

An EPR Investigation of Persistent Radicals from the Photolysis of *p,p'*-Dialkyl-Substituted Phenyl Benzyl Ketones Adsorbed on MFI Zeolites

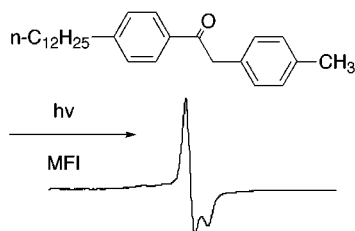
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ABSTRACT



The photolysis of isomeric pairs of *p,p'*-dialkyl-substituted phenyl benzyl ketones adsorbed on MFI zeolites has been investigated by EPR spectroscopy. Photolysis produces persistent “benzoyl type” and “benzyl type” radicals. The dominant persistent radical produced by photolysis of any particular isomeric pair depends on the length and position of the *p*-alkyl chain. The results are attributed to supramolecular stereoisomers resulting from preferential adsorption of the longer alkyl chain into the pores of the zeolite.

The adsorption and diffusion of benzene and alkylbenzenes on the external and internal surface of MFI zeolites (silicalite and ZSM-5) are generally accepted as playing an important role in the catalytic preparation and separation of alkyl benzenes by MFI zeolites.^{1–4} The kinetic diameter (molecular cross section) of a benzene ring is approximately the same as the pore diameters of MFI zeolites, leading to significant size/shape selectivity of adsorption and diffusion of alkylbenzenes.² The strength of adsorption of *n*-alkyl chains by the channel system of ZSM-5 increases with increasing chain

length because of the attractive dispersion forces resulting from the complementary and close fit of the chain and the void space of the internal surface of an MFI zeolite.⁴

Investigation of the photochemical reactions of molecules adsorbed on MFI zeolites has provided insights to the supramolecular structure and dynamics of adsorbed molecules and of the reactive radical intermediates produced by photolysis.⁵ For example, photolysis of dibenzyl ketone and its derivatives adsorbed on MFI zeolites results in the formation of persistent organic centered radicals which are readily detected by conventional EPR analysis.⁵ The degree of persistence has been shown to depend significantly on the initial supramolecular structure of the adsorbed ketone

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and on the supramolecular structure and dynamics of the radicals produced by photolysis.

We report here an EPR analysis of the persistent carbon centered radicals produced by photolysis of a family of pairs of isomeric *p,p'*-dialkyl phenyl benzyl ketones adsorbed on MFI zeolites 1_n @MFI and 2_n @MFI (Figure 1). This family

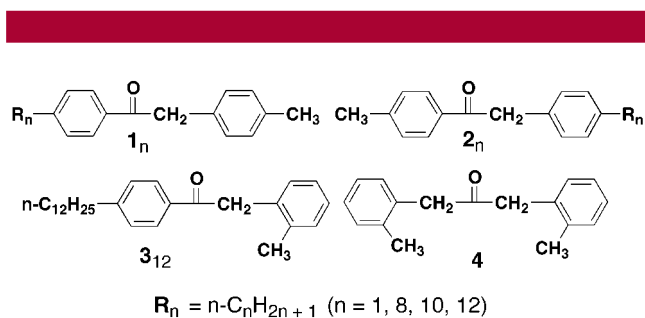


Figure 1. Structures investigated in this report.

allows a systematic EPR investigation of the influence of *n*-alkyl chains on the structure and persistence of radicals produced by photolysis of ketones@MFI. A striking dependence of the EPR spectra on the location (*p* or *p'*) and the length (*n*) of the alkyl chains of 1_n and 2_n is observed (Figure 2). These EPR results, together with those from the photolysis of the ketones 3_{12} @MFI and 4 @MFI (Figure 1), lead to the conclusion that there is preferential adsorption of the longer alkyl chains into the pores of MFI zeolites to

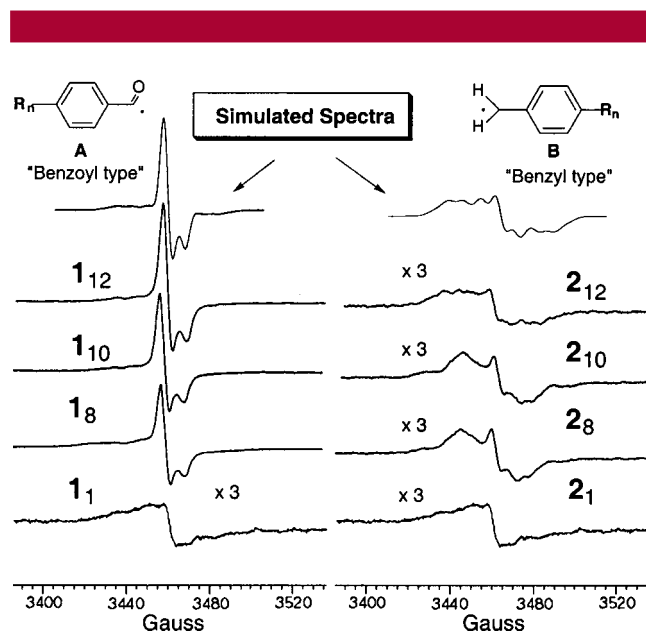


Figure 2. EPR spectra produced by the photolysis of 1_n @ZSM-5 (left) and 2_n @ZSM-5 (right). The simulations employed literature hyperfine coupling constants⁶ and line broadening parameter of ca. 5–6 G. Fits to the experimental spectra for the “benzoyl type” signal (top left) assumed a mixture of 95% **A** ($n > 1$) and 5% **B** ($n = 1$) and for the “benzyl type” signal (top right) assumed a mixture of 7% **A** ($n = 1$) and 93% **B** ($n > 1$). The benzoyl spectrum was simulated as a powder spectrum.

produce *two stereochemical supramolecular isomers*, one of which is preferred, depending on the position (*p* or *p'*) of the long alkyl chain of 1_n or 2_n . In the case of 1_n @ZSM-5, the EPR spectrum (i.e., the structure of the persistent radical produced by photolysis) depends strikingly on the preferred supramolecular stereoisomer.

The family of isomeric *p,p'*-dialkyl phenyl benzyl ketones 1_n and 2_n (Figure 1) was adsorbed from isooctane onto an MFI zeolite (silicalite or NaZSM-5 = ZSM-5, $SiO_2/Al_2O_3 = 40$, $Na_2O = 1.9\%$ by wt) at 1% wt/wt (ketone/zeolite) loading. After removal of solvent by argon flow, the samples were rotated and photolyzed under vacuum for ca. 7 min with a 450 W medium-pressure mercury lamp equipped with a chromate solution filter and then placed in the EPR spectrometer, and the EPR spectra were recorded within a period of 5 min. Representative EPR spectra resulting from the photolysis of 1_n @ZSM-5 (left) and 2_n @ZSM-5 (right) are shown in Figure 2. The simulated spectra⁶ (see figure caption for details) of a *p*-substituted alkyl benzoyl radical (left, top) and a *p*-substituted alkyl benzyl radical (right, top) are shown for comparison. The “benzoyl type” radicals produced from photolysis of 1_n @ZSM-5 are persistent⁷ for several hours (τ_{half} ca. 1 h for *p*-*n*-dodecyl benzoyl radicals), the “benzyl type” radicals produced from photolysis of 2_n @ZSM-5 are persistent for many hours ($\tau_{half} > 1$ day for *p*-*n*-dodecyl benzyl radicals), and the lifetime of both types of radicals increases with an increase in the alkyl chain length. Similar EPR results were obtained for photolysis of 1_n @silicalite and 2_n @silicalite. However, the lifetimes of both types of persistent radicals produced by photolysis were generally shorter for radicals produced on silicalite than for those produced on ZSM-5.

It is apparent that the length and, particularly, the position of the longer *p*-alkyl group have dramatic effects on the structure of the dominant persistent radical that is produced from photolysis of a given pair of isomeric ketones. As the *p*-alkyl chain on the benzoyl moiety of 1_n is lengthened from $n = 1$ to $n = 8$ to $n = 10$ to $n = 12$ (and the benzyl moiety maintains a *p*-methyl substituent), the EPR spectra are relatively strong in intensity and display dominantly the features of a “benzoyl type” radical (e.g., **A**, see Figure 2), with a minor “benzyl type” component (e.g., **B**). The relative intensity of the benzoyl type signal increases with increasing length of the alkyl chain. On the other hand, as the alkyl chain on the benzyl moiety of 2_n is lengthened from $n = 1$ to $n = 8$ to $n = 10$ to $n = 12$ (and the benzoyl moiety maintains a *p*-methyl substituent), the EPR spectra are relatively weak in intensity and display dominantly the features of a *p*-substituted alkyl “benzyl type” radical such as **B**, with a minor contribution from the “benzoyl type” component (e.g., **A**). For 2_n ($n = 8$ to $n = 10$ to $n = 12$), the “benzoyl type” signal decreases with increasing length of the alkyl chain. From simulation (Figure 2, top right) the observed EPR spectra fit well to “benzyl type” radicals such as **B** with a minor contribution of benzoyl type radicals such

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as **A**. The broad spectral lines show that the radicals are near the slow motion limit for EPR.

For comparison with other zeolites, the EPR resulting from photolyses of ketones adsorbed on Na5A were investigated. Na5A has pores leading to the internal surface which are smaller than the molecular cross section of benzene. The photolysis of **1**₁₂@Na5A and **2**₁₂@Na5A produced weak EPR signals (supporting material) which were not characteristic of either “benzoyl type” or “benzyl type” persistent radicals.

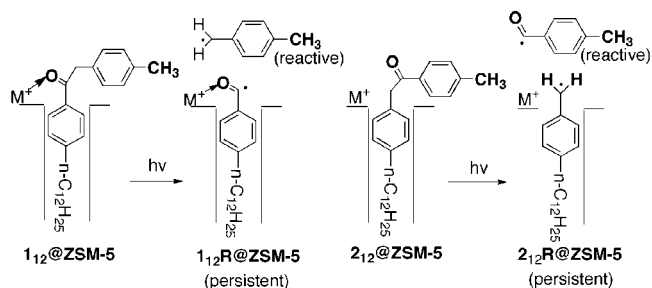
The influence of ortho substitution, which prevents entry of an alkyl benzene chain into the internal surface of MFI zeolites, was also investigated. Photolysis of **3**₁₂@ZSM-5 produces an EPR spectrum (Supporting Information) that is similar in intensity, lifetime, and structure to the “benzoyl type” EPR produced by photolysis of **1**₁₂@ZSM-5 (Figure 2). Photolysis of **4**@ZSM-5 did not produce EPR signals characteristic of persistent radicals of “benzoyl type” or “benzyl type” (Supporting Information).

The EPR spectra of Figure 2 demonstrate a strong preference for formation of persistent “benzoyl type” radicals from photolysis of **1**_{*n*}@ZSM-5 (*n* = 8, 10, and 12) and for the formation of persistent “benzyl type” radicals from photolysis of **2**_{*n*}@ZSM-5 (*n* = 8, 10, and 12). Of particular importance is the very strong and very selective “benzoyl type” signal that is produced for **1**_{*n*}@ZSM-5 (*n* = 8, 10, and 12) compared to **2**_{*n*}@ZSM-5 (*n* = 1, 8, 10, and 12). We suggest that the origin of these observations is the result of different supramolecular structures that are determined by the *p* or *p*' position of the longer alkyl chain and the characteristics of the pores at or near the external surface. We attempt to deduce the nature of the supramolecular structures whose photolysis produces the persistent radicals by first determining the most likely position of the adsorbed ketones, considering two possibilities: (1) adsorption mainly on the external surface; (2) adsorption partially or wholly in the internal surface. We then speculate on the reason for the most likely possibility being consistent with the EPR observations.

Possibility (1), that the initial ketone structures and the radicals produced by photolysis are mainly on the external surface, is considered unlikely on the basis of the following observations. Persistent radicals are not produced by photolysis of **1**₁₂@Na5A or **2**₁₂@Na5A although photolysis does occur. For Na5A the ketones and radicals produced are compelled to be adsorbed on and diffuse on the external surface, since the pores on the external surface are smaller than the aromatic rings of **1**_{*n*} and **2**_{*n*}. This conclusion is also supported by the absence of persistent radicals from the photolysis of **4**@ZSM-5 which is completely adsorbed on and produces only radicals on the external surface. These results imply that for photolysis to produce persistent radicals, the aromatic portion of the ketones must be adsorbed either deep in the internal structure or at least adsorbed near the external surface.

This leaves possibility (2) as a working paradigm for the initial supramolecular structures shown in Scheme 1. We distinguish adsorption deep within the internal surface from adsorption at or near the external surface with the following

Scheme 1 Favored Stereochemistry of **1**₁₂ and **2**₁₂ and Preference for Persistent Radical Formation



argument. Since *o*-xylene is not adsorbed into the pores of MFI zeolites at room temperature, the *o*-xylyl group of **3**₁₂ is expected to prevent the molecule from being adsorbed deeply into the MFI internal surface. However, a structure such as that shown in Scheme 1 for **1**₁₂@ZSM-5, for which the *p*-alkyl chain and associated benzoyl group are adsorbed into the internal surface, is plausible. The observation that photolysis of **3**₁₂@ZSM-5 produces a “benzoyl type” spectrum similar in intensity, lifetime, and structure to that produced by photolysis of **1**₁₂@ZSM-5 is particularly revealing. The observation of similar EPR spectra is consistent with similar initial supramolecular structures and dynamics. Since the initial supramolecular structure of **3**₁₂@ZSM-5 will possess the *o*-substituted ring to be at or near the external surface with the alkyl chain adsorbed internally, then **1**₁₂@ZSM-5 must also be sited at or near the external surface with the alkyl chain adsorbed internally. Thus, when **1**₁₂@ZSM-5 is adsorbed at or near the external surface,⁸ we deduce the structure shown in Scheme 1 is favored.

The issue arises as to why one supramolecular structure should be preferred for a given *p,p*'-dialkyl ketone. The heat of adsorption of *n*-alkyl chains in MFI zeolites increases with the length of the alkyl chain.⁴ It is plausible, therefore, that for structures such as **1**_{*n*} and **2**_{*n*} the adsorption of the longer chain into the holes on the external surface will be favored. If this is the case, two possible supramolecular stereoisomers will result: a stereoisomer that is adsorbed with the longer alkyl chain being closer to the external surface and a second stereoisomer that is adsorbed with the longer alkyl chain being farther away from the external surface.⁸

Scheme 1 provides a representation of the proposed mechanism to explain the EPR data for photolysis of **1**₁₂@ZSM-5 and **2**₁₂@ZSM-5. For clarity, the favored supramolecular stereoisomers are shown adsorbed near the pore openings on the external surface.

Photolysis of phenyl benzyl ketones results in α -cleavage to produce a “benzoyl type” radical and a “benzyl type” radical.⁹ If, at the time of the photolysis, structures such as those shown in Scheme 1 are adsorbed at or near the boundary of the external surface as proposed, on the basis

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of previous results,⁵ photolysis will produce a persistent radical from the moiety bound to the zeolite hole and a transient radical from the moiety that protrudes from the external surface. The absence of persistence of radicals produced on the external surface is confirmed from the results of photolysis of **4@ZSM-5** which does not produce persistent radicals upon photolysis. Applying this reasoning to **1₁₂@ZSM-5** and **2₁₂@ZSM-5**, it is concluded that **1₁₂R@ZSM-5** will mainly produce a persistent benzoyl radical (**1₁₂R@ZSM-5**) upon photolysis and that **2₁₂@ZSM-5** will produce a persistent benzyl radical (**2₁₂R@ZSM-5**) upon photolysis (Scheme 1). It is to be noted that the radicals observed by EPR are only a fraction of the actual radicals produced by photolysis. The transient radicals produced have reacted and are not observed in our experiments.

Some comments on the proposed stereoisomers shown in Scheme 1 are in order, in particular concerning the issue of why the molecules of **1₁₂** and the “benzoyl type” radicals produced by photolysis might prefer to be adsorbed in a pore yet remain close to the interface at the external surface. The “benzoyl type” spectrum (Figure 2) was best fit to a powder spectrum, indicating complete immobility of the radical on the EPR time scale, indicating significant binding of the radical to the zeolite. We speculate that the pore openings at the interface are able to bind the carbonyl group because of some polar interactions provided by SiOH (silicalite and ZSM-5) defects or by cations (ZSM-5) near the pores on the external surface. In support of this speculation, there is evidence in the literature that Al atoms, and, therefore, compensating cations, tend to concentrate near the pore on the external surface which would make the structure for **1₁₂@ZSM-5** shown in Scheme 1 plausible.¹⁰ Furthermore, there is evidence from time-resolved step-scan FT-IR¹¹ for significant bonding of the acyl radical to Na cations¹² in NaY, which is consistent with the persistence and slow motion of the “benzoyl type” radical deduced from the EPR data. Since photolysis of the isomeric partners, **2_n** ($n > 1$) show only weak EPR signals, it is clear that a long chain of the benzoyl moiety is more effective in producing radical persistence than a long chain on the benzyl moiety. This result is consistent with a weaker binding of the resulting *p*-alkyl benzyl radical and faster diffusion and resulting radical–radical reactions.

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The observation that the persistence of the radicals increases with the length of the alkyl chain is consistent with a diffusion mechanism in determining radical persistence. For example, radical–radical reactions may result if radicals diffuse from the internal to the external surface encounter and then react on the external surface. It is also possible that radical–radical reactions may occur between radicals that encounter at the intersections of the internal surface. It is also possible that photolysis produces some radicals in the framework of the zeolite which are not detected, because of their breadth or because they appear out of the range of detection, but which serve as scavengers of the persistent radicals. Finally, we note that both types of radicals decayed faster when adsorbed on silicalite than on ZSM-5. This result is also consistent with Scheme 1, since the pores of the silicalite framework do not possess the more strongly binding cations that are present on the ZSM-5 surface.

In closing, we comment that the persistence observed in this report may be closely related to a kinetic mechanism for radical persistence.¹³ When radicals are produced in pairs, if one of the radicals of the pair has a significantly different rate of radical–radical reaction than the other, there will be a build up in the concentration of the radical which reacts at the slower rate. In favorable cases this can lead to radical persistence. In the systems investigated here, the smaller radical produced by photolysis of either **1_n@MFI** or **2_n@MFI** will diffuse faster and undergo radical–radical reactions with a higher probability than the larger radical. This will eventually lead to an excess of the larger radical and would become persistent if its rate of radical–radical reaction is very slow.

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Supporting Information Available: EPR spectra of photolyzed **1₁₂@Na5A**, **2₁₂@Na5A**, **3₁₂@ZSM-5**, and **4@ZSM-5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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