Chemical Reactions of Organic Compounds on Clay Surfaces

by Yuko Soma* and Mitsuyuki Soma*

Chemical reactions of organic compounds including pesticides at the interlayer and exterior surfaces of clay minerals and with soil organic matter are reviewed. Representative reactions under moderate conditions possibly occurring in natural soils are described. Attempts have been made to clarify the importance of the chemical nature of molecules, their structures and their functional groups, and the Brönsted or Lewis acidity of clay minerals.

Introduction

Reactions of organic molecules on clay minerals have been investigated from various aspects. These include catalytic reactions for organic synthesis, chemical evolution, the mechanism of humus-formation, and environmental problems. Catalysis by clay minerals has attracted much interest recently, and many reports including the catalysis by synthetic or modified clays have been published (1,2). In this report we will limit the review to reactions on clays in moderate reaction conditions possibly occurring in natural soils.

The environmental aspects of organic compounds chemically reacting on clay surfaces relate to those in soils. Three main types of the transformation of organic compounds in soils are considered: photodecomposition, chemical transformation, and microbiological degradation (3,4). Although simultaneous chemical and microbiological transformations in soils are difficult to distinguish, it is generally accepted that the degradation of most organic compounds in soils involves microorganisms because the sterilization of soils greatly reduces the rate of degradation of many chemicals (5).

Many factors influence the adsorption of organic molecules on soils and clays. Khan (6) classified the mechanism of adsorption on soils depending on the natures of pesticides and soil surfaces, such as van der Waals attraction, hydrophobic bonding, hydrogen bonding, charge transfer, and ligand exchange. The adsorption process on soil surfaces plays an important role for chemical reactions, while adsorption—except when due to van der Waals attraction—might make microbiological degradation difficult (6). Thus, for certain organic compounds chemically activated by adsorption, chemical transformation may be significant.

Most experiments about the transformation of organic compounds in soils have been concerned with the decomposition of the parent molecules, but the complete metabolic degradation pathway; the degradation products; and the resultant residues in soils are relatively unknown and have received little attention (3). The transformation products may also exhibit significant biological activity. The degradation products observed in soils might be transformed further; for example, chloroaniline transformed from chloropropham (isopropyl N-(3-chlorophenyl)-carbamate) (7). The formation of azobenzene, azoxybenzene, and phenazine, which have a steric similarity to dioxin (8), were observed in the adsorption of aniline in sterile soils (9).

Components of the soil that may induce chemical reactions of organic compounds will be clay minerals, metal oxides, metal ions, and soil organic matter. The isolated reaction on pure clays might not be possible in actual soils, but the reaction on the surfaces of composite or complexed systems such as those of clays and organic matter should be considered (10). Moreover, rates of transformation in soils depend on many other factors such as temperature, humidity, and atmospheric oxygen (4). However, it is essential to clarify the role of clay minerals in the transformation of organic compounds in order to know the complete degradation pathways of organic pollutants such as pesticides in soils.

In this report, we review representative reactions on clay surfaces where the reaction mechanisms have been studied systematically in relation to the chemical natures of molecules and the surface properties of clays. The features thus obtained might be extended to apply to other organic reactions on other clay surfaces and those from field observations. Interactions of organic molecules with soil organic matter will be briefly discussed.

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Structures and Acidic Properties of Clay Minerals

Clay minerals are aluminosilicates. Most of them are classified as phyllosilicates, having layered structures comprising tetrahedral silicate and octahedral aluminate sheets. The tetrahedral cation, Si^{4+}, in the composition $O/Si = 2.5$, can be replaced by Al^{3+} or Fe^{3+} cations, and the octahedral cations normally are Al^{3+}, Mg^{2+}, Fe^{2+} and Fe^{3+}. The 1:1 layer type, which is represented by kaolinite, has a layer linking one tetrahedral sheet with one octahedral sheet (Fig. 1a). Montmorillonite clays, which have been most often used in organic reactions, have a 2:1 layer type, where one octahedral sheet is sandwiched by two tetrahedral sheets (Fig. 1b). In the 2:1 layer-type silicates, the substitution of Si^{4+} by Al^{3+} in a tetrahedral sheet (muscovite)—or that of Al^{3+} by Mg^{2+} (montmorillonite), Mg^{2+} by Li^{+} (hectorite) in an octahedral sheet—results in a positive charge deficiency (11). To balance the layer charge, cations are introduced between the layers. Interlayer cations in the smectite group (montmorillonite, hectorite) and the vermiculite group are hydrated exchangeable cations. In natural clays these are typically Na^{+}, K^{+} Ca^{2+} and Mg^{2+}; similar ions can be exchanged with these ions. The cation exchange capacity, intercalation, and swelling properties make smectite clays unique and are important factors in their activity for various reactions of organic molecules.

We note that clays dried to low water contents behave as acids (1,2). Cation-exchanged montmorillonites act as strong Brönsted acids, where the reactive protons are derived from the dissociation of hydrated water molecules because of polarization by exchangeable cations. This situation may be represented by the following equilibrium reaction:

$$[M(H_2O)_x]^{n+} \rightleftharpoons [M(OH)(H_2O)_{x-1}]^{(n-1)+} + H^{+} \quad (1)$$
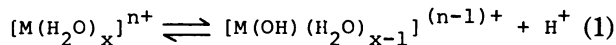
The interlayer acidity is found to increase with increasing charge to the radius ratio of the cations (Al^{3+}, Mg^{2+} > Ca^{2+} > Li^{+} > Na^{+} > K^{+}) and with decreasing water content of the interlayers (10). The dried clay minerals (H_2O < 5%) can develop a high-surface acidity as confirmed by measurements of acid strength, equivalent to 90 wt% or more of sulfuric acid (10). Hydroxyl groups in the lattice structure or at the crystal edge also act as Brönsted acids and play an important part under anhydrous conditions and/or at elevated temperatures. Acidity of pure kaolinite will arise from these sites.

Lewis-acid sites (electron-accepting sites) in clay minerals are considered to be derived from the interlayer transition-metal ions which are higher-valency-state Fe^{3+} ions within the silicate structure and Al^{3+} ions exposed at crystal edges (10,12). Organic molecules and water compete for Lewis-acid sites in the interlayer, and the interlayer water must be removed for the oxidative reaction of organic molecules to proceed. Thus, Lewis acidity may persist under dehydrated conditions.

Reactions due to Brönsted Acidity

A variety of catalytic reactions have been investigated on suitably cation-exchanged montmorillonites, and most of these reactions are believed to be catalyzed by the Brönsted acidity in clays (1,2). Adams, Ballantine, and their coworkers (13–21) examined the reactions of alkenes on cation-exchanged montmorillonites under moderate reaction conditions. The reaction of methanol and isobutylene using cation-exchanged smectites at 60°C in a sealed vessel gave methyl-t-butyl ether (MtBE) and a minor amount of t-butanol, which cor-

7.1 – 7.3 Å

KAOLINITE
(x - 0)

(a)

14.4 – 15.6 Å

SMECTITE (x-0.25-0.6)

(b)

• Tetrahedral cation
⊙ Octahedral cation
○ Exchangeable cation
O Oxygen
◎ Hydroxyl group
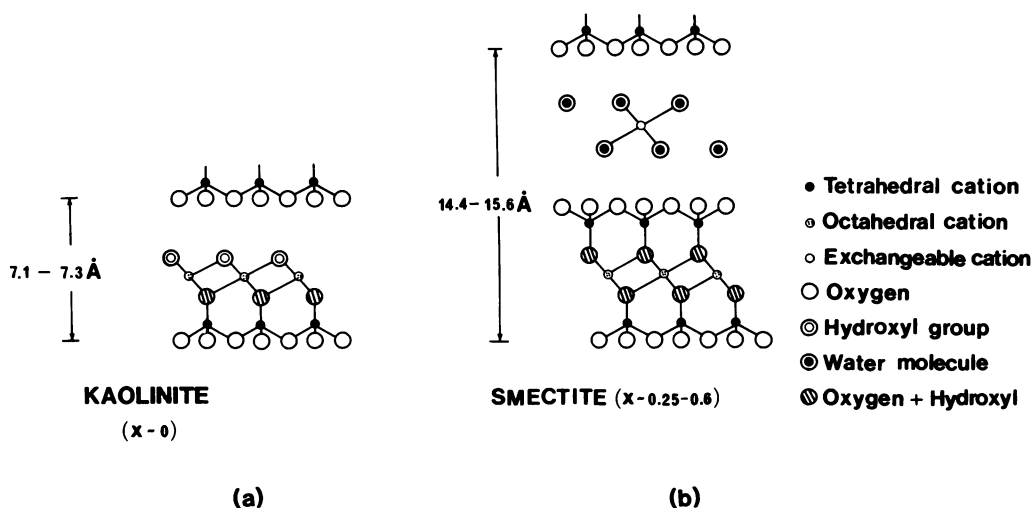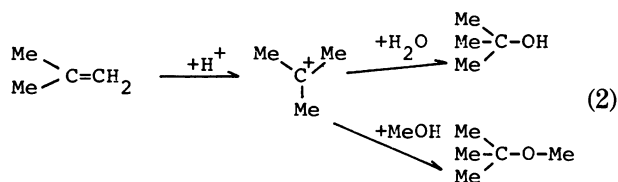◉ Water molecule
Ⓦ Oxygen + Hydroxyl

FIGURE 1.   View of structures of kaolinite (a), and smectite (b).

responded to the amount of the interlayer water (*13,14*). These products were considered to be formed via the following acid catalyzed reactions:

$$\begin{array}{ccc} \text{Me} \\ \diagdown \\ \text{C=CH}_2 \\ \diagup \\ \text{Me} \end{array} \xrightarrow{+\text{H}^+} \begin{array}{c} \text{Me} \quad +\text{Me} \\ \diagdown \quad / \\ \text{C} \\ | \\ \text{Me} \end{array} \xrightarrow{+\text{H}_2\text{O}} \begin{array}{c} \text{Me} \\ \text{Me--C--OH} \\ \text{Me} \end{array} \quad (2) \\ \xrightarrow{+\text{MeOH}} \begin{array}{c} \text{Me} \\ \text{Me--C--O--Me} \\ \text{Me} \end{array}$$

The yield of MtBE was greater where the interlayer cation was Fe^{3+}, Cr^{3+} or Al^{3+}, rather than with the monovalent or divalent cations. This resulting yield is probably because trivalent cations have a greater polarizing power for the hydration water.

Shape selectivity was found in the reaction of various alkenes with butanol over Al^{3+} ion-exchanged montmorillonite below 100°C (*15,16*). The only reactions occurring were those in which a tertiary carbocation could be formed from the reactant alkene directly on protonation; 2-methyl pent-1-ene, 2-methyl hept-2-ene gave their tertiary ethers with minor amounts of the tertiary alcohols. At temperatures above 100°C (150–180°C) the reaction involving secondary carbocation intermediates also occurred: cis-, trans-4-methyl pent-2-ene, 4-methyl pent-1-ene, which gave their secondary ethers.

The differences in reactivities below and above 100°C are related to the amount of water present in the interlayer of clays, which is then related to proton concentration in the interlayer. Tertiary and allylic carbocations are known to be more stable than secondary or primary carbocations. The interlayer environment below 100°C is considered (though less acidic than above 100°C) sufficiently acidic to produce tertiary and allylic carbocations, but insufficiently so as to produce secondary or primary carbocations (*16*).

When cation-exchanged montmorillonite was treated with straight-chain 1-alkenes below 100°C, the corresponding secondary ethers were produced using the interlayer adsorbed water (*13,17*). The whole of interlayer water converted to ether and the reaction ceased once the interlayer water was depleted (*17,19*). This reaction of 1-alkenes was unique because, usually, the reaction of alkenes occurring at low temperatures proceeded via tertiary or allylic carbocation intermediates. A secondary alcohol-type intermediate might be formed by the addition of water coordinated to the interlayer cation (*17,18*). Further reactions to the di(2,2'-alkyl) ether took place, provided the intermediate had a suitable configuration.

In the dehydration reaction of alcohols at 200°C on Al^{3+}-montmorillonites (*20*), primary alcohols mainly produced di-(1-alkyl) ether involving an intermolecular coupling reaction, but secondary and tertiary alcohols yielded alkenes almost exclusively. Esters were produced from the reaction between carboxylic acids and C_2–C_8 alkenes above 100°C on cation-exchanged mont-
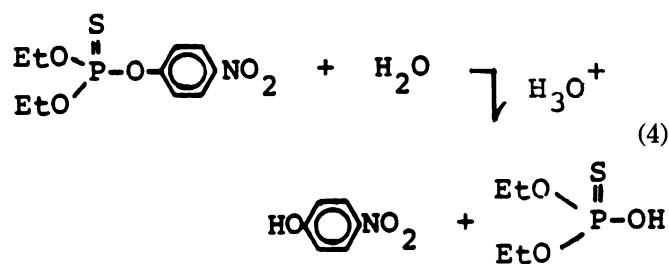
morillonite. The efficiency for conversion was high in 1-alkenes, whereas the reactions in solution were feasible only with alkenes that produced highly stabilized carbocation intermediates (*21*). Thus, in the interlayer of montmorillonite, molecules that have the reactive group at the end of the aliphatic chain may easily undergo an intermolecular coupling reaction above 100°C where secondary carbocations are easily formed.

Yaron and his coworkers studied organophosphorus pesticides-clay interactions, the adsorption and reaction on three types of clay (montmorillonite, kaolinite, and attapulgite) in detail, and summarized their results (*22,23*).

Organophosphorus pesticides such as parathion and methylparathion have the following chemical formula:

$$\begin{array}{c} \quad\quad \text{O (S)} \\ \text{RO} \diagdown \quad || \\ \quad\quad \text{P--O--X} \\ \text{RO} \diagup \quad \text{(S)} \end{array} \quad (3)$$

The pesticides adsorbed on clays degrade through the hydrolysis of the phosphate ester bond to nitrophenol and phosphate.

$$\begin{array}{c} \text{S} \\ \text{EtO} \diagdown \, || \\ \quad\quad \text{P--O--}\langle\bigcirc\rangle\text{NO}_2 \\ \text{EtO} \diagup \end{array} + \text{H}_2\text{O} \searrow \text{H}_3\text{O}^+ \\ \quad (4) \\ \text{HO}\langle\bigcirc\rangle\text{NO}_2 + \begin{array}{c} \text{EtO} \diagdown \, \text{S} \\ \quad\quad || \\ \quad\quad \text{P--OH} \\ \text{EtO} \diagup \end{array}$$

The rate of hydrolysis was affected by the clay's type, saturating cation, and hydration status. Kaolinite was found to enhance the degradation. The degradation of parathion after 40 days on oven-dried kaolinite was 93% for Cu-saturated kaolinite and 16% for Na- and Al-kaolinites (*20*).

Although montmorillonites adsorbed more parathion than the kaolinites, they were less efficient for the hydrolysis of parathion than kaolinites. Methylparathion was less stable than parathion in aqueous solutions, while that adsorbed on kaolinite surfaces seemed more stable than parathion adsorbed on kaolinite.

The addition of water to kaolinite corresponding to bound water at about 11% moisture content increased the degradation rate, but a slight increase in the moisture content above this percentage resulted in a steep decrease in the dehydration rate. The presence of free water hindered almost completely the catalytic effect of the clay surface (*24*).

From these results, a model was proposed where the attack of a ligand water molecule by an exchangeable cation on the P—O(S) bond induced hydrolysis, and the presence of free water blocked the active sites required for decomposition (*25*). Infrared spectra of parathion adsorbed on dehydrated clays showed that parathion directly coordinated to the metal cations through the

oxygen atoms of the nitro-group and through the P=S group (26).

In hydrated clays, parathion was observed to coordinate through water molecules to the cations. Thus, it was proposed that several cations may interact with one ester molecule, and a P—O bond is weakened through an inductive effect particularly through the nitro group (25). The difference in the hydrolysis rate of some organophosphorus pesticides may be explained because of the difference in the inductive field effect of electron-attracting groups for the weakening P—O bond.

Yaron's group extended their studies to the reaction in soils (23). Parathion is relatively nonpersistent in soils, and biological degradation is considered to be the predominant mode of degradation, while chemical degradation is considered to be a relatively slow process. Chemical decomposition in kaolinitic soils was faster than in montmorillonite soils, in agreement with the results in pure clays. Parathion degradation decreased with an increase in the soil organic matter, because of the decreased number of active sites available for the decomposition by coating the soil surfaces. This tendency, a decrease in the rate of hydrolysis by the addition of humic acid to clays, was also observed in the hydrolysis of 1-(4-methoxyphenyl)-2,3-epoxypropane on Na-kaolinite and montmorillonite (27).
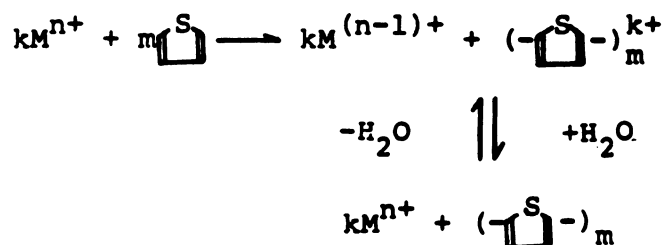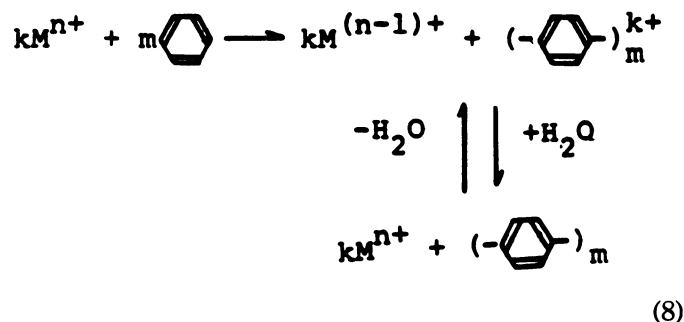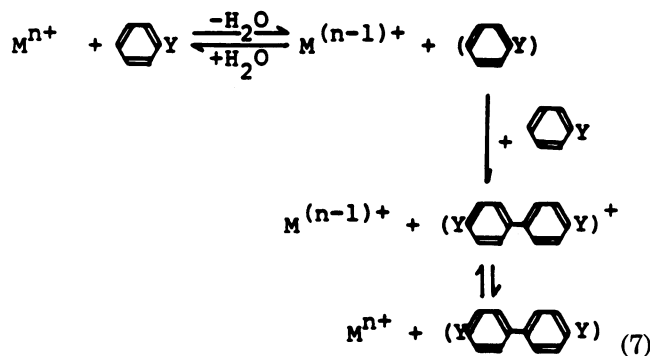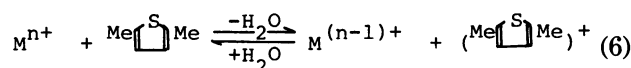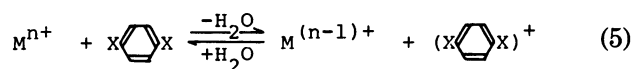
Hydrolysis of another organophosphorus pesticide, phosmet (O,O-dimethyl S-phthalimidomethyl phosphorothionate) has been studied using montmorillonite clays (28). The activity depended also on the interlayer cation in the following way: Ca > Ba > Cu > Mg > Ni. The formation of the bidentate complex through the P=S bond and aromatic ring was considered to be important for catalytic hydrolysis.

Reactions due to Lewis Acidity

The interaction between Lewis-acid sites and adsorbed organic molecules is an electron transfer from organic molecules to metal cations (29); thus, the formation of radical cations and the reduction of metal ions to lower valency are observed simultaneously. The successive dimerization, oligomerization, or polymerization proceeds through the radical cation formed. The reaction rate depends on the degree of dehydration of clay minerals, which ensures the direct coordination of organic molecules to metal ions replacing water molecules and the ionization potentials of organic molecules. In some oxidative reactions, such as those of aromatic amines and phenols, oxygen assists in the formation of radicals (cations), even in the absence of transition metal ions.

Certain aromatic molecules adsorbed on a transition-metal ion (Cu^{2+}, Fe^{3+}, VO^{2+}, Ru^{3+})-exchanged montmorillonite form colored adsorption complexes; the typical molecules studied are shown in Figure 2 (30–40). The initial step in forming these colored complexes involves an electron transfer from the adsorbed organic molecules to the interlayer transition-metal ion (31,32),

which may be followed by the oxidative transformations of the molecules. Several colored adsorption complexes have characteristic absorption in the near infrared region (so-called Type II complex) (30,31,33,34), besides an ESR signal of a free cation radical. However, the absorption in the near infrared region was not observed in some colored adsorption complexes, despite the ESR signal (31,35), which confused the reaction scheme of these aromatic molecules in the interlayer of transition-metal ion-exchanged montmorillonites. Recently, detailed spectroscopic information concerning the structure of adsorbed species was obtained from resonance Raman spectroscopy (36–40). Colored adsorption complexes (cation radicals), which are formed accompanying the reduction of metal ions, are divided into three types according to the structures of substituted benzenes and thiophenes:

$$M^{n+} + X\text{–}\bigcirc\text{–}X \xrightleftharpoons[+H_2O]{-H_2O} M^{(n-1)+} + (X\text{–}\bigcirc\text{–}X)^+ \qquad (5)$$

$$M^{n+} + Me\text{–}\boxed{S}\text{–}Me \xrightleftharpoons[+H_2O]{-H_2O} M^{(n-1)+} + (Me\text{–}\boxed{S}\text{–}Me)^+ \qquad (6)$$

$$M^{n+} + \bigcirc\text{–}Y \xrightleftharpoons[+H_2O]{-H_2O} M^{(n-1)+} + (\bigcirc\text{–}Y)$$

$$\downarrow + \bigcirc\text{–}Y$$

$$M^{(n-1)+} + (Y\text{–}\bigcirc\text{–}\bigcirc\text{–}Y)^+$$

$$\updownarrow$$

$$M^{n+} + (Y\text{–}\bigcirc\text{–}\bigcirc\text{–}Y) \qquad (7)$$

$$kM^{n+} + m\bigcirc \longrightarrow kM^{(n-1)+} + (\text{–}\bigcirc\text{–})^{k+}_m$$

$$-H_2O \updownarrow +H_2O$$

$$kM^{n+} + (\text{–}\bigcirc\text{–})_m$$

$$(8)$$

$$kM^{n+} + m\boxed{S} \longrightarrow kM^{(n-1)+} + (\text{–}\boxed{S}\text{–})^{k+}_m$$

$$-H_2O \updownarrow +H_2O$$

$$kM^{n+} + (\text{–}\boxed{S}\text{–})_m$$

The formation of these radical cations in the interlayer of montmorillonites [Reactions (5)–(7)] were enhanced by dehydration and returned reversibly to their neutral forms by hydration. Reaction (5) was observed in 1,4-disubstituted benzenes, 4,4'-disubstituted biphenyls, 2,5-dimethylthiophene as shown in Figure 2 (32,34). Mono-substituted benzenes tended to form the radial cation of 4,4'-disubstituted biphenyl type through their parent cation radical, as observed for anisole (31,34). Benzene, biphenyl, thiophene, and 3-ethylthiophene formed the stable polymer cations, poly-p-phenylene cation, polythiophene cation and polymethylthiophene cation respectively (37,40). Thus, the radical cations may remain stable when the para-positions of the benzene ring are occupied by stable substituents, or they undergo polymerization when the para-position is open. In the case of thiophene or pyrrole, the radical cation polymerizes at the 2 and 5 positions.

Strong absorption in the near infrared region (characterized by so-called Type II complex) was confirmed to be low-energy electronic absorption, which was characteristic in conjugated polymer ions (37). Thus, only molecules which undergo the Reaction (8) show Type II complex behavior.

These reactions depend both on the ionization potential of aromatic molecules and on the oxidizing power of the interlayer metal ion. Only metal ions with enough oxidizing power such as the Fe^{3+}, Cu^{2+} and Ru^{3+} ions can produce these radical cations and make the subsequent reactions possible.

For predicting the occurrence of free radical oxidation on soil and clay surfaces, Dragun and Helling (41) divided 93 organic chemicals into four groups, based on
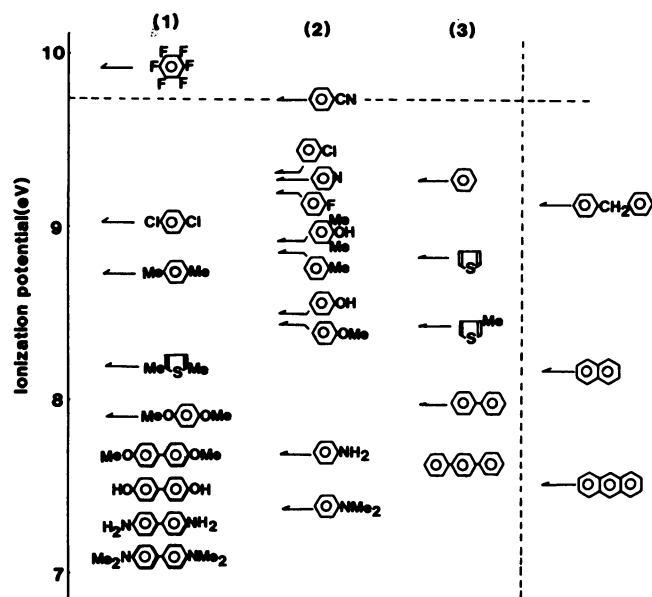

FIGURE 2. Ionization potentials of aromatic molecules grouped according to their adsorption behavior on transition-metal ion-exchanged montmorillonites. Sections 1, 2, and 3 in the figure correspond to the reaction schemes (5), (6), and (7) in the article.

the chemical structure (Hammett sigma constant for the para position on the benzene ring) and water solubility. Organic chemicals that have electron-withdrawing groups and low-water solubility, including halogen-containing aromatic chemicals, are considered to have structures that make free radical oxidation difficult on soil and clay surfaces. Organic chemicals with electron-donating groups usually have lower ionization potentials than those with electron-withdrawing groups; thus, Hammett sigma constants and ionization potentials have a similar trend.

Aromatic molecules that have low ionization potentials can be oxidized, not only by the interlayer transition-metal ion, but also by Al or Fe atoms at crystal edges (42,43) and, in part, by adsorbed oxygen. The typical examples are the reactions of several aromatic amines, such as the benzidine-blue reaction, which is the famous and classic reaction on clay minerals (10). Coordination of aromatic amines to metal ions is strong and can compete with that of water in colloidal clays; the oxidation proceeds even in aqueous suspension of clays. Silicate minerals other than montmorillonite, such as pyrophyrite, illite, attapulgite, and kaolinite, are able to oxidize benzidine to benzidine-blue (42). Some aromatic amines other than benzidine, such as N,N,N',N'-tetramethylbenzidine, triphenylamine, and p-phenylenediamine, exhibit blue or green color in contact with aqueous suspensions of Na^+-montmorillonite (44). In benzidine adsorption, the Na^+ ion was released into solution with the accompanying intercalation of the benzidine cation. Thus, benzidine was oxidized at Lewis-acid sites at the exterior surface; thereafter, the benzidine radical cation ion-exchanged with the interlayer Na ion and stabilized (44).

The benzidine radical cation is oxidized further to a yellow form under high acidity conditions (in low pH or dehydrated state of clay minerals). The structure of this yellow complex has been explained variously, such as a protonated monoradical cation, or a diimine or quinoidal cation. The following disproportionation mechanism to produce the yellow complex is supported from various experimental evidences (45–47):

$$2BZN^+ + 2H^+ \longrightarrow BZN^{2+} + BZNH_2^{2+} \qquad (9)$$
$$\text{blue} \qquad\qquad\qquad \text{yellow}$$
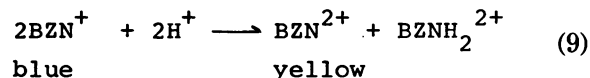
The radical cation of benzidine (BZN^+) adsorbed on montmorillonite is easily transferred to the di-cation (BZN^{2+}), compared with that of N,N,N',N'-tetramethylbenzidine ($TBZN^+$). This behavior occurs because of the presence of the sterically bulky methyl groups that may inhibit close approach of TBZN molecules necessary for the above reaction to proceed in the clay mineral interlayer (45).

Aniline and p-chloroaniline are oxidized on Fe-, Al- and H-montmorillonite in air to colored complexes (48,49), and the formation of a polymer with a linear polyaniline chain has been observed (43). Additionally, the formation of the benzidine cation in the adsorption

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of aniline or *N*,*N*-dimethylaniline of Fe- and Cu-mont-
morillonites was confirmed by resonance Raman spec-
troscopy, where the interlayer transition-metal ion was
necessary to form the benzidine type cation from aniline
or *N*,*N*-dimethylaniline (*50*).

Azobenzene, azoxybenzene, phenazine, and benzo-
quinone were extracted during the adsorption of aniline
on sterile soils (*9*). Thus, it is supposed that a similar
oxidative intermolecular coupling, as on metal-ion ex-
changed montmorillonite, may proceed chemically in
soils.

The oxidative polymerization of phenols also readily
proceeds with Al or Fe atoms at their crystal edges,
and it is enhanced by adsorbed oxygen. Reactions of
phenols on clay minerals have been investigated in re-
lation to the formation of humus in soils (*51*). Oxidative
polymerization easily proceeded for phenol, methyl-
phenols, and *o*-chlorophenol adsorbed on metal-ion (Fe,
Al, Ca, Na)-exchanged montmorillonites. Dimers, tri-
mers, and tetramers of the parent phenol, and the cor-
responding quinones were found by using HPLC and
mass-spectrometry. This polymerization reaction of
phenol and methylphenols was favored in the presence
of air, but not for chlorophenols (*52–54*). The degree of
polymerization and its amount was in the order of
Fe-> Al-> Ca-> Na-clay. The existence of substi-
tuents on the benzene ring markedly reduced polymer-
ization of phenols (*55*). Oligomers that have six to eight
benzene rings were detected in the adsorption of phenol
on Cu- or Fe-montmorillonite, while the main products
of 2,6-xylenol were dimer-diol (3,5,3',5'-tetramethyl-
4,4'-dihydroxy biphenyl) and the corresponding qui-
none. This demonstrates that the oxidative dehydro-
genation of phenol at the *ortho*-position to the OH group
allows the formation of polymers. The primary mech-
anism of polymerization involves the radical species.
Hydroperoxyl radicals (OOH) formed from surface-ad-
sorbed oxygen (*53*), and exchangeable transition-metal
ions such as Fe^{3+}, can provide organic radical cations.
The different behavior in polymerization of phenol from
the oxidation reaction of other aromatic molecules is the
negligible amounts of the transition-metal ion in a re-
duced state and the free radical observed during the
reaction. The amount of polymerized products far ex-
ceeds that of the transition-metal ion in the interlayer
(*55*). Thus, the re-oxidation of the interlayer transition-
metal ion by oxygen should be considered:

$$2Cu^+ + 1/2O_2 + 2H^+ \longrightarrow 2Cu^{2+} + H_2O \quad (10)$$
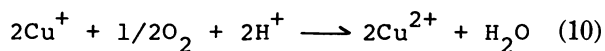
The formation of radical cations in the adsorption of
pentachlorophenol (PCP) and dioxins (dibenzo-*p*-dioxin,
1- and 2-chlorodioxins) on Cu^{2+}-smectite under mod-
erate conditions was observed (*56,57*). These radical
cations were dimers and trimers of the parent mole-
cules, as revealed by mass spectrometry. These oligo-
merization reactions may become new approaches for
the degradation or alteration of hazardous wastes such
as dioxins (*56,57*).

Differences between the oxidative reactions on the
clays described above and those in solution are as fol-
lows:

● The molecules that easily penetrate into the inter-
layer of clay minerals can react easily on clay sur-
faces. Molecules to the right side of the vertical dot-
ted line in Figure 2 are not appreciably adsorbed.
The amount of their radical cations formed is small,
probably because of their rigid and/or bulky struc-
tures. The conjugation length of polythiophene
formed in the interlayer of Cu-montmorillonite is
longer compared with that synthesized electrochem-
ically in solution; whereas that of polymethylthio-
phene is contrary (*40*). This difference may have
been caused from the steric hindrance in the ad-
sorption of methylthiophene in the interlayer.

● The radical cation is stabilized in the interlayer of
clay minerals. Also, the reactions are not as re-
stricted to highly stable cations as those in solution.
As Laszlo (*1*) explains, "Adsorption onto the sur-
faces of a layered mineral reduces the dimensionality
of reaction space from three to two. This constraint
translates into vastly increased encounter rates."

Interactions With Soil Organic Matter

In this section, we briefly discuss the interaction of
organic compounds with soil organic matter, especially
with humic substances (humus), which are the major
constituents of soil organic matter. Humus may be de-
fined as brown-colored organic polymers in soil with
irregular and varying arrangements of segments.
Humic substances are divided into three fractions ac-
cording to their aqueous solubility at different pH val-
ues. They are the alkali- and acid-soluble fulvic acid,
alkali-soluble and acid-insoluble humic acid, and alkali-
and acid-insoluble humin. The structure of blocking
units, which constitutes the skeleton of humic polymers,
is still a matter of debate (*58*). Often the phenolic unit
has been inferred as the major constituent (*59*). How-
ever, the importance of carbohydrate-amino acid con-
densate, melanoidin, known as the product of the Mail-
lard reaction, has been re-emphasized recently (*60,61*).
The inclusion of this topic in the present review is partly
because clay minerals are usually associated with humic
substances in the soil (*62–65*), and also because humus,
an organic colloid, itself is a constituent of the clay frac-
tion when soil is fractioned according to the particle size
of its constituents. Soil organic matter undoubtedly
plays an important role, directly or indirectly, in the
chemical transformation of organic compounds in soil.
Physical sorption of organic compounds by soil organic
matter (*66–70*) will not be discussed here.

Several mechanisms of the chemical activation of or-
ganic compounds by soil organic matter are expected.
The relevant interactions (*71*) may involve general acid-
base catalysis resulting from the acidity and basicity of

soil organic matter, catalysis by metal cations bound to humic substances, photochemical processes, and the bonding or strong complexation to humic substances. Because of a weaker acidity of humic substances, as compared with clay minerals, extensive works on their acid-base catalysis have not been reported. The last mechanism may include the formation of covalent bonding between organic compounds and humic substances and will be our principal interest.

The existence of strongly bound residues of organic chemicals in soil, not extracted by exhaustive extraction using various solvents, was demonstrated when the fate of pesticides in soil was studied by ^{14}C radiolabeled pesticides (72,73). They were bound mostly to humic fractions of soil. To date, the most studied class of compounds are anilines, which are the intermediates in the environmental degradation of many pesticides and other industrial chemicals. 3,4-Dichloroaniline is microbially liberated from the parent herbicide propanil (3,4-dichloropropionanilide). Bartha and Hsu (74,75) showed that the binding of 3,4-dichloroaniline to soil organic matter was not a microbial process and proceeded physicochemically. The addition of a free radical inhibitor to the 3,4-dichloroaniline-humic acid system had no effects on the bonding. Of several humic monomers, aldehydes and quinones were shown to react with 3,4-dichloroaniline. Parris studied the kinetics of bonding of aromatic amines to humate (76). The reaction could be divided into two parts, i.e., the initial rapid and reversible part (phase I) and the later slow, and not readily reversible part (phase II). Since the phase I reaction was reversible by hydrolysis, it was attributed to the reaction between the amino-group with carbonyl in humate to form imine (anil, Schiff's base) (75).

$$ArNH_2 \ + \ O{=}CR_2 \ \rightleftharpoons \ ArN{=}CR_2 \ + \ H_2O \qquad (11)$$
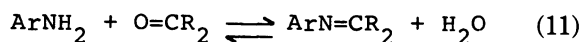
Because of its reversibility by hydrolysis, this binding mechanism contributes little to the persistence of anilines in soil. In phase II, anilines were considered to attach to the quinone ring of humate by Michael addition, followed by oxidation to form stable amino-substituted quinones, for example:

$$\text{(12)}$$

Amino-parathion (72) and amino-CNP (77), which are the intermediates of degradation of their corresponding parent nitro-pesticides, parathion (O,O-diethyl O-p-nitrophenyl monothiophosphate) and CNP (2,4,6-trichlorophenyl 4-nitrophenylether), respectively, were also shown to be bound in soils.

Ohisa and coworkers (78) studied the reaction between amino-CNP and humic acid in the presence of nitrite. When these compounds were mixed in solution, the absorbance in the wavelength-region characterizing

humic substances increased remarkably. The change corresponded to the progress of humification. The bound amino-CNP was not recovered by alkaline treatment, but by reduction with $Na_2S_2O_4$. Gel filtration chromatography of the products indicated the increase in the humic acid's degree of polymerization. It was suggested that amino-CNP was incorporated into the humic acid via diazocoupling, combining two humic acid molecules.

Khan and coworkers (73,79–81) used pyrolysis under an inert atmosphere in order to release ^{14}C residue of bound s-triazine pesticides, prometryn [2-methylthio-4,6-bis(isopropylamino)-s-triazine], and atrazine (2-chloro-4-ethylamino-6-isopropylamine-s-triazine) from soil and soil humic fraction. They recovered a considerable amount of the parent pesticides and suggested that these pesticides might be bound to the humic matrix, not by covalent bonding, but by a manner similar to the formation of inclusion compounds.

Worobey and Webster (82) applied a similar technique to release tightly complexed 4-chloroaniline from soils and soil humic acids and found intact 4-chloroaniline, though to a lesser extent. Accordingly, the nature of bonding between pesticides and humus remains to be studied further. The use of deuterated compounds may partly reveal the relative contribution of covalent bonding and molecular (inclusion) complexation.

Mathur and Morley demonstrated the incorporation of methoxychlor [1,1,1-trichloro-2,2-bis(p-methoxyphenyl)ethane], a relatively nonmobile pesticide, into humic substances during its formation both by microbial (83) and purely chemical processes (84). From the humic material formed from culture containing methoxychlor and a fungus, no methoxychlor was detected in the benzene extract. However, degradation of the same humic material by incubating with another fungus revealed methoxychlor. Hydroquinone was polyermized into a humic acid analogue in the presence of ^{14}C-methoxychlor. The polymer contained ^{14}C and was unextractable with acetone/hexane(1:1).

Cross-coupling of 2,4-dichlorophenol, degradation intermediate of 2,4-D (2,4-dichlorophenoxy acetic acid), with phenolic humus constituents such as orcinol, syringic acid, vanillic acid, and vanilline—catalyzed by phenoloxidase—resulted in the formation of oligomers as revealed by mass spectrometry (85). This mode of coupling may relate to the observation that, although pentachlorophenol was effectively bound to soil humic fraction, it was not bound to the isolated humic or fulvic acid (86).

As previously described, clay minerals can stimulate polymerization to form humiclike substances. They also accelerate the microbial formation of humic substances (63). Since humus in the soil is considered to be in a dynamic state ready to further reactions, clay minerals may catalyze the reaction of humic substances with organic molecules. The roles of humus-clay complexes in the reaction of organic compounds should be the subject of further studies.

Summary

Clay minerals are an important soil component. They act as Brönsted acids or Lewis acids for organic molecules. This property is derived from the minerals' characteristic structures. Various kinds of reactions for alkenes and dehydration of alcohols occur on clay minerals under moderate reaction conditions. These reactions proceed catalytically on Brönsted acid sites on clay minerals. The geometrical constraints imposed by the structure of clay minerals result in increased specificity of the reaction. Hydrolysis of organophosphorous pesticides is enhanced on kaolinite, and the rate of hydrolysis is affected by the Brönsted acidity, controlled by the hydration status of the clay.

Lewis acid sites on clays, which are interlayer transition-metal ions and Al or Fe atoms at crystal edges, oxidize various kinds of aromatic molecules in moderate reaction conditions to form their cation radicals. Oligomerization or polymerization proceeds through the aromatic cation radical formed. Aromatic amines and phenols that have low ionization potentials can be easily oxidized on clays; these reactions may proceed chemically in soils.

Soil humic matter also participates in the chemical transformation of organic compounds in soil. A possible importance of clay-humus complexes has been suggested.

REFERENCES

1. Laszlo, P. Chemical reactions on clays. Science. 235: 1473–1477 (1987).
2. Pinnavaia, T. J. Intercalated clay catalysts. Science. 220: 365–371 (1983).
3. Connell, D. W., and Miller, G. J. Chemistry and Ecotoxicology of Pollution. John Wiley & Sons, New York, 1984.
4. Goring, C. A. I., Laskowski, D. A., Hamaker, J. W., and Meikle, R. W. Principles of pesticides degradation in soil. In: Environmental Dynamics of Pesticides (R. Haque and V. H. Freed, Eds.) Plenum Press, New York, 1975, pp. 135–167.
5. Hance, R. J. Decomposition of herbicides in the soil by non-biological chemical processes. J. Sci. Fd. Agric. 18: 544–547 (1967).
6. Khan, S. U. Pesticides in the soil environment. In: Fundamental Aspects of Pollution Control and Environmental Sci., Vol. 5. Elsevier, New York, 1980.
7. Rajagopal, B. S., Brahmaprakash, G. P., Reddy, B. R., Singh, U. D., and Sethunathan, N. Effect and persistence of selected carbamate insecticides in soil. Residue Rev. 93: 1–199 (1984).
8. Poland, A., Glover, E., Kende, A. S., DeCamp, M., and Giandomenico, C. M. 3,4,3′,4′-Tetrachloroazoxybenzene and azobenzene: potent inducers of aryl hydrocarbon hydroxylase. Science 194: 627–630 (1976).
9. Pillai, P., Helling, C. S., and Dragun, J. Soil-catalyzed oxidation of aniline. Chemosphere 11: 299–317 (1982).
10. Theng, B. K. G. The chemistry of clay-organic reactions. Adam Hilger Ltd., London, 1974.
11. Brindley, G. W., and Brown, G. (Eds.), Crystal Structures of Clay Minerals and Their X-ray Identification. Mineralogical Society, London, 1980.
12. Voudrias, E. A., and Reinhard, M. Abiotic organic reactions at mineral surfaces. In: Geochemical Processes at Mineral Surfaces (J. A. Davis and K. F. Hayes, Eds.), American Chemical Society, Washington, 1986, pp. 462–486.
13. Adams, J. M., Ballantine, J. A., Graham, S. H., Laub, R. J., Purnell, J. H., Reid, P. I., Shaman, W. Y. M., and Thomas, J. M. Organic synthesis using sheet silicate intercalates: low temperature conversion of olefins to secondary ethers. Angew. Chem. Int. Ed. Engl. 17: 282–283 (1978).
14. Adams, J. M., Clement, D. E., and Graham, S. H. Synthesis of methyl-t-butyl ether from methanol and isobutene using a clay catalyst. Clays Clay Miner. 30: 129–134 (1982).
15. Adams, J. M., Clement, D. E., and Graham, S. H. Reactions of alcohols with alkenes over an aluminum-exchanged montmorillonite. Clays Clay Miner. 31: 129–136 (1983).
16. Adams, J. M., Clapp, T. V., and Clement, D. E. Catalysis by montmorillonites. Clay Miner. 18: 411–421 (1983).
17. Adams, J. M., Clapp, T. V., Clement, D. E., and Reid, P. I. Reactions of Alk-1-enes over ion-exchanged montmorillonites. J. Molec. Catal. 27: 179–194 (1984).
18. Adams, J. M., and Clapp, T. V. Infrared studies of 1-hexene adsorbed onto Cr^{3+}-exchanged montmorillonite. Clays Clay Miner. 33: 15–20 (1985).
19. Ballantine, J. A., Purnell, J. H., and Thomas, J. M. Organic reactions in a clay microenvironment. Clay Miner. 18: 347–356 (1983).
20. Ballantine, J. A., Davies, M., Purnell, H., Rayanakorn, M., Thomas, J. M., and Williams, K. J. Chemical conversions using sheet silicates: Novel intermolecular dehydrations of alcohols to ethers and polymers. J. Chem. Soc. Chem. Comm. 427–428 (1981).
21. Ballantine, J. A., Davies, M., Purnell, H., Rayanakorn, M., Thomas, J. M., and Williams, K. J. Chemical conversions using sheet silicates: Facile ester synthesis by direct addition of acids to alkenes. J. Chem. Ssoc. Chem. Comm. 8–10 (1981).
22. Yaron, B. Some aspects of surface interactions of clays with organophosphorous pesticides. Soil Sci. 125: 210–216 (1978).
23. Yaron, B., and Saltzman, S. Soil-parathion surface interactions. Residue Rev. 69: 1–34 (1978).
24. Saltzman, S., Mingelgrin, U., and Yaron, B. Role of water in the hydrolysis of parathion and methylparathion on kaolinite. J. Agric. Food Chem. 24: 739–743 (1976).
25. Mingelgrin, U., Saltzman, S., and Yaron, B. A possible model for the surface-induced hydrolysis of organophosphorous pesticides on kaolinite clays. Soil Sci. Soc. Am. J. 41: 519–523 (1977).
26. Saltzman, S., and Yariv, S. Infrared and X-ray study of parathion-montmorillonite sorption complexes. Soil Sci. Soc. Amer. J. 40: 34–38 (1976).
27. El-Amamy, M. M., and Mill, T. Hydrolysis kinetics of organic chemicals on montmorillonite and kaolinite surfaces as related to moisture content. Clays Clay Miner. 32: 67–73 (1984).
28. Camazano, M. S., and Martin, M. J. S. Montmorillonite-catalyzed hydrolysis of Phosmet. Soil Sci. 136: 89–93 (1983).
29. Theng, B. K. G. Clay-activated organic reactions. In: Developments in Sedimentology (H. Van Olphen and F. Vaniale, Eds.), Vol. 35, Elsevier, Amsterdam, 1982, pp. 197–238.
30. Mortland, M. M., and Pinnavaia, T. J. Formation of copper(II) arene complexes on the interlamellar surfaces of montmorillonite. Nature Phys. Sci. 229: 75–77 (1971).
31. Pinnavaia, T. J., and Mortland, M. M. Interlamellar metal complexes on layer silicates. I. Copper(II)-arene complexes on montmorillonite. J. Phys. Chem. 75: 3957–3962 (1971).
32. Rupert, J. P. Electron spin resonance spectra of interlamellar copper(II)-arene complexes on montmorillonite. J. Phys. Chem. 77: 784–790 (1973).
33. Mortland, M. M., and Halloran, L. J. Polymerization of aromatic molecules on smectite. Soil Sci. Soc. Am. J. 40: 367–370 (1976).
34. Stoessel, F., Futh, J. L., and Wey, R. Polymerisation de benzene en polyparaphenylene dans une montmorillonite cuivrique. Clay Miner. 12: 255–259 (1977).
35. Fenn, D. B., Mortland, M. M., and Pinnavaia, T. J. The chemisorption of anisole on Cu(II) hectorite. Clays Clay Miner. 21: 315–322 (1973).
36. Soma, Y., Soma, M., and Harada, I. Raman spectroscopic evidence of formation of p-dimethoxybenzene cation on Cu- and Ru-montmorillonites. Chem. Phys. Lett. 94: 475–478 (1983).
37. Soma, Y., Soma, M., and Harada, I. The reaction of aromatic molecules in the interlayer of transition-metal ion-exchanged

montmorillonite studied by resonance Raman spectroscopy. 1. Benzene and p-phenylenes. J. Phys. Chem. 88: 3034–3038 (1984).

38. Soma, Y., Soma, M., and Harada, I. Reactions of aromatic molecules in the interlayer of transitional-metal ion-exchanged montmorillonite studied by resonance Raman spectroscopy. 2. Monosubstituted benzenes and 4,4'-disubstituted biphenyls. J. Phys. Chem. 89: 738–742 (1985).

39. Soma, Y., Soma, M., and Harada, I. Resonance Raman spectroscopic study of cation radicals of aromatic molecules formed in the interlayer of transition-metal exchanged montmorillonites. J. Inclus. Phenom. 2: 135–142 (1984).

40. Soma, Y., Soma, M., Furukawa, Y., and Harada, I. Reactions of thiophene and methylthiophenes in the interlayer of transition-metal ion-exchanged montmorillonite studied by resonance Raman spectroscopy. Clays Clay Miner. 35: 53–59 (1987).

41. Dragun, J., and Helling, C. S. Physicochemical and structural relationships of organic chemicals undergoing soil- and clay-catalyzed free-radical oxidation. Soil Sci. 139: 100–111 (1985).

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

43. Tennakoon, D. T. B., Thomas, J. M., and Tricker, M. J. Surface and intercalate chemistry of layered silicates. Part II. An iron-57 Mössbauer study of the role of lattice-substituted iron in the benzidine blue reaction of montmorillonite. J. Chem. Soc. Dalton Trans. 2211–2215 (1974).

44. Tennakoon, D. T. B., Thomas, J. M., Tricker, M. J., and Williams, J. O. Surface and intercalate chemistry of layered silicates. Part 1. General introduction and the uptake of benzidine and related organic molecules by montmorillonite. J. Chem. Soc. Dalton Trans. 2207–2211 (1974).

45. Tennakoon, D. T. B., and Tricker, M. J. Surface and intercalate chemistry of layered silicates. Part V. Infrared, ultraviolet, and visible spectroscopic studies of benzidine-montmorillonite and related systems. J. Chem. Soc. Dalton Trans. 1802–1806 (1975).

46. Furukawa, T., and Brindley, G. W. Adsorption and oxidation of benzidine and aniline by montmorillonite and hectorite. Clays Clay Miner. 21: 279–288 (1973).

47. Kovar, L., DellaGuardia, R., and Thomas, J. K. Reaction of radical cations of tetramethylbenzidine with colloidal clay. J. Phys. Chem. 88: 3595–3599 (1984).

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

49. Moreale, A., Cloos, P., and Badot, C. Differential behaviour of Fe(III)– and Cu(II)–montmorillonite with aniline. I. Suspensions with contact solid:liquid ratio. Clay Miner. 20: 29–37 (1985).

50. Soma, Y., and Soma, M. Adsorption of benzidine and anilines on Cu- and Fe-montmorillonites studied by resonance Raman spectroscopy. Clay Miner. 23: 1–12 (1988).

51. Wang, T. S. C., Li, S. W., and Ferng, Y. L. Catalytic polymerization of phenolic compounds by clay minerals. Soil Sci. 126: 15–21 (1978).

52. Isaacson, P. J. and Sawhney, B. L. Sorption and transformation of phenols on clay surfaces: effect of exchangeable cations. Clay Miner. 18: 253–256 (1983).

53. Sawhney, B. L. Vapor-phase sorption and polymerization of phenols by smectite in air and nitrogen. Clays Clay Miner. 33: 123–127 (1985).

54. Sawhney, B. L., Kozloski, R. K., Isaacson, P. J., and Gent, M. P. N. Polymerization of 2,6-dimethylphenol on smectite surfaces. Clays Clay Miner. 32: 108–113 (1984).

55. Soma, Y., Soma, M., and Harada, I. The oxidative polymerization of aromatic molecules in the interlayer of montmorillonites studied by resonance Raman spectroscopy. J. Contami. Hydrol. 1: 95–106 (1986).

56. Boyd, S. A., and Mortland, M. M. Radical formation and polymerization of chlorophenols and chloroanisole on Cu(II)-smectite. Environ. Sci. Technol. 20: 1056–1058 (1986).

57. Boyd, S. A., and Mortland, M. M. Dioxin radical formation and polymerization on Cu(II)-smectite. Nature 316: 532–535 (1985).

58. Tate, R. L. III. Soil Organic Matter. John Wiley and Sons, New York, 1987.

59. Stevenson, F. J., and Butler, J. H. A. Chemistry of humic acids and related pigments. In: Organic Geochemistry (G. Eglinton and M. T. J. Murphy, Eds.), Berlin, Springer, 1969, pp. 534–557.

60. Benzing-Purdie, L., and Ripmeester, J. A. Melanoidines and soil organic matter: evidence of strong similarities revealed by ^{13}C CP-MAS NMR. Soil Sci. Soc. Am. J. 47: 56–61 (1983).

61. Ikan, R., Ioselis, P., Rubinsztain, Y., Aizenshtat, Z., Pugmire, R., Anderson, L. L., and Ishiwatari, R. Carbohydrate origin of humic substances. Naturwissenschaften 73: 150–151 (1986).

62. Schnitzer, M. Humic substances: chemistry and reactions. In: Soil Organic Matter (M. Schnitzer and S. U. Khan, Eds.), Elsevier, Amsterdam, 1978, pp. 1–64.

63. Theng, B. K. G. Formation and properties of clay-polymer complexes. Elsevier, Amsterdam, 1979, pp. 283–326.

64. Theng, B. K. G. Clay-polymer interactions: summary and perspectives. Clays Clay Miner. 30: 1–10 (1982).

65. Theng, B. K. G., Churchman, G. J., and Newman, R. H. The occurrence of interlayer clay-organic complexes in two New Zealand soils. Soil Sci. 142: 262–266 (1986).

66. Kenaga, E. E., and Goring, C. A. I. Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota. In: Aquatic Toxicology (J. G. Eaton, P. R. Parrish, and A. C. Hendricks, Eds.), ASTM STP 707, American Society for Testing and Materials, ASTM, Philadelphia, 1980, pp. 78–115.

67. Karickhoff, S. W. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10: 833–846 (1981).

68. Schwarzenbach, R. P., and Westall, J. Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. Environ. Sci. Technol. 15: 1360–1367 (1981).

69. Sabljic, A. On the prediction of soil sorption coefficients of organic pollutants from molecular structure: application of molecular topology model. Environ. Sci. Technol. 21: 358–366 (1987).

70. Chiou, C. T., and Shoup, T. D. Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity. Environ. Sci. Technol. 19: 1196–1200 (1985).

71. Khan, S. U. The interaction of organic matter with pesticides. In: Soil Organic Matter (M. Schnitzer and S. U. Khan, Eds.), Elsevier, Amsterdam, 1978, pp. 137–171.

72. Lichtenstein, E. P. Bound residues in soil and transfer of soil residues in crops. Residue Rev. 76: 147–153 (1980).

73. Khan, S. U. Bound pesticide residues in soil and plants. Residue Rev. 84: 1–25 (1982).

74. Bartha, R. Fate of herbicide-derived chloroanilines in soil. J. Agric. Food Chem. 19: 385–387 (1971).

75. Hsu, T.-S., and Bartha, R. Interaction of pesticide–derived chloroaniline residues with soil organic matter. Soil Sci. 116: 444–452 (1973).

76. Parris, G. E. Covalent binding of aromatic amines to humates. 1. Reactions with carbonyls and quinones. Environ. Sci. Technol. 14: 1099–1106 (1980).

77. Yamada, T. Bound residues of 4-aminophenyl 2,4,6-trichlorophenyl ether and 4-aminophenyl 2,4-dichlorophenyl ether in paddy soil treated with CNP (chloronitrofen). J. Pesticide Sci. 8: 33–39 (1982).

78. Ohisa, N., Matsumoto, S., and Yamaguchi, M. Reaction of 2,4,6-trichlorophenyl 4-aminophenyl ether with humic and fulvic acids in the presences of nitrite. J. Pesticide Sci. 9: 209–213 (1984).

79. Khan, S. U., and Hamilton, H. A. Extractable and bound (nonextractable) residues of prometryn and its metabolites in an organic soil. J. Agric. Food Chem. 28: 126–132 (1980).

80. Khan, S. U. Distribution and characteristics of bound residues of prometryn in an organic soil. J. Agric. Food Chem. 30: 175–179 (1982).

81. Capriel, P., Haisch, A., and Khan, S. U. Distribution and nature of bound (nonextractable) residues of atrazine in a mineral soil nine years after the herbicide application. J. Agric. Food Chem. 33: 567–569 (1985).

82. Worobey, B. L., and Webster, G. R. B. Pyrolytic release of tightly complexed 4-chloroaniline from soils and soil humic acids. J. Agric. Food Chem. 30: 164–169 (1982).

83. Mathur, S. P., and Morly, H. V. A biodegradation approach for investigating pesticide incorporation into soil humus. Soil Sci. 120: 238–240 (1975).

84. Mathur, S. P., and Morly, H. V. Incorporation of methoxychlor-^{14}C in model humic acids prepared from hydroquinone. Bull. En-

viron. Contam. Toxicol. 20: 268–274 (1978).

85. Bollag, J.-M., Lin, S.-Y., and Minard, R. D. Cross-coupling of phenolic humus constituents and 2,4-dichlorophenol. Soil Sci. Am. J. 44: 52–56 (1980).

86. Weiss, U. M., Scheunert, I., Klein, W., and Korte, F. Fate of pentachlorophenol-^{14}C in soil under controlled conditions. J. Agric. Food Chem. 30: 1191–1194 (1982).