

Supramolecular Effects on the Dynamics of Radicals in MFI Zeolites: A Direct EPR Investigation[†]

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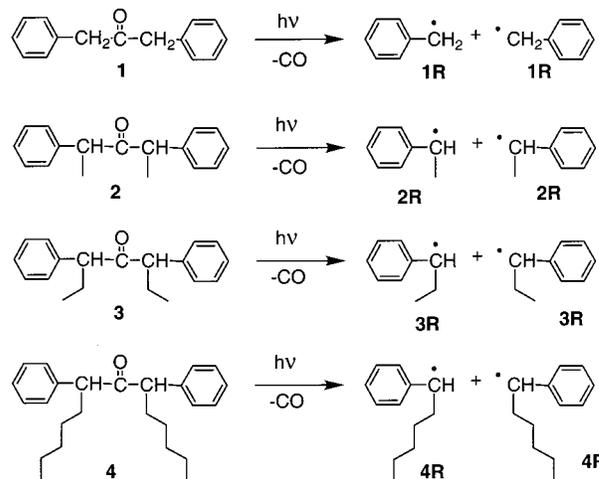
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Photolysis of the supramolecular complexes (dibenzyl ketones@ZSM-5) produced supramolecular complexes of benzyl radicals@ZSM-5, which were directly detected by CW-EPR spectroscopy, and provided information on the dynamics of the radicals. The lifetimes of the radicals increased as the group X attached to the carbon atom at the radical center increases from X = H ($t_{1/2}$ ca. 2 min) to X = (CH₂)₄CH₃ ($t_{1/2}$ > 200 min). In addition, line broadening of the EPR signal was observed as the group X increases. Experiments involving cation-exchanged zeolites (MZSM-5; M = Li, Na, K, Rb, Cs) showed a strong dependence of the radical lifetime on the size of the cation ($t_{1/2}$ ca. 10 min for Li and $t_{1/2}$ > 200 min for Cs). The results are discussed in terms of supramolecular steric effects on the radical–radical reactions in the zeolite supercages.

Introduction

In inert solvents and in the absence of scavengers the lifetimes of reactive radical intermediates are limited by self-reaction, i.e., radical–radical coupling or radical–radical disproportionation.¹ Classically, radical–radical reactions may be minimized or even eliminated by severely reducing diffusional motion or by imposing significant steric effects on the radical center.² Carbon-centered radicals produced by the photolysis of ketones adsorbed on MFI zeolites are sufficiently persistent at room temperature that they may be readily characterized by steady-state CW EPR.^{3–5} Although a number of studies of the EPR of carbon-centered radicals have been reported, there have been no reports on the relationship between the dynamics of radical decay and the supramolecular structure of the radicals. We report here a systematic investigation of the molecular structure of guest radicals and the exchangeable cations of zeolite host structures on the steady-state CW EPR spectra and the decay of carbon-centered radicals adsorbed on MFI zeolites. A series of symmetrically substituted dibenzyl ketones, **1–4** (Scheme 1), were selected as radical precursors. After photoexcitation, the ketones undergo α -cleavage from the triplet state to produce an acyl–benzyl radical pair in a primary process, followed by rapid decarbonylation of the acyl radical to generate a secondary radical pair consisting of benzyl radicals **1R–4R** (Scheme 1).^{6–8}

SCHEME 1



Results

The ketones **1–4** (Scheme 1) were adsorbed on NaZSM-5 (Si/Al = 20).^{9,10} In addition, ketone **2** was adsorbed on cation-exchanged zeolites MZSM-5 (M = Li, Na, K, Rb, and Cs). The complexes formed by the adsorbed ketones are termed **1–4**@MZSM-5. Photolysis of **1–4**@MZSM-5 produces radicals **1R–4R** (Scheme 1),⁵ and the complexes of the radicals with zeolites are termed **1R–4R**@MZSM-5.

Figure 1 displays the decay (left) and CW-EPR spectra (right) of radicals **1R–4R**@NaZSM-5. The most salient

[†] Dedicated to Waldemar Adam on the occasion of his 65th birthday.
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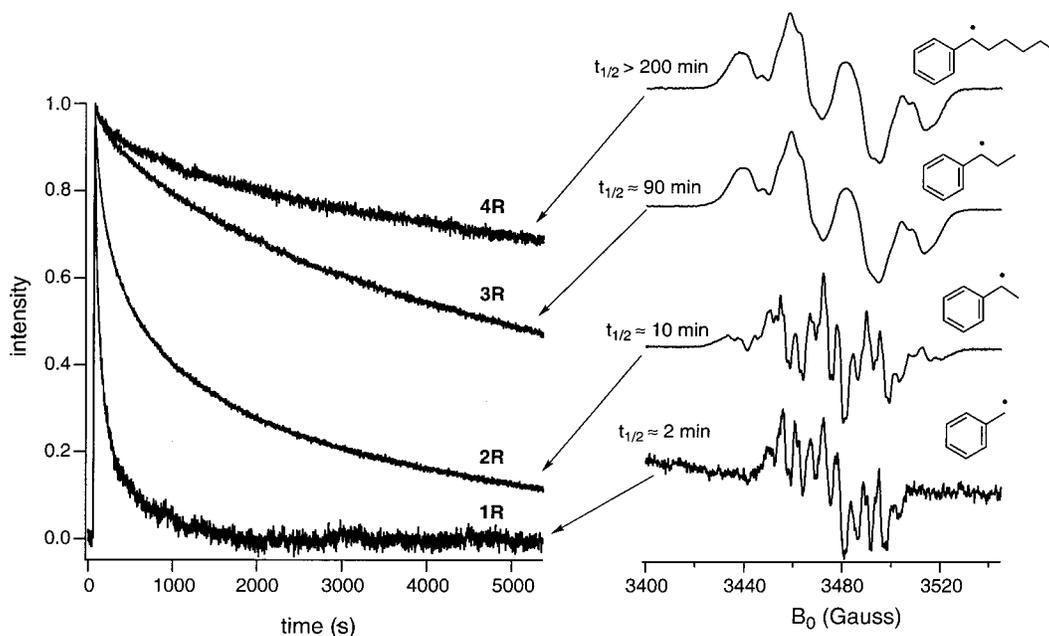


FIGURE 1. CW-EPR spectra (right) of radicals **1R**–**4R**@NaZSM-5 produced by photolysis of **1**–**4**@NaZSM-5 ($\lambda_{\text{irr}} > 280$ nm) and corresponding decay kinetics of the EPR signal (left) after short irradiation (10 s, $\lambda_{\text{irr}} > 280$ nm).

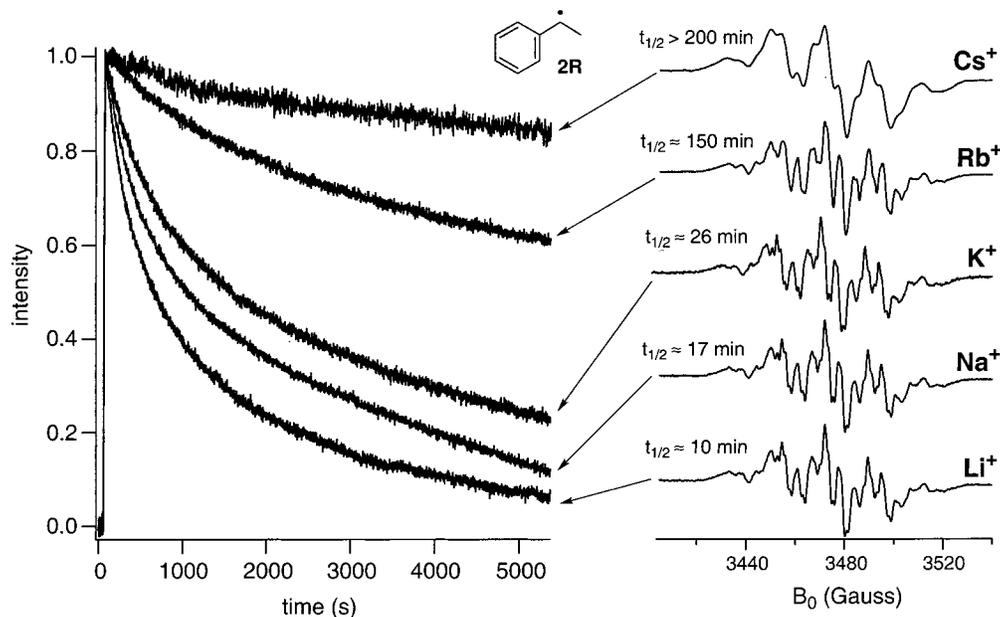


FIGURE 2. CW-EPR spectra (right) of the radical **2R** on cation-exchanged zeolites (**2R**@M-ZSM-5) produced by photolysis of **2**@M-ZSM-5 ($\lambda_{\text{irr}} > 280$ nm) and corresponding decay kinetics of the EPR signal (left) after short irradiation (10 s, $\lambda_{\text{irr}} > 280$ nm).

structural feature associated with the EPR decay curves is the clear correlation of the rate of the decay with the size of the radical: *the larger the radical, the slower the decay*. For example, the smallest radical **1R** shows the fastest decay ($t_{1/2}$ ca. 2 min) and the largest radical **4R** shows the slowest decay ($t_{1/2} > 200$ min). The most salient structural feature associated with the EPR spectra is the clear correlation of the line width of the spectrum with the size of the radical: *the larger the radical, the broader the signals*. It is also noted that the signal/noise is poorest for the benzyl radical spectrum, which decays the fastest.

Figure 2 displays the decay (left) and steady-state CW-EPR spectra (right) of radical **2R**@M-ZSM-5. The most

salient structural feature associated with the EPR decay curves is the clear correlation of the rate of decay with the size of the cation: *the larger the cation, the slower the decay*. For $M = \text{Li}$ the radical shows the fastest decay ($t_{1/2}$ ca. 10 min), and for $M = \text{Cs}$ the radical shows the slowest decay ($t_{1/2} > 200$ min). The line widths of the EPR spectra are similar for $M = \text{Li}$, Na , and K . However, a definite increase in line width occurs with $M = \text{Rb}$ and a significant increase in line width occurs with $M = \text{Cs}$.

Discussion

The external surface of ZSM-5 crystals consists of pores (circular diameter of pores ca. 5.5 Å) and a solid frame-

work between the pores. The internal void space consists of channels (ca. 5.5 Å in diameter) that intersect to produce roughly spherical supercages of ca. 9 Å in diameter.^{9,10} The molecular cross section of the guest ketone **1** is small enough to enter the pores on the external surface of ZSM-5. Under low-loading conditions **1** is exclusively adsorbed on the internal surface. Conversely, the guest ketones **2–4** are adsorbed on the external surface, because the molecular cross sections of the ketones are too large to enter the pores of ZSM-5. Evidence has been produced that the ketones **2–4** predominantly adsorb at the pore openings of the external surface.⁵

Photolysis of the complexes **1–4**@ZSM-5 generated the benzyl radical pairs **1R–4R**@ZSM-5. The decay curves shown in Figures 1 and 2 represent an example of “flash photolysis” with a time resolution in the orders of seconds. In this experimental configuration only radicals with a lifetime longer than ca. 1 s can be observed. The highly mobile benzyl radicals **2R–4R** on the external surface are expected to recombine rapidly and are, therefore, “invisible” in our EPR measurements. It is expected that only the radicals, which can escape into the pores on the internal surface, possess a lifetime long enough to be detected by EPR in our experimental configuration.

The resulting lifetimes followed by EPR of radicals **1R–4R** increase monotonically in the order **1R** < **2R** < **3R** < **4R**; i.e., as the group X attached to the radical center increases from X = H to X = (CH₂)₄CH₃, the rate of decay of the radicals decreases. We attribute this correlation to a supramolecular steric effect on radical–radical reactions which determine the lifetime of the radicals under observation. From computer-simulated molecular models, only the radical–radical combination of benzyl radicals, **1R**, to form 1,2-diphenylethane is sterically plausible in the supercages of the internal surface of the MFI zeolite. Product studies showed that the radicals **2R–4R** predominantly undergo radical–radical disproportionation on ZSM-5 zeolites.⁵ The concept of a steric effect on the radical–radical reactions in the internal supercages explains the correlation between radical size and radical decay. This is a dramatic *supramolecular steric effect* on the radical–radical reaction, since in ordinary solvents *all of the radicals investigated* undergo radical–radical combination at close to the diffusion-controlled rate.^{11,12}

In addition to a steric effect on the reaction step of two radicals, there may also be a steric effect on the diffusion of the radicals into a supercage. In other words, *in the zeolite internal surface, the diffusion of the smallest radical 1R may be much faster than the diffusion of the largest radical 4R*. A dramatic dependence of the diffusion rate on subtle changes in size is well established for molecular diffusion in zeolites. This possibility is consistent with the observed increase in line broadening in the EPR spectra as the size of the radical increases. The increased line broadening can be associated with a decrease in the correlation time for rotational motion of

the radicals.¹³ A decrease in rotational motion is consistent with a concomitant decrease in diffusional motion.

The data in Figure 1 are consistent with a correlation of the variation of the molecular structure of the guest on the observed decay of the guest@zeolite system. However, since we are dealing with a supramolecular system, the decay is expected to depend on the variation of the structure of the host zeolite also. The most subtle variation of the host structure is the variation of the exchangeable cations associated with the negatively charged Al atoms of the zeolite framework. The cations can be expected to interact with the radicals, both sterically and electrostatically. Previous studies have indicated that electrostatic interactions of the cations with hydrocarbon radicals are not as important as steric interactions.¹⁴ The data in Figure 2 speak for a dominating steric effect on the decay of the radicals through radical–radical reactions in the zeolite supercages. The larger the cation, the slower the decay. However, for cations Li, Na, and K, the line widths of the EPR spectra are similar and relatively sharp, indicating a similar and relatively high degree of rotational motion (and, by inference, diffusional motion) for these radicals. Only in the case of M = Rb and Cs is line broadening significant. These results are consistent with the main effect of the cation as being due to steric inhibition of radical–radical reaction in the zeolite supercages. This conclusion in turn suggests that the cations are associated with the supercages so that they are effective at the time of radical–radical reaction. It is also possible that Rb and Cs cause an increase in line broadening due to an increase in radical relaxation resulting from increased spin–orbit coupling.¹⁵

Conclusions

CW-EPR analysis of supramolecular complexes **1R–4R**@MZSM-5, generated by photolysis of **1–4**@MZSM-5, provided information on the supramolecular dynamics of the radicals. The lifetimes of the radicals increased as the group X attached to the radical center increases from X = H to X = (CH₂)₄CH₃. This correlation was attributed to a supramolecular steric effect on the radical–radical reactions, which determine the radical lifetimes. In addition, line broadening of the EPR signal (associated with a decrease in rotational motion) is consistent with the notion of decreased mobility as the group X attached to the radical center increases. EPR experiments involving cation-exchanged zeolites (MZSM-5; M = Li, Na, K, Rb, Cs) showed a strong dependence of the radical lifetime on the size of the cation; i.e., the larger the cation, the slower the decay. This is consistent with steric inhibition of radical–radical reaction in the supercages.

Experimental Section

1,3-Diphenyl-2-propanone (**1**) was obtained from Aldrich and purified by recrystallization from 5% (v/v) ether in hexane. 2,4-Diphenylpentan-3-one (**2**), 3,5-diphenylheptan-4-one (**3**), and

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6,8-diphenyltridecan-7-one (**4**) were synthesized and characterized previously.⁵

NaZSM-5 (Si/Al = 20), a Chemie Uetikon product, was supplied as a generous gift by Dr. V. Ramamurthy, Department of Chemistry, Tulane University, New Orleans, LA. The mean crystal lateral dimension was determined by scanning electron microscopy as ca. 0.3 μm . The external surface area was determined by mercury porosimetry¹⁶ to be 16 m^2/g . This zeolite (5 g) was then ion-exchanged two times at 70 $^\circ\text{C}$ for 24 h with 50 mL of 0.5 M solutions of LiCl, KCl, RbCl, and CsCl, washed thoroughly with deionized water, and dried.^{17,18} The zeolites were activated in a furnace at 500 $^\circ\text{C}$ for at least 8 h and cooled to room temperature in a desiccator before use.

The ketones **1–4** were adsorbed on ZSM-5 from an isooctane solution at ca. 1% (w/w) loading. After removal of the isooctane

solvent by evaporation under a stream of argon, the ketone-loaded zeolites were further degassed under vacuum (2×10^{-5} Torr) to remove traces of water, solvents, and oxygen. The photolysis was performed inside the cavity of a CW-EPR spectrometer (EMX, Bruker) employing a 1000 W Xe lamp (LX1000UV; ILC Technology, Inc.) in conjunction with a long wave pass filter (cutoff at 280 nm). For kinetic measurements the zeolite sample was briefly irradiated (10 s) in the cavity of the EPR spectrometer, and the decay of the EPR signal at a fixed magnetic field was monitored over time.

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