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POLYMERIZATION OF 2,6-DIMETHYLPHENOL ON SMECTITE SURFACES

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Abstract—Air-dried samples of homoionic Na-, Ca-, Al-, and Fe-smectite were equilibrated with 2,6-dimethylphenol vapor for 24 hr. Infrared spectra of the complexes formed indicated that a portion of the sorbed phenol was transformed into quinone-type compounds. Both sorption and transformation were greatly influenced by the nature of the exchangeable cation and followed the order Fe $\gg$ Al > Ca > Na. Changes in the electron spin resonance spectra of the clays following interaction with the phenol followed the same order, indicating that these reactions are enhanced by a transition metal cation, such as Fe^{3+}, on the exchange complex. The reaction products from the clay complexes were extracted with methanol and identified using ultraviolet/visible spectrophotometry, high-pressure liquid chromatography (HPLC), and mass spectrometry. The extracts contained mixtures of products including the parent phenol, di-, tri-, and tetramers of the phenol, as well as quinone and quinone dimers. The identities of these compounds were further confirmed by the coincidence of the retention times of HPLC peaks obtained from extracts of the clays with those from compounds produced by oxidation of 2,6-dimethylphenol with Ag_2O.

Key Words—Adsorption, Electron spin resonance, Phenol, Polymerization, Quinone, Smectite.

INTRODUCTION

A number of reports have shown that clay minerals catalyze reactions of organic compounds; various aspects of clay catalysis have recently been reviewed by Pinnavaia (1983). The reactions often result in transformation and polymerization of the organic compounds. In many reports, the products were inferred from the colored complexes, as in the oxidation of benzene to benzidine blue (Solomon *et al.*, 1968) and of phenols to colored complexes (Thompson and Moll, 1973). The colored products of phenols were shown by gel filtration to be polymers with as high as 3000 molecular weight (Larson and Hufnal, 1980). In a study by Mortland and Halloran (1976), mass spectroscopic (MS) analysis of the reaction products of benzene and phenol with smectite containing transition metal cations on exchange sites showed that the products had higher molecular weights than the parent compounds. Whereas di-, tri-, and tetracondensates of phenols were identified in the phenol system, no rational multiples of benzene were produced in the benzene system.

Isaacson and Sawhney (1983) recently studied sorption of a number of phenols by a smectite with transition metal cations Cu^{2+} and Fe^{3+} and nontransition metal cations, Na^+, Ca^{2+}, and Al^{3+} on the exchange sites. Infrared spectra of the clay-phenol complexes revealed that all of the clays transformed the sorbed phenols; however, the transformation of the phenols occurred to a much greater extent in clays with transition metal cations than in those with nontransition metal cations. 2,6-dimethylphenol appeared to undergo the greatest change. Furthermore, ultraviolet/visible spectrophotometric analysis indicated the formation of quinone-type alteration products.

Free radicals from organic matter contamination of clays, transition metal atoms in clay structure, and the hydroperoxyl radical (·OOH) on clay surfaces have been invoked as catalysts for these reactions (Friedlander *et al.*, 1963; Wauchope and Haque, 1971; Larson and Hufnal, 1980). Mortland and coworkers (Mortland and Pinnavaia, 1971; Fenn *et al.*, 1973; Pinnavaia *et al.*, 1974; McBride *et al.*, 1977) investigated reactions of benzene and other organic molecules, including phenols, with smectite containing transition metal cations on the exchange sites. Their results and those of Rupert (1973) show that, in some instances, these reactions produce free radical cations on the clay surfaces through transfer of unpaired electrons from the aromatic ring to the transition metal cation, leading to polymerization of organic molecules.

In the present investigation, we examined the transformation of 2,6-dimethylphenol by Na-, Ca-, Al-, and Fe-saturated clay using infrared (IR) and electron spin resonance (ESR) analysis of the clay-phenol complexes. The altered phenols were identified by extracting the phenolic material from the clay and analyzing the extract using ultraviolet/visible spectrophotometry (UV/VIS), high-pressure liquid chromatography (HPLC), and mass spectrometry (MS). Further confirmation of the reaction products was obtained by comparison with the products produced by the oxidation of the phenol with Ag_2O.

MATERIALS AND METHODS

Clay preparations

Smectite clay (Wyoming bentonite, API No. 26) was obtained from Ward's Natural Science Establishment, Rochester, New York.

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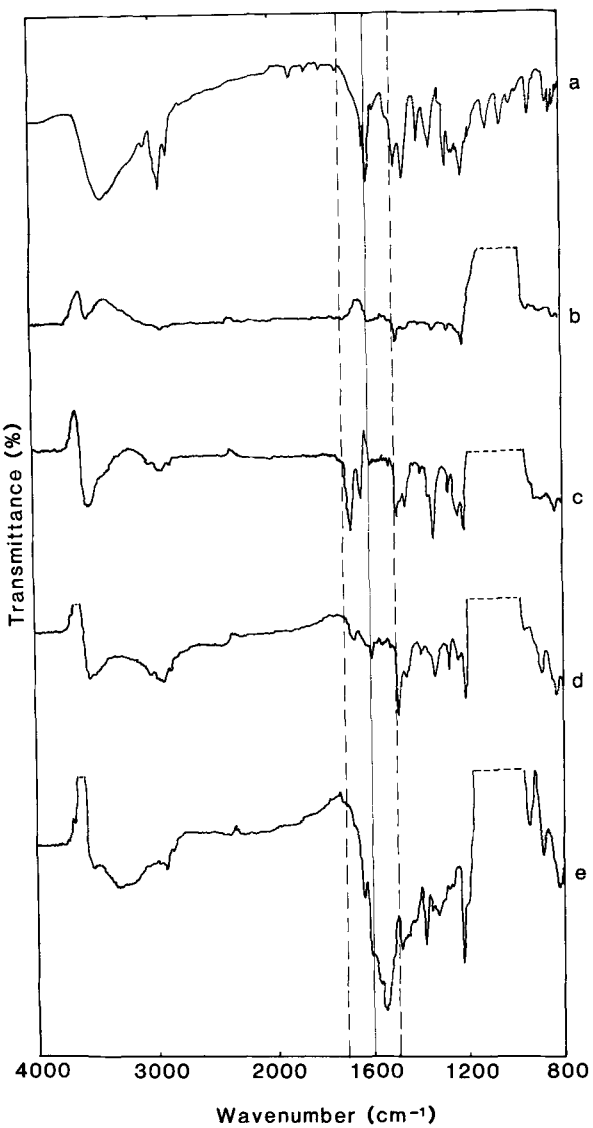


Figure 1. (a) Infrared spectrum of 2,6-dimethylphenol (KBr disc); (b) differential spectra of 2,6-dimethylphenol complexes with Na-smectite, (c) with Ca-smectite, (d) with Al-smectite, and (e) with Fe-smectite. Vertical dotted lines are for reference indicating wavenumbers (cm^{-1}) 1700 and 1500.

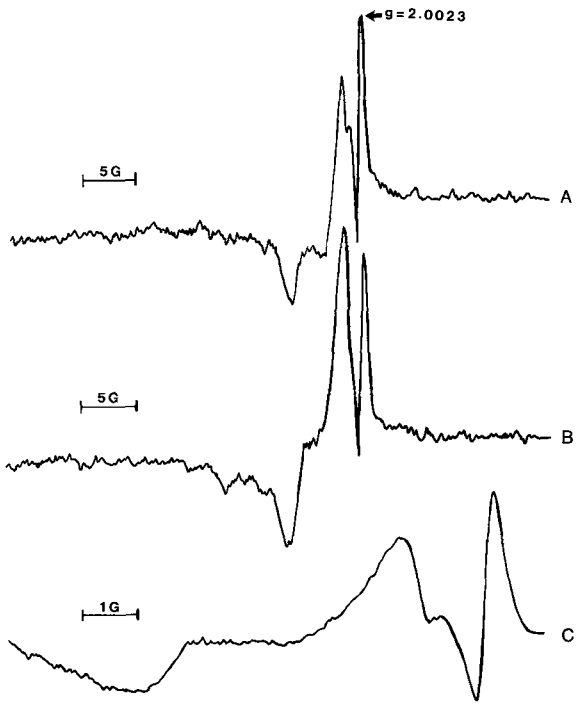


Figure 2. Electron spin resonance spectra of Fe-smectite (A); and Fe-smectite-2,6-dimethylphenol complex (B), both at a ±50 G sweep width; and Fe-smectite-2,6-dimethylphenol complex at ±10 G sweep width (C).

Homoinic clay. Na-, Ca-, Al-, and Fe^{3+}-smectites were prepared by three centrifuge washings of the clay fraction (<2 μm) with 0.1 N chloride solution of the respective cations, followed by three washings with distilled water. The washing procedure may hydrolyze Al and Fe on the clay, but the extent of hydrolysis is uncertain. The colloids were then suspended in distilled water to give about 2% suspension.

Thin clay films. Clay suspensions containing about 38 mg clay were filtered through a 0.45-μm Millipore membrane filter (47-mm diameter) to give clay concentrations of about 2.0 mg/cm^2 on the filter. The films were washed with distilled water and dried at 50°C for about 10 min when they could be easily peeled off.

Clay-phenol complexes. Aliquots of homoionic clays were dried at 110°C and ground to uniform powders. Portions (~2.0 mg) of the powdered clay, thinly spread on a watch glass, were placed in a desiccator with 2,6-dimethylphenol in a crucible at the center of the desiccator and equilibrated for 24 hr at 50°C. The phenol source was then removed, and the clays were placed in a fume hood for an additional 24 hr to remove excess phenol that may have condensed on the clays. Clay films were similarly treated to form complexes.

Instrumental analysis

IR analysis. Differential IR spectra of the thin films were recorded using a Perkin-Elmer 281 Infrared Spectrophotometer (Isaacson and Sawhney, 1983). Differential spectra record changes in the absorption peaks resulting from the treatment when the treated sample is balanced against the control sample in a dual-beam IR instrument.

ESR analysis. Powdered clay samples were packed in 5-mm o.d. Pyrex tubes, and ESR spectra were obtained

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Table 1. Ratios of peak heights of resonance at g = 2.0023 to g = 2.0071 of smectite with different exchange cations and their 2,6-dimethylphenol complexes, taken at 1 G × 1 mW.

Sample[1]	Ratio of peak heights
Fe-clay	1.42
Fe-clay-X	0.89
Al-clay	0.96
Al-clay-X	0.75
Ca-clay	0.77
Ca-clay-X	0.80
Na-clay	0.81
Na-clay-X	0.92

[1] X denotes complex formed on 2,6-dimethylphenol sorption.

at room temperature using a JEOL ME3X spectrometer with automatic field control. The instrument was operated in X band mode at 3350 gauss field strength, a modulation frequency of 100 kHz, and an amplitude of 0.4 or 1 gauss. Microwave power used was 1.0 mW for sweep widths of 100 gauss and 0.1 mW for sweep widths of 20 gauss. To make comparison among different samples, peak heights of the derivative spectra were normalized to the peak height at g ~ 2.0071. The peak at g = 2.0071 was chosen to normalize intensities of all spectra because this peak had high intensity and was not affected by variation in sweep width or modulation power.

UV/VIS and HPLC analysis. The UV/VIS spectra of the methanol extracts of clay-phenol complexes were obtained from 220 nm to 700 nm using a Perkin Elmer/Hitachi 200 spectrophotometer. HPLC analysis of the methanol extract was conducted at 270 nm and at 420 nm using a LDC SPECTRO MONITOR III spectrophotometric detector and CONSTA/METRIC II pump. A 10-μl aliquot of the extract was eluted with 75:25 methanol : water solution through an EXCALIBAR C-18 column, 25 cm × 4.5 mm i.d. at 1-ml/min nominal flow rate.

MS analysis. The methanol extracts were scanned over 122 to 800 mass units (m/e) using a HP 5985 GC/MS system. An aliquot of the extract contained in a capillary tube was placed directly into the MS probe, and the temperature was increased from 30° to 300°C at a rate of 15°C/min. Total ion spectra, followed by mass spectra of the individual peaks were obtained. Mass spectra of the extracts corresponding to individual peaks eluted from the HPLC column were analyzed similarly.

Oxidation products of 2,6-dimethylphenol

To 1.2 g of 2,6-dimethylphenol dissolved in 20 ml of absolute ether, 1 g Na_2SO_4 and 1.24 g Ag_2O were added slowly while the contents were continually stirred. The reaction was allowed to continue for 24 hr. The mixture was then filtered through a sintered glass funnel. The precipitate was washed with 10 ml of ether, and the combined ether fractions were evaporated to a resinous oily material. The precipitate was extracted with acetone on a soxhlet apparatus. The acetone extract was evaporated on a steam bath, yielding a red precipitate. A portion of the red solid was reduced with $NaBH_4$ to give a light yellow precipitate.

Table 2. Ultraviolet/visible absorbance by methanol extracts from complexes of 2,6-dimethylphenol and smectite with different exchange cations.

Exchange cation	269 nm	412 nm
Fe	1.34 (1:10)[1]	.976 (1:10)
Al	.886 (1:10)	.026
Ca	.762 (1:10)	.01
Na	.236 (1:10)	.02

[1] 1:10 refers to 10 times dilution of the extract.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectrum of 2,6-dimethylphenol (KBr disc) and differential spectra of Na-, Ca-, Al-, and Fe-clay complexed with 2,6-dimethylphenol. The absorption bands in the 1670–1630-, 1570–1530-, and 1480–1450-cm^{-1} regions, absent in the phenol spectra, indicate the presence of alteration products of the phenol. These absorption bands indicate that the transformation of the phenol varied with exchange cation following the order Fe > Al > Ca > Na, and may result from quinone-type transformation products (Isaacson and Sawhney, 1983).

Inasmuch as these transformation reactions are generally attributed to radical ion reactions, ESR spectra were obtained of all the clays both before and after reaction with the phenol to understand the role of free radicals. All samples showed similar resonances. The spectra for the Fe-saturated clay with and without the adsorbed phenol (Figure 2) are representative of spectra from all the clay samples. These detailed spectra show a complex radical system with a major resonance of 10-gauss width centered at g = 2.0071 and two small peaks towards lower field and a shoulder towards higher field. It is not clear whether all these peaks derived from a single radical. Another very sharp peak with 0.7 gauss width occurs at g = 2.0023. As noted by Wauchope and Haque (1971), this sharp resonance is easily saturated, and it appeared to be partially saturated even at 0.1-mW microwave power used here in the spectrum taken over a 20-gauss sweep (Figure 2).

Although all samples showed similar resonances, the relative intensities (or heights) of the free radical peaks at g = 2.0023 and g = 2.0071 were altered differently on phenol sorption. The ratios of peak heights at g = 2.0023 and g = 2.0071 (Table 1) increased slightly in the Na-clay and remained essentially the same in Ca-

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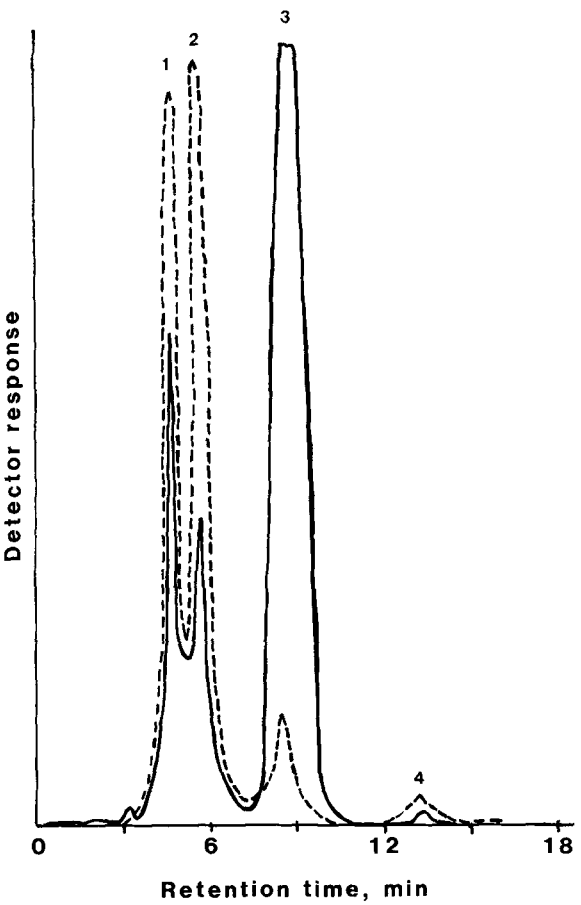


Figure 3. High pressure liquid chromatographic spectra of methanol extract from Fe-smectite-2,6-dimethylphenol complex taken at 270 nm (– – –) and 420 nm (——).

clay. The ratios, however, decreased appreciably in the Al-clay and markedly in the Fe-clay. These changes in the free radical signals follow the reactivity of the clays Fe > Al > Ca > Na-clay as determined by IR analysis.

The more extensive reaction of 2,6-dimethylphenol with the clay having transition metal (Fe^{3+}) cations on

Table 3. Heights of high-pressure liquid chromatographic absorption maxima at 270 nm and 420 nm obtained from methanol extracts of complexes of 2,6-dimethylphenol and smectite with different exchange cations.

Exchange cation	Peak heights (mm)							
	270 nm				420 nm			
	1[1]	2	3	4	1	2	3	4
Fe	211	225	30	9	120	90	220	5
Al	266	57	2	—	165	60	6	—
Ca	254	52	—	—	152	51	8	—
Na	20	66	—	—	36	37	8	—

[1] 1, 2, 3, 4 refer to peaks identified in Figure 3.

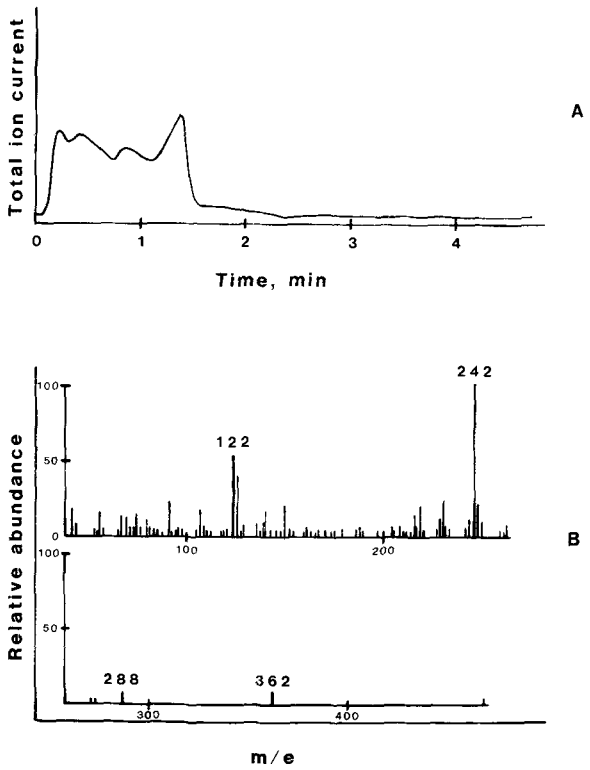


Figure 4. Total-ion mass chromatogram (A) and mass spectrum of methanol extract from Fe-smectite-2,6-dimethylphenol complex taken at 1 min (B), showing the presence of phenolic compounds of m/e = 122, 242, 288, and 363.

the exchange sites than with the non-transition metal cations may involve electron transfer from the aromatic ring to the metal cation as observed by Pinnavaia *et al.* (1974) and Mortland and Halloran (1976). If an organic free radical was formed in this manner, it would be obscured in the clay system because of the sharp resonance at g = 2.0023. This resonance is very sharp and too easily saturated to be that of an organic free radical. As the intensity of this resonance relative to others decreased, not increased, after reaction with 2,6-dimethylphenol, the formation of an organic free radical with the same g value is unlikely. The sharp resonance is possibly due to a stable ·OH free radical (Suflita *et al.*, 1981) which is likely involved in oxidative transformation of the phenol with clays saturated with non-transition metal cations. If this free radical is involved, it must have a catalytic role in the reaction because, despite a high concentration of the phenol, the resonance signal was not eliminated, although it was somewhat reduced in proportion to the extent of the reaction described above.

Identification of reaction products

UV/VIS spectra of methanol extracts of the clay-phenol complexes showed absorption peaks at 269 nm

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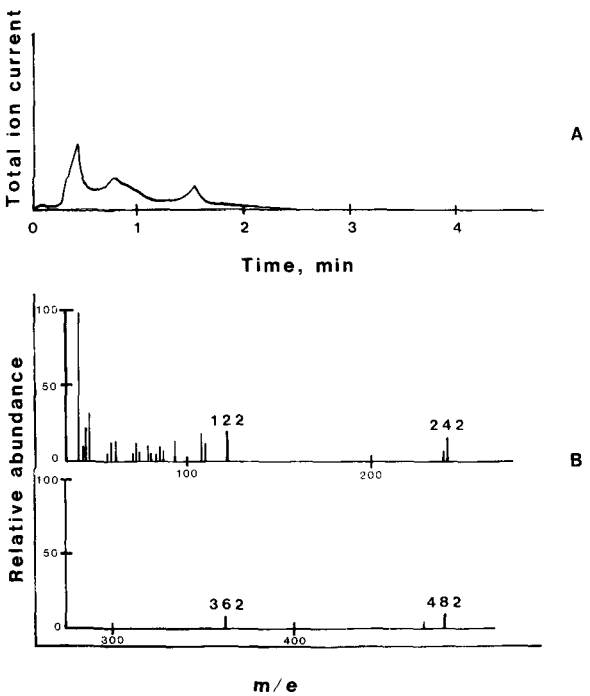


Figure 5. Total-ion mass chromatogram (A) and mass spectrum of methanol extract from Ca-smectite-2,6-dimethylphenol complex taken at 2.57 min (B), showing the presence of phenolic compounds of m/e = 122, 242, 362, and 482.

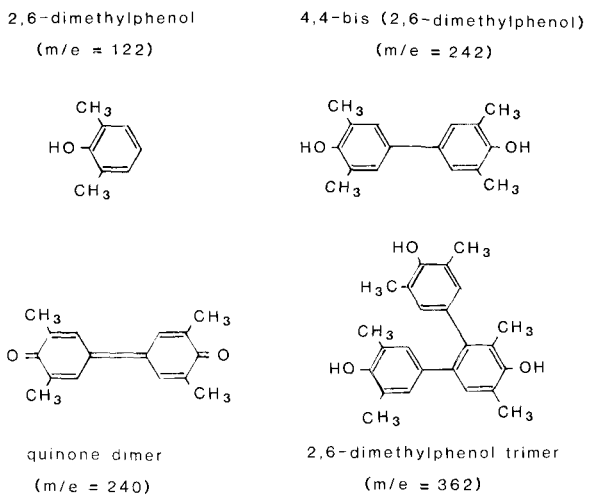


Figure 6. Phenolic compounds identified in methanol extracts of clay complexes by gas chromatography/mass spectrometry.

and 412 nm, attributable, respectively, to phenols and the quinone-type alteration product. Intensities of the peaks at 412 nm (Table 2) show, as in IR and ESR spectra, that the Fe^{3+}-clay is the most reactive not only in the formation of altered products, but also in the sorption of unaltered phenol.

HPLC spectra of the methanol extract from Fe-clay-phenol complex obtained by absorption at 270 nm and 420 nm (Figure 3) show several peaks at both wavelengths, indicating that the phenol is transformed into several different compounds. Similar spectra were obtained for the extracts from phenol complexes with clays saturated with other cations. The relative intensities of the maxima, however, varied with exchange cation. Table 3 contains heights of the four distinct peaks identified on the HPLC chromatograms of the extracts. The heights of peaks 2, 3, and 4, which correspond to the transformation products of the phenol, are largest from the Fe-clay complex followed by the Al-, Ca-, and Na-clay complexes. Thus, whereas the transformation and polymerization (as seen below) of phenols on clay surfaces are enhanced in the presence of a transition metal exchange cation, such as Fe^{3+}, these reactions can occur in the absence of a transition metal cation as also observed by Cloos *et al.* (1979) for anilines.

Mass spectrometric analysis of the methanol extracts of clay-phenol complexes show a number of peaks of m/e higher than the parent phenol, indicating the formation of a number of higher molecular weight compounds. Mass spectra obtained from selected individual peaks revealed the presence of at least four compounds with m/e = 122, 242, 362, and 482 shown in Figures 4 and 5 for the Fe- and Ca-clay complexes. In addition, m/e = 240 was also obtained for both Fe- and Ca-clay complexes when HPLC peak 3 (Figure 3) was eluted and analyzed separately. The phenolic compounds corresponding to 122, 240, 242, and 363 are given in Figure 6. The compound having m/e = 482 corresponds to dimethylphenol tetramer. Small amounts of quinone monomer of m/e = 136 were also identified when peak 3 was analyzed. Mortland and Halloran (1976) also observed mass spectral peaks for di-, tri-, and tetra condensates of phenol on its reaction with Cu^{2+}- and Fe^{3+}-smectite. Mass spectral data reported by these authors indicate the formation of quinones also, although they did not allude to these compounds.

Identity of the HPLC peaks

Each of the four peaks in the HPLC chromatogram (Figure 3) was eluted from the HPLC column with 75% methanol and analyzed by MS. The peaks were not completely resolved and contained some impurities. The major component of peak 1, however, appeared to be the parent phenol (m/e = 122); of peak 2, the phenolic dimer (m/e = 242); of peak 3, the quinone dimer (m/e = 240) and phenolic trimer (m/e = 362); and of peak 4, the phenolic tetramer (m/e = 482).

Identities of the peaks were further established by their coincidence with retention times of the phenolic compounds formed on oxidation of 2,6-dimethylphenol with Ag_2O. The three products (see above) obtained were: (1) ether extract—a viscous oily material;

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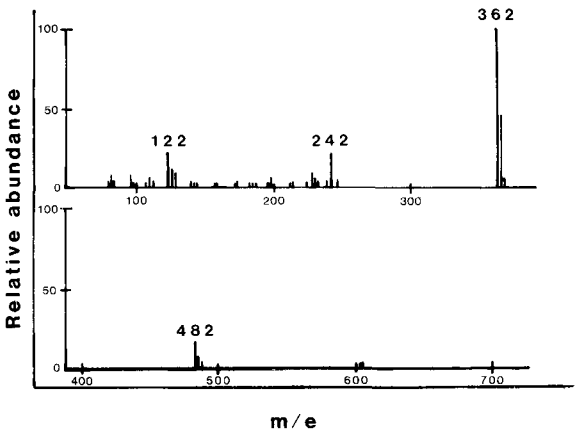


Figure 7. Mass spectrum of the viscous oil obtained on oxidation of 2,6-dimethylphenol by Ag_2O taken at 2.52 min.

(2) acetone extract—a red precipitate; and (3) a portion of red precipitate reduced with $NaBH_4$ to give a light yellow precipitate. Mass spectrometric analysis showed that the viscous liquid was a mixture of phenolic oligomers and the unreacted phenol (Figure 7). The red precipitate was identified as the quinone dimer and the light yellow product as 4,4-bis(2,6-dimethylphenol).

HPLC peak 2 obtained from methanol extract of clay complexes corresponded to the bis-phenol obtained on reduction of the quinone dimer. The retention time of peak 3 was notably different from that of the quinone dimer when the chromatogram was run at 270 nm; but at 420 nm (where quinone absorption is strong), peak 3 increased considerably in height, and its retention time approached the quinone dimer. At 270 nm the peak corresponded to the phenolic trimer of the viscous oily material. Thus, peak 3 appears to be a mixture of quinone dimer and phenolic trimer.

The results of this investigation show that interactions of phenols with clays may be mediated not only by transition metal cations, but also by a stable free radical. The reaction produces a variety of transformation products, including quinone and phenolic oligomers. IR and ESR analysis of the clays, saturated with different cations, both before and after reaction with the phenol showed that the reactions are strongly influenced by the nature of the exchangeable cation. Transition metal cations such as Fe^{3+} on the exchange complex enhance these reactions. Identifications of the reaction products in methanol extracts of the clay complexes, using UV/VIS, HPLC, and MS techniques, further support these conclusions.

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REFERENCES

Cloos, P., Moreale, A., Broers, C., and Badot, C. (1979) Adsorption and oxidation of aniline and p-chloroaniline by montmorillonite: *Clay Miner.* **14,** 307–321.

Fenn, D. B., Mortland, M. M., and Pinnavaia, T. J. (1973) The chemisorption of anisole on Cu-montmorillonite: *Clays & Clay Minerals* **21,** 315–322.

Friedlander, H. Z., Saldick, J., and Frink, C. R. (1963) Electron spin resonance spectra in various clay minerals: *Nature* **199,** 61–62.

Isaacson, P. J. and Sawhney, B. L. (1983) Sorption and transformation of phenols on clay surfaces: effect of exchangeable cations: *Clay Miner.* **18,** (in press).

Larson, R. A. and Hufnal, J. M., Jr. (1980) Oxidative polymerization of dissolved phenols by soluble and insoluble inorganic species: *Limnol. Oceanogr.* **25,** 505–512.

McBride, M. B., Pinnavaia, T. J., and Mortland, M. M. (1977) Adsorption of aromatic molecules by clays in aqueous suspension: *Adv. Environ. Sci. Technol.* **8,** 145–154.

Mortland, M. M. and Halloran, L. J. (1976) Polymerization of aromatic molecules on smectite: *Soil Sci. Soc. Amer. J.* **40,** 367–370.

Mortland, M. M. and Pinnavaia, T. J. (1971) Cu-arene complexes on montmorillonite: *Nature, Phys. Sci.* **229,** 75–77.

Pinnavaia, T. J. (1983) Intercalated clay catalysts: *Science* **220,** 365–371.

Pinnavaia, T. J., Hall, P. L., Cady, S. S., and Mortland, M. M. (1974) Aromatic radical cation formation on the intracrystal surfaces of transition metal layer silicates: *J. Phys. Chem.* **78,** 994–999.

Rupert, J. P. (1973) Electron spin resonance spectra of interlamellar copper(II)-arene complexes on montmorillonite: *J. Phys. Chem.* **77,** 784–790.

Solomon, D. H., Loft, B. C., and Swift, J. D. (1968) Reactions catalysed by minerals IV. The mechanism of the benzidine blue reaction on silicate minerals: *Clay Miner.* **7,** 389–397.

Suflita, J. M., Loll, M. J., Snipes, W. C., and Bollag, J. M. (1981) Electron spin resonance study of free radicals generated by a soil extract: *Soil Sci.* **131,** 145–150.

Thompson, T. D. and Moll, W. F. (1973) Oxidative power of smectites measured by hydroquinone: *Clays & Clay Minerals* **21,** 337–350.

Wauchope, R. D. and Haque, R. (1971) ESR in clay minerals: *Nature, Phys. Sci.* **233,** 141–142.

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Резюме—Образцы однородных Na-, Ca-, Al- и Fe-смектитов, осушенные в воздухе уравновешивались с 2,6-двуметилфениловым паром в течение 24 часов. Инфракрасные спектры формированных комплексов указывали на то, что часть адсорбированного фенола преобразовывалась в соединения типа хинона. Оба процесса, сорбция и трансформация, зависили очень сильно от типа обменного катиона и располагались в порядке Fe ≫ Al > Ca > Na. Изменения спектров электронного спинового резонанса глин после взаимодействия с фенолом следовали в том же самом порядке, указывая на то, что эти реакции усиливались присутствием катиона переходного металла, такого как Fe^{3+}, на обменном комплексе. Продукты реакции из глинистых комплексов извлекались при помощи метаноля и идентифицировались при помощи ультрафиолетовой и видимой спектроскопии, жидкой хроматографии высокого давления (ЖХВД) и масс-спектрометрии. Экстракты содержали смеси продуктов, включая исходный фенол, ди-, три-, и тетрамеры фенола, а также хинон и димеры хинона. Тождественности этих соединений дальше подтверждались совпадением времени удержания пиков ЖХВД, полученных из экстрактов глин, с соответствующими величинами для продуктов окисления 2,6-двуметилфенола Ag_2O. [E.G.]

Resümee—Luftgetrocknete Proben von homoionischen Na-, Ca-, Al-, und Fe-Smektiten wurden mit 2,6-Dimethylphenol-Dampf über einen Zeitraum von 24 Stunden ins Gleichgewicht gebracht. IR-Spektren der gebildeten Komplexe deuteten darauf hin, daß ein Teil des adsorbierten Phenols in Verbindungen des Quinon-Typs umgewandelt wurde. Sowohl die Adsorption als auch die Umwandlung wurden in hohem Maße von der Art der austauschbaren Kationen beeinflußt mit der Reihenfolge Fe ≫ Al > Ca > Na. Veränderungen in den ESR-Spektren der Tone nach der Wechselwirkung mit Phenol folgten der gleichen Reinhenfolge. Dies deutet darauf hin, daß diese Reaktionen durch übergangsmetallkationen, wie Fe^{3+}, am Austauschkomplex behindert werden. Die Reaktionsprodukte aus den Tonkomplexen wurden mit Methanol extrahiert und mit UV/VIS-, MS-Spektren, und HPLC identifiziert. Die Extrakte enthielten Mischungen aus Produkten inklusive dem Ausgangsphenol, Di-, Tri-, und Tetrameren von Phenol, sowie Quinon und Quinondimere. Die Identität dieser Verbindungen wurde zusätzlich bestätigt durch die übereinstimmung der Retentionszeiten der HPLC-Peaks, die von den Extrakten aus den Tonen erhalten wurden, mit denen von Verbindungen, die durch die Oxidation von 2,6-Dimethylphenol mit Ag_2O hergestellt wurden. [U.W.]

Résumé—Des échantillons de smectite-Na, -Ca, -Al, et -Fe, sechés à l'air, ont été équilibrés avec la vapeur diméthylphénol-2,6 pendant 24 heures. Les spectres infrarouges des complexes formés ont indiqué qu'une portion du phénol sorbé avait été transformée en composés du type quinone. A la fois la sorption et la transformation étaient fortement influencées per la nature du cation échangeable, dans l'ordre suivant: Fe ≫ Al > Ca > Na. Les changements dans les spectres de résonnance à spin d'électrons des argiles après l'interaction avec le phénol ont suivi le même ordre, indiquant que ces réactions etaient augmentées par un cation métal de transition, tel que Fe^{3+}, sur le complexe d'échange. Les produits de réaction des complexes argile ont été extraits avec du méthanol, et identifiés utilisant la spectroscopie visible/ultraviolette, la chromatographie liquide à haute pression (HPLC), et la spectroscopie de masse. Les extraits contenaient des mélanges de produits y compris le parent phénol, des di-, tri-, et tétramères du phénol, ainsi que de la quinone et des dimères de la quinone. Les identités de ces composés ont été d'avantage confirmées par la coïncidence des temps de rétention des sommets HPLC obtenus des extraits des argiles avec ceux des composés produits par oxidation du diméthylphénol-2,6 avec Ag_2O. [D.J.]

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