchange reactions. The first was between the metal ion and benzene, and the second was between the resulting benzene cation and neutral benzene or other available species. These two factors are closely related because the rates of electron transfer reactions depend on the relative orientations of the reacting species (Marcus, 1965). The radicals which were observed by EPR would have formed subsequent to the initial electron-transfer reactions. The temperature dependence of the EPR signal of the radical products indicates that any exchange reactions involving these products had an activation energy of essentially zero or that exchange reactions were not significant in the final system. This latter conclusion is compatible with the idea of radicals at localized sites in the interlayer.

ACKNOWLEDGMENTS

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Резюме—Реакция бензена с обменивающимися Cu(II) и Fe(III) в фильмах гекторитовой глины исследовалась при помощи электронного парамагнетического резонанса (ЭПР). Эта реакция, когда происходила в герметической трубке при температурах между 60° и 100°C, давала различные продукты с органическими радикалами. Природа этих продуктов зависила от концентрации воды в реакционной среде и времени реакции. Формированию свободных радикалов сопутствовала редукция состояния окисления ионов металла; этот процесс характеризовался зависимостью нулевого порядка от концентрации ионов металла. Энергии активации, определенные на основании постоянных скоростей нулевого порядка, равны 67 ± 11 кДж/моль (Cu(II)) и 46 ± 6 кДж/моль (Fe(III)). Свободные радикалы, формированные первоначально в безводных условиях, вероятно, заполняли места в межслойном пространстве; энергии активации, определенные для этого процесса первого порядка, были равны 57 ± 9 кДж/моль (Cu(II)) и 42 ± 3 кДж/моль (Fe(III)). Эти энергии активации находятся в пределах экспериментальной погрешности значений, определенных при использовании кинетики ионов металла. Сигнал ЭПР, соответствующий органическим радикалам, не зависел от температуры, в связи с чем процессы обмена, включающие свободные органические радикалы не имели, вероятно, значения при определении формы линии ЭПР. [E.G.]

Resümee—Die Reaktion von Benzol mit austauschbaren Cu(II) und Fe(III) in Hektorit-Tonfilmen wurde mittels elektronenparamagnetischer Resonanz (EPR) untersucht. Wenn die Reaktion in einem geschlossenen Meßrohr zwischen 60° und 100°C durchgeführt wurde, führte sie zur Bildung verschiedener organischer Radikale. Die Art dieser Produkte hing von der Wasserkonzentration im Reaktionsmedium und von der Reaktionszeit ab. Die Bildung freier Radikale wurde von einer Verminderung der Oxidationsstufe der Metallionen begleitet. Dieser Prozeß hängt von der Metallionenkonzentration kinetisch von nullter Reaktionsordnung ab. Die Aktivierungsenergien, die aus den Geschwindigkeitskonstanten für nullte Reaktionsordnung bestimmt wurden, waren 67 ± 11 kJ/Mol (Cu(II)) und 46 ± 6 kJ/Mol (Fe(III)). Die freien Radikale, die sich ursprünglich unter wasserfreien Bedingungen bildeten, schienen Plätze im Zwischenschichtbereich zu besetzen. Die Aktivierungsenergien, die für eine Reaktion erster Ordnung bestimmt wurde, betrugen 57 ± 9 kJ/Mol (Cu(II)) und 42 ± 3 kJ/Mol (Fe(III)). Diese Aktivierungsenergien liegen innerhalb des experimentellen Fehlers der aus den Metallionen-kinetischen Werten bestimmten Aktivierungsenergien. Das EPR-Signal, das von organischen Radikalen verursacht wird, zeigte eine geringe Temperaturabhängigkeit; das bedeutet, daß die Austauschprozesse, die organische freie Radikale mit einschließen, wahrscheinlich keine Rolle bei der Bestimmung der EPR-Linienform spielten. [U.W.]

Résumé—La réaction du benzène avec Cu(II) et Fe(III) échangeables dans des films d'argile hectorite a été etudiée par résonnance paramagnétique d'électrons (EPR). Lorsqu'on a provoqué la réaction dans un tube hermétiquement fermé entre 60° et 100°C, elle a produit une variété de produits organiques radicaux. La nature de ces produits était dépendante de la concentration de l'eau dans le milieu de réaction et du temps de réaction. Les radicaux libres étaient accompagnés d'une réduction de l'état d'oxidation des ions métalliques; ce procédé avait une dépendance d'ordre zéro sur la concentration de l'ion métallique. Les énergies d'activation déterminées à partir des constantes de taux d'ordre zéro sont 67 ± 11 kJ/mole (Cu(II)) et 46 ± 6 kJ/mole (Fe(III)). Les radicaux libres initialement formés sous des conditions anhydrées semblaient habiter les sites dans la région interfeuillet; les énergies d'activation déterminées pour ce procédé de premier ordre sont 57 ± 9 kJ/mole (Cu(III)) et 42 ± 3 kJ/mole (Fe(III)). Ces énergies d'activation sont endéans l'erreur expérimentale de celles déterminées à partir des kinétiques d'ion métallique. Le signal EPR dû aux radicaux organiques a montré peu de dépendance sur la température; ainsi, les procédés d'échange impliquant les radicaux organiques libres n'étaient probablement pas importants pour la détermination des formes de droites EPR. [D.J.]