TRANSFORMATION OF 1-AMINONAPTHTHALENE AT THE SURFACE OF SMECTITE CLAYS

Calvin C. Ainsworth, Bruce D. McVeety, Steven C. Smith, and
John M. Zachara

Pacific Northwest Laboratory P.O. Box 999, MSN K3-61, Richland, Washington 99352

Abstract—One-aminonaphthalene is sorbed onto the Na-saturated smectite clays, montmorillonite and hectorite, by cation exchange. In the presence of Fe^{3+}, either in the clay structure or on the clay surface, sorption is followed by the formation of a blue-colored complex, with the continuous disappearance of aminonaphthalene from solution and the clay surface. The rate of aminonaphthalene disappearance decreases as pH increases. With time, four major products that appear to be structural isomers of N(4-aminonaphthyl)-1-naphthylamine are produced. A simplified model of this transformation is suggested to be the oxidation by Fe^{3+} of sorbed aminonaphthalene forming a radical cation-clay complex. A subsequent reaction between the radical-cation and a neutral aminonaphthalene molecule takes place, with the products being strongly sorbed to the clay surface.

Key Words—Polymerization, Smectite, Sorption, Surface catalysis.

INTRODUCTION

Clay surfaces have the capacity to act as catalysts in chemical oxidation/reduction, acid-base neutralization, and hydrolysis reactions (McBride, 1979; Theng, 1974; Solomon, 1968). The formation of colored clay-organic complexes is well documented (Hauser *et al.,* 1941; Solomon *et al.,* 1968; Theng, 1971; Voudrias and Rienhard, 1986), and has been related to transformation reaction intermediates, and products at the clay surface (Solomon *et al.,* 1968; Theng, 1971; Soma *et al.,* 1984, 1985, 1986; Furukawa and Brindley, 1973; Cloos *et al.,* 1981). Color development is often ascribed to charge transfer reactions (McBride, 1979; Soma *et al.,* 1984, 1985, 1986; Teenakoon *et al.,* 1974), but color development and intensity are dependent on the clay type (Hauser *et al.,* 1941; Voudrias and Rienhard, 1986; Thompson and Moll, 1973), reaction mechanism (Fenn *et al.,* 1973), and saturating inorganic cation (Furukawa and Brindley, 1973; Soma *et al.,* 1983; Vansant and Yariv, 1977). The formation of a colored complex in the montmorillonite-benzidine system is the result of benzidine sorption and subsequent oxidation to a radical cation by the reduction of structural ferric iron; although O_2, or freshly sorbed Fe^{3+} and Cu^{2+} can also act as oxidants (McBride, 1979). Interestingly, with time, sorbed Fe^{3+} loses its ability to oxidize benzidine, and freshly precipitated $Fe(OH)_3$ fails to produce a reaction at all (McBride, 1979). The oxidative polymerization of aromatic compounds at the surface of transition metal exchanged clays has also been demonstrated (Soma *et al.,* 1986; Fenn *et al.,* 1973).

The most studied aromatic amine, aniline, and several of its ethyl- and chloro-substituted analogs have been shown to undergo biotic and abiotic transformations in soils resulting in: (1) colored-clay complexes,

(2) formation of multiring compounds (i.e., azobenzene, and azoxybenzene; Pillai *et al.,* 1982; Barta and Pramer, 1967; Parris, 1980), (3) other higher molecular weight products from chemical interactions with soil organic matter (Hsu and Barta 1974, Bollag *et al.,* 1978, 1987), and 4. mineralization to CO_2. Multiring amines are suggested to be far more recalcitrant than aniline to microbial utilization. The behavior of aminonaphthalene is poorly understood. However, because of its similarity to aniline in structure, its pK_a (3.92), and its high solubility (1700 ppm), it would be expected that these two aromatic amines would behave in a similar manner. Graveel *et al.* (1985) found 1-aminonaphthalene to behave similarly to aniline and suggested that aminonaphthalene is rapidly and reversibly sorbed by electrostatic interactions, hydrophobic binding, and through reversible imine linkages with soil colloids. A subsequent slow reaction, irreversible in nature, bonding the amine to the organic carbon fraction of the soil was also hypothesized.

Preliminary sorption studies in this laboratory with 1-aminonaphthalene on two subsoils low in organic carbon, dominated by smectitic clays, and with little extractable iron showed very rapid uptake of the sorbate (98% in 24 hr). Methanol extraction of these subsoils, however, showed approximately 95–98% recovery of ^{14}C, but the aminonaphthalene concentration of the extracts (determined by HPLC) was below detection limits. Additionally, the ^{14}C was almost entirely associated with compounds (unidentified) with considerably longer HPLC elution times than aminonaphthalene. Similar studies with isolated clay fractions from the above soils showed that the disappearance of aminonaphthalene was related to the clay and not the organic carbon or Fe-oxide content. These studies suggest that 1-aminonaphthalene does not behave in a manner

416

Table 1. Properties of the clay minerals.

| Material[a] | Organic C | CEC[a] | | | Interlayer charge[b] | Octahedral Fe[c] |
		pH 4.5	pH 6.5	pH 8.5		
	%	------------------------------- meq/100 g -------------------------------			%	%
Na-SWy-1	<0.01	75.7	82.7	83.6	0.84 (38%)	10.5
Na-SHCa-1	<0.01	16.6	40.2	58.2	0.76 (<1%)	<0.01

[a] Cation exchange capacity based on ^{22}Na exchange.
[b] Interlayer charge per $O_{20}(OH)_4$; values in parentheses are the % tetrahedral charge (Newman and Brown, 1987).
[c] Based on the number of Fe^{3+} cations per $O_{20}(OH)_4$/total number of cations per $O_{20}(OH)_4$ (Newman and Brown, 1987).

similar to aniline, and that irreversible binding of 1-aminonaphthalene is more rapid than previously suggested, even in soils with low organic carbon content. Therefore, the present study was undertaken to address the lack of published data, and reconcile conjecture with the above qualitative observation on the behavior and fate of 1-aminonaphthalene. The pure clay minerals montmorillonite and hectorite are used as surrogates of soil clays to discern the effect of Fe^{3+} location and the role of pH in the transformation of aminonaphthalene.

EXPERIMENTAL PROCEDURES

Clay preparation and analysis

Earlier work with the aromatic amine, benzidine (Furukawa and Brindley, 1973; McBride, 1979; Teenakoon et al., 1974), demonstrated that color development was due to the oxidation and subsequent production of a benzidine cation radical with the concomitant reduction of structural ferric iron. Therefore, the dioctahedral smectite, SWy-1 montmorillonite, with octahedral Fe^{3+} isomorphic substitution and the trioctahedral smectite, SHCa-1 hectorite, with little, if any, Fe^{3+} isomorphic substitution were selected for this study (Table 1). Bulk samples of montmorillonite (SWy-1, Crook County, WY) and Hectorite (SHCa-1, San Bernardino County, CA) were obtained from the Source Clays Repository of The Clay Minerals Society. The clays were purified and suspensions prepared in the sodium form (Sposito et al., 1981). The final clay suspensions were steam autoclaved for 30 min on three successive days, clay densities determined (Sposito et al., 1981), and suspensions stored under UV light. The cation exchange capacity (CEC) of the clays was determined by ^{22}Na exchange (Babcock and Schulz, 1970) over a pH range of 4.0–9.3. The variation of CEC (meq/100g) with pH is described by the equations CEC = 57.15 + 19.55(pH) + 0.703(pH)^2 and CEC = 37.73 + 11.84(pH) − 0.758(pH)^2 for the hectorite and montmorillonite, respectively (Table 1).

Constant pH sorption studies

Although previous experiments showed laboratory lighting to have no discernable effect on the reactions, all experiments were carried out in a reduced-light en-

vironment by wrapping the reaction vessel with aluminum foil. A double-side-arm, water-jacketed stir cell (250 ml), and a Radiometer Copenhagen pH meter with titrator and autoburette system were employed for all experiments. Specific masses of stock clay suspension (montmorillonite or hectorite), deionized water, and NaCl background electrolyte were added to the stir cell. The pH was adjusted and held constant using the autotitrator system and 0.1 M HCl or 0.1 M NaOH as titrants. Humidified N_2 was passed through the suspension overnight (and for the duration of the experiments). After the overnight equilibration, the titrant volume was recorded and the total mass of the stir-cell system determined. Water circulation around the cell was initiated (maintained at 25 ± 0.5°C). After temperature equilibration, the appropriate amount of 1-aminonaphthalene (ANP) was introduced rapidly into the stir cell from a tared test tube and the added mass determined by difference. The addition of ANP marked T = 0. By designing the studies in this manner, precise determinations of clay and ANP concentrations were possible. Previous work with ANP (Graveel et al., 1985) suggested that the rapid uptake of the amine was related to the cation exchange capacity of the sorbent. Therefore, the clay concentrations for these experiments were determined on total exchange capacity of the suspensions and were about 3.8, 7.6, or 11.4 meq/liter. The initial ANP concentrations were 1×10^{-5}, 10^{-4}, or 10^{-3} M, and, when desired, ^{14}C-1-aminonaphthalene was used (5000 cpm/ml).

At timed intervals (15, 30, 45, 60, 90, 180, 360, 1440, and 2880 min) approximately 25 ml of the reacting suspension was removed to tared corex tubes and centrifuged at 5000 rpm for 20 min. The time at which phase separation was accomplished, while arbitrary do to the length of centrifugation, was assumed to be the point when the centrifuge reached its maximum rpm (5000). Centrifugate (3 ml) was removed to amber glass HPLC vials for quantification, and where appropriate, a 1-ml aliquot was removed for ^{14}C liquid scintillation counting. The remaining liquid was carefully removed and discarded, and the sorbed ANP and products extracted with MeOH. ANP concentration in the MeOH solution was determined by HPLC. Additionally, a complete HPLC chromatogram was col-

lected. Selected sampling time MeOH extracts were prepared for GC/MS analysis.

A hectorite suspension at approximately 3.8 meq/liter, pretreated as discussed above, was rapidly adjusted to pH 2, and approximately 10 ml of 2.61×10^{-4} M Fe^{3+} solution added. The Fe was allowed to sorb for 10 min then a 2 ml sample was taken, and the supernatant analyzed for Fe. At this time the suspension was rapidly adjusted up to pH 4.5. After the pH stabilized (about 5 min) enough ANP was added to give an initial concentration of 1×10^{-4}M. Beyond this point the system was treated as described above, except that periodic supernatant samples were taken for Fe determination by inductively-coupled argon plasma spectrophotometry (ICP).

Extraction procedure and efficiency

The efficiency of the MeOH extraction to remove ANP and any transformation products quantitatively was determined using a suspension of SWy-1 montmorillonite (7.6 meq/liter) and 1×10^{-4} M ANP with a known amount of ^{14}C-1-aminonaphthalene (5000 cpm/ml). The clay-sorbate system was allowed to react for 48 h. An aliquot of suspension was removed to a tared glass centrifuge tube, mass determined, and then centrifuged for 20 min at 5000 rpm. A 1-ml aliquot of the supernatant was removed to a tared scintillation vial, weighed, and the activity of ^{14}C determined by liquid scintillation counting. The remaining supernatant was carefully removed and discarded, and the occluded solution mass determined. The clay plug was resuspended in 20 ml of MeOH, mass determined, the capped centrifuge tube vigorously shaken, and then centrifuged. The quantity of MeOH used for each extraction was dependent on the clay and ANP concentrations, and ranged between 10 and 20 ml. The supernatant was removed and placed in a tared amber 100-ml volumetric flask. The MeOH extraction procedure was repeated a total of four times. After the extraction procedure was completed the volumetric flask was filled to volume with MeOH and mass determined. The ^{14}C activity was determined by liquid scintillation counting. Using the above technique 96.4% of the ^{14}C activity was recovered. This procedure was used throughout these studies to quantify the ANP on the surface and collect reaction products for HPLC and GC/MS analyses.

Organic compounds and analysis

ANP (99% purity, Aldrich Co.) was used without further purification. Radiolabeled ^{14}C-ANP was custom synthesized (Sigma Chem. Co.). The radiochemical purity was >99% and specific activity was 8.0 mCi/mmol. Approximately 0.4 g of ANP was dissolved in 0.1 M Ultrex HCl, diluted to about 200 ml with deionized H_2O, pH adjusted to 4.0 with 10 M NaOH, and then diluted to a total volume of 0.25 liter. The final

ANP concentration was 1.12×10^{-2} M (1609 mg/liter). The clay extracts and clay-free centrifugates were analyzed on a HPLC system consisting of a Waters 721 pump controller, two Waters 510 pumps, a Waters 710A WISP auto-injector, and a Katros Spectroflow 773 UV detector. When necessary, the HPLC column effluents were fractionated using an Isco Model 328 fraction collector. Data were acquired with either a Hewlett-Packard 3390 integrator, or a Rainin Macintosh-based data acquisition and analysis system. The samples were run on a Waters μ-bondapak C18 reverse phase column using the following parameters: flow rate 1.5 ml/min; isocratic 55/45 acetonitrile/water for the first 4 minutes, with a linear gradient up to 100% acetonitrile over the following 16 minutes. The variable wavelength UV detector was set to 234 nm.

For a more detailed analysis, the clay extracts and the solution supernatants were run on a gas chromatographic mass spectrometer (GC/MS) that consisted of a HP5880 capillary gas chromatograph coupled with an HP5970B bench top mass spectrometer. An HP1000 computer running RTE/6 software was used for data acquisition and analysis. The samples were separated on a J and W (J and W Scientific, Folsom, CA) 30 m, 0.25 mm ID DB-5 capillary column. The injection port and transfer line were set to 280°C. The column oven temperature was held at 40°C for the first 4 minutes of the runs, and increased to 280 at 6°C/min. Before GC/MS analysis, the aqueous solution samples were extracted 3 times with 50 ml of methylene chloride in a glass separatory funnel fitted with a Teflon stopcock. The solution extracts were combined and the volumes were reduced via rotary evaporation to about 4 ml. The samples were further concentrated to a 1-ml volume under a stream of dry nitrogen. The MeOH clay extracts were exchanged into methylene chloride and concentrated to a 1-ml volume prior to injection.

Adsorption-edge experiments

A hectorite clay-ANP suspension (approximately 3.8 meq/liter clay and 1×10^{-4} M ANP), using the procedure described above, was equilibrated at pH 8.91 for 2 hr, a 10 ml aliquot removed, the phases separated, and the supernatant concentration determined by HPLC. Following the sampling the pH was adjusted downward by one pH unit, allowed to equilibrate for 1 hr, and then sampled again. This procedure was repeated 5 times.

Microbial degradation

An organism isolated from the deep (176 m) Middendorf sediments of the southeast Coastal Plain that is capable of utilizing aniline, pyridine, quinoline and other organic compounds as its sole source of carbon was used to test the microbial degradation rate of ANP in a solution under aerobic conditions (Brockman *et al.*, 1989). Additionally, a consortia of organisms com-

mon to the subsurface environment were also tested. A solution of 1 or 10 ppm ANP (^{14}C-ANP) and basic mineral media in flasks equipped with 1 M KOH CO_2 traps were inoculated with the requisite organisms, and placed in a constant temperature incubator-shaker at 25°C. This study was carried out in triplicate and with controls consisting of ANP without organisms, and ANP plus organism plus 100 ppm $HgCl_2$. KOH traps were changed periodically and the mineralization of ANP determined by ^{14}C liquid scintillation counting of the KOH trap fluid.

RESULTS

Microbial mineralization of ANP was not observed until approximately 26 days after innoculation. Even after this lag time the mineralization rate was slow. Additionally, mineralization was only noted at the lower ANP concentration and then only in the flasks innoculated with the single isolate that had previously been shown to utilize aniline and several N heterocyclic compounds. Therefore, microbial degradation of ANP was felt to be of no concern in the present study.

Montmorillonite-ANP interactions

Aminonaphthalene sorption to Na-montmorillonite, like benzidine (Furukawa and Brindley, 1973), produced a blue color within 15 to 30 min, and its intensity appeared to increase slightly with the amount of ANP sorbed. Rigorous exclusion of air by flushing the system with N_2 prior to and during the sorption experiments did not affect color development. HPLC analyses of the supernatant showed only ANP in solution regardless of pH, clay, or ANP concentration. However, extraction of the clay pellet with four washings of methanol removed the blue color from the clay and left a montmorillonite pellet that appeared (at the higher initial concentrations of ANP) to be bleached of its pale green-yellow color. HPLC chromatograms of the methanol extracts, with time, showed a build up of later-eluting compounds with a concomitant decrease of ANP (Figure 1). The intensities (peak heights, areas) of the transformation products were less at the higher pH values for a set reaction time. At pH 9.0, for example, it took approximately 120 hr to attain an HPLC chromatogram similar to those attained at 48 hr at pH 4.5, and consume approximately the same total amount of ANP. Sorption of ANP to Na-montmorillonite, over the pH range of 4.5 to 9.0 (1 × 10^{-5} M ANP and 3.8 meq/liter) did not reach a steady-state solution concentration in 48 hr (Figure 2). Additionally, there was little or no observable ANP associated with the surface (Figure 2). At pH 4.5 about 40% of the ANP was unaccounted for after 30 min, and 92% was gone after 48 hr.

GC/MS analyses of the clay extracts from the high concentration clay-ANP systems (11.4 meq/liter and 10^{-3} M, respectively), at pH 4.5, showed the presence
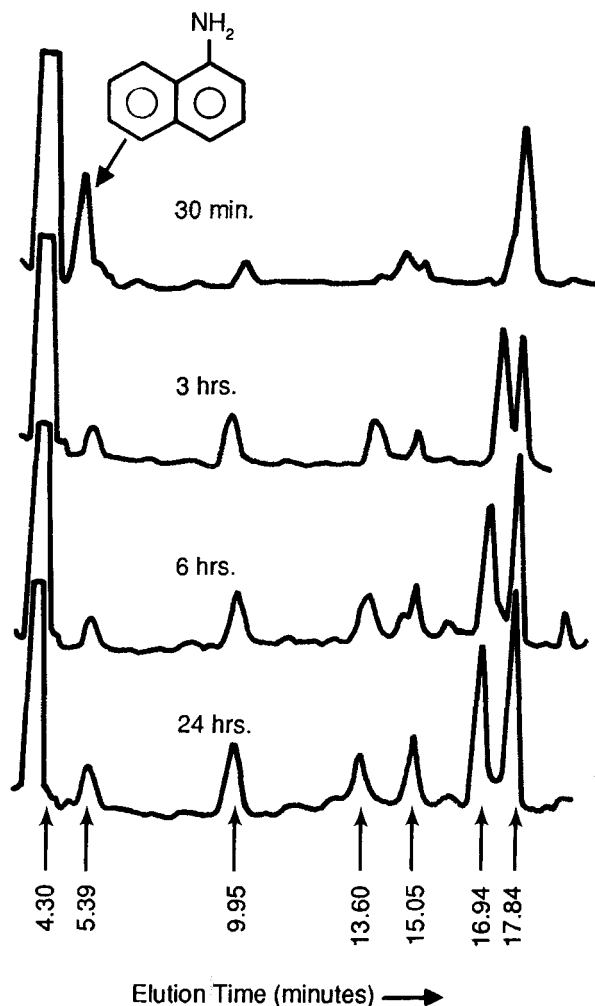

Figure 1. Representative HPLC chromatographs of clay extracts from sorption of 10^{-5} M ANP to montmorillonite (3.8 meq/liter) at pH 4.5 with time (the 4.30 min peak is ANP).

of four major products (Figure 3a). Each of these compounds has the same molecular ion at m/z 284 (100%). The mass spectra are relatively featureless and similar, implying that they are four isomers of a highly aromatized compound (Figures 3b–e). The mass weights are, interestingly, only 2 mass units shy of being equal in mass to two ANP molecules (ANP M.W. = 143). The above GC/MS data were basically the same for those clay-ANP systems that were high enough in concentration to yield any GC/MS data, i.e., clay $\geq$ 3.8 meq/liter and ANP $\geq$ 10^{-4} M. Occasionally, other peaks were noted to elute downfield of m/z 284 compounds. In particular, two peaks of m/z 298 and 307 (100%) were the most often noted. However, these were minor and not always observable. While the four m/z 284 products were observed in the clay extracts from the pH 9 (120 hr) sample, the intensity or distribution of the four product peaks were slightly different.
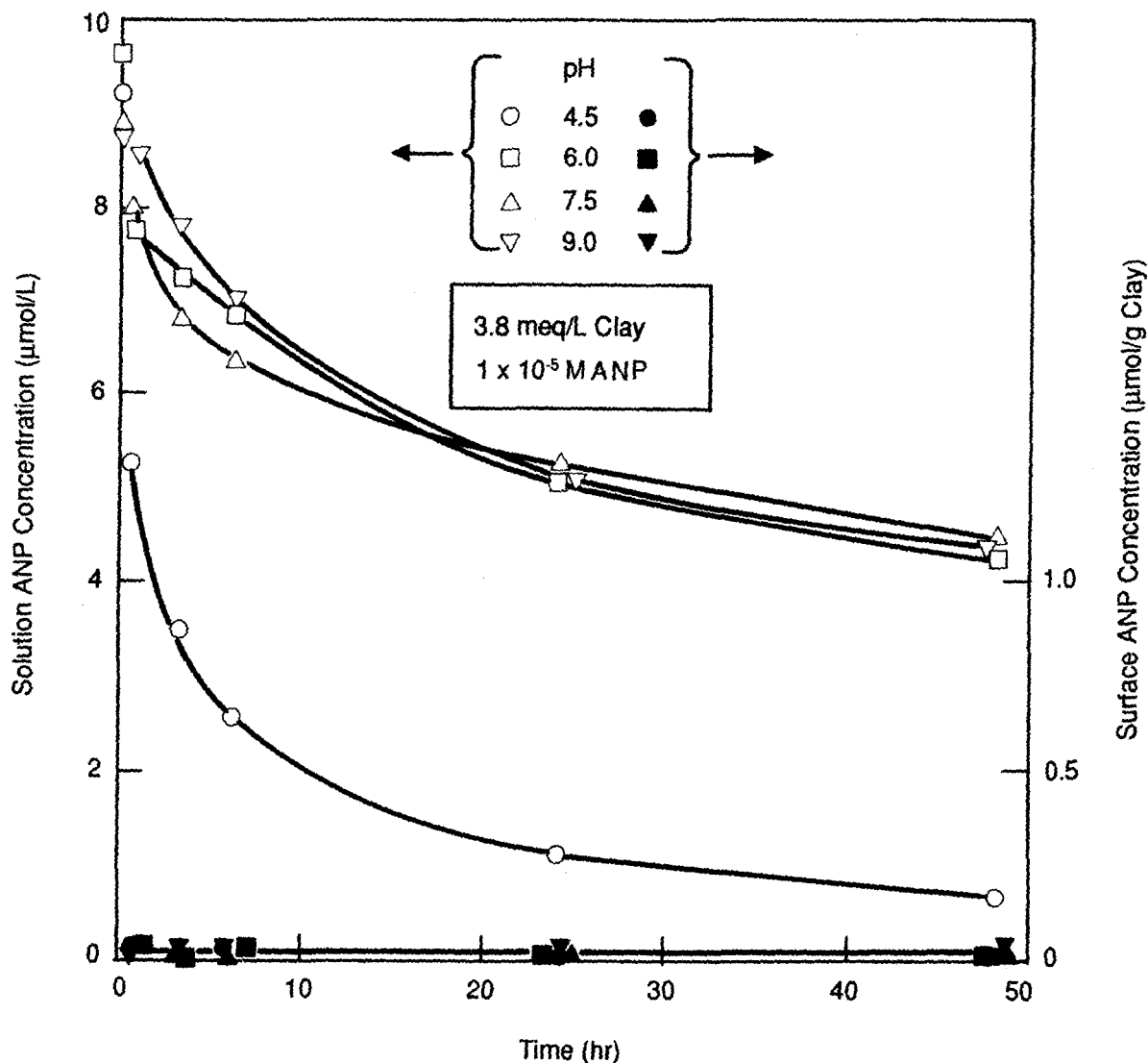
Figure 2.   Effect of pH and time on the disappearance of ANP from solution.

The HPLC analysis of the clay extracts (Figure 1) shows evidence of more than four products being formed in the transformation of ANP, but GC/MS analysis of the clay extracts does not mirror the HPLC results. The relative peak size noted in the HPLC chromatograms cannot be used to directly estimate the relative significance of a potential transformation product. Additionally, the inability to observe more compounds by GC/MS than the six noted previously (four major peaks at m/z 284 and two minor peaks at m/z 298 and 307) may be due to a compound: (1) being thermally labile (i.e., breakdown during the GC volatilization process), (2) having a low ionization efficiency, or (3) having an extremely low concentration but a high extinction coefficient at 235 nm that would allow minute concentrations to yield a UV/VIS response.

As would be expected, increasing either the clay concentration or the initial ANP concentration while keeping the other constant caused an increase in the initial rate of transformation. Here the initial rate is simply the amount of ANP transformed over the initial 30 min of the reaction (Table 2). Above an initial concentration of 1×10^{-5} M ANP (regardless of clay concentration), a clay surface ANP concentration was observed in the 30 min clay extracts. However, the clay-bound concentration in each system decreased with time (Figure 4). Interestingly, the rate of ANP loss from the surface conformed to a 2nd-order rate with respect to the surface concentration of ANP (as determined by plotting the inverse of the surface ANP concentration versus time). As expected the rate constant (k_{obs}), determined from the slope of the 2nd-order plot, in-
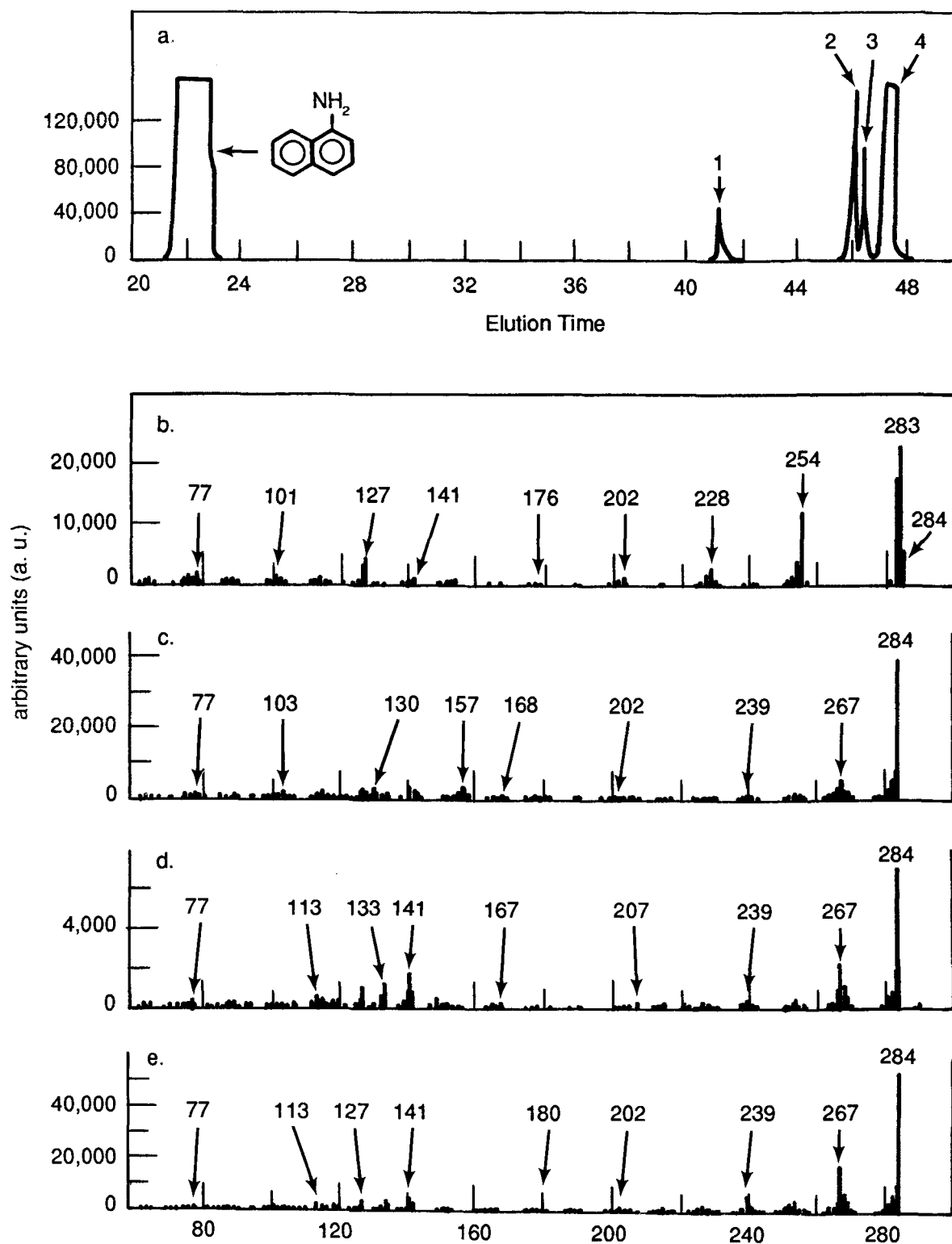
Figure 3.   a) Total ion chromatograph of MeOH extract from a montmorillonite suspension (11.4 meq/liter and 1×10^{-3} M ANP) at pH 4.5 after 48 hr, b) mass spectra of peak 1 in Figure 3a, c) mass spectra of peak 2 in Figure 3a, d) mass spectra of peak 3 in Figure 3a, e) mass spectra of peak 4 in Figure 3a.
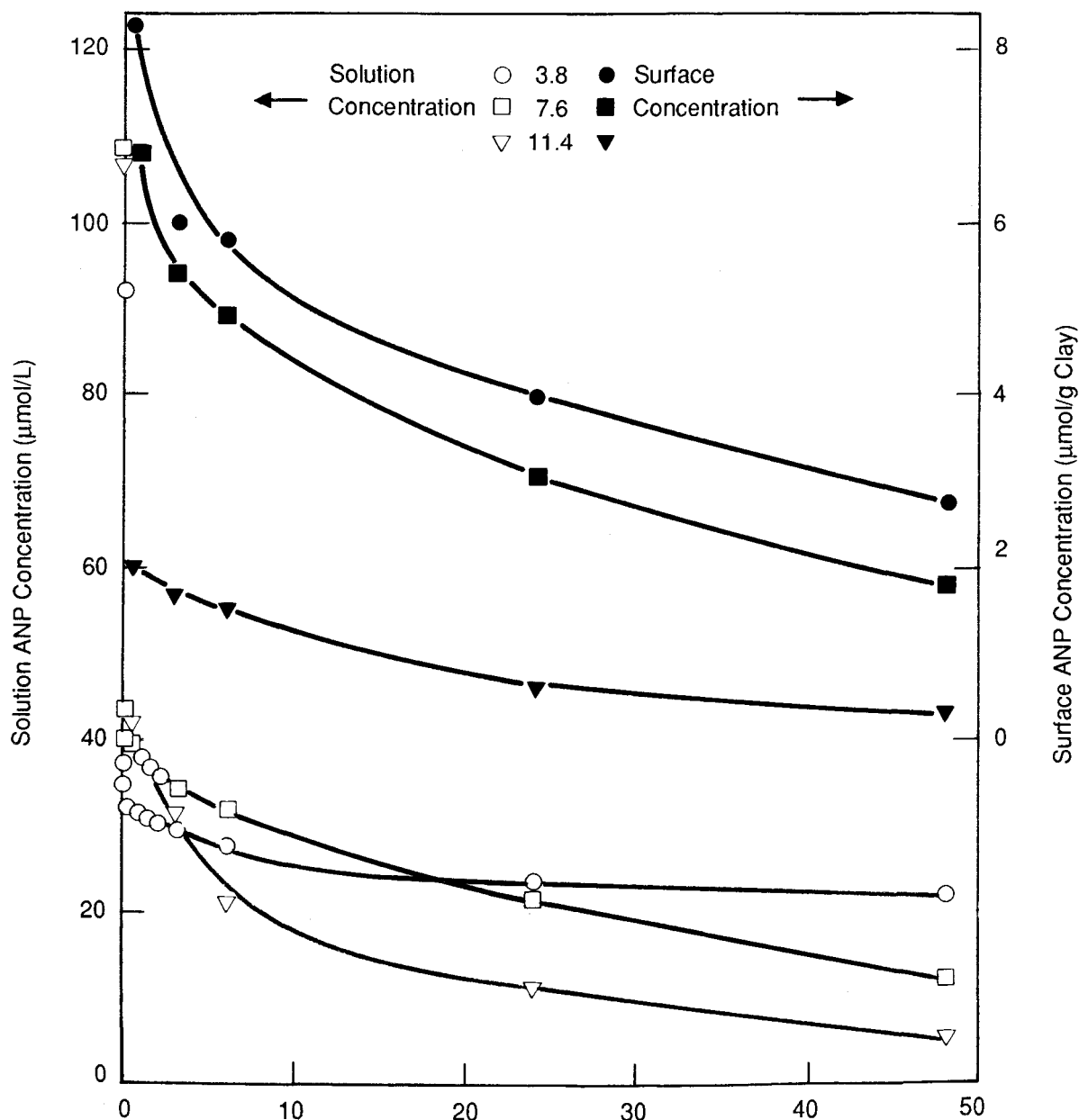
Figure 4. The effect of increasing clay concentration (3.8, 7.6, and 11.4 meq/liter) and time on the solution and surface concentration of ANP (1×10^{-4} M).

creased with increasing clay concentration, but the k_{obs} decreased with increasing initial ANP concentration (Table 2).

The decrease in k_{obs} observed as the initial concentration of ANP was increased may be due to the formation of quasi-crystalline structure in the clay suspensions. Dilute suspensions of Na-montmorillonite, as in the present study, are suspended as single crystals; i.e., there is no stacking of the hydrated clay units, and hence no interlayers (Sposito, 1984). However, the addition of ANP at the higher concentrations may cause a clustering of ANP on the surface, a demixing of Na^+ and the protonated ANP species, and formation of a quasi-crystalline structure, with the Na^+ being relegated to the external surfaces. This would allow the ANP to be sequestered in the interlayers, thereby isolating the sorbed species and stabilizing surface-activated species against further reaction. This could explain the observed decrease in the rate of surface ANP loss when the ANP concentration is increased at a constant clay density. A simple settling study using Na-montmorillonite and ANP in graduated cylinders was performed

Table 2. Variation of the initial rate of solution ANP disappearance and the 2nd-order rate constant for the disappearance of the surface-ANP complex as a function of clay and ANP concentration.

Clay concentration	Solution concentration	pH	Initial rate	k_{obs}	r^2
meq/liter	M/liter		μM/liter/min	g/μM/h	
3.8	10^{-4}	4.5	0.957	$4.9 \times 10^{-3} \pm 1.3 \times 10^{-3}$	0.994
7.6	10^{-4}	4.5	0.658	$8.7 \times 10^{-3} \pm 2.7 \times 10^{-3}$	0.991
11.4	10^{-4}	4.5	1.443	$5.0 \times 10^{-2} \pm 1.6 \times 10^{-2}$	0.991
7.6	10^{-5}	4.5	0.130	—	—
7.6	10^{-3}	4.5	9.548	$5.4 \times 10^{-5} \pm 2.0 \times 10^{-5}$	0.990

and the rate of settling determined as a function of ANP concentration. The results of this study showed that as the ANP concentration increased, the settling time decreased, suggesting the formation of quasi-crystalline structure.

Hectorite-ANP interactions

Hectorite, a low-iron trioctahedral smectite, pale white in color (Table 1), readily sorbs ANP, but no blue color or transformation products are observed, and a steady-state solution and surface concentration is obtained rapidly (Figure 5). In the presence of freshly-sorbed Fe^{3+} on the hectorite surface, the sorption of ANP results in the development of a blue color as ANP is continuously removed from solution. Additionally, the ANP surface concentration decreases with time (Figure 6). GC/MS analysis of the Fe^{3+}-hectorite extracts showed that three major compounds, besides ANP, were present. Each of these compounds had a molecular ion m/z 284 (100%). The MS spectra were very similar to the three most prominent products found with montmorillonite at pH 4.5 (i.e., peaks 2, 3, and 4 in figure 3a). The order of intensity of the three peaks observed in the hectorite-Fe^{3+} system were peak 4 > 3 > 2. This is slightly different than observed with the montmorillonite suspension. Additionally, there was no evidence of peak 1 (Figure 3a). There were two minor peaks with m/z 307, and these same peaks were also observed sporadically with the montmorillonite systems (pH 4.5). The total amount of Fe^{3+} added to the hectorite suspension of 3.8 meq/liter was slightly more than half that present in an equivalent amount (charge basis) of montmorillonite, but less than 10% of the total cation exchange capacity of the suspension. The initial rate of transformation for hectorite-Fe^{3+}-ANP was 0.161 μmol/liter/min. This compares favorably to a similar montmorillonite suspension (3.8 meq/liter and 1×10^{-4} M ANP; table 2). Additionally, the disappearance of hectorite surface-bound ANP conformed to a 2nd-order rate with respect to the surface concentration of ANP, as did the montmorillonite systems. The k_{obs} of the two clay systems, at 3.8 meq/liter and 1×10^{-4} M ANP, were statistically identical (k_{obs} = $4.7 \times 10^{-3} \pm 2.6 \times 10^{-3}$ and $4.9 \times 10^{-3} \pm 1.3 \times$

10^{-3} g/μm/hr for hectorite and montmorillonite suspensions, respectively).

DISCUSSION

Qualitative reaction model

A proposed simplified model of the transformation of ANP on montmorillonite would be: (1) sorption of the protonated ANP species by cation exchange, (2) select sorbed species oxidized (and Fe^{3+} reduced) forming a radical-cation (or a free radical with the loss of a proton), and (3) formation of the products through a reaction of the radical-cation and neutral ANP. The clay surface appears to be acting as a catalytic surface since there is no evidence of a reaction between Fe^{3+} and ANP in solution (after about 190 min reaction time under an N_2(g) atmosphere). Addition of a montmorillonite or hectorite slurry results in the immediate development of the classic blue color and production of the above products. The placement of the iron (structural or exchangable), at least in the above systems, does not appear to be crucial to the rate of transformation. However, it does seem to direct the products and their respective yields. Clearly, the Fe^{3+} (or at least a transition metal cation with similar properties) is a necessary reactant in the transformation of ANP, and a clay surface appears necessary as a catalytic surface.

The sorption of ANP to hectorite as a function of pH parallels the ionization fraction of ANP; as pH increases sorption decreases. This type of coincident decrease in sorption and ionization fraction of the sorbate has been seen before. Sorption of quinoline, a N-heterocyclic organic base, to soils has been previously observed to decrease with a decrease in the ionization fraction (Zachara et al., 1986), and has been demonstrated to be related to a cation exchange process (Ainsworth et al., 1987). These data suggest strongly that an exchange process controls the rapid sorption of ANP to hectorite, and probably is the first reaction in the transformation process of ANP on the surface of montmorillonite.

Using the ANP sorption data to pure hectorite, a conditional equilibrium constant or Vanslow selectivity coefficient for the exchange of Na^+ by $ANPH^+$ on hectorite may be written as:
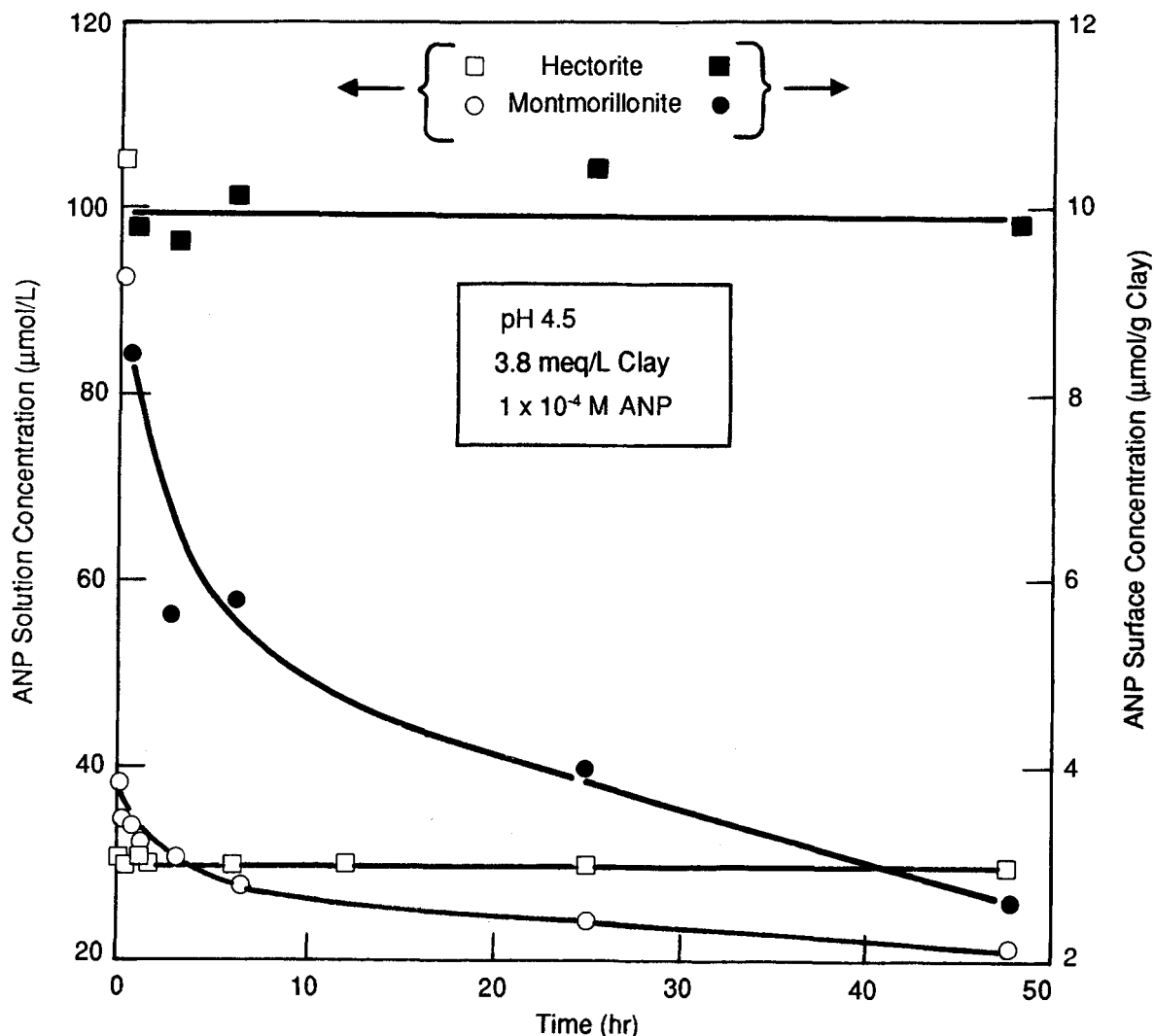
Figure 5. Comparison of ANP solution and surface concentrations as a function of time between a pure hectorite and montmorillonite clay suspension at pH 4.5.

$$XNa + ANPH^+ = XANPH + Na^+ \qquad (1)$$

and

$$K_v = (X_{ANPH}a_{Na^+}/X_{Na}a_{ANPH^+}), \qquad (2)$$

where X_{ANPH} and X_{Na} are the respective mole fractions on the surface, and a_{Na^+} and a_{ANPH^+} are the respective solution activities. The calculated K_v for $ANPH^+$-hectorite, at pH 4.5–6.5 ranges between 94 and 150. At pH >6.5 the K_v starts increases dramatically (i.e., K_v = 150 at pH 6.5 and increases to 800 at pH 9.0). The increase in K_v at pH >6.5 is believed to be due to underestimation of the small quantity of sorbed ANP. Therefore K_v values at pH >6.5 are highly questionable. Selectivity coefficients (K_v) for tetraethylammonium ions on Na-montmorillonite were observed to be as high as 22.4 (Theng *et al.,* 1967). Quinoline K_v

values ranged from 200 to 1200, depending on surface loading, in a montmorillonite suspension similar to that used in the present study (Ainsworth *et al.,* 1987). Additionally, the adsorption of benzidine and aniline to montmorillonite and hectorite have been suggested to be via a cation exchange reaction (Furukawa and Brindley, 1973).

While an exchange mechanism is believed to be responsible for the rapid uptake of ANP in the clay systems used in the present study, only the sorption sites associated with the ditrigonal cavities in the tetrahedral layers of the 2:1 layer clays are believed to act as sites of "activation" for the transformation of ANP on montmorillonite surfaces. Association with the ditrigonal cavities would bring the ANP in closer proximity to the Fe^{3+} that is incorporated into the octahedral layer, at least in montmorillonite. Additionally, the
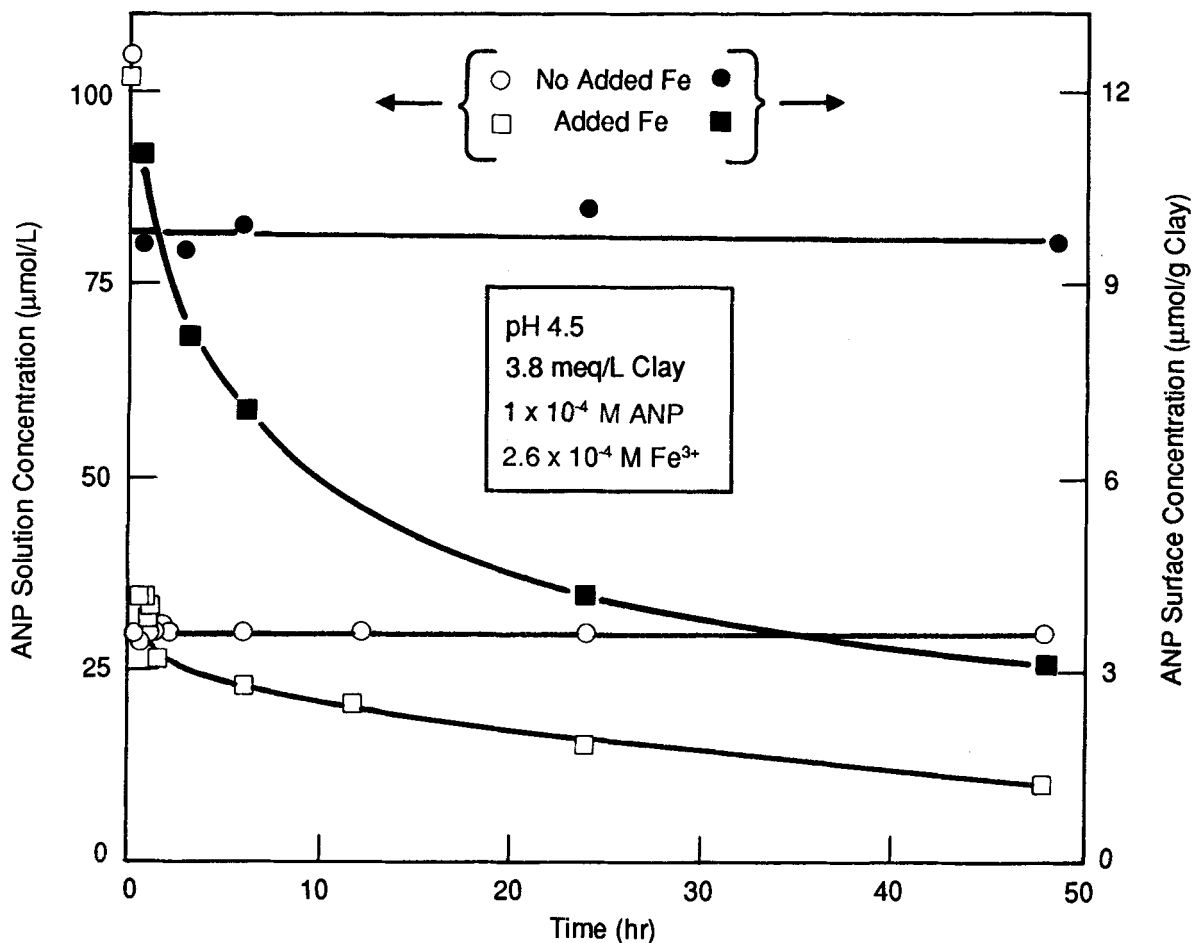
Figure 6. Comparison of ANP solution and surface concentrations as a function of time between a suspension of hectorite with and without Fe^{3+} sorbed to the surface.

amine group is the correct size in terms of fit, and it is well known that the inorganic ammonium ion, and alkylammoniium cations, similar in size to the amine, readily occupies the diatrigonal cavities. Anilinium-vermiculite intercalate is nearly perpendicular to the plane of the surface with the amine group directed at the siloxane ditrigonal cavities (Slade and Stone, 1983). Additionally, at higher concentrations of ANP in solution and low clay concentrations (Figure 4) surface ANP is still detectable after as much as 30 days, even though substantial amounts of Fe^{3+} are still available. This implies that only a subset of the total exchange sites are active in the transformation of ANP.

The ability of sorbed transition metals such as Fe^{3+} and Cu^{2+} to act as Lewis acids in the oxidative formation of colored surface complexes is well known (McBride, 1979, Fenn et al., 1973, Soma et al., 1983, 1985, 1986). Copper(II) sorbed to hectorite has also been shown to oxidize anisole to a radical cation with subsequent reaction between the radical cation and neutral anisole producing a 4-4'-dimethylbiphenyl

complex (Fenn et al., 1973). Soma et al. (1985, 1986) found sorbed phenol, via oxidative polymerization, forms dimers, trimers, and tetramers when reacted with Fe^{3+}- and Cu^{2+}-montmorillonite. Aniline undergoes oxidation at the surface of smectite clays in the presence of adsorbed Fe^{3+} or Cu^{2+} (Cloos et al., 1979; Cloos et al., 1981). While all of the experiments in the present study were conducted with rigorous exclusion of O_2, air was bubbled through the hectorite-ANP system (no added Fe^{3+}) for approximately 24 hr without any observable color development or loss of ANP. Additionally, past work has demonstrated that octahedral layer iron substitution in smectite clays like hectorite (McBride, 1979), or montmorillonite (Teenakoon et al., 1974; Theng, 1971; Furukawa and Brindley, 1973) oxidize benzidine and leads to a blue-colored radical cation surface complex.

Of interest is the apparent limited, or lack of, effect due to Fe^{3+} location (exchangeable versus structural). It is apparent that the physical and chemical environment of the two ferric iron species are different. Yet
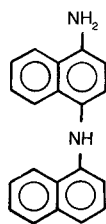
Figure 7. Proposed structure of the dominant ANP transformation product.

Figure 8. Deuteration of ANP, and diphenylamine.

the initial rates of transformation of ANP on montmorillonite and Fe-hectorite are similar, the rates of disappearance of ANP from the surface of the two clays are similar, and the transformation products are largely identical. This would suggest that the interaction of ANP on the hectorite-Fe surface and montmorillonite surface are similar. However, aniline interaction with exchangeable Fe^{3+} is suggested to be through the π-electrons of the aniline benzene ring, but is thought to coordinate via the amino group with Cu^{2+} (Voudrias and Rienhard, 1986). Dimethyl methylphosphonate has been shown to interact, through an ion-dipole interaction, between the cationic surface species and the phosphaphonate oxygen directly rather than through the waters of hydration (Bowen *et al.,* 1988). At present, the difference in surface-ANP interactions leading to the formation of a free radical (or radical cation) in the montmorillonite and Fe-hectorite systems can only be speculated upon. However, the protonation and subsequent cation exchange reaction believed to be of importance in the montmorillonite system is inconsistent with a coordination reaction between ANP and sorbed Fe^{3+}-hectorite system as suggested by studies with aniline.

Proposed product structure

The four principal products formed in the montmorillonite system and the three products in the hectorite systems are only 2 mass units different than the mass of two ANP molecules. We have not been able to isolate enough of the products to identify their structure definitively. However, from deuterium exchange studies carried out on the clay extract solutions and mass spectra of the deuterated products. N(x-amino-aphthyl)-1-naphthylamine are believed to be the primary products with x = 4 being the predominant isomer (Figure 7). The proposed product(s) has one hydrogen associated with the secondary amine, similar to that of diphenylamine, and two hydrogens associated with the primary amine and, hence, is similar to ANP. The rate of deuteration for these hydrogen atoms associated with ANP and diphenylamine are different (Figure 8). The rate of isotopic exchange of the secondary amine is slow, as determined by experiments at pH 3, 50°C. After 30 days clear mass spectra evi-
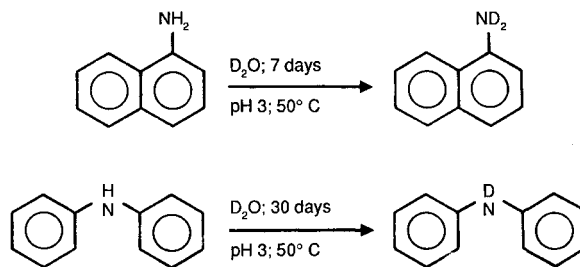
dence for one proton exchange was observed. The primary amine hydrogens of ANP, under similar conditions, are completely exchanged in about a week (Figure 8). Similar rates, or rate differences, of deuteration for the two types of hydrogens would be expected if the proposed product is reasonable. In fact, when deuteration is carried out, the mass spectra of the product compounds show an increase of two mass units in each of the four 284 peaks after about 7–10 days. After 30–35 days, while not complete, there is clear evidence of a third deuterated site. Therefore, we feel that the compounds represented by the four GC/MS 284 peaks are isomers of the structure depicted in Figure 7.

It is unclear at this time if the products that are seen in the pure clay systems of this study are also observed in the soil or soil clay systems. Additionally, it is unclear if the observed products are end products or, if given longer periods of time to react would continue to do so, eventually forming oligomer-type compounds. For example, aniline percolated through columns containing Fe^{3+}-montmorillonite developed colored spots and stripes, with the final products suggested to be soil-humin or kerogen-like polymers (Cloos *et al.,* 1981). Similarly, a mixture of phenolic compounds mixed in aqueous suspensions of montmorillonite, illite, kaolinite and quartz resulted in a mixture of polymers of humic and fulvic-like materials (Wang *et al.,* 1978).

ACKNOWLEDGMENTS

REFERENCES

Ainsworth, C. C., Zachara, J. M., and Schmidt, R. L. (1987) Quinoline sorption of Na-montmorillonite: Contributions of the protonated and neutral species: *Clays & Clay Minerals* **35,** 121–128.

Babcock, K. L. and Schulz, R. K. (1970) Isotopic and conventional determination of exchangeable sodium percentage of soil in relation to plant growth: *Soil Sci.* **109,** 19–22.

Barta, R. and Pramer, D. (1967) Pesticide transformation to aniline and azo compounds in soil: *Science* **156**, 1617–1618.

Bollag, J-M., Blattmann, P., and Laanio, T. (1978) Adsorption and transformation of four substituted anilines in soil: *J. Agric. Food Chem.* **26**, 1302–1306.

Bollag, J-M., Liu, S-Y., and Deune, E. G. (1987) Transformation of 2,6-diethylaniline in soils: *Soil Sci.* **143**, 56–65.

Bowen, J. M., Powers, C. R., Ratcliffe, A. E., Rockley, M. G., and Hounslow, A. W. (1988) Fourier transform infrared and Raman spectra of dimethyl methylphosphonate adsorbed on montmorillonite: *Environ. Sci. Technol.* **22**, 1178–1181.

Brockman, F. J., Denovan, B. A., Hicks, R. J., and Fredrickson J. K. (1989) Isolation and characterization of quinoline-degrading bacteria from subsurface sediments: *Appl. Environ. Microbiol.* **55**, 1029–1032.

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

Cloos, P., Badot, C., and Herbillon, A. (1981) Interlayer formation of humin in smectites: *Nature* **298**, 391–393.

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

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

Graveel, J. G., Summers, L. E., and Nelson, D. W. (1985) Sites of benzidine, 1-napthylamine and *p*-toluidine retention in soils: *Environ. Toxicol. Chem.* **4**, 607–613.

Hauser, C. R. and Leggett, M. B. (1941) Color reactions between clays and amines: *J. Am. Chem. Soc.* **62**, 1811–1814.

Hsu, T. S. and Barta, R. (1974) Interaction of pesticide-derived chloroaniline residues with soil organic matter: *Soil Sci.* **116**, 444–452.

McBride, M. B. (1979) Reactivity of adsorbed and structural iron in hectorite as indicated by oxidation of benzidine: *Clays & Clay Minerals* **27**, 224–230.

Newman, A. C. D. and Brown, G. (1987) The chemical constitution of Clays: in *Chemistry of Clays and Clay Minerals*, A. C. D. Newman, ed., Mineralogical Society Monograph No. 6, Wiley, New York, pp. 1–128.

Parris, G. E. (1980) Environmental and metabolic transformations of primary aromatic amines and related compounds: *Residue Rev.* 76, 1–30.

Pillai, P., Helling, C. S., and Dragun, J. (1982) Soil-catalyzed oxidation of aniline: *Chemosphere* **11**, 299–317.

Slade, P. G. and Stone, P. A. (1983) Structure of a vermiculite-aniline intercalata: *Clays & Clay Minerals* **31**, 200–206.

Solomon, D. H. (1968) Clay minerals as electron acceptors and/or electron donors in organic reactions: *Clays & Clay Minerals* **16**, 31–39.

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

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

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

Soma, Y., Soma, M., and Harada, I. (1984) 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.

Soma, Y., Soma, M., and Harada, I. (1983) Resonance Raman spectroscopy of benzene adsorbed on Cu²⁺-montmorillonite. Formation of poly(*p*-phenylene) cations in the interlayer of the clay mineral: *Chem. Phys. Letters* **99**, 153–156.

Sposito, G. (1984) *The Surface Chemistry of Soils*: Oxford University Press, New York, 234 pp.

Sposito, G., Holtzclaw, K. M., Johnston, C. T., and LeVesque, C. S. (1981) Thermodynamics of sodium-copper exchange on Wyoming bentonite at 298 K: *Soil Sci. Soc. Am. J.* **45**, 1079–1084.

Teenakoon, D. T. B., Thomas, J. M., and Tricker, M. J. (1974) Surface and intercalate chemistry of layer silicates. Part II. An iron-57 Mössbauer study of the role of lattice-substituted iron in the benzidene blue reaction of montmorillonite: *J. Chem. Soc. Dalton Trans.* **20**, 2211–2215.

Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reactions:* Wiley: Adam Hilger, London, 343 pp.

Theng, B. K. G. (1971) Mechanisms of formation of colored clay-organic complexes. A review: *Clay & Clay Minerals* **19**, 383–390.

Theng, B. K. G., Greenland, D. J., and Quirk, J. P. (1967) Adsorption of alkylammonium cations by montmorillonite: *Clay Miner.* **7**, 1–17.

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

Vansant, E. F. and Yariv, S. (1977) Adsorption and oxidation of dimethylaniline by laponite: *J. Chem. Soc. Faraday Trans.* **73**, 1815–1824.

Voudrias, E. A. and Rienhard, M. (1986) Abiotic organic reactions at mineral surfaces: in *Geochemical Processes at the Mineral Surface*, J. A. Davis and K. F. Hayes, eds., ACS Symposium Ser. No. 323, Amer. Chem. Soc.: Washington DC, pp. 462–487.

Wang, T. S. C., Li, S. W., and Ferng, Y. L. (1978) Catalytic polymerization of phenolic compounds by a latosol: *Soil Sci.* **126**, 81–86.

Zachara, J. M., Ainsworth, C. C., Felice, I. J., and Resch, C. T. (1986) Quinoline sorption to subsurface materials: Role of pH and retention of the organic cation: *Environ. Sci. Technol.* **20**, 620–627.