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PYROGALLOL TRANSFORMATIONS AS CATALYZED BY NONTRONITE, BENTONITE, AND KAOLINITE

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Abstract—The catalytic power of Ca-nontronite, Ca-bentonite, and Ca-kaolinite in promoting the abiotic ring cleavage of pyrogallol (1,2,3-trihydroxybenzene) and the associated formation of humic polymers was studied in systems free of microbial activity. The presence of Ca-kaolinite and especially Ca-nontronite in the pyrogallol solutions at pH 6.00 greatly enhanced the absorbance at both 472 and 664 nm of the supernatants. At an initial pH of 6.00 and at the end of a 90-hr reaction period, the amounts of CO_2 released from the ring cleavage of pyrogallol and the yields of the resultant humic polymers formed in the reaction systems followed the same sequence: Ca-nontronite > Ca-kaolinite > Ca-bentonite. The data indicate that the catalytic power of Fe(III) on the edges and in the structure of nontronite was substantially greater than that of Al on the edges of kaolinite and montmorillonite and of a small amount of Fe(III) in the structure of montmorillonite in promoting the reactions. The infrared and electron spin resonance spectra and the solid-state, cross-polarization magic-angle-spinning ^{13}C nuclear magnetic resonance spectra of humic polymers formed in the reaction systems resembled those of natural humic substances.

Key Words—Bentonite, Catalysis, Humic polymers, Infrared spectroscopy, Kaolinite, Nontronite, Nuclear magnetic resonance, Pyrogallol.

INTRODUCTION

Kumada and Kato (1970) reported the catalytic role of montmorillonite and kaolinite in the polymerization of pyrogallol based on the increase in the optical density of pyrogallol solution in the presence of these minerals. By investigating the O_2 uptake and yields of polymers formed and by comparing the infrared spectra of synthesized polymers with those of natural humic substances, Wang *et al.* (1978a, 1978b, 1986) reported that montmorillonite and kaolinite catalyzed the polymerization of phenolic compounds. Furthermore, the relative effectiveness of montmorillonite and kaolinite in the abiotic synthesis of humic acid (HA) from hydroquinone was reported by Shindo and Huang (1985). Recently, Wang and Huang (1986) showed that hydroquinone, in aqueous solution at near-neutral pH (6.5), can be transformed to humic macromolecules, which are deposited in the interlayers of nontronite that are saturated with Ca, the most common exchangeable cation of soils and sediments. They also reported (1987) that Fe(III) on the edges and in the structure of Ca-nontronite promoted the polymerization of hydroquinone.

Despite the significant advances in describing the catalytic role of clays in the transformations of phenolic compounds and the subsequent formation of humic polymers, the surface and structural properties of phyllosilicate clays, which determine their catalytic capabilities, in the transformations of polyphenols are still obscure. Phyllosilicate clays, such as nontronite, montmorillonite, and kaolinite, are the most important clay minerals in soils and sediments (Borchardt, 1977; Dixon, 1977), and polyphenols are commonly present in soils (Flaig *et al.*, 1975; Martin and Haider, 1980). The present study was therefore undertaken to investigate the influence of the structural and surface properties of nontronite, montmorillonite, and kaolinite on the ring cleavage and associated reactions of pyrogallol, a common polyphenol in natural systems.

MATERIALS AND METHODS

Materials

The nontronite (SWa-1, ferruginous smectite, Grant County, Washington) and kaolinite (KGa-1, well crystallized, Washington County, Georgia) were obtained from the Source Clays Repository of The Clay Minerals Society. The bentonite (Upton, Wyoming) was obtained from the Ward's Natural Science Establishment, Rochester, New York. The nontronite, kaolinite, and bentonite were lightly ground and suspended in dilute Na_2CO_3 solution (pH 9.5) at a 1:10 (w/v) ratio (Jackson, 1979). Each mineral suspension was dispersed by ultrasonification at 50 watts for 3 min. The 0.2–2-μm particle size fraction of each mineral sample was collected by the combination of sedimentation and centrifugation methods (Jackson, 1979).

Thirty grams of each mineral sample was washed 5 times with 180 ml of 0.5 M $CaCl_2$ solution, adjusted to pH 6.5 with 0.01 M HCl, washed with water, dialyzed against deionized distilled water until Cl-free,

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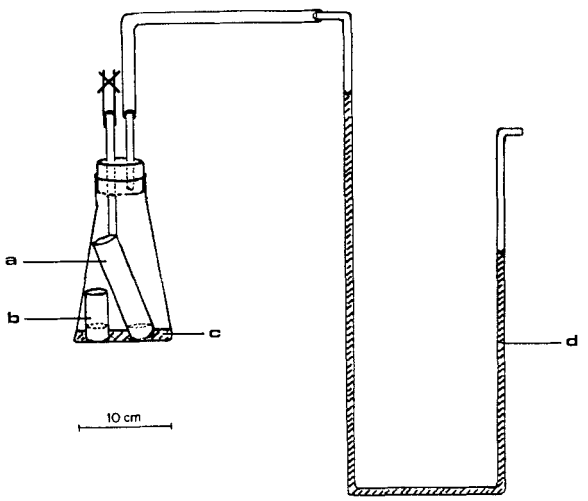


Figure 1. Diagram of apparatus used to determine amount and distribution of CO_2 released in system upon uptake of O_2. (a) 5 ml of 50% KOH, (b) 5 ml of 1 M pyrogallol, (c) 25 ml of aqueous solution which contained 0.02% thimerosal and 1000 mg of Ca-nontronite, Ca-bentonite, or Ca-kaolinite, and (d) Brodie solution.

and then freeze-dried. The freeze-dried samples were examined by X-ray powder diffraction (XRD) and infrared (IR) absorption analyses. The specific surfaces of the freeze-dried mineral samples (0.2–2 μm) were estimated by the ethylene glycol-monoethyl ether retention method (Eltantawy and Arnold, 1973).

Pyrogallol (99.988% purity) was obtained from BDH Chemicals.

Determination of released CO_2

One gram of autoclaved Ca-nontronite, Ca-bentonite, or Ca-kaolinite was suspended in about 20 ml of autoclaved deionized distilled water, which contained 0.02% (w/v) thimerosal (an antiseptic), in a 25-ml plastic vial. The suspension was adjusted to pH 6.00 with 0.01 M HCl. The pH adjustment was carried out for several days until the pH of each mineral suspension was stabilized. An apparatus (Figure 1) was designed to determine the amounts of CO_2 released upon the uptake of O_2 in the systems. All the suspension was transferred to the autoclaved 500-ml wide-mouth Erlenmeyer flask (Figure 1). A small amount of sterilized distilled water (pH 6.00) was used to rinse the plastic vial; the suspension was then transferred to the Erlenmeyer flask. The flask containing the suspension was weighed, and sterilized deionized distilled water (pH 6.00) was added to adjust the volume of the suspension to 25 ml. An autoclaved 50-ml polyethylene centrifuge tube containing 5 ml of 50% KOH was placed in the flask in such a way that it leaned against the wall of the flask. A 20-ml autoclaved polyethylene vial (flat bottom) containing 5 ml of 1 M pyrogallol (pH 6.00) was similarly placed in the flask. Finally, each flask was capped tightly with a rubber stopper, which was connected by Tygon tubing to a manometer containing the same manometer fluid, Brodie solution (23 g of NaCl and 5 g of sodium choleate dissolved in 500 ml of water), as that used in a Gilson Respirometer (Umbreit *et al.*, 1964). Each flask was shaken slowly to mix the pyrogallol with the mineral suspension and then gently agitated in a water bath at 25°C for 90 hr under air. All the experiments including the controls were duplicated. At the end of the reaction period, the end of the Tygon tubing that was connected to the manometer was closed with a clamp. Each flask was disconnected from the manometer and flushed with N_2 to sweep the gases that were present into a test tube containing 20 ml of 0.15 M KOH to absorb the CO_2 present. The amounts of the CO_2 absorbed by the KOH solution after flushing N_2 through the system and by the KOH solution that was placed in a flask to absorb the released CO_2 during the reaction period were determined by titration (Tiessen *et al.*, 1981).

Examination of microbial activity

Small amounts of individual suspensions, which contained pyrogallol, thimerosal, autoclaved mineral, and sterilized water in the experiment as described above, were inoculated to agar plates of GYEN (Germida and Casida, 1980), AIA, and Czapek-Dox (Olson *et al.*, 1984), both at the beginning and at the end of the 90-hr reaction period to check for microbial growth in the systems. All inoculated plates were incubated at 25°C for 15 days.

Formation of humic polymers

At the end of the 90-hr reaction period, the pHs of the suspensions were measured. The suspensions were then centrifuged at 7800 *g* for 10 min to separate the supernatants from the sediments. The absorbances of the supernatants at 472 and 664 nm were determined. The sediments were washed repeatedly with deionized distilled water at 1:10 (w/v) ratio to remove water-soluble humic polymers until the extracts were clear. The water extracts and the supernatants described above were combined. The combined solutions were acidified to pH 1.0 with 6 M HCl, according to the method recommended by the International Humic Substances Society (Aiken, 1985; Hayes, 1985; Leenheer, 1985; Swift, 1985). The acidified solution was equilibrated at room temperature for 24 hr and then centrifuged at 2000 *g* to separate the HA fraction (precipitate) from the FA fraction (supernatant). The precipitated HA fractions were suspended in a 0.1 M HCl:0.3 M HF solution in plastic containers and shaken overnight at room temperature. The suspensions were centrifuged at 2000 *g* to precipitate the HA fractions. The HA fractions were suspended in deionized distilled water and transferred to dialysis tubes with a molecular-weight

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Table 1. Examination of growth of microorganisms in reaction systems during 15-day incubation period.

Catalyst	Pyrogallol	Thimerosal[1]	Inoculum[2]	Growth of microorganisms in various media[3] GYEN	AIA	Czapek-Dox
Nontronite	P[4]	P	A[5]	—[6]	—	—
Bentonite	P	P	A	—	—	—
Kaolinite	P	P	A	—	—	—
No catalyst	P	P	A	—	—	—
No catalyst	A	A	P	+[7]	+	+

[1] This antiseptic does not affect the oxidation process of phenolic compounds (Wang *et al.*, 1983).

[2] Centrifugate obtained at 1000 g from a soil-water suspension (soil : water = 1:10) was used as the inoculum. Fresh soil was taken from the Ap horizon of an Orthic Dark Brown Soil (Vertic Argiboroll), a member of the Sutherland Soil Association (106°14′W, 52°18′N).

[3] GYEN = agar plate made of glucose, yeast extract, nutrient broth, and agar for incubation of bacteria (Germida and Casida, 1980); AIA = actinomycetes isolation agar for incubation of actinomycetes (Olson *et al.*, 1984); Czapek-Dox = agar plate for incubation of fungi (Olson *et al.*, 1984).

[4] In presence.

[5] In absence.

[6] No growth.

[7] Growth detected.

Table 2. Release of carbon dioxide in mineral-pyrogallol systems at end of 90-hr reaction period.

Mineral[1]	CO_2 release (μmole)
Nontronite	263.1 ± 0.4
Bentonite	92 ± 2
Kaolinite	135 ± 2
No catalyst	54 ± 2

[1] 1000 mg of Ca-nontronite, Ca-bentonite, or Ca-kaolinite (0.2–2 μm) was suspended in 30 ml of sterilized deionized distilled water (pH 6.00), which contained 0.02% (w/v) thimerosal (an antiseptic) and 5 mmole of pyrogallol.

cutoff of 1000 to separate the fractions of HA (MW > 1000). The supernatants containing the FA fractions were passed through XAD-8 resin to adsorb FA, and the effluents were discarded. The FA adsorbed by XAD-8 was eluted with 0.1 M NaOH, the NaOH eluates were immediately acidified with 6 M HCl to pH 1.0, and HF was added to each eluate to make 0.3 M HF. The solutions were stirred for at least 48 hr in a fumehood. The solutions were passed through XAD-8 resin to adsorb FA, and the effluents were discarded. The FA adsorbed by XAD-8 was eluted with 0.1 M NaOH and the NaOH eluates were collected. The eluates were then immediately passed through H^+-saturated cation-exchange resin (Bio-Rad AG MP-50) to convert all FA to H^+-saturated FA. The H^+-saturated FA solutions were concentrated by using a rotary evaporator to an adequate volume. The concentrated FA solutions were transferred to dialysis tubes with a molecular-weight cutoff of 1000 to separate the fractions of FA (MW > 1000). The equilibrated solutions outside the dialysis tubes were then concentrated by using a rotary evaporator to collect the fraction of FA (MW < 1000). All HA and FA samples were freeze-dried and their yields determined.

Characterization of humic polymers

To synthesize the large amount of polymers required for electron spin resonance (ESR), IR, and solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopies, the same procedure as described above was used, except that the amounts of pyrogallol and the minerals were increased accordingly. The IR spectra of the freeze-dried HA and FA samples were obtained from KBr discs (each disc contained 1 mg sample and 300 mg KBr). The spectra were recorded in the 300–4000-cm^{-1} range on a Perkin-Elmer 983 IR spectrophotometer. The ESR spectra of freeze-dried powders of HA and FA were obtained with a Bruker B-ER418S spectrometer operating at 100 kHz and a nominal frequency of 9620 MHz at room temperature. The freeze-dried HA samples formed in the nontronite-pyrogallol and pyrogallol systems were subjected to solid-state ^{13}C NMR analysis with cross polarization and magic-angle spinning (CPMAS), proton decoupling, using a spectrometer frequency of 37.735000 MHz and an acquisition time of 51.25 ms.

Organic-C determination of mineral-humic polymer complexes

After extraction of the mineral-humic polymer complexes with water as described above, the sediments were freeze-dried and the organic-C content determined (Tiessen *et al.*, 1981). The organic-C contents of the untreated nontronite, bentonite, and kaolinite were also determined.

RESULTS AND DISCUSSION

Microbial growth was not evident in the systems studied (Table 1), indicating that all reactions were abiotic in nature. At the end of a 90-hr reaction period, the sequence for the amounts of CO_2 released from the reaction systems was: nontronite-pyrogallol > kaolinite-pyrogallol > bentonite-pyrogallol > pyrogallol (Table 2). The data on CO_2 release indicate that bentonite and especially nontronite and kaolinite significantly promoted the ring cleavage of pyrogallol (Table 2).

At the end of the reaction period, the pH of the suspensions, which were initially adjusted to pH 6.00, decreased substantially (Table 3). This decrease is attributable to the generation of protons during the polymerization of pyrogallol and polycondensation of its fragments either in the presence or in the absence of minerals. The final pH of the suspension in the nontronite-pyrogallol system was much lower than that in the pyrogallol system (Table 3), apparently because of a higher degree of humification of pyrogallol in the

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Table 3. Final pH of suspension, absorbance of supernatants, and yield of humic polymers for mineral-pyrogallol systems.

Mineral	Final pH	Absorbance		Supernatant			
		472 nm	664 nm	Humic acid (MW > 1000) (mg)	Fulvic acid (MW > 1000) (mg)	Humic polymers adsorbed in sediment[1] (mg)	Total humic polymers (mg)
Nontronite	3.57 ± 0.01	6.58 ± 0.05	3.42 ± 0.05	8.1 ± 0.2	68.5 ± 0.4	4.9 ± 0.4	82 ± 1
Bentonite	4.10 ± 0.01	0.59 ± 0.01	0.08 ± 0.00	2.6 ± 0.0	21.9 ± 0.2	2.5 ± 0.2	27.0 ± 0.4
Kaolinite	4.28 ± 0.02	1.34 ± 0.04	0.25 ± 0.02	3.8 ± 0.1	32.2 ± 0.2	3.9 ± 0.3	39.9 ± 0.6
No catalyst	4.9 ± 0.1	0.62 ± 0.04	0.10 ± 0.01	2.8 ± 0.0	20.0 ± 0.2	N.A.[2]	22.8 ± 0.2

[1] Weights of humic polymer-mineral complexes formed in the nontronite-, bentonite-, and kaolinite-pyrogallol systems after extraction were 1009 ± 1, 729 ± 1, and 776 ± 1 mg, respectively; organic-C contents of the complexes were 0.55 ± 0.01, 0.24 ± 0.01, and 0.38 ± 0.02%, respectively. Organic-C contents of nontronite, bentonite, and kaolinite were 0.31 ± 0.01, 0.05 ± 0.00 and 0.10 ± 0.00%, respectively. Organic-C contents of the minerals were subtracted, then amounts of humic polymers in the sediments were estimated on the basis of the previous finding that synthesized humic polymers contain about 50% organic C (Wang *et al.*, 1983).

[2] Not applicable.

presence of nontronite. A decrease in the final pH in the kaolinite-pyrogallol and bentonite-pyrogallol systems was observed, but it was not as substantial as in the nontronite-pyrogallol system (Table 3).

The presence of kaolinite and especially nontronite in the pyrogallol solutions greatly enhanced the absorbance of the supernatants at both 472 and 664 nm (Table 3). The absorbances of the supernatants at both 472 and 664 nm in the reaction systems studied decreased in the order: nontronite-pyrogallol ≫ kaolinite-pyrogallol > pyrogallol ≅ bentonite-pyrogallol (Table 3). The absorbances of the supernatants at 472 nm in the nontronite-pyrogallol and kaolinite-pyrogallol systems were 10.6 and 2.2 times higher, respectively, than that in the pyrogallol system, whereas the absorbances at 664 nm in the same systems were 34.2 and 2.5 times higher, respectively (Table 3). The total yields of humic polymers formed in the reaction systems decreased in the order: nontronite-pyrogallol > kaolinite-pyrogallol > bentonite-pyrogallol > pyrogallol (Table 3). The total yields of humic polymers formed in the nontronite-pyrogallol, kaolinite-pyrogallol, and bentonite-pyrogallol systems were 3.6, 1.8, and 1.2 times higher, respectively, than of those formed in the pyrogallol system (Table 3).

The phyllosilicates used in this experiment had the same particle size range (0.2–2 μm); however, their specific surface areas differed greatly. The surface areas of nontronite, bentonite, and kaolinite were 855 ± 8, 477.7 ± 0.3, and 42 ± 2 m^2/g, respectively. The specific surface of the nontronite was 1.8 times greater than that of the bentonite, whereas the specific surface of the bentonite was 11.4 times greater than that of the kaolinite. Nevertheless, the amounts of CO_2 released from the systems (Table 2), the absorbances of the supernatants, and the yields of humic polymers formed in these three systems (Table 3) did not differ accordingly, indicating that the nature of surfaces and atomic bonding and crystal structure of aluminosilicates were far more important than the total surface areas. The nontronite, bentonite, and kaolinite differed substantially in their ability to catalyze the release of CO_2 as a result of ring cleavage of pyrogallol, the polymerization of pyrogallol, and the polycondensation of its fragments. Silicate minerals can tenaciously adsorb O_2 (Solomon and Hawthorne, 1983). This O_2 is chemisorbed and, thus, a strong oxidant. Therefore, the O_2 molecules adsorbed and polarized by exposed structural cations on the edge sites of the minerals apparently played an important role in the ring cleavage of pyrogallol and the related reactions in the systems. The Fe content in bentonite (1.29% Fe) was much lower than that in nontronite (9.35% Fe). Although bentonite contained more Fe than kaolinite (0.11% Fe), the former contained much less Al (6.51%) than the latter (24.80%). Therefore, bentonite was not even as reactive as kaolinite in promoting the oxidation of pyrogallol. The data indicate that the catalytic power of Fe(III) on the edges and in the structure of nontronite was much greater than that of Al on the edges of kaolinite and montmorillonite and of a small amount of Fe(III) in the structure of montmorillonite in promoting the ring cleavage of pyrogallol and the associated reactions.

The IR spectra of HA (MW > 1000), FA (MW > 1000), and FA (MW < 1000) of all reaction systems were similar. Therefore, only the IR spectra of HA (MW > 1000), FA (MW > 1000), and FA (MW < 1000) formed in the nontronite-pyrogallol system are shown (Figure 2). The IR spectrum of FA (MW < 1000) was similar to that of unpolymerized pyrogallol (Figure 2), but this FA (MW < 1000) fraction displayed an IR absorption band at about 1715 cm^{-1}, which may be attributable to carboxyl groups. The IR spectra of FA (MW > 1000) and HA (MW > 1000) were entirely different from that of unpolymerized pyrogallol (Figure 2) and very similar to those of natural humic substances (Schnitzer, 1977; Hatcher *et al.*, 1980; Schnitzer and Ghosh, 1982). Absorption bands were observed at 3000–3400 cm^{-1} (hydroxyl groups of varying degrees of H bonding), 2800–2900 cm^{-1} (the stretching vibra-

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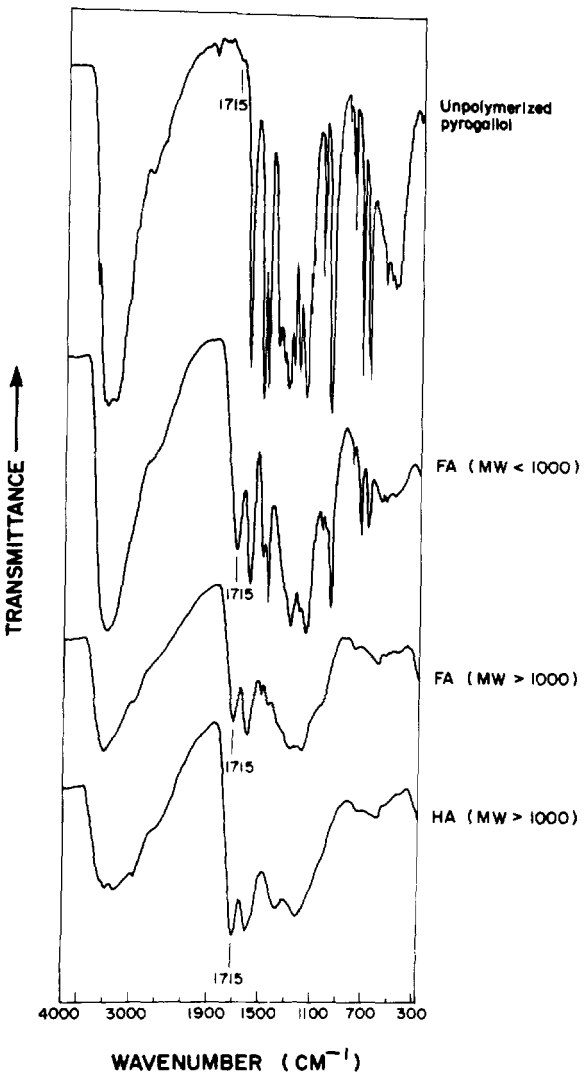


Figure 2. Infrared spectra of unpolymerized pyrogallol and humic polymers formed in Ca-nontronite-pyrogallol system.

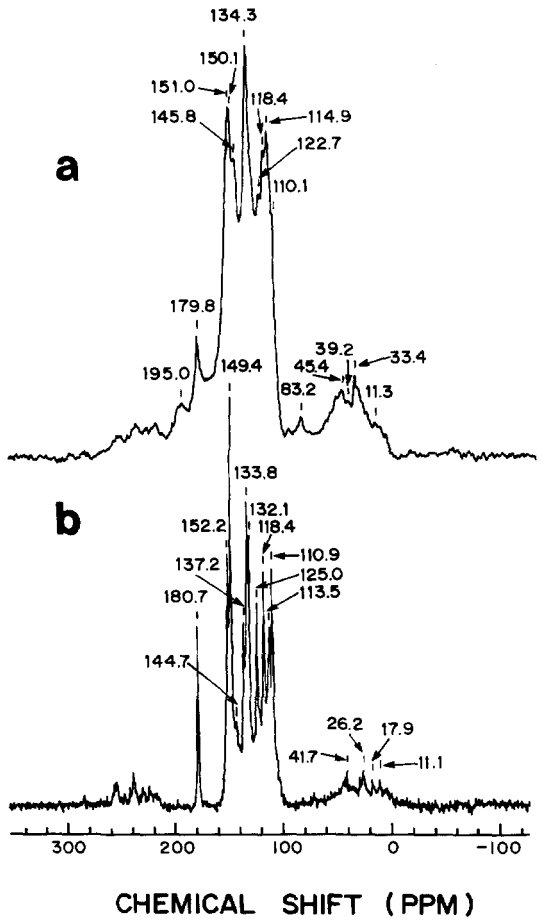


Figure 3. Solid-state, cross-polarization magic-angle-spinning ^{13}C nuclear magnetic resonance spectra of humic acid (MW > 1000) formed in: (a) Ca-nontronite-pyrogallol and (b) pyrogallol systems, with proton decoupling, spectrometer frequency of 37.735000 MHz, and acquisition time of 51.25 ms. The chemical shifts are relative to tetramethylsilane (TMS) using hexamethyl benzene (HMB) as a secondary standard (methyl signal at 17.35 ppm).

tions of aliphatic CH, CH_2, and CH_3 groups), 1715 cm^{-1} (carboxyl and aldehydic and ketonic carbonyl), 1610 cm^{-1} (C=C stretching vibrations in aliphatic and aromatic compounds), 1380 cm^{-1} (symmetric bending or deformation vibration of CH_3, δ_s-CH_3; salts of carboxylic acid, and/or aliphatic CH vibration of esters, ethers, and phenols), 1230 cm^{-1} (C–O stretching vibration of esters, ethers, and phenols), and 1030 cm^{-1} (ethers).

No significant differences were noted in the ESR spectra of the FA (MW > 1000) and HA (MW > 1000) synthesized in the reaction systems. All the spectra were single lines, devoid of hyperfine splitting. The g-values and breadths (G) between two extreme peaks on the derivative curves of FA and HA (MW > 1000) formed in the reaction systems studied were 2.0032–2.0038 and 3.2–3.5, respectively. The ESR spectra were similar to those of natural FAs and HAs (Schnitzer, 1977; Senesi and Schnitzer, 1977; Schnitzer and Lévesque, 1979).

The solid-state CPMAS ^{13}C NMR spectrum of pyrogallol-derived HA formed by the catalysis of nontronite (Figure 3a) resembled that of natural HA (Hatcher *et al.*, 1981; Schnitzer and Preston, 1983; Schnitzer and Chan, 1986). The spectrum (Figure 3a) shows the presence of carbons in aldehydes and ketones (195.0 ppm), carboxyl carbon in carboxyl and ester groups (179.8 ppm), aromatic carbons and olefinic carbons (151.0–110.1 ppm), CO carbons in alcohols, esters, ethers, carbohydrates (83.2 ppm), and alkyl carbons (45.5–11.3 ppm) in the HA formed in the

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nontronite-pyrogallol system. The NMR spectrum of HA formed in the pyrogallol system (Figure 3b) shows the presence of carboxyl carbon in carboxyl and ester groups (180.7 ppm), aromatic carbons and olefinic carbons (152.2–110.9 ppm), and trace amounts of alkyl carbons (41.7–11.1 ppm). The NMR spectra (Figure 3) corroborate the IR evidence (Figure 2) and the CO_2-release data (Table 2), revealing the catalytic power of nontronite in the ring cleavage of pyrogallol and the concomitant formation of aliphatic fragments.

Oxidation of pyrogallol observed in the present study appeared to be promoted by the following processes: (1) electron transfer with Fe^{3+} or other variable-valence transition metal ions on the edges or in the structure (Solomon, 1968), (2) strong oxidation power of chemisorbed O_2 on silicate minerals (Solomon and Hawthorne, 1983), and (3) complexation by Al^{3+} through displacing protons from phenolic groups to delocalize electrons from phenolic O atoms into π-orbital systems (Eaton, 1964). Electrons seem to be able to diffuse or tunnel to octahedral sites from layer edges or basal surfaces (Tennakoon *et al.,* 1974). Spectroscopic evidence has demonstrated that Al^{3+} increases the rate of oxidation of a phenolic compound, catechol, by O_2 (McBride *et al.,* 1988). Our data indicate that oxidation of pyrogallol resulted in the formation of the semiquinone radical, ring cleavage, polymerization of pyrogallol, polycondensation of its fragments, and the subsequent release of protons. Under an N_2 atmosphere, the amounts of CO_2 released and humic polymers formed drastically decreased (authors' unpublished work).

In summary, the sequence of the catalytic power that promoted the oxidation of pyrogallol and the associated formation of humic polymers is: nontronite > kaolinite > bentonite (Tables 2 and 3). The data indicate that the catalytic power of Fe(III) on the edges and in the structure of nontronite is substantially greater than that of Al on the edges of kaolinite and montmorillonite and of a small amount of Fe(III) in the structure of montmorillonite in promoting the reactions. The ring cleavage of pyrogallol and the release of CO_2 as catalyzed by kaolinite, montmorillonite, and especially nontronite (Table 2, Figures 2 and 3) can be a pathway of C turnover. Furthermore, the abiotic ring cleavage of polyphenols as catalyzed by soil inorganic components, such as nontronite, kaolinite, and montmorillonite (Table 2, Figures 2 and 3), merits attention in understanding the origin of the aliphaticity of humic substances in soils (Schnitzer, 1977; Preston *et al.,* 1982; Wilson and Goh, 1977; Hatcher *et al.,* 1981).

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