

Interaction of 1-Naphthol and Its Oxidation Products with Aluminum Hydroxide

K. G. KARTHIKEYAN

Soil Science Program, Department of Agronomy,
The Pennsylvania State University,
University Park, Pennsylvania 16802

JON CHOROVER*

Soil Science Program, Department of Agronomy,
116 ASI Building, The Pennsylvania State University,
University Park, Pennsylvania 16802

JACKIE M. BORTIATYNSKI

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

PATRICK G. HATCHER

Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210

Sterile batch experiments were conducted to investigate the effects of pH, dissolved O₂ concentration, and reaction time on interaction of 0.1 mM ¹⁴C-1-hydroxynaphthalene [1-naphthol] with poorly crystalline Al(OH)₃(s). Negligible (<4%) sorption of 1-naphthol to Al(OH)₃(s) was observed after 20 h reaction time (conditions — dark, w/ O₂). However, a significant increase in sorption of ¹⁴C labeled compound occurred with increasing equilibration time to 7 days, and a clear pH dependent trend emerged. The extent of removal was minimal below pH 6.8, increased sharply over a narrow pH range, and leveled off around pH 8.2. A similar pH-dependent trend was observed for 1-naphthol transformation in controls [no Al(OH)₃(s)]. In the absence of O₂, 1-naphthol transformation and removal were negligible even after 7 d reaction time. Therefore, sorption of ¹⁴C labeled compound is due to a stronger interaction between the naphthol oxidation product and Al(OH)₃(s). ¹³C CPMAS NMR spectra of 1,4-¹³C-labeled 1-naphthol reacted with Al(OH)₃(s) showed a chemical shift change at the C₄ position and also the progressive emergence of a new peak attributable to naphthoquinone. Possible mechanisms for interaction of naphthoquinones with Al(OH)₃(s) include hydrophobic sorption and/or surface complexation. The Al(OH)₃(s) surface provides a “sink” for irreversible binding of the quinone transformation product.

Introduction

Mineral surfaces catalyze various abiotic reactions of organic compounds via hydrolysis, substitution, redox, and polymerization. Hydrated oxides of Fe and Mn, in particular, are known to promote oxidative polymerization of phenolic compounds (1–3). Mineral surface-organic contaminant

interactions affect the fate of pesticides and pollutants in soils and sediments, and contribute to clay-catalyzed humification processes (4). In porous media with low organic C contents as encountered in subsoils and aquifers, mineral surfaces provide an important barrier to retard the transport of organic contaminants (5). Therefore, the mechanism of interaction between organic contaminants and mineral surfaces must be understood in order to predict chemical fate and transformation.

In natural systems, many polycyclic aromatic hydrocarbons (PAHs) are readily degraded to hydroxylated metabolites (6), which may exhibit higher toxicity than the parent compound (7, 8). However, the environmental fate of hydroxylated metabolites, including sorptive interactions with mineral surfaces, is poorly understood. 1-Hydroxynaphthalene [1-naphthol] is a toxic metabolite of the PAH naphthalene. It is also a major component of the pesticide napropamide and a principal reaction product in hydrolysis of the pesticide carbaryl (9). 1-Naphthol is weakly acidic (pK_a = 9.34), with intermediate hydrophobicity (K_{ow} = 700) and water solubility (10^{-2.22} M) (10). Its stability in aqueous systems is thought to be affected by irradiation, oxygenation, and microbial decomposition (11), but functional relations are not well-known.

Poorly crystalline aluminum hydroxide [Al(OH)₃(s)] is an important constituent of many soils. However, there are relatively few studies on interactions of Al(OH)₃(s) with model phenolic compounds typical of PAH metabolites. Kummert and Stumm (12) showed that specific adsorption of 1,2-dihydroxybenzene [catechol] and salicylic acid onto γ-Al₂O₃ occurs through a ligand exchange reaction. McBride and Wesseling (13) found that sorption of catechol to Al hydroxides occurs via bidentate complexation.

In addition to providing a surface for adsorption, Al (hydr)oxide surfaces may also catalyze the oxidative transformation of phenolic compounds. McBride et al. (14, 15) demonstrated that, at low pH, dissolved Al³⁺ catalyzes the oxidation of catechol and promotes the formation of hydroxyquinone polymers. Soluble Al³⁺ stabilizes semiquinone radicals [resulting from catechol oxidation] through the formation of aqueous complexes and also influences the nature of dimers and polymers that are subsequently formed (15). It has also been suggested that Al oxide may catalyze the oxidative polymerization of catechol and pyrogallol (16).

The present study was conducted to examine the nature of mineral-organic interactions in the case of 1-naphthol, a polycyclic aromatic compound possessing a single phenolic functional group. 1-Naphthol is known to be unstable under certain solution conditions [alkaline pH] and could potentially be oxidized in the presence of dissolved O₂ (11). Our objective was to determine the effect of Al(OH)₃(s) on the fate of 1-naphthol in model systems. Experiments were designed to assess whether this mineral phase (i) directly complexes 1-naphthol, (ii) promotes its oxidative polymerization, or (iii) does not catalyze oxidation but serves as a scavenger for transformation products that are formed in solution. Our approach was to manipulate key variables [pH and dissolved O₂ concentration] and examine their effect on the rate and extent of reaction. The structure of reaction products was elucidated using spectroscopic methods.

Materials and Methods

Poorly Crystalline Aluminum Hydroxide [Al(OH)₃(s)] was synthesized by gradual neutralization of a 0.5 M AlCl₃ solution to pH 7 using 0.5 M NaOH (17). The suspension was aged for 48 h at room temperature and then centrifuged in 250 mL

* Corresponding author phone: (814)863-5394; fax: (814)863-7043; e-mail: jdc7@psu.edu.

polypropylene copolymer bottles at 10 300 relative centrifugal force (RCF) for 20 min. Supernatant solutions were discarded. The precipitate was dialyzed to remove Cl^- and then freeze-dried.

1-Naphthol (99+%) was obtained from Aldrich Chemical and was purified by recrystallization before use. Recrystallization in CH_3OH was observed to increase water solubility of 1-naphthol to levels that were in agreement with published values (10). 1-Naphthol was added to 0.01 M LiCl and equilibrated in a water bath at 313 K with constant stirring for at least 2 h. The solution was passed through a 0.22 μm filter, and 1-naphthol concentration was determined by high-performance liquid chromatography (HPLC). 1-Naphthol solution was thoroughly mixed with radiolabeled 1- ^{14}C - α -naphthol (specific activity = 7.71 mCi mmol $^{-1}$, Sigma Chemical) to provide a stock with <5% of the total 1-naphthol ^{14}C labeled. Fresh stock solutions were prepared for each experiment.

Batch sorption experiments and controls [no solid phase] were conducted as a function of pH [4–11], dissolved O_2 concentration [with and without ambient O_2], and reaction time [20 h and 7 d]. For each batch system, 15.3 mg (oven dried mass) of $\text{Al}(\text{OH})_3(\text{s})$ were added to tared 50 mL PTFE centrifuge tubes. Variable proportions of 0.01 mol kg $^{-1}$ LiCl, LiOH, and HCl were added to each tube to obtain a range of final pH values. Sodium azide (NaN_3 , 5 mg kg $^{-1}$) was added to prevent microbial growth. Negligible differences in sorption of ^{14}C labeled compound were observed between experiments performed in the presence and absence of NaN_3 . Stock 1-naphthol solution was added to give a total concentration of 0.1 mmol kg $^{-1}$ in a total suspension mass of 41.0 g. Control experiments [no $\text{Al}(\text{OH})_3(\text{s})$ addition] were also conducted, using a similar preparatory scheme as indicated above, to account for losses as sorption to PTFE tubes, volatilization, and transformation. Centrifuge tubes were closed with PTFE sealing caps and covered with aluminum foil to prevent exposure to light. The suspensions were equilibrated at 25 $^\circ\text{C}$ by end-over-end rotation at 7 rpm for the desired reaction time. All the experimental plastic/glass ware was autoclaved before use, and solutions were prepared using distilled water that was passed through a MilliQ UV-plus water purification system.

At the end of the reaction period, suspensions were centrifuged at 26 700 RCF and 25 $^\circ\text{C}$ for 20 min. Supernatant solutions were aspirated into amber vials, and final proton concentration was measured immediately using an Orion 8401 combination glass electrode calibrated by Gran titration at the experimental ionic strength (18). 1-Naphthol concentration in the supernatant solution was measured by HPLC on a reverse-phase (Beta-basic 18, Keystone Scientific) column followed by UV detection (HPLC, Waters Inc. equipped with a photodiode array [PDA] detector) within 4 h. Solution ^{14}C activities were determined using liquid scintillation counting [LSC] (Beckman LS8100). The mobile phase consisted of 80% (v/v) methanol. HPLC measurement is specific for 1-naphthol. Conversely, since each mol of 1- ^{14}C - α -naphthol contains 1 mol of ^{14}C , LSC provides a measure of the total carbon contribution deriving from 1-naphthol, i.e.,

$$[^{14}\text{C}]_{\text{LSC}} = [1\text{-naphthol}]_{\text{HPLC}} + [1\text{-naphthol}]_{\text{transformed}}$$

Therefore, the difference between concentrations measured by LSC and HPLC provides an estimate of the amount of 1-naphthol that has been transformed. Using PDA, UV absorption spectra corresponding to the 1-naphthol peak in the HPLC chromatogram were obtained for verification. New peaks in the chromatogram, resulting from transformation reactions, were also characterized on the basis of UV absorption spectra.

O_2 -exclusion experiments required the use of serum bottles with Teflon-lined rubber septa as reaction vessels to achieve complete dissolved O_2 (DO) elimination. The experimental procedure was similar to that described above, with the following modifications. After the addition of all solutions and $\text{Al}(\text{OH})_3(\text{s})$, the contents of the serum bottle were purged with $\text{N}_2(\text{g})$ for 1 h and sealed. The bottle headspace was then purged for an additional 30 min. This purge had a negligible effect on volatilization of 1-naphthol as reflected in ^{14}C recoveries consistently greater than 95%. At the end of the reaction period, DO was measured using an Orion DO Meter [range 0–8.5 mg/L].

1,4- and 1,2-naphthoquinones (97%, Aldrich Chemical), which are known oxidation products of 1-naphthol, were subjected to aqueous solubility measurement and spectroscopic analysis. A known amount of naphthoquinone was added to MilliQ water and equilibrated for 24 h. This suspension was centrifuged at 26 700 RCF and 25 $^\circ\text{C}$ for 20 min and then passed through a 0.2 μm , nylon filter. The filtrate was then analyzed by HPLC to determine the aqueous solubility.

Spectroscopic Analysis. Samples for nuclear magnetic resonance (NMR) spectroscopy analysis were obtained using 1,4- ^{13}C -labeled 1-naphthol [1.33 mmol kg $^{-1}$] reacted with $\text{Al}(\text{OH})_3$ [4960 mg kg $^{-1}$]. The 1-naphthol- $\text{Al}(\text{OH})_3$ slurry obtained after centrifugation was washed with 0.01 M LiCl to remove any entrained and weakly sorbed products. The samples were then dried in a vacuum desiccator, and solid state ^{13}C NMR spectra were obtained at 300.133 MHz with cross-polarization magic angle spinning (CPMAS) on a Bruker DPX-300 MHz spectrometer. Similarly, samples containing 1,2- and 1,4-naphthoquinones [no ^{13}C label] reacted with $\text{Al}(\text{OH})_3(\text{s})$ were also analyzed by ^{13}C CPMAS NMR for comparison. In addition, NMR chemical shifts for the pure solids of 1,4- ^{13}C -labeled 1-naphthol and the naphthoquinones (1,2- and 1,4-) were determined. Fourier transform infrared (FTIR) analysis [transmission mode; 1% sample by weight; 400 scans; 4 cm^{-1} resolution] was performed on the dried solid sample pelletized with KBr using a Nicolet Magna 560 FTIR spectrometer. Liquid state ^{13}C NMR spectra of the supernatant solutions were obtained on a Bruker DRX-500 MHz spectrometer. The ^{13}C sensitivity of the NMR instrument required concentrating the 1-naphthol/transformation products prior to analysis. For this purpose, the contents of the aqueous supernatant solution were transferred into CH_2Cl_2 and concentrated under $\text{N}_2(\text{g})$. The supernatant solutions were also subjected to HPLC-MS (Waters Inc.) analysis to identify the structure of the reaction products.

Results and Discussion

Batch Sorption Experiments. Figure 1 shows the amount of ^{14}C labeled compound sorbed onto $\text{Al}(\text{OH})_3$ [measured as loss from solution of ^{14}C label] as a function of pH for three different reaction conditions: (i) 20 h equilibration ($\text{O}_2 \approx 8 \text{ mg L}^{-1}$), (ii) 7 d equilibration ($\text{O}_2 \approx 8 \text{ mg L}^{-1}$), and (iii) 7 d equilibration ($\text{O}_2 \approx 0 \text{ mg L}^{-1}$). In the presence of O_2 at pH > 6.5, sorption of ^{14}C labeled compound increases from being negligible after 20 h (<10.4 $\mu\text{mol/g}$ or < 4% removal) to 83.2 $\mu\text{mol/g}$ (33% removal) for 7 d reaction with $\text{Al}(\text{OH})_3$. In addition, for the 7 d reaction condition there is a clear pH-dependent trend with the extent of removal being minimal below pH 6.8, increasing sharply over a narrow pH range, leveling off around pH 8.2, and then decreasing at pH > 9.0. Under these high removal conditions we also noticed the formation of a dark-pinkish coating on $\text{Al}(\text{OH})_3(\text{s})$, with the degree of pigmentation increasing in proportion to sorption of ^{14}C labeled compound. Contact time of 20 h should be sufficient to permit direct sorption/complexation interactions between 1-naphthol and $\text{Al}(\text{OH})_3(\text{s})$, whereas chemical transformation of 1-naphthol is expected to proceed more

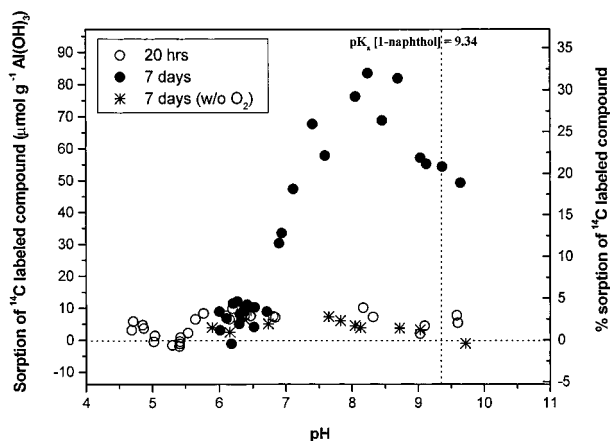


FIGURE 1. Sorption of ^{14}C labeled compound [measured as loss from solution of ^{14}C label] to $\text{Al}(\text{OH})_3(\text{s})$ as a function of pH and reaction time [with and without O_2] (1-naphthol = 0.1 mmol kg^{-1} ; $\text{Al}(\text{OH})_3(\text{s}) = 373 \text{ mg kg}^{-1}$; $0.01 \text{ mol kg}^{-1} \text{ LiCl}$).

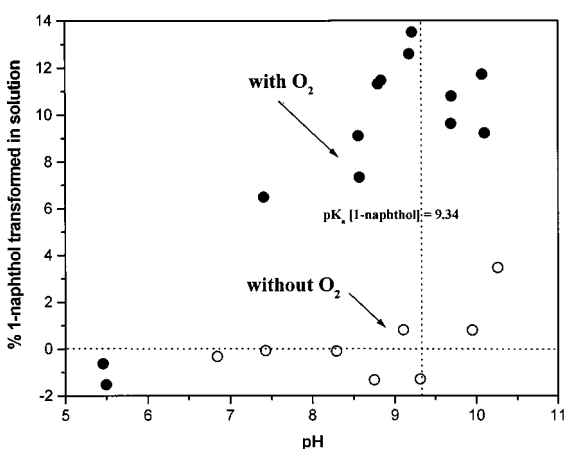


FIGURE 2. Transformation of 1-naphthol in controls [no $\text{Al}(\text{OH})_3(\text{s})$] in the presence and absence of O_2 [1-naphthol = 0.1 mmol kg^{-1} ; $0.01 \text{ mol kg}^{-1} \text{ LiCl}$; equilibration time = 7 d].

slowly. Since a 7 d equilibration resulted in a significant increase in sorption of ^{14}C labeled compound, it is possible that transformation of 1-naphthol (either in solution or surface-catalyzed) is a necessary prerequisite for sorption under these conditions. Independent HPLC analysis indicated that mostly untransformed 1-naphthol remained in solution. The decrease in removal above pH 9 could be related to the increased negative surface charge of $\text{Al}(\text{OH})_3(\text{s})$ [$\text{pzc} = 8.2\text{--}9.5$ (19)] and proton dissociation of 1-naphthol [$\text{p}K_a = 9.34$].

In the absence of O_2 , very little sorptive removal of label was observed even after 7 d [comparable to 20 h equilibration in the presence of O_2]. Evidently, 1-naphthol itself exhibits a low affinity for the $\text{Al}(\text{OH})_3$ surface, and the presence of dissolved O_2 promotes the transformation of 1-naphthol to a more strongly sorbing product. These data are consistent with prior reports that promotion of phenolic compound oxidation by clays is facilitated at higher pH [circumneutral and alkaline regions] (1).

The effects of dissolved O_2 and pH on aqueous phase transformation of 1-naphthol was measured by HPLC in control systems [no $\text{Al}(\text{OH})_3(\text{s})$] (Figure 2). In the absence of a solid phase, the percent 1-naphthol transformed increases above pH 7.0 and levels off around pH 9.0. This trend correlates well with that observed for sorptive removal in the presence of $\text{Al}(\text{OH})_3(\text{s})$. Even in the absence of $\text{Al}(\text{OH})_3(\text{s})$, about 14% transformation was observed. Lamberton and Claeys (11) found that 1-naphthol was unstable under alkaline conditions. Below pH 6.5, 1-naphthol appears stable even in

the presence of O_2 . There is essentially no transformation after 7 d in the absence of dissolved O_2 (Figure 2).

Photolytic transformation of 1-naphthol produces 2-hydroxy-1,4-naphthoquinone (lawsone), 1,4-naphthoquinone, and 1,2-naphthoquinone (20), and similar products may result in the presence of an oxidizing species in solution. The byproducts of naphthalene biodegradation [with 1-naphthol as an intermediate] have been shown to include 1,4-naphthoquinone and 4-hydroxy-1-tetralone (21). In the HPLC chromatogram, peaks corresponding to compounds other than 1-naphthol were observed in the presence of O_2 [in both $\text{Al}(\text{OH})_3$ and control (no $\text{Al}(\text{OH})_3(\text{s})$) experiments] at pH values corresponding to high removal conditions. The UV spectrum for the peak with an elution time of 2.6 min (insert in Figure 3) contained certain features [λ_{max} at 249 and 335 nm] similar to those present in the reference spectrum for lawsone (22). Although it was not possible to match exactly the corresponding UV spectra with these known degradation products of 1-naphthol, a clear, linear trend [$r^2 > 0.9$] was observed between chromatogram peak areas and percent transformation in controls [no $\text{Al}(\text{OH})_3(\text{s})$] (Figure 3) or percent sorption of ^{14}C labeled compound to $\text{Al}(\text{OH})_3(\text{s})$ [data not shown]. The UV spectra obtained at those peak positions had strong absorbances at 228, 268/272 nm and were very different from that of 1-naphthol (insert in Figure 3). In addition, based on the concentrations of transformation products in solution, it was found that between pH 7 and 9 greater than 80% of the transformed product was sorbed to $\text{Al}(\text{OH})_3(\text{s})$ (assuming that sorption as 1-naphthol is negligible). These data suggest that sorption to $\text{Al}(\text{OH})_3(\text{s})$ is facilitated by the formation of oxidation products. Since direct 1-naphthol complexation is negligible [$<4\%$ from Figure 1 after 20 h reaction in the presence of O_2] and there is about 14% transformation in the absence of $\text{Al}(\text{OH})_3(\text{s})$ [control experiments, Figure 2], it is likely that $\text{Al}(\text{OH})_3(\text{s})$ does not catalyze oxidation but rather serves as a strong scavenger of the transformed secondary products. The structural composition of these sorbed products was investigated using ^{13}C CPMAS NMR and FTIR spectroscopy.

^{13}C CPMAS NMR Spectra. 1-Naphthol used in this study was labeled with ^{13}C at C_1 and C_4 positions. Chemical shifts corresponding to these carbons are 151.16 and 120.73 ppm, respectively, for the liquid state and 149 and 121.5 ppm, respectively, for the solid state. Figure 4 provides the ^{13}C CPMAS NMR spectra for pure $\text{Al}(\text{OH})_3(\text{s})$ (topmost spectrum) and those for 1-naphthol reacted with $\text{Al}(\text{OH})_3(\text{s})$ as a function of pH. The spectrum for 1-naphthol reacted with $\text{Al}(\text{OH})_3(\text{s})$ shows peaks around 149.0 and 128.7 ppm. Therefore, the peak at 128.7 ppm is shifted relative to that of the C_4 position of 1-naphthol. This shift indicates a change in the electron configuration of 1-naphthol following oxidation reaction and subsequent sorption to $\text{Al}(\text{OH})_3(\text{s})$. Since the structural composition of the sorbed component is different from that of 1-naphthol, it appears that the surface is comprised mainly of the reaction products of 1-naphthol. In addition, with increasing pH there is a progressive emergence of a signal at 186 ppm, which is attributed to the carbonyl ($\text{C}=\text{O}$) functional group in naphthoquinone. The ^{13}C CPMAS spectra for pure 1,2-naphthoquinone and 1,4-naphthoquinone (not shown) show chemical shifts corresponding to $\text{C}=\text{O}$ at 182.6 and 185.8 ppm, respectively. In contrast, the chemical shift corresponding to the C_1 position (149 ppm) was not affected by reaction.

Liquid-state NMR spectra for the supernatant solutions were obtained while generating the solids [$\text{Al}(\text{OH})_3(\text{s})$ system] for ^{13}C CPMAS analysis [spectra not shown]. At pH 6.71 (low surface loading) chemical shifts were observed at 120.7 and 151.5 ppm corresponding to the C_4 and C_1 labeled positions of 1-naphthol. However, for the sample at pH 9.05 (high surface loading) chemical shifts for naphthoquinones were

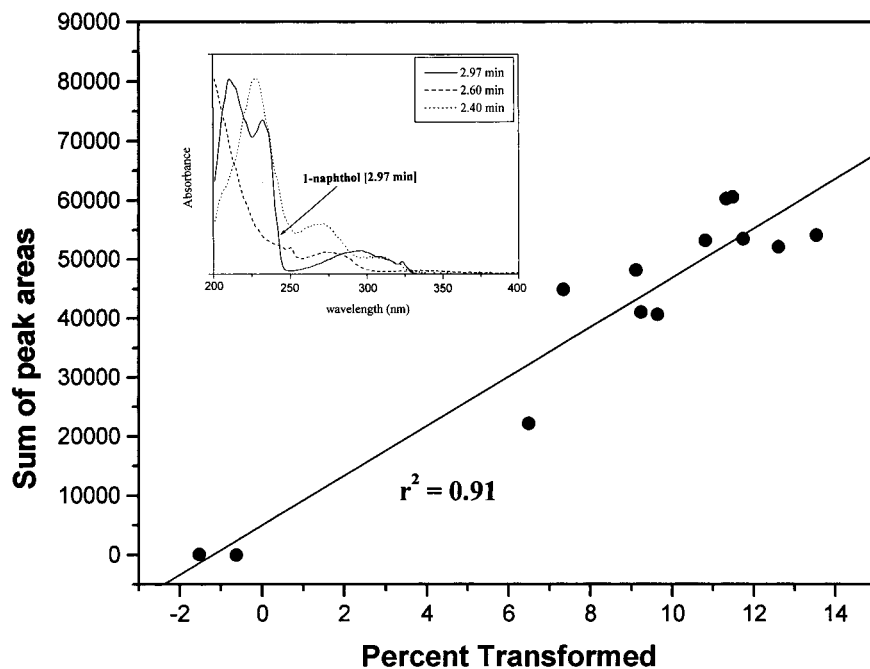


FIGURE 3. Percent 1-naphthol transformation versus sum of the HPLC chromatogram peak areas [detection wavelength = 270 nm] of the transformation products. UV spectra of 1-naphthol (elution time 2.97 min) and transformation products (elution times 2.40 and 2.60 min) are provided as inserts.

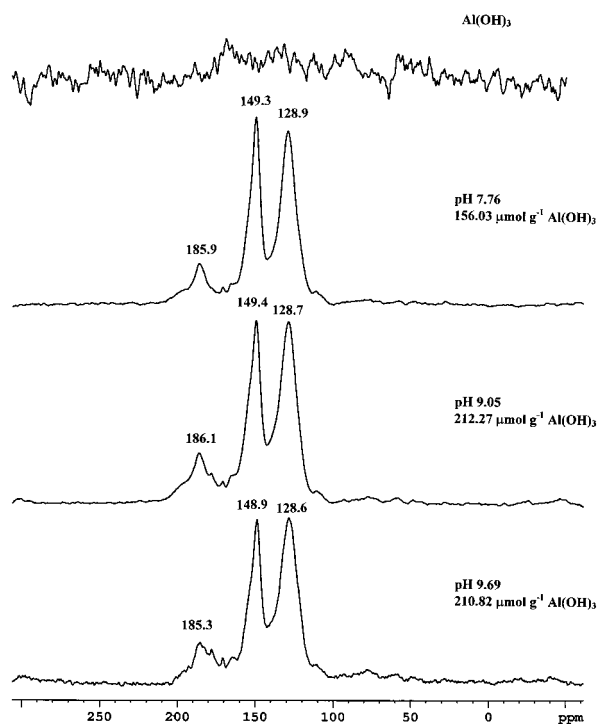


FIGURE 4. ^{13}C CPMAS NMR spectra of 1,4- ^{13}C -1-naphthol reacted with $\text{Al}(\text{OH})_3(\text{s})$ as a function of pH [$0.01 \text{ mol kg}^{-1} \text{ LiCl}$; equilibration time = 7 d; with O_2].

seen between 180 and 186 ppm. These liquid-state NMR data indicate the presence of naphthoquinone in solution as well as sorbed to the surface of $\text{Al}(\text{OH})_3(\text{s})$.

FTIR Spectra. Figure 5 shows the FTIR spectra of (a) 1-naphthol reacted with $\text{Al}(\text{OH})_3(\text{s})$, (b) $\text{Al}(\text{OH})_3(\text{s})$, (c) the difference spectrum, and (d) 1-naphthol with the appropriate band assignments [using ref 23]. The “difference spectrum”, which pertains to the sorbed product, is obtained by subtraction of the $\text{Al}(\text{OH})_3(\text{s})$ spectrum from that of 1-naphthol-reacted with $\text{Al}(\text{OH})_3(\text{s})$. The sorbed product has a few

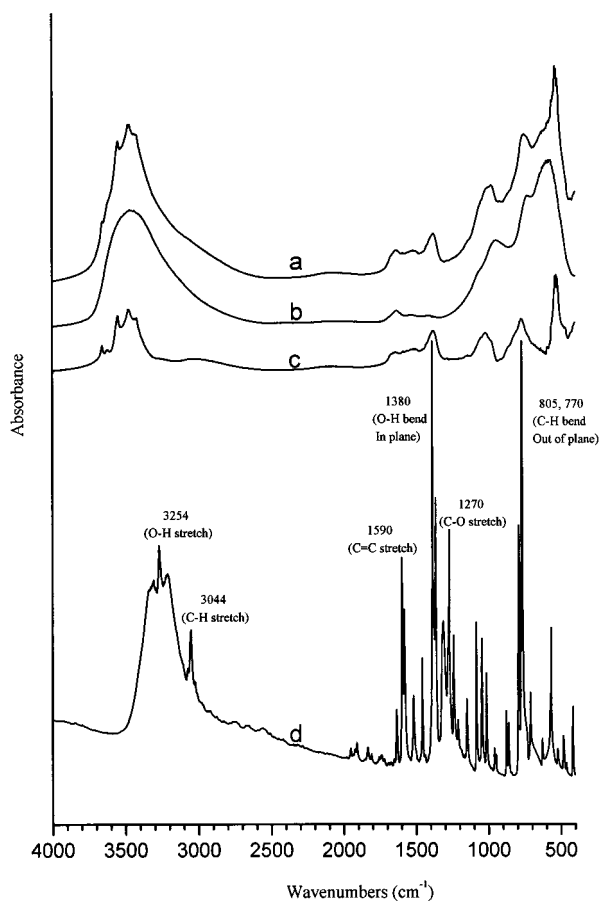


FIGURE 5. FTIR spectra of 1-naphthol reacted with $\text{Al}(\text{OH})_3(\text{s})$ [a], $\text{Al}(\text{OH})_3(\text{s})$ [b], difference spectrum [c], and 1-naphthol [d]. The difference spectrum is obtained by subtraction of the $\text{Al}(\text{OH})_3(\text{s})$ spectrum [b] from the 1-naphthol reacted with $\text{Al}(\text{OH})_3(\text{s})$ spectrum [a]. Experimental conditions for obtaining sample [a]: $0.01 \text{ mol kg}^{-1} \text{ LiCl}$; equilibration time = 7 d; pH = 8.87; surface loading = $190.57 \mu\text{mol g}^{-1} \text{ Al}(\text{OH})_3(\text{s})$; with O_2 .

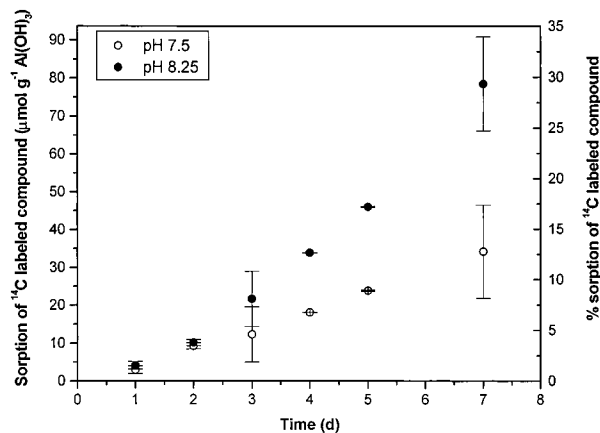


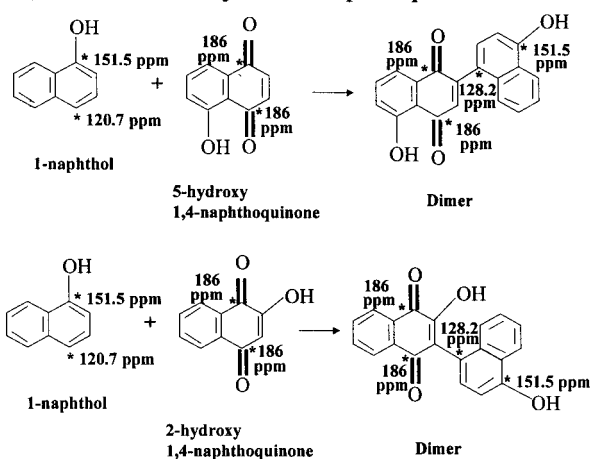
FIGURE 6. Time-dependent sorption of ¹⁴C labeled compound to Al(OH)₃(s) (1-naphthol = 0.1 mmol kg⁻¹; Al(OH)₃(s) = 373 mg kg⁻¹; 0.01 mol kg⁻¹ LiCl).

bands at positions corresponding to those observed for 1-naphthol suggesting some structural similarities. Significant broadening of bandwidths is observed in the sorbed product spectrum, which could result from strong interaction with the surface or the presence of a polymerized product. Also, the emergence of a band at 1653 cm⁻¹ in the sorbed product may be attributed to the C=O stretch of naphthoquinones (14, 24).

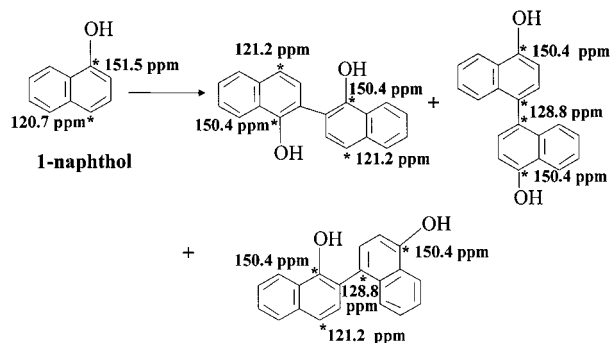
Sorption Kinetics. As indicated above, an increase in equilibration time from 20 h to 7 d in the presence of O₂ resulted in a tremendous increase in ¹⁴C labeled compound sorption [measured as loss from solution of ¹⁴C label]. To further investigate the effect of reaction period, long-term kinetic studies were performed. Time-dependent removal of 1-naphthol in the presence of Al(OH)₃(s) at two different pH values [7.5 and 8.25] is shown in Figure 6. Sorption (measured as loss of ¹⁴C label) followed second-order kinetics at pH 7.5 and 8.25 with *t*_{1/2} values of 35 and 16 days, respectively. At pH 8.25, both faster uptake and higher sorption levels were observed. Removal of 1-naphthol from solution continued to occur for the entire experimental duration of 41 d. After 41 d there was no statistically significant difference in percent removal between pH 7.5 and 8.25 systems [52.33 ± 6.02 and 53.71 ± 6.02, respectively]. If 1-naphthol interaction with Al(OH)₃(s) was solely through complexation reactions, sorption would have attained a maximum at short times corresponding to saturation of available sites on Al(OH)₃(s). Since this did not occur, sorption appears to be controlled by transformation to a more reactive product.

Mechanistic Interpretations. The ¹³C NMR and FTIR data also indicate a time-dependent accumulation of naphthoquinones on the surface of Al(OH)₃(s). In addition, the ¹³C CPMAS NMR spectra show chemical-shift changes at the C₄ labeled position of 1-naphthol. The FTIR spectra of the sorbed product also suggested some structural similarities to 1-naphthol. Therefore, oxidative polymerization of 1-naphthol [either before or after sorption to Al(OH)₃(s)] is possible. Colored coatings on mineral surfaces reacted with phenolic compounds have been attributed to oxidative polymerization reactions (1, 2, 13, 14, 16, 25), and dark-pinkish coatings on Al(OH)₃(s) were observed in the present study also. As a starting point, we considered a few dimerization reactions (Figure 7): (a) addition of 1-naphthol to naphthoquinones and (b) coupling of 1-naphthol mediated by an oxidizing agent (26, 27). The naphthoquinones considered were 5-hydroxy-1,4-naphthoquinone (juglone) and 2-hydroxy-1,4-naphthoquinone (lawsone). The dimerized products shown in Figure 7 containing these hydroxynaphthoquinones are consistent with our analysis of supernatant solutions by

a) Addition of 1-naphthol to naphthoquinones:



b) Coupling Reactions



Reactions occur at *ortho* and *para* positions to the OH group

FIGURE 7. Dimerization reactions of 1-naphthol: (a) addition of 1-naphthol to naphthoquinones and (b) coupling of 1-naphthol caused by an oxidizing agent (* indicates ¹³C-labeled carbon positions).

HPLC-MS. It is important to note that the HPLC-MS analysis did not reveal the existence of monomers of naphthoquinone in solution, which could help explain the difficulty in exactly matching the UV spectra obtained from PDA to known reference compounds. Besides that of 1-naphthol, other MS peaks were observed for compounds with molecular weight (MW) 290 [1-naphthol dimer; it is important to note that the 1-naphthol used was 1,4-¹³C labeled and, hence, its MW is 146.15] and 320 [1-naphthol bound with either lawsone or juglone; MWs of ¹³C-labeled lawsone and juglone are both 176.15].

The ¹³C chemical shifts at the C₁ and C₄ positions of the dimer structures that are indicated in Figure 7 were calculated using ChemWindows (SoftShell International). Clearly, dimerization involving 1-naphthol would change the chemical shift of the C₄ carbon from 121 to 128/129 ppm, as observed in our solid NMR spectra (Figure 4). Such a transformation would also explain an increased reactivity of the dimer (relative to 1-naphthol) toward mineral surfaces. The presence of peaks at 128, 149, and 186 ppm necessitates the consideration of a dimerized structure for the sorbed product. If sorption involved monomers of 1-naphthol and its oxidation products [i.e., naphthoquinone/hydroxy-naphthoquinone], then the peak positions would be observed at 121, 149, and 186 ppm.

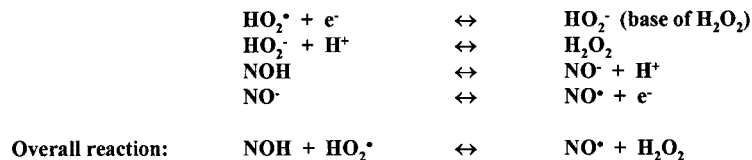
McBride and Wesselink (13) have shown that catechol and hydroquinone, both containing two phenolic-OH functional groups [at *ortho* and *para* positions, respectively] have a greater affinity toward Al oxides compared to phenol, which has a single hydroxyl group. Similar results were obtained for catechol and phenol sorption to goethite by Evanko and

REACTION PATHWAY

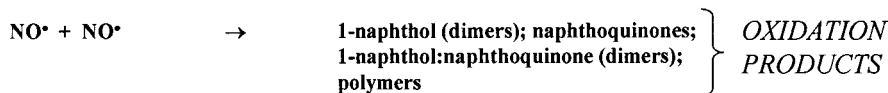
I. Reaction of 1-naphthol (NOH) with dissolved oxygen:



II. Reaction of 1-naphthol (NOH) with hydroxyperoxyl radical:



III. Coupling and Further Oxidation:



IV. Interaction with mineral surfaces:



FIGURE 8. Possible reaction pathway for 1-naphthol interaction with mineral surfaces.

Dzombak (28). In addition, significant removal levels (>50%) were measured for 2,3-dihydroxynaphthalene, whereas extremely low (<5%) amounts of 2,7-dihydroxynaphthalene were sorbed onto goethite (28). These observations are consistent with our own: low surface affinity for 1-naphthol (single phenolic-OH group) and stronger sorption of the transformation products (dimerized compounds shown in Figure 7 possessing hydroxyl groups at ortho and para positions). The presence of two oxygen containing substituents on the ring may contribute to the formation of bidentate or binuclear complexes with the $Al(OH)_3(s)$ surface.

Dimerization reactions could also represent the onset of polymer formation. Indeed, reaction of 1,2-naphthoquinone with $Al(OH)_3(s)$ (data not shown) resulted in the formation of a dark colored surface precipitate similar to that observed in the 1-naphthol sorption experiments. The NMR spectrum of the product resulting from the above reaction also contained a peak at 186 ppm. The pinkish coating formed in both cases was extremely insoluble, and the material could not be desorbed from the $Al(OH)_3(s)$ surface by washing the solid with water or other solvents including CH_3OH , CH_2Cl_2 , and 0.1 M NaOH. Naphthoquinones are more hydrophobic and have a lower water solubility [e.g., we measured values of $10^{-3.12}$ M and $10^{-2.92}$ M for 1,2-naphthoquinone and 1,4-naphthoquinone, respectively] than 1-naphthol [$10^{-2.22}$ M (10)]. Therefore, 1-naphthol oxidation products and quinone-containing dimers/polymers may exhibit enhanced sorption to mineral surfaces because of hydrophobic interaction.

Based on the above findings and using the suggested mechanisms for the oxidation of phenol by O_2 (29) and metal ion oxidants (30), we postulate the reaction pathway shown in Figure 8. Although O_2 is considered a weak oxidant at pH 7 [$O_2 + e^- \leftrightarrow O_2^{\cdot -}$; $E_H^0 = -0.16$ V], compounds such as phenols that can be oxidized very easily will react readily with O_2 (31). Oxidation of 1-naphthol in solution to naphthoxy radicals could be facilitated by the reaction of $O_2^{\cdot -}$ [superoxide radical] in water yielding HO_2^{\cdot} [hydroxyperoxyl radical] (29), which subsequently forms HO_2^- and O_2^{2-} . These peroxide ions are

considered to be the operative oxidizing species in aerated water (32). Naphthoxy radicals are highly reactive and could combine to form 1-naphthol dimers, naphthoquinones, and 1-naphthol:naphthoquinone dimers (30). Oxidation of 1-naphthol has been shown to produce free radicals, which dimerize to form dinaphthols (27).

While coupling of 1-naphthol monomers to form insoluble hydrophobic oligomers is a very likely explanation for the observed changes in chemical shift at the C_4 position, we must also consider other less likely possibilities. One is a shift induced by the sorption reaction itself. However, it is not likely that such a reaction would only affect the C_4 -carbon and not the C_1 -carbon. In addition, the requirement of a reaction period of more than 20 h and the need for dissolved O_2 to produce significant removal preclude the existence of any significant sorption reaction between 1-naphthol and $Al(OH)_3(s)$. Another possibility is that the sorption process induces motional restriction of 1-naphthol along the C_1 to C_4 axis and this causes a change in the isotropic chemical shift value obtained for C_4 in the solid-state ^{13}C NMR spectrum. Such an effect has been commonly observed for carbons whose intra- or intermolecular orientations are fixed in the solid state but rotational freedom exists in the liquid state. However, such a condition would require that all 1-naphthol species be in fixed orientation on the surface of the sorbent (see ref 33).

For environmental systems contaminated with naphthalene, the formation of similar recalcitrant polymers is probable. The pathway for microbial metabolism of naphthalene (through 1-naphthol) also involves the formation of 1,4-naphthoquinone and 4-hydroxy-1-tetralone (21). Strong binding of these products to soil constituents likely explains the formation of nonextractable residues observed during long-term biodegradation of naphthalene in soil (34). However, an important result of the present study is that such residue formation from 1-naphthol can also occur *abiotically* in the presence of mineral surfaces.

Role of Mineral Surfaces. The results indicate clearly that hydrous Al oxide serves as a surface for accumulation (i.e., "scavenging") of naphthol transformation products. By effectively removing the reaction products from solution, the mineral surface provides a driving force for further oxidative transformation of 1-naphthol. The degree to which Al(OH)₃(s) itself mediates the oxidative transformation reaction is less clear and requires further study. Since Al³⁺ cannot participate in electron-transfer processes as mediated by Fe³⁺ or Mn⁴⁺, its direct role in oxidation might not be significant. However, the Al(OH)₃(s) surface comprises Lewis acid sites that are capable of electron sharing with O-containing functional groups of substituted aromatic compounds. McBride et al. (14) has proposed that Al³⁺ could indirectly facilitate oxidation of catechol through complexation reactions. By shifting the electronegativity from the O atom to the ring, such complexation reactions make the ring more susceptible to oxidation. In the present study, when O₂ was absent, Al(OH)₃(s) was unable to mediate oxidative polymerization. Furthermore, there is no evidence for strong complexation of 1-naphthol by Al(OH)₃(s), and coordination of a compound with the surface has been shown to facilitate surface catalyzed oxidation (1). Therefore, the role of Al(OH)₃(s) appears to derive primarily from a high capacity to strongly bind the transformation products. Since similar reactions may affect the fate of PAHs and metabolites in soil systems, these results underscore the importance of intermediate compounds in the environmental reactivity of organic contaminants.

Acknowledgments

Research was supported by the U.S. Department of Energy, Office of Biological and Environmental Research, Joint Bioremediation Program, Grant No. DE-FG02-97ER62356.

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Received for review March 10, 1999. Revised manuscript received August 24, 1999. Accepted August 24, 1999.

ES990274Q