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Time Resolved CW-EPR Spectroscopy of Powdered Samples: Electron Spin Polarization of a Nitroxyl Radical Adsorbed on NaY Zeolite, Generated by the Quenching of Excited Triplet Ketones

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Chemically induced dynamic electron polarization (CIDEP) generated in a faujasite zeolite (NaY) by the interaction between a stable free radical (4-oxo-TEMPO) and the triplet state of benzophenone was investigated by time-resolved electron spin resonance spectroscopy (TR-CW-EPR). The TR-CW-EPRs were performed by either pulling a long tube containing powdered zeolite through the EPR cavity during the laser irradiation, or by flowing a liquid transport medium (polydimethylsiloxane) for the zeolite powder, through a flat cell in the EPR cavity. CIDEP was observed for intermolecular triplet quenching (benzophenone triplets with 4-oxo-TEMPO) and intramolecular triplet quenching using a covalently linked TEMPO-benzophenone molecule. The identification of the polarized nitroxide structure was confirmed by employing both ^{14}N and ^{15}N 4-oxo-TEMPO isotopomers. The kinetics of the triplet quenching inside the zeolite were studied by diffuse reflection laser flash photolysis.

Introduction

The quenching of excited triplet state ketones by nitroxides in isotropic solutions has been the subject of considerable attention.[1−4] For sensitizers with triplet energies higher than 225 kJ/mol, quenching rate constants close to the diffusion limit were found.[4,5] As a result of triplet quenching, chemically induced dynamic electron spin polarization (CIDEP) of the nitroxides has been observed by time resolved electron paramagnetic resonance (TR-EPR).[2,3,5] For quenching of aromatic ketone triplet states by nitroxides, exclusively emissive electron spin polarization was observed, which was explained by a radical-triplet pair mechanism (RTPM).[1,6,7]

TR-EPR experiments to generate spin polarization of nitroxides by the quenching of ketone triplets have been reported mainly in solutions. Because of our combined interest in CIDEP[8] and the photochemistry of ketones adsorbed on zeolites,[9] we have initiated TR-EPR investigations of the photochemistry of molecules adsorbed in zeolites. The motion of guest molecules adsorbed on zeolites is limited compared to molecules in fluid solutions. Therefore, processes that lead to electron spin polarized radicals can be influenced.

TR-EPR in solutions is usually performed by irradiation of a sample inside the EPR cavity, usually with a pulsed laser.[10−12] Because of photo decomposition due to laser irradiation, the solutions of the sample are flowed through the cavity in order to ensure a fresh sample at each laser pulse. Flowing a powdered sample through the cavity is problematic and is a reason for the dearth of reports on TR-EPR of powders. Blaettler and Paul solved the flow problem by using a liquid transport medium for particles of zeolite.[13] Zeolite-polydimethylsiloxane-slurries, which are relatively transparent, were flowed through the EPR cavity during laser irradiation.[13] Forbes et al. studied photochemically generated radical pairs at solid/solution interfaces.[14] Ketones were covalentely anchored to silica surfaces, and the silica slurries in organic solvents were flowed during laser irradiation to produce the radicals.[14] We have previously reported CW-EPR spectra for benzyl radicals on porous silica generated by continuous irradiation of dibenzylketone adsorbed on silica with a HgXe lamp.[15] To reduce photo decomposition during the irradiation, the sample-containing cell was slowly moved through the EPR cavity. In this paper, we apply two techniques, pulling a long tube containing powdered zeolite and the flowing slurry technique, through the EPR cavity to employ TR-EPR to investigate photochemical processes of molecules adsorbed in zeolites. We report the nitroxide CIDEP that is generated by the quenching of benzophenone triplets with 4-oxo-TEMPO, both of which were adsorbed on NaY zeolite.

The faujasite cavities of NaY zeolites ($Na_x(AlO_2)_y(SiO_2)_z$; dehydrated: $y + z = 192$, $x/y = 0.7$ to 1.1, $z/y = 1.5$ to 3)[16] consist of supercages possessing a diameter of ca. 13 Å. Therefore, both an aromatic ketone as triplet sensitizer and a nitroxide as triplet quencher can occupy the same supercage of NaY. When both the triplet sensitizer and ketone occupy the same supercage, no long range diffusion is necessary for efficient quenching. For studies in NaY zeolites, benzophenone (**1**) was selected as the triplet sensitizer because quenching of benzophenone triplets by TEMPO derivatives (**2**) generated one of the strongest observed electron spin polarization of **2** in solutions.[2,5,6]

Experimental Section

Materials. Unless otherwise stated, all reagents were purchased from Aldrich Chemical Co. and used as received. n-Pentane (HPLC grade; Fisher Scientific) and dichloromethane (Optima; Fisher Scientific) were used as received. Benzophenone (**1**, Chart1) was recrystallized twice from ethanol and once from hexane.

The ^{15}N labeled 4-oxo-TEMPO (**2**-^{15}N, Chart1) was prepared as follows: 2,2,6,6-tetramethyl-4-piperidone-^{15}N was synthesized based on a literature procedure [17] by stirring 6.47g phorone (46.8mmol) in 15 mL of benzene with 2 g of $(^{15}NH_4)_2SO_4$ (14.9mmol), 1.56 g of NaOH (39mmol), 3.67g $Na_2HPO_4 \cdot 7H_2O$, and 5 mL of water at 95° C in a heavy-walled glass pressure

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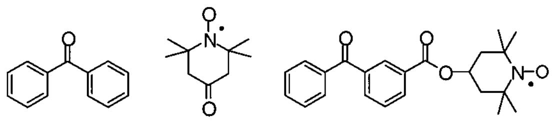
CHART 1: Structures of molecules investigated in this report.



1 2 (^{14}N) 2 (^{15}N) 3

vessel for 10 days. The reaction mixture was diluted with 50 mL of water and 50 mL of ether. The aqueous layer was washed three times with 50 mL of ether, and the combined ether extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification was achieved by flash column chromatography on silica gel using solvent mixtures of increasing polarity (5:1 to 2:1; hexane:ethyl acetate), and then methanol yielding 4g of 2,2,6,6-tetramethyl-4-piperidone-^{15}N (25.8mmol, 86% yield). **2**-^{15}N was then synthesized by oxidation of crude 2,2,6,6-tetramethyl-4-piperidone-^{15}N according to a published procedure[18] using H_2O_2 and Na_2WO_4. **2**-^{15}N was purified by flash column chromatography using 4:1 hexane:ethyl acetate and was obtained in 10% yield as an amber-colored solid. EPR, GC/MS (EI): $m/z = 171$ (M^+). The purity (>98 %) of **2**-^{15}N was determined by GC.

The TEMPO labeled benzophenone (**3**) was synthesized by a procedure analogous to that described by Hassner.[19] 3-Benzoylbenzoic acid was esterified with 4-hydroxy-TEMPO in the presence of 1,3-dicyclohexylcarbodiimide and 4-dimethylaminopyridine in THF under argon for 10 h. After removal of the THF, the residue was dissolved in methylene chloride, washed with water, 5% acetic acid, and chromatographed over silica gel (9:1 to 8:2; hexane: ethylacetate) to obtain **3** in 85% yield. The structure and purity (>98 %) of **3** were determined by NMR and EPR.

NaY (CBV100, $SiO_2/Al_2O_3 = 5.1$) was purchased from Zeolyst International. The unit cell formula of this sample was calculated to be $Na_{54}(AlO_2)_{54}(SiO_2)_{138}$ when dehydrated.[16] NaY was activated at 500° C in an oven for at least 8 h and cooled to room temperature in a desiccator before use. NaY was added to a solution of the ketone and nitroxide in *n*-pentane and dichloromethane (5 mL of *n*-pentane and 3.2 mL of dichloromethane per gram of NaY). The slurry was stirred for at least 8 h in a closed vessel, and then the solvent was removed by argon flow and subsequently placed in a vacuum chamber for 2 h.

Time-Resolved CW-EPR. TR-CW-EPR experiments employed the pulses (308 nm, 10 ns) from a Lambda Physik Lextra 50 excimer laser, a Bruker ER 100D X-band EPR spectrometer, and a PAR boxcar integrator and signal processor (Models 4420 and 4402, respectively).[20,21] To obtain spectra from dry powders, quartz tubes (diameter 4 mm, length 1 m) filled with NaY containing the ketones and TEMPO derivatives were evacuated to at least 5×10^{-5} Torr to remove traces of water, solvents and oxygen and closed with a vacuum stopcock. During the irradiation with laser light, the sample container was pulled through the cavity of the EPR spectrometer at a constant rate of 5 cm/min. A schematic of the experimental setup is shown in Figure 1. CW-EPR measurements were recorded before and after the TR-EPR experiments and showed no difference by visual inspection of the line shape and intensity of the CW-spectra, demonstrating that the laser irradiation during the TR-ESR experiments did not cause significant decomposition of the TEMPO derivatives.

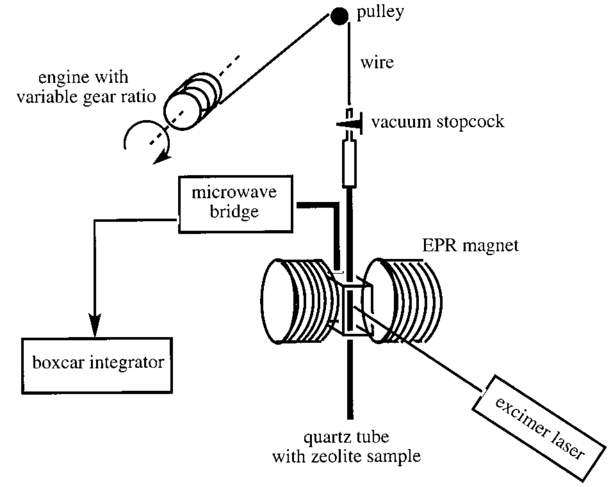


Figure 1. Schematic representation of the instrumentation used to measure electron spin polarization in powder samples by TR-EPR.

To obtain spectra using a fluidized transport medium, a slurry of NaY containing **3** and polydimethylsiloxane (viscosity: 500 cP) was prepared as follows: NaY containing **3** was evacuated to at least 1×10^{-4} Torr to remove traces of water, solvents and oxygen and was then filled with argon. Deoxygenated polydimethylsiloxane was added to the zeolite complex and homogenized in an ultrasonic bath for about 20 min. The emulsion was transferred into a gas tight Hamilton syringe and bubbled with argon. To measure TR-EPR spectra the emulsion was flowed through a flat quartz cell (~0.3 mm thick) in the rectangular cavity of the EPR spectrometer with a flow rate of 1 mL/min.

CW-EPR. CW-EPR experiments were performed on a Bruker EMX-EPR spectrometer.

Diffuse Reflectance Laser Flash Photolysis. Diffuse reflectance laser flash photolysis experiments employed pulses (308 nm, 10 ns) from a Lambda Physik Lextra 50 excimer laser and a computer-controlled system that has been described elsewhere.[22] The optical configuration was similar to that used by Wilkinson and Kelly.[23] The data analysis was based on the fraction of reflected light absorbed by the transient (reflectance change ($\Delta J/J_o$) where J_o is the reflectance intensity before laser excitation and ΔJ is the change in the reflectance after excitation.

Results and Discussion

Figure 2a shows the CW-EPR of **2**-^{14}N loaded into NaY, which was coadsorbed with **1** at a loading of 2% and 10%, respectively (*w*/*w*). Assuming a random adsorption in supercages, this loading corresponds in average to one molecule of **2**-^{14}N and five molecules of **1** in five supercages of NaY. For direct comparison with the TR-CW-EPR spectra, the CW spectrum is presented in its integrated form in Figure 2. Spectra simulation showed that the observed CW-EPR spectrum corresponds to **2**-^{14}N in the slow motion limit (see Supporting Information 1). The magnetic parameters used in the simulation are in good agreement with previously published values for TEMPO in NaX zeolite.[24] For efficient triplet quenching, it would be desired that each loaded supercage of NaY contains only one molecule of **1** and only one molecule of **2**. Because the molecules are loaded randomly, the occupation of the supercages probably deviate from the ideal condition. Furthermore, the maximum amount of nitroxide which can be loaded is limited by spin-spin exchange interactions, which would complicate the interpretation of the CIDEP data, i.e., if nitroxide

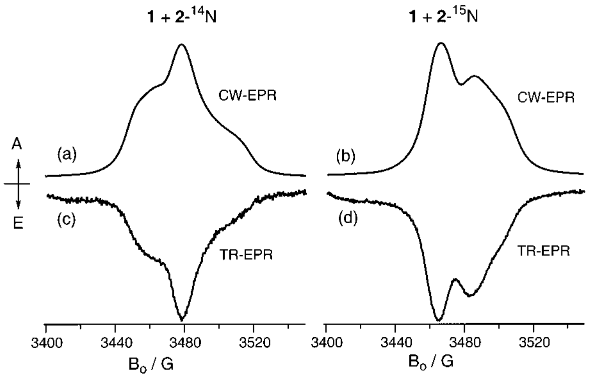


Figure 2. CW-EPR (a, b) and TR-EPR (c, d) spectra of powder samples of **2**-^{14}N (a, c) and **2**-^{15}N (b, d) in NaY (one molecule of **2** in five supercages), which also contains **1** (one molecule of **1** in one supercage). TR-EPR spectra (c, d) were recorded $1.0 - 1.7$ μs following laser excitation (308 nm, 10 ns). The CW-EPR spectra (a, b) are displayed in its integrated form.

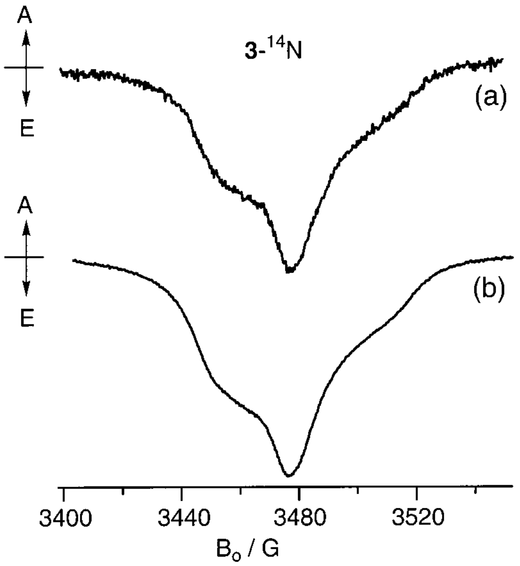


Figure 3. TR-EPR spectra recorded $1.0 - 1.7$ μs following 308 nm laser excitation of **3** in NaY (one molecule in five supercages) as powder sample (a), or as slurry in polydimethylsiloxanes (5% zeolite complex) as transport medium (b).

molecules are located close to each other, then Heisenberg exchange interactions alter the EPR spectrum.[25−27] This is expected to be the case when on average one molecule of **2** occupies each supercage. Therefore, for our experiments, the loading of nitroxides was reduced to one molecule of **2** in five supercages, where spectral changes due to spin-spin exchange interactions are minor.

Laser irradiation (308 nm) of NaY containing on average five molecules of **1** for every one molecule of **2**-^{14}N (natural isotope) affords a broad emissive polarized TR-EPR spectrum shown in Figure 2c. The spectrum obtained by TR-EPR exhibits the same features as the spectrum of **2**-^{14}N obtained by CW-EPR spectroscopy (Figure 2a). The observation of emissive spin polarization is in agreement with TR-EPR experiments in solution, where emissive spin polarization was also observed.[28,29]

In normal EPR practice, the identity of the paramagnetic species under study is uniquely determined by measuring coupling constants and *g* factors. However, due to the broadening of the EPR spectrum of the nitroxide on NaY surface, these parameters cannot be reliably obtained from the TR-EPR spectra. The anisotropic components of the magnetic tensor parameters are detectable, which is common for free radicals under slow motion conditions.[25,26] To circumvent this problem and unambiguously support the proposed interpretation, benzophenone and 4-oxo-TEMPO−^{15}N (**2**-^{15}N) were employed. Because ^{15}N possesses a spin multiplicity of $^{1}/_{2}$, in contrast to the spin multiplicity of ^{14}N of 1, both nitroxide EPR spectra are readily distinguishable from each other.[25,26]

Figure 2b shows the CW-EPR of **2**-^{15}N adsorbed in NaY, which also contains the sensitizer ketone **1** (one molecule of **2** and five molecules of **1** in five supercages of NaY), which is easily distinguishable from the ^{14}N isotope (Figure 2a). Spectra simulation is in good agreement with previously published values for **2**-^{15}N in slow motion condition (see Supporting Information 1).[25,26] Laser irradiation (308 nm) of **1** and **2**-^{15}N in NaY produced an emissive polarized TR-EPR spectrum shown in Figure 2d. The spectrum obtained by TR-EPR (Figure 2d) exhibits the same features as the spectrum obtained by CW-EPR spectroscopy (Figure 2b).

The electron spin polarizations shown above were generated by intermolecular triplet quenching of benzophenone (**1**) by a nitroxide (**2**). If both ketone and nitroxide are chemically linked through a short tether (i.e., **3**, Chart 1), then triplet quenching can occur intramolecularly, as has been demonstrated successfully in homogeneous solution.[3,5,30] The following experiment shows that intramolecular triplet quenching inside NaY supercages also produces spin polarized nitroxides. The nitroxide linked benzophenone (**3**) was loaded into NaY (one molecule of **3** per five supercages of NaY). The CW-EPR spectrum of **3** adsorbed on NaY is identical to that obtained for **2**-^{14}N (Figure 2a). Laser irradiation (308 nm) produced a strong emissive spin polarized TR-EPR spectrum (Figure 3a), which is identical to the TR-EPR spectrum generated by intermolecular triplet quenching (Figure 2c).

The time evolution of the nitroxide spin polarization after irradiation with a short laser pulse (308 nm, 10 ns) was measured at 3485 G for inter- and intramolecular triplet quenching (Figure 4a,b). In both cases, the buildup of the polarization occurred within the first 300 ns, which is the instrument response function. The decay of the electron spin polarization of the nitroxides **2**-^{14}N and **3** followed first order kinetics. The spin polarization lifetimes of both nitroxides **2**-^{14}N and **3** are the same within experimental error (3.9 and 3.8 μs, respectively), and are in agreement with reported values of TEMPO spin polarization lifetimes in solution.[1,29]

To study the benzophenone triplet quenching kinetics by nitroxides inside the zeolites in more detail, diffuse reflectance laser flash photolysis was performed. Laser flash photolysis (308 nm, 10 ns) of **1** loaded on NaY affords a readily detectable transient absorption at 525 nm corresponding to the triplet state of **1** (Figure 5a).[31] The transient decayed with multiexponential kinetics, as expected for intermediates in a heterogeneous environment.[4] In the presence of the nitroxide **2** the triplets of **1** are strongly quenched (Figure 5b). Most of ^{3}(**1**)* is quenched within the first 300 ns. This is consistent with the buildup kinetics of the electron spin polarization measured by TR-EPR, which occurred within $\leq$300 ns (Figure 4c). Intramolecular triplet quenching of **3** occurred faster (Figure 5c) than the response time of our experimental setup for transient diffuse reflectance. The fast decay is consistent with the short triplet lifetime of **3**, which was determined in benzene solution by laser flash photolysis ($\tau_T = 85$ ns).[5]

The TR-EPR experiments presented above were performed on zeolite powder samples, where the sample containing cell was slowly moved through the EPR cavity during laser

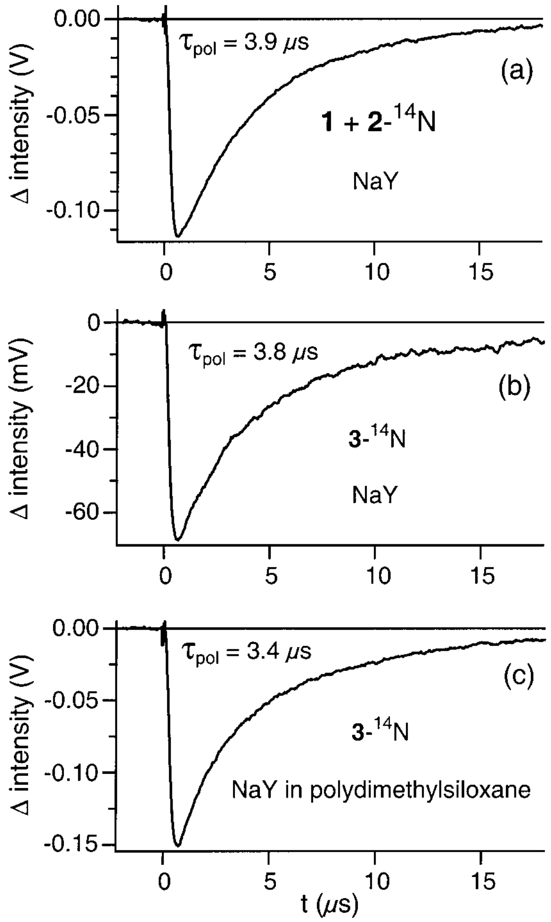


Figure 4. Transient EPR decay kinetic observed at 3485 G following laser excitation (308 nm, 10 ns) excitation of **1** and **2**-^{14}N in NaY (five molecules of **1** and one molecule of **2** in five supercages) (a), and **3** in NaY (one molecule in five supercages) (b) as powder samples (a, b), and **3** in NaY (one molecule in five supercages) as slurry in polydimethylsiloxanes as transport medium (c).

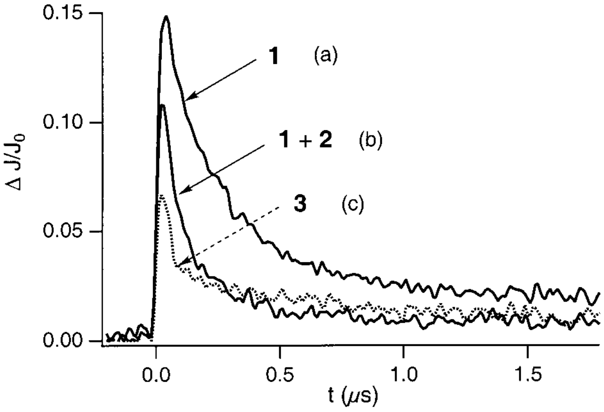


Figure 5. Transient diffuse reflectance kinetic traces observed at 525 nm following laser excitation (308 nm, 10 ns) of NaY containing one molecule of **1** in one supercage (a), five molecules of **1** and one molecule of **2** in five supercages (b), and one molecule of **3** in five supercages (c).

irradiation to reduce photo decomposition. Blaetter and Paul showed that transport of zeolite particles through the EPR cavity during irradiation can also be achieved by using a liquid transport medium, which is flowed through a flat cell in the EPR cavity.[13] Polydimethylsiloxane (viscosity 200 cP) was used for the following reasons: (i) it is viscous enough to prevent sedimentation of the zeolite particles, (ii) polydimethylsiloxane molecules are too large to enter the NaY cavity, and (iii) the refractive indexes of polydimethylsiloxane and zeolite crystals are similar to produce relatively transparent slurries.[13]

Accordingly, we used polydimethylsiloxane as the transport medium for zeolite complexes to study electron spin polarization of a nitroxide generated by quenching of a triplet ketone inside of NaY. Laser irradiation of an emulsion of polydimethylsiloxane and NaY loaded with **3** (one molecule in five supercages) that is flowed through the EPR cavity affords a broad emissive polarized TR-EPR spectrum (Figure 3b) which is experimentally identical to the TR-EPR spectrum obtained from photolysis of **3** adsorbed on zeolite powder (Figure 3a). The time evolution of the nitroxide spin polarization after laser irradiation using polydimethylsiloxane as transport medium (Figure 4c) was compared to powder samples (Figure 4b). The spin polarization lifetimes of **3** in polydimethylsiloxane slurries and in the zeolite powder sample NaY are the same within experimental error (3.4 and 3.8 μs, respectively).

Using a liquid transport medium for zeolites loaded with organic molecules has the risk of the organic molecules relocating from the zeolite phase to the liquid phase of the transport medium. To ensure that **3** remained inside NaY, CW-EPR experiments were performed (experimental spectra shown in Supporting Information). The nitroxide **3** dissolved in polydimethylsiloxane (500 cP) shows a three line isotropic EPR spectrum typical for nitroxides in fast motion condition.[25,26] The CW-EPR powder spectrum of **3** loaded into NaY cavities is broadened due to the hindered motion (resolution of the anisotropic components of the magnetic tensor parameters) and easily distinguishable from the spectrum in polydimethylsiloxane solution. The CW-EPR spectrum of a slurry of polydimethylsiloxane and NaY loaded with **3** is identical within the experimental error to the spectrum of **3** adsorbed in powdered NaY without the transport medium. This demonstrates that **3** remained in the NaY zeolite phase and that no nitroxide is extracted into the liquid phase of the transport medium.

Conclusion

The use of TR-CW-EPR to investigate photochemical reactions has been mainly limited to systems in solutions, which can be flowed through a flat cell in the EPR cavity to prevent chromophore depletion due to laser irradiation. TR-CW-EPR investigations of photochemical reactions of molecules adsorbed in zeolites can be performed conveniently by pulling a long tube containing powdered zeolite through the EPR cavity during the laser irradiation, or by using a liquid transport medium (polydimethylsiloxane) to produce a slurry of zeolite powder, which can be flowed through a flat cell in the EPR cavity. Both methods showed a strong CIDEP, generated by quenching of benzophenone triplets with TEMPO, which were adsorbed on NaY zeolite. These findings suggest that it should be possible to employ TR-CW-EPR to investigate a range of photochemical reactions of molecules adsorbed on zeolites and other porous solids. Because the generation of electron polarization from radicals produced by photolysis depends on a number of factors, including the extent of diffusional separation and the diffusional and rotational motions of radicals, the investigation of CIDEP in porous solids promises to be a method that will be of value for determining the dynamics of reactive intermediates in constrained spaces.

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Supporting Information Available: CW-EPR spectra and simulation of **2**-^{14}N, **3**-^{14}N , and **2**-^{15}N loaded into NaY zeolite. CW-EPR spectra of **3**-^{14}N in polydimethylsiloxane solution, NaY zeolite powder, and slurry of NaY in polydimethylsiloxane. This material is available free of charge via the Internet at http://pubs.acs.org.

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