Reversible Oxygenation of a Diphenylmethyl Radical Rendered Supramolecularly Persistent

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Received April 20, 1999
Revised Manuscript Received June 16, 1999

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 (TMP2), 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 O2 in fluid solution, however, TPM reacts with oxygen to give a peroxy radical.4 Although TPMO2 is a reactive intermediate in fluid media, it is persistent in a solid glass.5 In a glassy matrix, a remarkable deoxygenation of TPMO2 to TPM has been observed (eq 1), demonstrating that the addition of O2 to TMP is reversible to a measurable extent.6

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 7 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.

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For instance, when for which the sample was allowed to stand at room temperature. Add tion 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 1B) 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. The features of the EPR spectrum of a peroxy radical R$\cdot$O$\cdot$O 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 $\pm$23 to $\pm$150 $^\circ$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. $5 \times 10^{-5}$ 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 cycle. The decrease in DPM during an oxygenation–deoxygenation cycle is assigned to thermal instability of DPM$_2$@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$_2$@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$_2$@LZ-105 was oxygenated at low temperature. The sample was cooled to $\sim$123 $^\circ$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. The similarity of the persistence of the supramolecular system, DPM$_2$@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$_2$@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$_2$H$_4$ bond in TPM.

Reversible oxygenation–deoxygenation reactions of carbon-centered radicals are possible for a resonance-stabilized radicals, such as TPM, 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. Energetically, oxygenation of alkyl, allyl, and benzylic radicals has been evaluated with standard heats of formation and dissociation of the corresponding peroxy radicals in the gas phase. An estimate of the C–O bond strength in DPM may be made as follows. For a benzyl radical, the $\Delta H$ of the oxygenation reaction was calculated to be $\sim 13$ kcal/mol. Since the resonance stabilization energy by substitution of a phenyl group on a molecule is $\leq$3 kcal/mol, the $\Delta H$ for the oxygenation of DPM is estimated to be ca. $\sim 10$ kcal/mol. Since the deoxygenation is entropically favorable, it is expected from this calculation that DPM should be reversible at room temperature. Experimentally, the value of $\Delta H$ for oxygenation of TPM in a solid glass lattice was determined to be ca. $\sim 9$ kcal/mol 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 DPM$_2$ 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.

**Acknowledgment.** The authors at Columbia thank the National Science Foundation for Grant CHE-93-13102. This work was supported (in part) by the National Science Foundation and the Department of Energy under Grant No. NSF CHE-98-10367 to the Environmental Molecular Sciences Institute (EMSI) at Columbia University. Mr. Xuegong Lei is thanked for helpful discussions.

**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.

JA9912628