

Reactivity of Nitroxide Spin Probes toward Photochemically Generated Benzyl Radicals in Clay Mineral Suspensions

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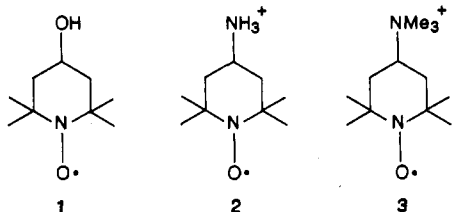
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The ESR spectra of three nitroxide probes in laponite (synthetic hectorite)/cyclohexane slurries show up to three components assigned to probes dissolved in solution, bound to the surface, and aggregated near the surface. Addition of dibenzyl ketone (DBK) to the probe/clay suspensions results in partial probe desorption. Upon ultraviolet irradiation of these mixtures, the component of the ESR spectra assigned to bound probe changes to a lesser extent than that corresponding to solubilized probe, which disappears as benzyl radicals react with the nitroxide. With the probe aggregates, irradiation of samples containing DBK leads to a diminishment of spin exchange and resulting sharpening of the peaks. This paper demonstrates a novel use of nitroxide traps for unstable radicals as structural probes of heterogeneous systems.

Layered silicates (clay minerals) represent a class of compounds studied widely in relation to soil science, as well as having a range of industrial applications.² The structure of these compounds in suspensions consists of thin silicate sheets which form groups of clay layers. Isomorphous substitution renders the clay anionic with the corresponding exchangeable cationic counterions between the layers. The separation between layers is affected by the solvent and by the nature of the exchangeable cation. Nitroxide and metal ion spin probes have been useful in studying the environment of oriented films of silicates in the presence of various solvents.³ ESR spectroscopy has shown that the rotational mobility of a nitroxide spin probe is significantly hindered when adsorbed on films saturated with nonpolar solvents. This indicates that there can be strong interactions between nitroxide probes and clay surfaces.

In this study, we report on the use of three nitroxide spin probes, 4-hydroxy-TEMPO (1), 4-amino-TEMPO (2), and 4-(trimethylammonio)-TEMPO chloride (3) (TEMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxy), to study clay sus-



pensions (rather than films). These probes were expected to equilibrate between interstitially bound and solubilized material depending on the nature of the probe and the polarity of the solvent. ESR spectroscopy can provide information about this distribution. Moreover, since photochemically generated benzyl radicals react with nitroxides to give diamagnetic products,⁴ by generating

benzyl radicals (e.g., by photolysis of dibenzyl ketone, DBK) in the presence of layered silicates and nitroxide spin probes, we can follow the relative rates of changes of the two components in the ESR spectrum. This then provides us with information on the relative reactivity, location, and in some cases mobility of organic compounds around clay minerals as compared to the bulk solution.

Experimental Section

Materials. DBK, diphenylethane (DPE), 4-hydroxy-TEMPO (1), and 4-amino-TEMPO (2) were purchased from Aldrich. 4-(Trimethylammonio)-TEMPO chloride (3) was prepared by addition of excess methyl iodide to an acetone solution of 4-amino-TEMPO and NaHCO₃. After filtration, the solid was dissolved in hot ethanol/water, and a large excess of LiCl was added. The mixture was gravity filtered, and crystals formed from the filtrate on cooling. These crystals were recrystallized from methanol. That the ammonium salt was formed was demonstrated by precipitation of AgCl from a test sample with AgNO₃.⁵ The samples of XLG-laponite used in these experiments were obtained from Laporte Industries (U.K.)

Instrumentation. All ESR spectra were conducted by using a Bruker ER100D ESR spectrometer operating at the X-band. Sample irradiations were performed by using an Oriel Model 6141 1000-W Xe-Hg lamp with an optical filter (transmission between 320 and 360 nm). (Note that the filter is necessary since the nitroxide radicals decompose photochemically below 320 nm.⁶)

Procedures. For preparation of samples with 1: A sample of 1.0 mL of 0.05 wt. % aqueous XLG-laponite was freeze-dried. To this sample were added 0.4 mL of 10 μM 1 in cyclohexane and (where appropriate) 0.1 mL of 0.11 M DBK in cyclohexane.

For preparation of samples of 2: To a sample of 1.0 mL of 0.05 wt. % aqueous XLG-laponite and 0.4 mL of 10 μM of 2 was added sufficient dilute HCl to bring the pH to 3. At this point, flocculation was observed due to the high acid concentration. The mixture was freeze-dried, then cyclohexane (0.4 mL) and (where appropriate) 0.1 mL of 0.11 M DBK in cyclohexane were added to the dry solid.

For preparation of samples with 3: A sample of 1.0 mL of 0.05 wt. % XLG-laponite and 0.4 mL of 10 μM 3 was freeze-dried, then 0.4 mL of cyclohexane and (where appropriate) 0.1 mL of 0.11 M DBK in cyclohexane were added to the dry solid.

All ESR spectra were run several minutes after UV irradiation to ensure temperature equilibration.

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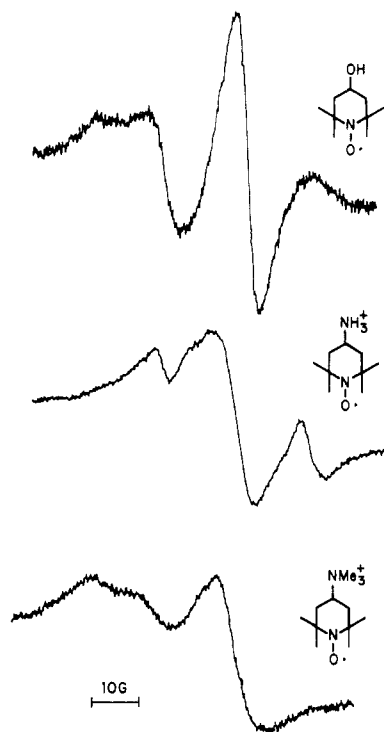


Figure 1. ESR spectra of clay/cyclohexane slurries with nitroxide probes.

Results and Discussion

The ESR spectra of the three TEMPO spin probes in clay/cyclohexane slurries differ substantially in the relative contributions of two components in the spectra (Figure 1).⁷ With 3, a broad, anisotropic spectrum is obtained which is characteristic of a highly immobilized (frozen) probe.⁸ The positively charged ammonium functionality probably binds tightly between the layers of the negatively charged silicate. With 2, the ESR spectrum shows what will be interpreted below as a combination of three superimposed spectra. This spectrum can be interpreted as being composed of the frozen probe spectrum seen with 3, the solution spectrum of the probe, and a component that appears to be due to probe which is broadened isotropically by spin exchange. The presence of this last component is difficult to detect from the spectrum shown in Figure 1 alone, but its presence is suggested by the spectral changes on UV irradiation. With 1, the ESR spectrum shows mostly the immobilized spectrum, with a slight contribution from the solution spectrum. Centrifugation and ESR analysis of the supernatant for this sample demonstrate the presence of some probe in solution.

Addition of DBK (2 mM) to probe/clay slurries in cyclohexane (8 μ M probe) results in nearly complete desorption of the probe with 1 (Figure 2) and partial desorption with 2 (Figure 3). With the desorption of 1, the isotropic (solution) spectral component obtained is relatively broad, suggesting aggregation of this probe. With 3, no effect is observed upon addition of DBK. The polar carbonyl moiety of DBK can interact with the cations between the clay layers and therefore penetrate into these layers. Since the DBK is present in much higher concentrations than are the probes, the DBK is able to dis-

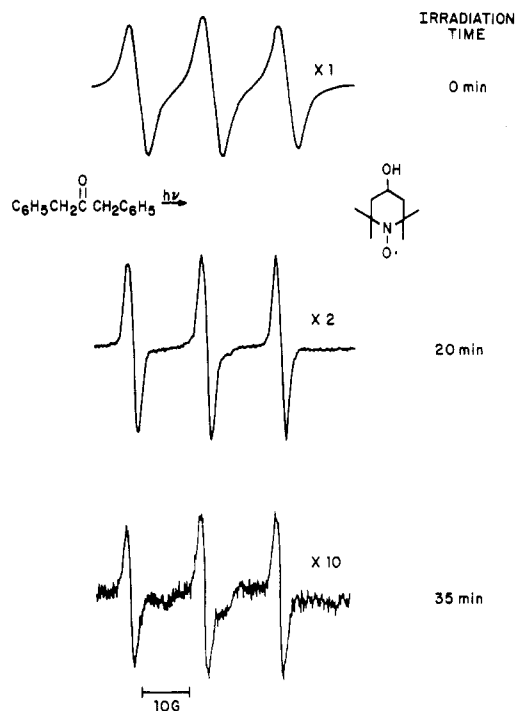


Figure 2. ESR spectra of clay/cyclohexane slurry with 1 and DBK as a function of UV irradiation (320–360 nm) time.

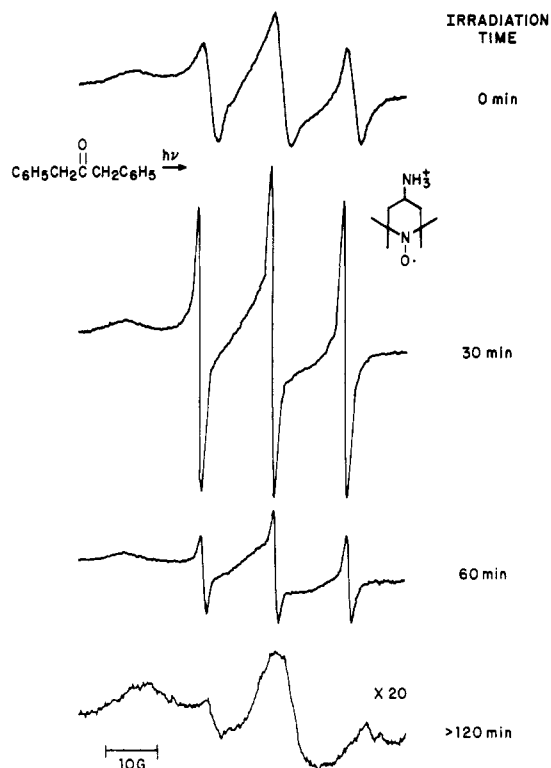


Figure 3. ESR spectra of clay/cyclohexane slurry with 2 and DBK as a function of UV irradiation (320–360 nm) time.

place a large portion of the bound probes, depending on the nature of the probe. In contrast, when a nonpolar compound, such as DPE, is added to 1, 2, or 3, there is no discernible change in the ESR spectra. In this case, DPE does not interact sufficiently with the charged clay surface to displace the polar probes.

On irradiation (320–360 nm) of the cyclohexane suspensions with probe and DBK, each probe shows a different behavior. With 1, irradiation as a function of time results in some immediate sharpening of the peaks followed by a uniform diminishment of the ESR peak in-

(7) The exact concentrations of probe, DBK, and clay were uncertain due to the possible adhesion of the clays to the surface of the glassware used in the freeze-drying. Because of this, the ESR spectra are quantitatively difficult to reproduce, especially in the case of 2; however, the general spectral patterns and photochemical reactivity on irradiation of DBK remain the same in each case. The spectral patterns are also reasonably similar between laponite samples from different batches.

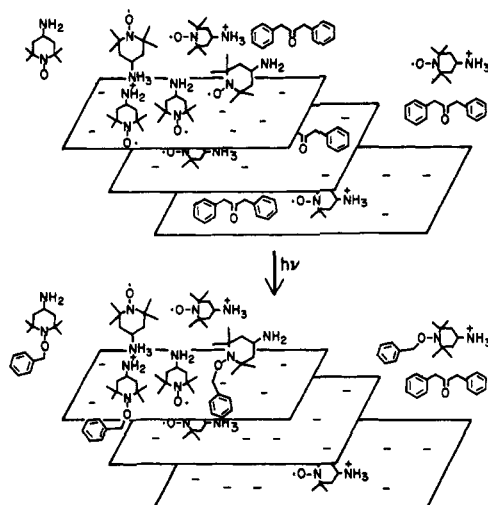


Figure 4. Schematic representation of the probe (2) in a clay/cyclohexane slurry with DBK. The probe is present in three environments: tightly bound between the clay layers, in solution, and in aggregates near the surface. (Note that the probe is present in both the protonated and neutral form, though probably most of the tightly bound material is protonated.) Upon UV irradiation, DBK gives benzyl radicals which react with probe in solution but not with that bound between the clay layers. The probe aggregates are diluted by the diamagnetic reaction product.

tensities (Figure 2). In contrast to this behavior, with the clay-bound 3, no reaction could be detected by ESR spectroscopy on a comparable time scale. This lack of reactivity may be due to either a small affinity of the benzyl radicals for the polar clay atmosphere, to decreased benzyl radical mobility on the clay surface, to reduced photochemical reactivity of the DBK on the clay, or to an inherent lack of reactivity of this nitroxide on the clay surface.⁸ These issues are currently being pursued by flash photolysis techniques. With 2, irradiation results in an intermediate behavior (Figure 3) between the extreme cases of 1, where a uniform decrease in signals is observed, and 3, where no signal decrease is observed. Irradiation in this case results in an *increase* in signal intensity (solution peaks) with only a small change in the immobilized component. With time, the solution peaks diminish leaving mostly the immobilized component to the original spectrum. This observation can be explained by assuming that before irradiation, aggregation of the probe near the surface occurs which results in a broad spin-exchanged component to the spectrum. As the probes within the aggregates react with the benzyl radicals, the nitroxides in the aggregates are diluted by the diamagnetic coupling product. Spin exchange is therefore diminished, and the signal intensity of the sharp, solution peaks is enhanced. Similarly, with 1, the peak sharpening observed on irradiation can be rationalized by assuming that probe aggregates are dispersed as some of the probe reacts with the

benzyl radicals. That the bound 1 and 2 react with benzyl radicals (albeit slowly with 2) while bound 3 does not show comparable reactivity may reflect the kinetics of the desorption/adsorption equilibration; that is, the nitroxide reacts with benzyl radicals in solution but not on the clay. Since 1 is not charged, it is not unreasonable that such equilibration is most facile with this probe. That the clay plays an important role in promoting aggregation on the surface is clear, since at these concentrations both 1 and 2 show sharp spectra with essentially no evidence of spin exchange in cyclohexane solution. The differences between 2 and 3 probably result from the presence in the case of 2 of both protonated and deprotonated forms which may equilibrate on the surface. The deprotonated form of 2, being neutrally charged, will have less tendency to intercalate or surface bind to the anionic clay. With 3, only a cationic form exists and therefore 3 is always attracted to the surface.

Following irradiation of 2 in the clay/cyclohexane slurries, the relative intensities of the sharp, solution peaks increase again upon sitting in the dark. This also suggests that the adsorption/desorption process on the clay is an equilibrium process where the rate of equilibration is slow with respect to the rate of reaction between the nitroxide and benzyl radicals with this probe.

Conclusion

The combination of ESR spectroscopy on stable nitroxide radicals and the corresponding reactivity of these species toward photochemically generated unstable radicals provides a facile method for probing the structure and dynamics of the microenvironment surrounding clay mineral suspensions. Moreover, the methodology allows the monitoring of effects of different environments within a single, heterogeneous mixture. That such microenvironments display different reactivity is demonstrated by the lack of reactivity for clay surface bound nitroxides. The results of this study are shown pictorially in Figure 4 for the case of 2. The nitroxide is present in three nominal environments: between the clay layers (unreactive toward benzyl radicals), in solution (reacts with the benzyl radicals), and aggregated near the surface (reacts to dilute spin exchange). The probe 2 is also shown in both protonated and deprotonated forms. Equilibration of different forms of binding can occur depending on the nature of the probe. The use of nitroxide spin traps for unstable radicals represents a new method for probing the structure of heterogeneous systems and demonstrates the use of reactive species in the probing of such interactions. In this way, not only is structure indicated but also dynamics of different microenvironments.

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Registry No. 1, 2226-96-2; 2, 58237-03-9; 3, 67036-09-3; laponite, 53320-86-8; benzyl radical, 2154-56-5.

(8) VPC analysis of an irradiated sample of 3 and DBK in a cyclohexane/clay slurry demonstrated that DPE is formed during irradiation.