Reversible Oxygenation of a Diphenylmethyl Radical Rendered Supramolecularly Persistent

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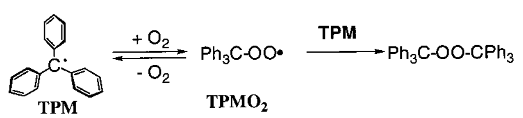
The preparation of the triphenylmethyl radical (TPM) by Gomberg in 1900 launched carbon-centered, free radical chemistry.[1] Under deaerated conditions in an inert solvent, TPM exists in measurable equilibrium with its dimer (TMP_2) as the result of an *intramolecular steric effect* which severely inhibits radical−radical reactions that render the radical "persistent", i.e., with a lifetime greater than seconds.[2,3] In the presence of O_2 in fluid solution, however, TPM reacts with oxygen to give a peroxide ($TMPO_2$, eq 1) via a peroxy radical.[1] Although $TPMO_2$ is a reactive intermediate in fluid media, it is persistent in a solid glass.[4] In a glassy matrix, a remarkable deoxygenation of $TPMO_2$ to TPM has been observed (eq 1), demonstrating that the addition of O_2 to TMP is reversible to a measurable extent.[4]



(1)

In contrast to the TPM radical, the diphenyl methyl radical (DPM) is not persistent at all in fluid solution at room temperature and undergoes nearly diffusion-controlled radical−radical coupling to quantitatively form 1,1,2,2-tetraphenylethane.[5] Evidently, the occurrence of two benzene rings on a carbon radical does not provide sufficient steric inhibition to radical−radical recombination reactions which is required for persistence. We report here that photolysis of 1,1,3,3-tetraphenylacetone (**1**) adsorbed on a MFI zeolite,[6−8] the sodium form of LZ-105, produces DPM radicals (eq 2) which are extremely persistent (half-life for many weeks) and that these DPM radicals react *reversibly* with oxygen. TPM is rendered persistent through *supramolecular steric effects*.

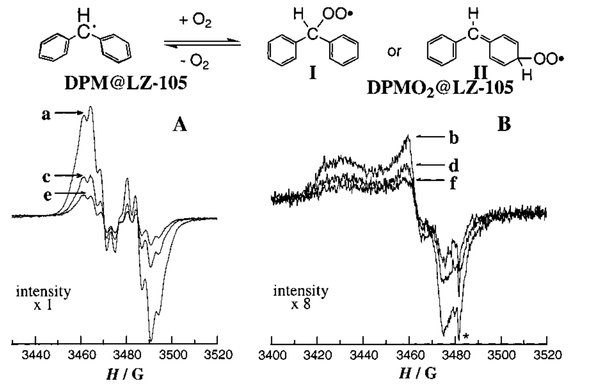


Figure 1. EPR spectra of DPM (A) and $DPMO_2$ (B) adsorbed on LZ-105 at room temperature. DPM (a) was generated by a photoreaction of **1** (0.5% loading) adsorbed on LZ-105. $DPMO_2$ (b) was obtained by exposing the sample (a) to air. DPM (c) was regenerated by degassing the sample (b) to 1×10^{-4} Torr at room temperature. Spectra d−e correspond to the samples in the oxygenation−deoxygenation cycles shown in Scheme 1. A sharp signal of irradiated quartz glass is present as indicated by the asterisk (∗).

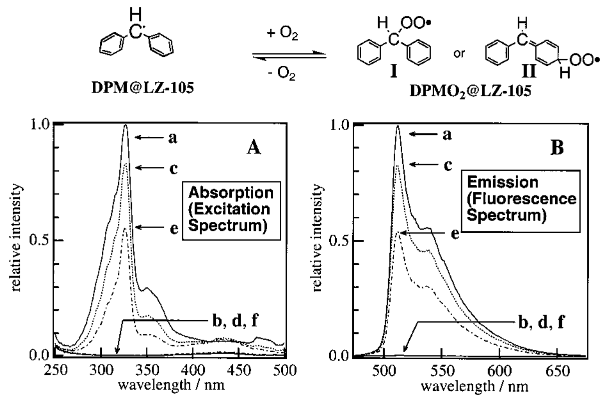


Figure 2. Fluorescence excitation (A, em 520 nm) and emission (B, ex 325 nm) spectra of DPM and $DPMO_2$ adsorbed on LZ-105 at room temperature. DPM (a) was generated by a photoreaction of **1** (0.5% loading) adsorbed on LZ-105. Spectra a−f correspond to those of Figure 1 and the samples in the oxygenation−deoxygenation cycles shown in Scheme 1.

1,1,3,3-Tetraphenylacetone (**1**) is an efficient photochemical precursor of DPM.[5,11,12] **1** was adsorbed on the LZ-105 surface from an isooctane solution at ca. 0.3−0.5% loading, which is sufficient to fill all holes on the LZ-105 surface with **1** to form a supramolecular system, termed (eq 2) **1**@LZ-105.[6,13] After removing the solvent by evaporation under a stream of argon, the **1**@LZ-105 sample was further degassed under vacuum. Irradiation of **1**@LZ-105 produced an intense EPR spectrum (Figure 1) and fluorescence spectrum (Figure 2), both of which are persistent for many weeks at room temperature as long as the sample is maintained under vacuum. The EPR spectrum is convincingly assigned to DPM by simulation. The fluorescence excitation spectra (**a** in Figure 2A) showed a maximum at 327

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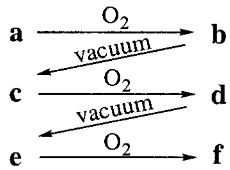
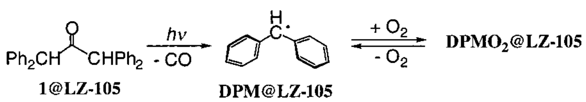
Scheme 1. Reversible Cycling of **DPM**@LZ-105 and **DPMO$_2$**@LZ-105



nm and the emission spectra (**a** in Figure 2B) showed maxima at 512 and 538 (sh) nm. These fluorescence maxima were assigned to those of DPM by comparing the reported values.[12,14] Thus, we conclude that photolysis of **1**@LZ-105 produce a persistent radical, **DPM**@LZ-105 (eq 2), and that the spectral properties of the supramolecular radical are similar to those of the molecular radical, a property expected if the intermolecular bonding of the supramolecular system is relatively weak.



(2)

Addition of air to a sample of **DPM**@LZ-105 causes the replacement of the EPR spectrum of **DPM**@LZ-105 with that of a new spectrum (b in Figure 1 B) within 30 s. The fluorescence of **DPM**@LZ-105 also disappeared under the same conditions (b in Figures 2A and 2B). The EPR spectrum which is assigned to a supramolecular peroxy radical, **DPMO$_2$**@LZ-105 by comparison with literature examples of peroxy radicals shows a strong *g*-factor anisotropy as the result of immobilization in a rigid matrix or at low temperature.[15] Because the features of the EPR spectrum of a peroxy radical R−OO• are relatively insensitive to the structure of R, the observed DPMO$_2$ could be assigned to either **I** or **II** (Figure 2). The EPR spectrum of **DPMO$_2$**@LZ-105 did not vary significantly with temperature in the range of −23 to −150 °C. This result confirms the immobilization of DPMO$_2$ resulting from adsorption to the internal surface of LZ-105 even at room temperature.

When **DPMO$_2$**@LZ-105 was degassed to ca. 5×10^{-5} Torr at room temperature, the EPR signals and fluorescence of DPM both reappeared and both could be partially recovered by addition of air (Figures 1 and 2). As in the case of TPM (eq 1) deoxygenation/reoxygenation was reversible (Figures 1 and 2 and Scheme 1). However, the intensities of the EPR and fluorescence of DPM decreased during the oxygenation−deoxygenation cycling. The decrease in DPM during an oxygenation−deoxygenation cycle is assigned to thermal instability of **DPMO$_2$**@LZ-105. The EPR signal of the peroxy radical gradually decreased with a half-life of ca. 1 h at room temperature. The EPR intensity of the regenerated **DPM@**LZ-105 was dependent on the period for which the sample was allowed to stand at room temperature. For instance, when **DPMO$_2$**@LZ-105 was degassed 10 min or 5 h after exposure of DPM to air, 47 or 9% of the original EPR intensity of DPM was recovered, respectively.

In an effort of increase the yield of DPM recovered after deoxygenation−reoxygenation cycling, **DPM**@LZ-105 was oxygenated at low temperature. The sample was cooled to −123 °C, and then air was introduced into the sample to form **DPMO$_2$**@LZ-105. After degassing the sample at room temperature, 66% of the original EPR intensity of DPM was observed.

From the results reported above, a reversible oxygenation reaction of **DPM**@LZ-105 (eq 2) is established at room temperature and is similar to the behavior of TPM generated in a solid glass lattice.[4] The similarity of the persistence of the supramolecular system, **DPM**@LZ-105, and the molecular system, TPM in fluid solution, is ascribed to a supramolecular steric effect. In both cases the persistence results from the steric inhibition of radical−radical reactions as two radicals approach each other. The persistence of **DPM**@LZ-105 results from the creation of an intermolecular, supramolecular "bonding" between the host system and the entire DPM is analogous to the persistence that results from the replacement of an intramolecular covalent C−H bond by a C−C_6H_5 bond in TPM.

Reversible oxygenation−deoxygenation reactions of carbon-centered radicals are possible for a resonance-stabilized radicals, such as TPM,[4,17] and a pentadienyl radical for which the energetic differences between the peroxy radical and the deoxygenated radical is relatively small, i.e., for which the C−O bond is weak.[18] Energetically, oxygenation of alkyl, allyl, and benzyl radicals has been evaluated with standard heats of formation and dissociation of the corresponding peroxy radicals in the gas phase.[19] An estimate of the C−O bond strength in DPM may be made as follows. For a benzyl radical, the ΔH of the oxygenation reaction[19] was calculated to be −13 kcal/mol. Since the resonance stabilization energy by substitution of a phenyl group on a molecule is 2−3 kcal/mol, the ΔH for the oxygenation of DPM is estimated to be ca −10 kcal/mol. Since the deoxygenation is entropically favored, it is expected from this calculation that DPM should be reversible at room temperature. Experimentally, the value of ΔH for oxygenation of TPM in a solid glass lattice was determined to be ca. −9 kcal/mol[4] which is consistent with the calculation for DPM. In our studies, the secondary reaction of **DPMO$_2$**@LZ-105 is inhibited, compared to the reaction of DPMO$_2$ in solution, by the *supramolecular steric effect* resulting from adsorption onto LZ-105.

Application of the concept of a *supramolecular steric effect* should be useful as a general strategy to make reactive intermediates more persistent through noncovalent, intermolecular interactions. The concept of supramolecular steric effects is related to, but differs from, the strategy of persistence that results from immobilization by *matrix isolation.* Supramolecularly stabilized reactive intermediates may be able to experience considerable rotational and diffusional freedom that allows the exploration of extensive *intermolecular reactivity*; however, the selectivity of the reactive intermediate is determined by steric control of this reactivity by the host. Thus, in the case of DPM, the bimolecular reaction between two DPM radicals is completely inhibited for **DPM**@LZ-105, yet the bimolecular reaction between **DPM**@LZ-105 and oxygen is still facile. In summary, a supramolecular host, such as a zeolite cavity, may, through intermolecular noncovalent binding, prevent or inhibit the approach of two guest molecules in analogy to the steric effect of *tert*-butyl groups preventing or inhibiting the approach of a reagent to a functional group.

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Supporting Information Available: Experimental details and Figures 3 and 4 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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