

¹³C NMR Study of Co-Contamination of Clays with Carbon Tetrachloride and Benzene

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Both solid-sample and liquid-sample ¹³C NMR experiments have been carried out to identify the species produced by the reaction between carbon tetrachloride and benzene when adsorbed on clays, kaolinite, and montmorillonite. Liquid-sample ¹³C and ¹H NMR spectra of perdeuteriobenzene extracts confirm the identities determined by solid-sample ¹³C NMR and provide quantitative measures of the amounts of the products identified—benzoic acid, benzophenone, and triphenylmethyl carbocation (or triphenylmethanol, the product of hydrolysis of the carbocation). Montmorillonites are much more effective than kaolinite in promoting this chemistry, and their reactivity is dramatically enhanced by Zn²⁺ exchange of the montmorillonite. The results can be explained by invoking reaction mechanisms of the Friedel–Crafts type. ²⁷Al MAS NMR spectra were obtained to provide structural information on the clays.

Introduction

The release and dispersion of organic contaminants in soil have become a matter of increasing concern with respect to environmental and health issues (1). Some chlorinated organics, such as carbon tetrachloride, are known to cause ozone depletion and to affect the human central nervous system, while aromatic compounds, e.g., benzene and its derivatives, can result in blood dyscrasias, including lymphopenia, thrombopenia, and pancytopenia; a decrease in all types of circulating blood cells; and the development of aplastic anemia and leukemia (2). Therefore, it is important to understand the detailed chemical/physical behaviors of and complex interactions among such organic pollutants in soil. Knowledge of such fundamental chemical/physical detail is a prerequisite to the formulation of reliable models of contaminant behavior for optimizing technology to minimize these contamination problems.

Recently, we reported (3, 4) a “ship-in-a-bottle” synthesis of the triphenylmethyl cation, (C₆H₅)₃C⁺, from carbon tetrachloride and benzene inside the supercage of zeolite HY. In view of the well-known chemical similarities and properties of certain clays and zeolites, this provocative result prompted our interest in exploring analogous chemistry in clay systems. Clay minerals are primary soil components with largely aluminosilicate structures that have large surface areas and strong adsorbing properties (5), which markedly affect the behaviors of contaminants in soil and groundwater systems (6). Along with cation exchange capability, the surface acidity of a clay can be one of its most prominent and remarkable features; the acidic character of a clay can

sometimes make it the equal of solid acids like zeolites or silica-aluminas. Benesi (7–9) measured the Hammett acidity function H_0 for a number of clays; these H_0 values range from +1.5 to –8.2 (in comparison to $H_0 = -12$ for 100% sulfuric acid and $H_0 = 5$ for pure acetic acid). Therefore, one can expect that certain chemical transformations might occur in/on clays that are similar to what are observed in zeolite systems. Thus, it is of interest to examine what happens when carbon tetrachloride and benzene are “co-contaminants” in a clay. This kind of information would be useful in a long-term view for understanding chemical transformations of contaminants in soil at contaminated sites. Data on these phenomena could also be useful for designing predictive models and/or effective pollution remediation strategies.

Solid-state NMR results, based on ¹³C detection and line narrowing by magic angle spinning (MAS) and high-power ¹H decoupling (10), have been reported on a variety of organic soil components such as humic samples (11–13). Apparently, there have been few NMR studies concerned directly with elucidating the interactions of organic compounds with soil or its major components. Most of the few such reports have concentrated on soil–pesticide interactions (14), although some work has addressed other species, e.g., benzene (15), dimethylsulfoxide (16), trichloroethylene (17), and amine or alkyl ammonium ion systems (18, 19). To the best of our knowledge, studying chemical transformations in co-contamination systems on clays by solid-state ¹³C NMR or any other technique has not previously been reported, although clays have been widely used as catalysts in organic syntheses (20). In this paper, we report ¹³C NMR results (from both solid and liquid samples) on the co-contamination of clays with carbon tetrachloride and benzene.

Experimental Section

Materials. Three clay samples were used in this study. Camontmorillonite and kaolinite were obtained from the Source Clay Minerals Repository, University of Missouri at Columbia. K-10 montmorillonite was purchased from Aldrich. ¹³C-labeled carbon tetrachloride was obtained from Cambridge Isotopes Laboratory and was used without further purification. Benzene (from Aldrich) was dried by refluxing with calcium hydride and distilled.

NMR Spectroscopy. All solid-state ¹³C MAS NMR spectra shown were obtained at 22.71 MHz at room temperature on a Chemagnetics M-90S spectrometer. Kel-F rotors (2.4 cm³ sample volume) were used at a spinning speed of about 2.5 kHz. For cross-polarization (CP) experiments, the following experimental conditions were employed: ¹H decoupling, 45 kHz; CP contact time, 2 ms; delay between scans, 1 s. For direct polarization (DP) experiments (no cross polarization): a 90° pulse length of 5.5 μs, 45 kHz ¹H decoupling; repetition time, 5 s. ¹³C spectra were externally referenced to liquid tetramethylsilane (TMS) based on substitution of the secondary reference, solid hexamethylbenzene (peaks at 16.9 and 132.3 ppm, relative to TMS). Solid-state ²⁷Al MAS NMR spectra of the clays were obtained at 156.4 MHz at room temperature on a Chemagnetics CMX Infinity spectrometer, with a 29° pulse length of 0.8 μs and a repetition time of 0.2 s; Chemagnetics 3.2 mm PENCIL rotors were used at a spinning speed of about 18 kHz. ²⁷Al spectra were externally referenced to Al(H₂O)₆³⁺ in 1 M aqueous Al(NO₃)₃ solution. A Bruker AC-300P spectrometer was used to obtain all of the liquid-solution ¹H and ¹³C spectra, at 300.13 and 75.47 MHz, respectively.

Sample Preparations. Zn²⁺-Exchanged Clays. All three clay samples were doped with zinc ion by the following

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TABLE 1. Clay-Pollutant Samples Studied and Contents of C₆D₆ Extracts of ¹³CCl₄/Benzene/Clay Samples Based on ¹H NMR Analysis

sample no.	type of clay	Zinc content ^a (wt %)	weight proportions of clay/ ¹³ CCl ₄ /benzene (g/g/g)	sample weight for extraction (g) ^b	TTMSM (0.2 ppm) mol × 10 ⁻⁷ c	(C ₆ H ₅) ₃ ¹³ COH (7.3 ppm) mol × 10 ⁻⁶ c	(C ₆ H ₅) ₂ ¹³ CO (7.7 ppm) mol × 10 ⁻⁶ c	C ₆ H ₅ ¹³ CO ₂ H (8.1 ppm) mol × 10 ⁻⁷ c
1	Ca-montmorillonite	<0.0050	1.98/0.0315/0.132	0.176	8.4	0.50 (2.8) ^d	0.66 (3.7)	0 (0)
2	K-10 montmorillonite	<0.0050	2.02/0.0320/0.131	0.174	9.4	0.73 (4.1)	0.82 (4.6)	0 (0)
3	kaolinite	<0.0010	2.03/0.0324/0.136	0.170	8.3	0 (0)	0 (0)	0 (0)
4	Zn ²⁺ -exchanged Ca-montmorillonite	2.02 ± 0.02	2.06/0.0328/0.133	0.177	11	2.5 (14)	8.2 (45)	5.7 (31)
5	Zn ²⁺ -exchanged K-10 montmorillonite	1.86 ± 0.02	2.08/0.0325/0.132	0.172	11	2.3 (13)	11 (64)	2.1 (12)
6	Zn ²⁺ -exchanged kaolinite	0.49 ± 0.02	2.03/0.0318/0.133	0.175	8.3	0 (0)	0 (0)	0 (0)

^a Zn contents were determined by Huffman Laboratories, Golden, CO. ^b Weight of ¹³CCl₄/C₆H₆/clay sample used for C₆D₆ extraction after 30 days. ^c Number of moles of individual components in concentrated C₆D₆ extracts. ^d The numbers in parentheses correspond to percent yield relative to ¹³CCl₄.

procedure: A 10.0-g portion of the clay was gradually added to a stirred slurry of 1.63 g of zinc chloride in 60 mL of acetonitrile. The suspension was stirred at room temperature for 48 h, and the mixture was filtered and washed with two 25-mL portions of acetonitrile. The resulting solid was dried at 80 °C in an oven under atmospheric pressure (~645 Torr) for 12 h and ground with a mortar/pestle. The Zn contents of the ion-exchanged clays were analyzed by Huffman Laboratory, Golden, CO, and the results are shown in Table 1.

Pretreatment of Clays. Before mixing with an organic reagent, each clay sample (as received, as well as Zn²⁺-ion exchanged) was calcined in vacuum (<10⁻³ Torr) by (i) first slowly heating the clay to 200 °C in 1 °C/min increments, (ii) maintaining that temperature for 8 h, and then (iii) gradually cooling back to room temperature. The activated clays were used immediately after preparation.

Preparation of Clay-Pollutant Samples. A 2.00-g sample of each pretreated clay sample (from the steps described above) was mixed with 0.020 mL (0.032 g, 0.21 mmol) of ¹³C-labeled carbon tetrachloride and 0.15 mL (0.13 g, 1.7 mmol) of benzene in a glovebox under a dry N₂ atmosphere at room temperature. Weight ratios of the six clay-pollutant samples prepared for this study are summarized in Table 1. All samples were stored in a dry N₂ glovebox at room temperature for 30 days before they were transferred into MAS rotors for solid-state ¹³C NMR measurements.

C₆D₆ Extraction of Clay-Pollutant Samples. After clay-pollutant samples were examined by solid-state ¹³C NMR, they were opened to ambient (air) moisture in a laboratory hood for 24 h. A 0.173 ± 0.004 g sample of each such moisture-contacted sample was individually refluxed with 5.0 mL of perdeuteriobenzene (C₆D₆) for 10 h; the mixture was then filtered and washed with an additional 5.0 mL of C₆D₆. The resulting filtrate-wash was concentrated on a rotary evaporator to a volume of 0.70 ± 0.02 mL, which was then transferred to a 5 mm NMR tube, and 3.2 ± 0.6 × 10⁻⁴ g (1.0 ± 0.2 × 10⁻⁶ mol) of tetrakis(trimethylsilyl)silane (TTMSS) in 30.0 μL of C₆D₆ was added into the extract for an NMR intensity reference.

Results and Discussion

Structure and Properties of Clay Minerals. Naturally-occurring layered silicates, with various arrangements of tetrahedral and octahedral "layers", are generally called clay minerals; these materials have important sorptive and ion exchange properties. The crystal structure of a clay mineral was first proposed by Pauling (21), and the validity of his model was ascertained by the X-ray diffraction technique

(22). A tetrahedral layer within a clay mineral consists primarily of a sheet of tetrahedral silicons linked via oxygens (SiO₄) with other silicons. One of the four corners of each tetrahedron is shared with an adjacent octahedral layer, which typically contains Al³⁺ (or Mg²⁺) at the center and -OH or -O- at the apices, where -O- occupied apices are corner shared with adjacent tetrahedra and -OH occupied apices are not shared. The general structure of 1:1 clay minerals, such as kaolin or kaolinite, consists of parallel stacked sheets, each being a composite of one tetrahedral and one octahedral layer. The general structure of 2:1 clay minerals, e.g., montmorillonite, consists of parallel stacked sheets, each composed of two tetrahedral layers and one octahedral layer. Figure 1 presents the ²⁷Al MAS spectra of the three kinds of clays involved in this study; the tetrahedral Al contents in these clays are in the order montmorillonite K-10 > Ca-montmorillonite > kaolinite, as shown by the relative intensities of the peaks at about 60 ppm.

Kaolinite is an abundant, common, naturally-occurring clay, often found in relatively pure deposits; this clay has a relatively low porosity and cation exchange capacity. The ²⁷Al MAS NMR spectrum of untreated kaolinite shown in Figure 1A-a indicates that most of the Al sites in kaolinite are in the form of octahedral coordination and only a very small portion of the Al sites are in the form of tetrahedral coordination. With only very small portions of isomorphous substitution of Si sites by tetrahedral Al, it is not surprising that kaolinite has a much lower (about four times lower) cation exchange capacity with Zn²⁺ than montmorillonite (Table 1). Heating kaolinite at 200 °C or treating it with ZnCl₂ does not bring about significant changes in the ²⁷Al MAS spectra (Figures 1A-b and 1A-c) in comparison to the spectrum of untreated kaolinite (Figure 1A-a).

Montmorillonite is the most important clay mineral used in catalytic applications (23). The high cation exchange capacities of montmorillonites allow a wide variety of catalytically active forms (e.g., containing acidic cations, metal complexes, photocatalytically active cations, etc.). Montmorillonites are most frequently used as solid acid catalysts, where exchangeable cations, such as protons or metal cations (Al³⁺, Zn²⁺, Fe³⁺, etc.) produce Brønsted acid sites and Lewis acid sites. The ²⁷Al MAS spectrum of untreated Ca-montmorillonite given in Figure 1B-a shows a higher content of tetrahedral Al sites than in kaolinite (Figure 1A-a). When Ca-montmorillonite and Zn²⁺-exchanged montmorillonite were heated at 200 °C and 10⁻³ Torr, the intensities of the tetrahedral Al sites shown in the ²⁷Al spectra (Figures 1B-b and 1B-c) decreased. This behavior might result from the transformation of some tetrahedral Al sites to trivalent Lewis acid sites, e.g., as indicated in eq 1. These Lewis acid sites

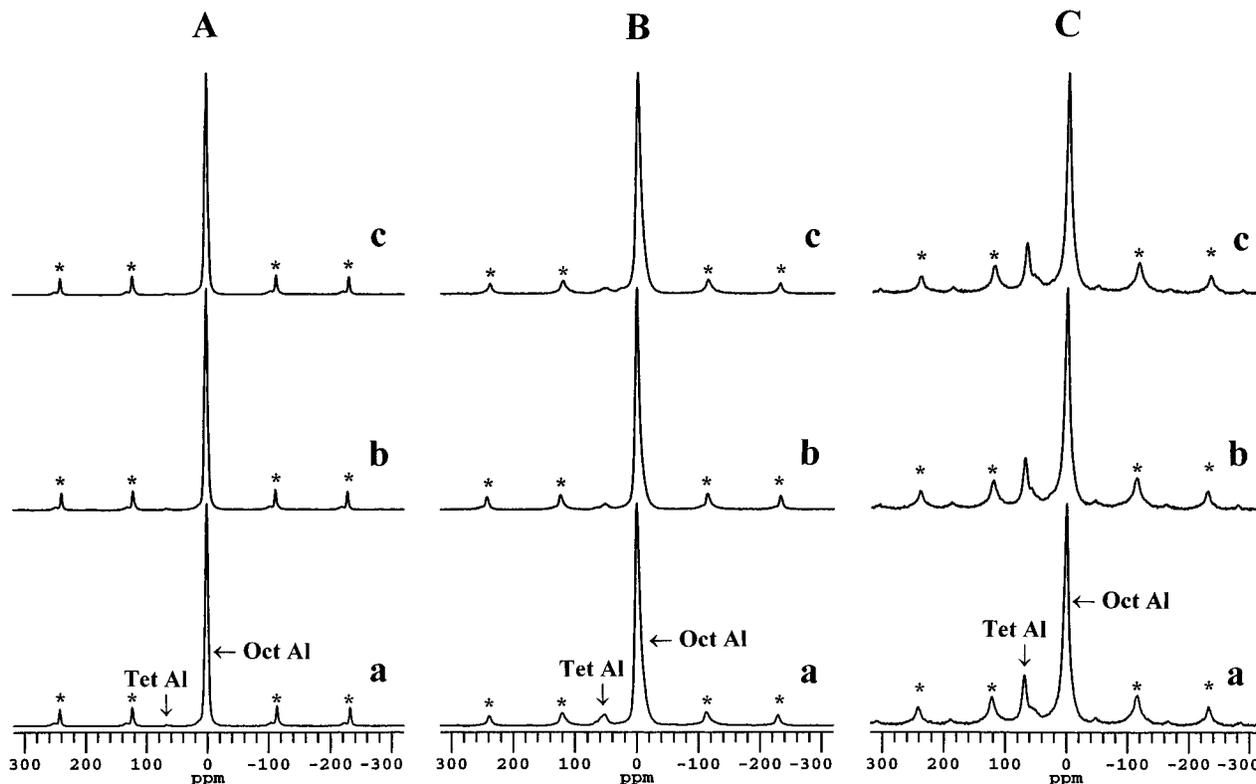
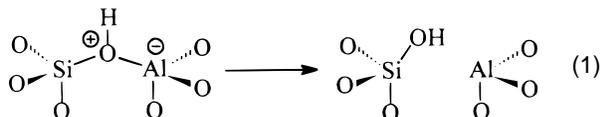
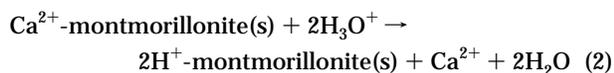


FIGURE 1. ^{27}Al MAS NMR spectra of (A) kaolinite, (B) Ca-montmorillonite, and (C) K-10 montmorillonite. (a) Untreated, (b) preheated (200 °C, 10^{-3} Torr), (c) Zn^{2+} -exchanged, heated (200 °C, 10^{-3} Torr). Each spectrum obtained with a 29° pulse of 0.8 μs , a repetition delay of 0.2 s, and 4000 scans. Spinning side bands indicated by asterisks.



probably exist in highly unsymmetrical surroundings, e.g., three-coordinate (as shown), which might not be readily detected in a ^{27}Al MAS spectrum because of a very large electric field gradient and resulting large second-order quadrupolar broadening (24).

Acidic montmorillonites can be prepared by direct impregnation of natural montmorillonite with a mineral acid, presumably leading to partial proton exchange of the original interlayer cations and the formation of an extraneous salt (eq 2). While treatment of montmorillonite with mineral



acids results in increased concentration of Brønsted acid sites, it can also lead to breakdown of the laminar (sheet) montmorillonite structure. Recently, Onaka et al (25) suggest a "card-house" structure for an acid-treated montmorillonite after the laminar montmorillonite lattice is degraded by mineral acids. The commercially available montmorillonite, K-10, used in this study is an acid-leached montmorillonite and is known to be especially useful in catalyzing organic reactions (26–29). The ^{27}Al MAS spectrum of "untreated" K-10 montmorillonite (Figure 1C-a) shows the highest content of tetrahedral Al sites in the three clay samples used in this study. The ^{27}Al MAS NMR spectra shown in Figure 1C-b and 1C-c indicate that neither heat treatment nor Zn^{2+} exchange causes dramatic changes in the population of tetrahedral Al sites in the K-10 montmorillonite system.

There has been considerable growth in interest in using montmorillonite-supported transition metal salts as catalysts in recent years, especially for the catalysis of organic reactions (30–32). The emergence of zinc chloride supported on acid-treated montmorillonite, Clayzic, was a definite breakthrough in the search for environmentally friendly catalysts (33). ZnCl_2 in its supported form is very much more active than the unsupported salt itself; nevertheless, the supported catalyst is not as active as solid AlCl_3 (34). Clayzic offers significant environmental advantages over homogeneous catalysts in terms of the regeneration and ease of disposal of the used catalyst.

Recent studies on Clayzic have revealed a number of interesting and important capabilities, including (i) effectively catalyzing benzylation in minutes at room temperature, demonstrating a remarkable effect on Friedel–Crafts alkylation reactions (35); (ii) the presence of both Brønsted and Lewis acid sites (36, 37); and (iii) a strong dependence on activation temperature of Clayzic's catalytic activity in Friedel–Crafts benzylation reactions (38). Based on the provocative zeolite-based results cited above (3, 4), one might expect that a Friedel–Crafts type reaction of carbon tetrachloride with benzene could take place on clay minerals that are pretreated with acids or activated at an appropriate temperature.

Solid-State ^{13}C NMR Results on Pollutant/Clay Samples. While the pollutant/clay samples 1–6 listed in Table 1 were being stored in a dry N_2 atmosphere, one could see the development of color in some samples. Color generating reactions of clays with organic compounds have previously been reported (39, 40). For the samples of benzene- CCl_4 adsorbed on Ca-montmorillonite (sample 1) and on Zn^{2+} -exchanged Ca-montmorillonite (4), a green-yellow color became obvious within 2 days after mixing carbon tetrachloride and benzene with the clays; the color changed from light to dark during the first week, and no further color change

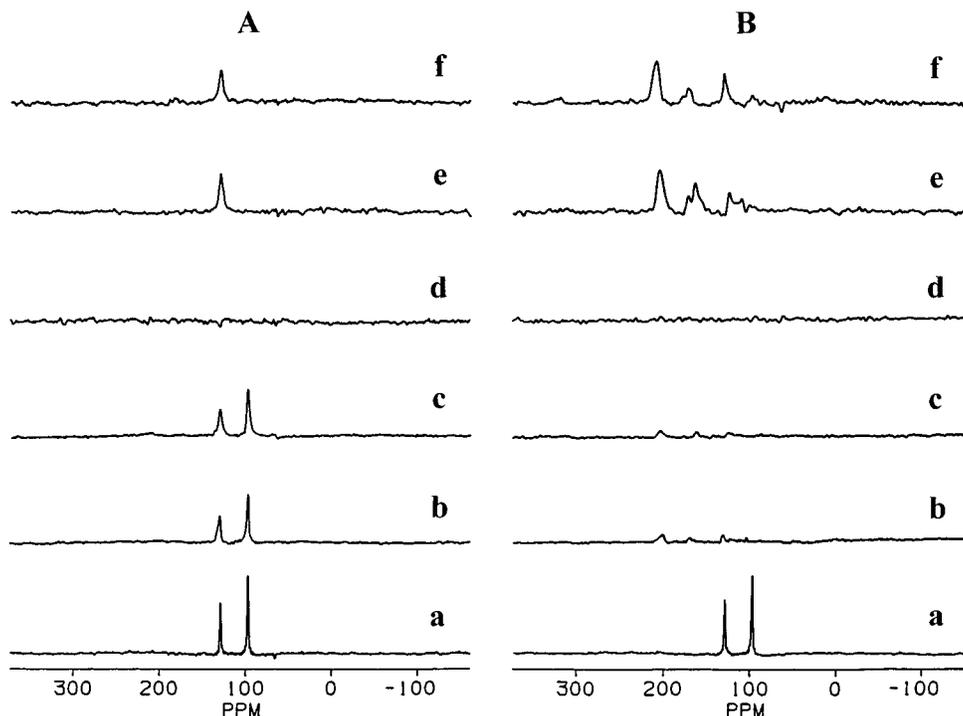


FIGURE 2. ^{13}C DP-MAS (a–c) and CP-MAS (d–f) NMR spectra of samples of benzene and ^{13}C -labeled carbon tetrachloride on (A-a, A-d) kaolinite (sample 3), (A-b, A-e) Ca-montmorillonite (sample 1), (A-c, A-f) K-10 montmorillonite (sample 2), (B-a, B-d) Zn^{2+} -exchanged kaolinite (sample 6), (B-b, B-e) Zn^{2+} -exchanged Ca-montmorillonite (sample 4), and (B-c, B-f) Zn^{2+} -exchanged K-10 montmorillonite (sample 5). Each DP-MAS spectrum was obtained with a 90° pulse of $5.5 \mu\text{s}$, 45 kHz ^1H decoupling, a repetition delay of 5 s, and 3000 scans. Each CP-MAS spectrum was obtained with a 90° ^1H pulse of $5.7 \mu\text{s}$, a CP contact time of 2 ms, 43 kHz ^1H decoupling, a 1 s repetition delay, and 20 000 scans (A) or 40 000 scans (B).

appeared to occur during the last 3 weeks of observation. For benzene– CCl_4 loaded onto K-10 montmorillonite (2) and on Zn^{2+} -exchanged K-10 montmorillonite (5), a bright yellow color developed in both samples during the first week, and no significant color change was observed for the remainder of the 3-week observation period. For benzene– CCl_4 loaded onto kaolinite (3) and on Zn^{2+} -exchanged kaolinite (6), no significant color change could be seen during the entire 4-week storage period.

Figure 2A-a–c shows solid-state DP-MAS ^{13}C NMR spectra of samples consisting of a mixture of ^{13}C -labeled carbon tetrachloride and natural abundance benzene loaded onto (a) kaolinite (Figure 2A-a), (b) Ca-montmorillonite (Figure 2A-b), and (c) K-10 montmorillonite (Figure 2A-c). Only benzene and $^{13}\text{CCl}_4$ signals are seen in these three spectra; thus, there is no dramatic evidence that the co-existence of carbon tetrachloride and benzene on/in those three clays yields any obvious chemical transformation, although some products with low concentration can be detected by liquid-sample NMR experiments on C_6D_6 extracts of these samples (*vide infra*). The ^{13}C NMR line shapes observed for these samples of carbon tetrachloride and benzene loaded onto these clays differ from each other, as summarized in terms of line widths in Table 2.

Although chemical shift differences are small in the different samples represented in Figure 2A-a–c, one can nevertheless see a small variation from high shielding to low shielding in the order of kaolinite, Ca-montmorillonite, and K-10. Apparently, the line widths of the organic species significantly depend upon the type of clay, which may simply reflect the facts that (i) line-broadening effects due to trace amounts of iron and other paramagnetic species are varied in different clays and (ii) the strength and detailed nature of interactions between the organic pollutants and the clay depend on the structure of the clay.

TABLE 2. ^{13}C Chemical Shifts and Line Widths of ^{13}C DP-MAS Spectra of ^{13}C -Labeled Carbon Tetrachloride and Benzene Adsorbed onto Kaolinite, Ca-Montmorillonite, and K-10 Montmorillonite

	carbon tetrachloride		benzene	
	$\Delta\nu_{1/2}$ (Hz) ^a	δ (ppm) ^b	$\Delta\nu_{1/2}$ (Hz) ^a	δ (ppm) ^b
Ca-montmorillonite sample 1	41.3	95.4	61.1	128.2
K-10 montmorillonite sample 2	75.6	96.1	92.8	128.6
kaolinite sample 3	34.1	95.3	39.3	127.5

^a ± 3.4 Hz. ^b ± 0.2 ppm.

In the ^{13}C CP-MAS spectra of the samples of Figure 2A-a–c, shown in Figure 2A-d–f, no signal was detected from the C_6H_6 - $^{13}\text{CCl}_4$ /kaolinite system (Figure 2A-d), but one of the organic components (benzene) could be detected in the C_6H_6 - $^{13}\text{CCl}_4$ /Ca-montmorillonite sample (Figure 2A-e) and in the C_6H_6 - $^{13}\text{CCl}_4$ /montmorillonite K-10 sample (Figure 2A-f). It is reasonable that ^{13}C NMR signals of carbon tetrachloride do not show up in CP-MAS spectra, because there is no intramolecular proton source that can contribute to ^1H - ^{13}C cross polarization. The mobility of benzene adsorbed on a specific clay mineral is expected to affect the efficiency of the cross polarization process in that system. During cross polarization, magnetization is transferred from protons to carbon with a rate governed by a time constant, T_{CH} , that depends on an unaveraged ^1H - ^{13}C magnetic dipole–dipole interaction. However, while the ^{13}C polarization is being built up by CP transfer from protons, the decay of ^1H and ^{13}C polarization occurs simultaneously at a rate determined primarily by a time constant $T_{1\rho}(\text{H})$, which is independent of the rate of cross polarization. If $T_{1\rho}(\text{H})$ is smaller than T_{CH} , then ^{13}C signals will be reduced in intensity and in the extreme

case become lost in the background noise. The efficiency of cross polarization depends on molecular motion; a very long T_{CH} might occur because the sample is liquid-like.

Figure 2A-d shows no cross polarization ^{13}C signal of benzene on kaolinite, which might indicate a liquid-like or fast-motion behavior and hence a weak benzene-clay interaction for benzene adsorbed on this solid surface. Figure 2A-e,f shows the ^{13}C CP-MAS signals of benzene in $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ loaded on these montmorillonites. In contrast to the benzene-on-kaolinite system, benzene in these $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ /montmorillonite samples appears to be less mobile, implying much stronger interactions between benzene and these clays. The cause of this stronger interaction in the case of montmorillonites could result from the isomorphous metal-ion substitution that occurs in the framework of the clay. Some of the silicons in the tetrahedral layers are replaced by aluminums in montmorillonites, as evidenced by the 60–70 ppm peaks in the ^{27}Al MAS spectra in Figure 1B,C. Accordingly, there must be some positively-charged counterions, such as Ca^{2+} , Na^+ or H^+ , between the layers. These acidic cations might have an important influence on the adsorption of an organic pollutant. The fact that the ^{13}C chemical shift of the benzene peaks in Figure 2A-e,f is 134 ppm, rather than the 128 ppm obtained in the corresponding DP-MAS spectra of Figure 2A-b,c (compared to 128.5 ppm for liquid benzene), reflects the fact that the CP-MAS technique emphasizes less mobile species while the DP-MAS technique emphasizes more mobile species. Hence, it may be that the benzene signal observed in DP-MAS spectra represents a non-interacting (e.g., adsorbed) or weakly physisorbed fraction of the benzene, while the CP-MAS spectra represent a more strongly interacting adsorbed fraction.

The fact that loading zinc chloride into clays has been shown to generate much more active catalysts for Friedel–Crafts alkylation reactions (32, 35) suggests that carbon tetrachloride might readily react with benzene under catalysis by Zn^{2+} -exchanged clays. Figure 2B presents ^{13}C DP-MAS and CP-MAS spectra of a mixture of carbon tetrachloride and benzene adsorbed on three Zn^{2+} -exchanged clays. The ^{13}C DP-MAS spectrum shown in Figure 2B-a for $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ / Zn^{2+} -kaolinite is very similar to that shown in Figure 2A-a for $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ /kaolinite, just as the fact that no ^{13}C signal is seen in the CP-MAS spectrum of Figure 2B-d (also for $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ / Zn^{2+} -kaolinite) resembles the CP-MAS result shown in Figure 2A-d for the $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ /kaolinite system. These results indicate that zinc ion does not appreciably change the catalytic activity of kaolinite for the reaction of carbon tetrachloride with benzene.

In contrast to the kaolinite behavior described above, we note that Zn^{2+} -exchanged montmorillonites catalyze the reaction of carbon tetrachloride and benzene effectively. Figure 2B-e,f shows that carbon tetrachloride and benzene can be converted, by using Zn^{2+} -exchanged montmorillonites as catalysts, into the triphenylmethyl carbocation (~209 ppm peak for the positively charged sp^2 carbon center) or benzophenone [197 ppm peak for the carbonyl carbon in solution (41) and a lower-shielding chemical shift when adsorbed on solid acid surfaces (42)]. Although the low-shielding peak at 209 ppm in the DP-MAS spectra (Figure 2B-b,c) has poor signal-to-noise, the ^{13}C CP-MAS spectra of the same samples shown in Figure 2B-e,f confirm the chemical transformations to species yielding an intense peak at 209 ppm.

It has been established that Lewis acid sites can be very important for catalyzing a Friedel–Crafts type reaction between carbon tetrachloride and benzene in zeolite HY (3, 4). The results presented here suggest that the acid sites in clay minerals may have a similar property for converting organic pollutants into other compounds. Parry has

described the use of pyridine as a probe to differentiate Brønsted acid sites from Lewis acid sites in K-10 montmorillonite and in Zn^{2+} -exchanged montmorillonite (Clayzic) (43). Parry's FTIR study showed that the vibrational bands at 1449 and 1607 cm^{-1} are due to pyridine molecules coordinatively bound to Lewis acid sites. The fact that these bands are present in a Clayzic sample but not in a K-10 sample suggests that montmorillonite K-10 does not possess significant Lewis acidity and that it is the zinc ions which create effective Lewis acid sites in these clays. This is in agreement with our ^{13}C NMR results, which indicate that the transformation of organic species in Zn^{2+} -exchanged montmorillonites (Figure 2B-e,f) is much more efficient than in the corresponding unexchanged montmorillonites themselves (Figure 2A-e,f).

These studies demonstrate that modern solid-state NMR techniques constitute very useful methods to study the behaviors of organic pollutants in soil and its components. Since solid-state NMR can provide *in situ* information regarding pollutants adsorbed on soil components, the fates of pollutants in soil can be investigated non-invasively at the molecular level of detail. For example, relatively unstable species, such as the carbocation intermediates involved in this study, can be detected directly by solid-state NMR techniques.

Liquid-Solution ^{13}C NMR Results on C_6D_6 Extracts of $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ /Clay Samples. After solid-state ^{13}C NMR spectra were obtained, the $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ /clay samples were exposed to ambient (air) moisture for 12 h in a laboratory hood. The moisture-contacted samples were then extracted by C_6D_6 , and the extracts were concentrated. Only non-volatile compounds that had formed by chemical transformation of carbon tetrachloride and benzene are expected to be present after this isolation procedure because any volatile species, including unreacted carbon tetrachloride and benzene, would most likely be lost in the processes of extract preparation, exposure to air, and rotary evaporation.

Figure 3A shows the liquid-sample ^{13}C NMR spectra of the C_6D_6 extracts from three $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ /clay samples, based on kaolinite, Ca-montmorillonite, and montmorillonite K-10 without Zn^{2+} exchange. The only prominent ^{13}C NMR peaks seen in these spectra appear at 128 ppm due to C_6D_6 solvent. No other species (peaks) were found in the extract prepared from the $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ /kaolinite sample (Figure 3A-a). Very small amounts of triphenylmethanol (82 ppm) and benzophenone (196 ppm) were detected in the extracts from the $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ /montmorillonite samples (Figure 3A-b,c). In spite of the fact that the peaks at 82 and 196 ppm are barely detectable in Figure 3A-b,c, those peak assignments were confirmed by ^1H NMR results (*vide infra*). As seen in Figure 3B-b,c, the extracts from the $\text{C}_6\text{H}_6\text{-}^{13}\text{CCl}_4$ / Zn^{2+} -exchanged montmorillonites, the concentrations of reaction products detected by liquid-sample ^{13}C NMR are much higher than in extracts from the samples without zinc ions. Figure 3B-a indicates that, in contrast, Zn^{2+} exchange on kaolinite does not substantially improve the catalytic activity of the clay for transforming carbon tetrachloride and benzene into such species as benzoic acid (176 ppm), benzophenone, and triphenylmethyl carbenium ion (or triphenylmethanol).

Postulated Reaction Pathways. The liquid-sample and solid-sample ^{13}C NMR results presented above demonstrate that there are three major products in the reaction of carbon tetrachloride with benzene on Zn^{2+} -exchanged montmorillonites. The mechanisms of the reactions appear to be, in general terms, of the well-known Friedel–Crafts type (44). In the present case, one can postulate that ionization of the C–Cl bond of carbon tetrachloride is first promoted by an acid site (M^+) on the clay; then the resulting cation undergoes an electrophilic substitution reaction with benzene, as shown in eqs 3 and 4.

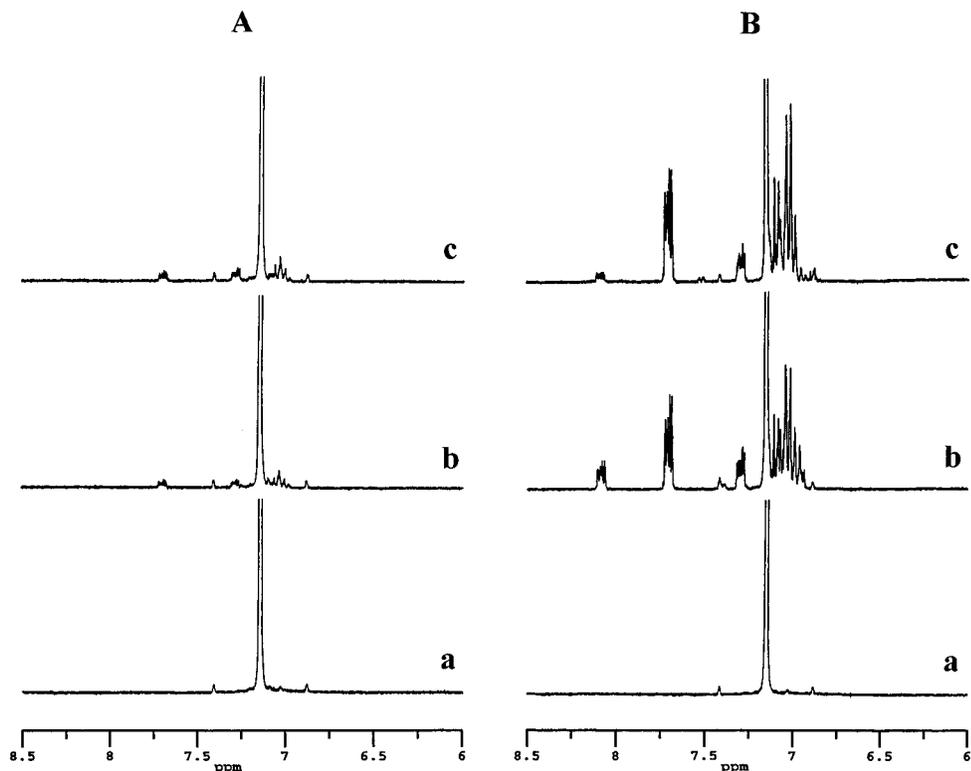
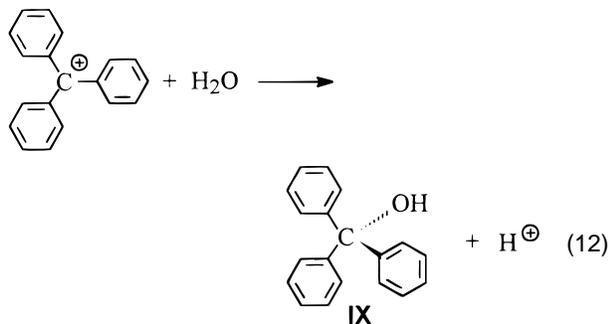
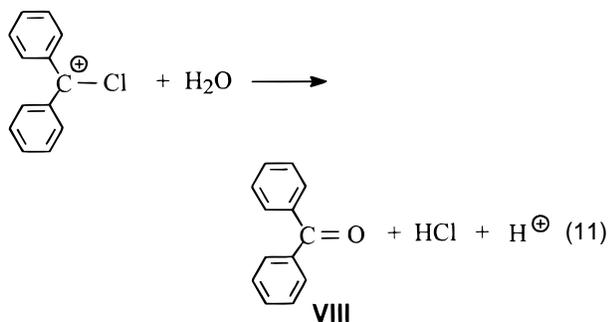


FIGURE 4. Liquid-sample 300.13 MHz ^1H NMR spectra of the concentrated (rotovapped) C_6D_6 extract from a mixture of benzene and ^{13}C -labeled carbon tetrachloride adsorbed on (A-a) kaolinite (sample 3), (A-b) Ca-montmorillonite (sample 2), (A-c) Zn $^{2+}$ -treated kaolinite (sample 6), (B-a) Zn $^{2+}$ -treated Ca-montmorillonite (sample 4), and (B-b) Zn $^{2+}$ -treated K-10 montmorillonite (sample 5); each obtained with a 45° pulse of $3.0 \mu\text{s}$, a repetition delay of 10 s, and 128 scans.

Hydrolysis of **V** and **VII** finally gives rise to benzophenone **VIII** and triphenylmethanol **IX**, respectively (eqs 11 and 12).



On the basis of the reaction schemes outlined above, we can expect that the peaks at 209 ppm in Figure 2B-e,f might consist of two components, i.e., triphenylmethyl cation (**VII**) and strongly perturbed benzophenone (**VIII**), although the ^{13}C chemical shift of pure benzophenone is 197 ppm. Also, it can be reasonably concluded that the detection of triphenylmethanol (**IX**) in the extracts (Figure 3B-b,c) but

not in solid samples before exposure to moisture is due to the conversion of the carbocation **VII** to the corresponding triphenylmethanol **IX** when the samples were put into contact with air-moisture. The fact that there is a peak in the spectra of Figure 3B-b,c at about 197 ppm implies that some of the 209 ppm peak intensity in the solid-sample spectra (Figure 2B-e,f) is due to benzophenone. The chemical shift of some portion of the ^{13}C -carbonyl functionality in these samples would have a low-shielding shift when adsorbed on solid acid surfaces. A reference ^{13}C NMR spectrum of benzophenone adsorbed on Zn $^{2+}$ -exchanged montmorillonite (not shown here) yields a chemical shift of 207 ppm for the ^{13}C -carbonyl functionality; a 10 ppm decrease in the ^{13}C shielding of the ^{13}C -carbonyl carbons of acetone and di-*tert*-butyl ketone was also observed upon adsorption on preheated silica (42). Therefore, it is possible that an overlap might occur between the signals corresponding to the triphenylmethyl cation and benzophenone in Figure 2B-e,f.

Liquid-Solution ^1H NMR Results on C_6D_6 Extracts of C_6H_6 - $^{13}\text{CCl}_4$ /Clay Samples. Liquid-sample ^1H NMR spectra of all six extract samples were obtained for quantitatively determining the percentage conversion of $^{13}\text{CCl}_4$ into each of the three major extraction products: triphenylmethanol, benzophenone, and benzoic acid. One might worry about the fact that splittings due to *J*-coupling of the aromatic protons of these three compounds could complicate these analyses due to severe peak overlapping. Fortunately, for quantitative analysis, ^1H NMR spectra of three authentic samples of these compounds in C_6D_6 (not given here) show that the *ortho* proton resonances are distinguishable from one another, occurring at 8.1 ppm for benzoic acid, 7.7 ppm for benzophenone, and 7.3 ppm for triphenylmethanol. They are well resolved for quantitative analysis.

Figure 4A shows the liquid-state ^1H NMR spectra of the C_6D_6 extracts of the three C_6H_6 - $^{13}\text{CCl}_4$ /clay samples with no

prior Zn²⁺ exchange. *Ortho* proton signals from neither triphenylmethanol nor benzophenone (nor benzoic acid) were found in the extract prepared from the C₆H₆-¹³CCl₄/kaolinite sample (Figure 4A-a). Only small amounts of triphenylmethanol (7.3 ppm, *ortho* protons) and benzophenone (7.7 ppm, *ortho* protons) were detected in the extracts from the C₆H₆-¹³CCl₄/montmorillonite samples (Figure 4A-b,c). No *ortho* proton signals from benzoic acid (8.3 ppm) were found in the spectra of any of these samples. From the samples of C₆H₆-¹³CCl₄/Zn²⁺-exchanged montmorillonites, liquid-sample ¹H NMR spectra of the extracts (Figure 4B-b,c) show all three major products (benzoic acid, benzophenone, and triphenylmethanol) with much higher concentrations than those found in the samples prepared from non-Zn²⁺-exchanged clays. Similar to what was found in the ¹³C spectra in Figure 3B-a, Figure 4B-a indicates that Zn²⁺-exchanged kaolinite does not catalyze the reaction between carbon tetrachloride and benzene.

By using tetrakis(trimethylsilyl)silane (TTMSS) as an intensity reference, one can estimate the contents of each individual product from the intensities of the *ortho* proton peak relative to the intensity of the reference peak, based on the formula:

$$\text{amount of Y (mol)} = I_o A_r N_r / (I_r N_o)$$

where **Y** could be triphenylmethanol or benzophenone or benzoic acid. In this formula *I*_o and *I*_r are the integrated intensity of the *ortho* proton peak and the integrated intensity of the reference peak, respectively, *A*_r is the amount of reference compound in mol, *N*_r = 36 (the number of protons in a TTMSS molecule), and *N*_o is the number of protons in the *ortho* position of a **Y** molecule (where *N*_o = 6 for triphenylmethanol, 4 for benzophenone, and 2 for benzoic acid). The results are summarized in Table 1. For the samples of C₆H₆-¹³CCl₄/Zn²⁺-exchanged montmorillonites (samples 4 and 5, as defined in Table 1), almost 90% of the initial ¹³CCl₄ was converted into triphenylmethanol, benzophenone, and benzoic acid, although the distributions of the products are somewhat different between these two samples. For the samples of C₆H₆-¹³CCl₄/non-Zn²⁺-exchanged montmorillonites (samples 1 and 2), less than 10% of the initial ¹³CCl₄ was converted into triphenylmethanol and benzophenone. No detectable amount of these products was found in the samples of C₆H₆-¹³CCl₄/kaolinite (samples 3 and 6), whether or not the kaolinite was initially treated with Zn²⁺.

Liquid-sample ¹³C and ¹H NMR results provide the important information that montmorillonites, even without Zn²⁺ pretreatment, can catalyze the reaction of carbon tetrachloride with benzene (albeit in low yield in the absence of Zn²⁺). Therefore, one can expect that co-contamination of carbon tetrachloride and benzene in soil might result in similar chemical transformations under certain conditions (e.g., a dry and/or hot climate or over a very long time). The reactions that occur between these organics adsorbed on montmorillonites lead to chemical transformations that convert more volatile (and probably more toxic) organic pollutants into less volatile (and probably less toxic) compounds. This study can readily be extended to other pollutant systems (e.g., chloroform, toluene, trichloroethane, etc.) that might have analogous chemical behaviors. Such studies are underway.

Acknowledgments

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