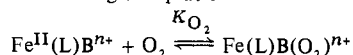


Table I. Oxygen Binding Constants for Reversible Oxygen Adducts of lacunar-Fe<sup>II</sup>(L)B<sup>n+</sup> at -41.5 °C<sup>a</sup>

B	solvent	K <sub>O<sub>2</sub></sub> , torr <sup>-1</sup> b
pyridine	acetone/py/water = 3/1/1	0.16 ± 0.01
chloride	acetone/py = 4/1	0.015 ± 0.003
pyridine	acetone/py = 4/1	0.08 ± 0.01
1-MeIm	acetone/MeIm = 4/1	1.7 ± 0.2

<sup>a</sup> K<sub>O<sub>2</sub></sub> defined according to equation



<sup>b</sup> O<sub>2</sub>, average of values at four wavelengths across the spectrum using nonlinear least-squares fit to absorbance data.<sup>4</sup>

is sufficient to facilitate complete conversion to the 5-coordinate neutral base derivative (electronic spectrum identical with that of the complex prepared independently from the CO complex<sup>5</sup>). The water is apparently necessary to solvate the chloride, thereby assisting its displacement by neutral base. The resulting 5-coordinate complexes are high spin ( $\mu_{\text{eff}} \sim 5.2\text{--}5.4 \beta$ ) and very sensitive to oxygen in solution.

Cooling solutions of the complex Fe(L)B<sup>2+</sup> (B is pyridine or 1-methylimidazole) to -35 °C in a combination of acetone/water/axial base as solvent produces a system that reacts with O<sub>2</sub> in a fully reversible manner. Gas uptake measurements<sup>15</sup> at -35.7 °C in pyridine solvent show that 1.0 ± 0.1 mol of O<sub>2</sub> is absorbed per mol of Fe(II); the resulting O<sub>2</sub> adduct is ESR silent. Visible spectral changes in a mixed solvent (Figure 1, see caption) show the reversibility of the O<sub>2</sub> reaction. The two spectral maxima, in the 500–650-nm region, associated with the O<sub>2</sub> adduct, increase in intensity as the partial pressure of O<sub>2</sub> is increased and the isosbestic point at 462 nm remains sharp. Following exposure to 1 atm of O<sub>2</sub>, the system may be quantitatively reversed by flushing with N<sub>2</sub> to regenerate the original spectrum while retaining the sharp isosbestic point at 462 nm. This, of course, strongly supports the conclusion that reversible oxygenation is occurring.

A close parallel in qualitative spectral behavior further supports the presence of an O<sub>2</sub> adduct. The visible spectrum of the O<sub>2</sub>-saturated solution of Fe(L)py<sup>2+</sup> shows absorption maxima at 523 and 610 nm. These bear a striking similarity to the bands observed at 541 and 577 nm for oxyhemoglobin.<sup>16</sup>

Equilibrium constants for oxygen binding by the lacunar complexes Fe(L)B<sup>n+</sup> have been estimated at -41.5 °C and are presented in Table I. The trends in values are very much as anticipated, with the progression increasing for axial bases in the sequence Cl < py < 1-MeIm. This parallels the behavior of the cobalt complexes<sup>17</sup> and modified porphyrin complexes.<sup>18</sup> The presence of water in the mixed solvent increases the O<sub>2</sub> affinity, as was found for the lacunar cobalt(II) derivatives.<sup>4</sup> Comparison of the values of K<sub>O<sub>2</sub></sub> for the iron complexes with those for the corresponding cobalt complexes shows that the O<sub>2</sub> adducts of iron are stronger by the expected factor.

At higher temperatures, for example at 20 °C, the O<sub>2</sub> complexes are unstable, rapidly producing iron(III)-containing species. The mode of irreversible oxidation is itself a fascinating problem in the fundamental chemistry of iron-dioxygen systems. Preliminary results indicate that the synthetic systems react in accord with a superoxide mechanism similar to that proposed for the auto-oxidation of Hb and Mb.<sup>19</sup> The thorough understanding of this process is essential to further refinements in the design of synthetic iron(II)-oxygen carriers and our studies are continuing.

The series of iron complexes of general structure I offer the exciting possibility of producing totally synthetic, non-porphyrin

iron containing heme protein analogues capable of closely mimicking biological functions. The susceptibility of structure I toward systematic variation fosters the belief that further rational structure changes will lead to greater success in controlling Fe-O<sub>2</sub> systems. Prior to the studies reported here the only unchallenged example of a non-porphyrin iron O<sub>2</sub>-carrying complex was that reported in 1973 by Baldwin and Huff.<sup>20</sup> That complex only attained reversibility at -85 °C while suffering irreversible oxidation at -50 °C in toluene/pyridine.

**Acknowledgment.** The support of the National Science Foundation is gratefully acknowledged.

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## Isotope Enrichment by Photolysis on Ordered Surfaces

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Recent reports of Turro<sup>1</sup> and other<sup>2,3</sup> have verified that under some conditions there exists an unusually large ratio of the rate of reaction of <sup>12</sup>C vs. <sup>13</sup>C compounds when compared to the ratio expected from the ordinary "mass" isotope effect. The so-called magnetic isotope effect<sup>3</sup> appears to be responsible whereby a reaction producing triplet biradicals as intermediates (e.g., Scheme I) reverts more frequently back to the starting compound when the odd electron density is on <sup>13</sup>C than on <sup>12</sup>C.

Turro has demonstrated that in order to observe substantial <sup>13</sup>C enrichment in the photolysis of dibenzyl ketone (DBK), the triplet diradicaloid arising from photolysis must be constrained within a cage long enough for electron nuclear hyperfine coupling to take place between an unpaired electron and a magnetic nucleus (<sup>13</sup>C). The hyperfine coupling (hfc) induces singlet-triplet mixing in the radical pair (*k*<sub>ST</sub>) followed by release of energy as the singlet radical pair undergoes bond reformation. Apparently in solution the weak solvent cage provides little resistance to the rapid diffusional separation of the radicals (*k*<sub>escape</sub>). Thus the reaction in solutions, including viscous solutions, forms escape products which do not exhibit the effects of hfc. However, a dramatic isotope effect, which is apparently due to the differences in the nuclear magnetic moments rather than the masses of <sup>13</sup>C and <sup>12</sup>C, was observed when DBK was photolyzed in micellar cages in solution. The "restricted dimensionality" of the micelles holds the triplet radical pairs sufficiently long for hfc to cause intersystem crossing, thus recycling predominantly <sup>13</sup>C back to the starting material.

Clearly, it would be worthwhile to optimize the "magnetic isotope effect" to give <sup>13</sup>C enrichments that are as high as possible. Unfortunately, it is not possible to systematically alter the size, interior viscosity, and similar properties of a micelle<sup>4</sup> to optimize the effect by "moving" the reflecting boundaries closer together

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(15) We are indebted to Drs. R. A. Wilkins and D. J. Olszanski for this datum.

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(17) Stevens, J. C.; Kojima, M.; Busch, D. H., unpublished results.

(18) Chang, C. K.; Traylor, T. G. *J. Am. Chem. Soc.* 1976, 98, 6765 and references therein.

(19) Reference 16, pp 1 and 69.

## Scheme I. Transformations in Dibenzyl Ketone Photochemistry

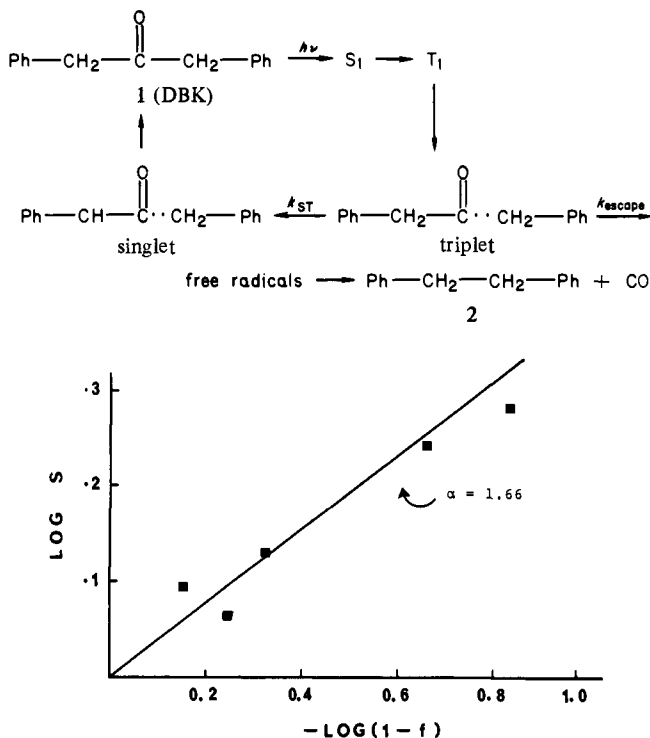


Figure 1. <sup>13</sup>C content of recovered dibenzyl ketone (DBK). Plot of separation factor, *S*, vs. fraction, *f*, of reacted DBK.

and farther apart. Since there is a great similarity in the physicochemical behavior of micelles, bilayers, vesicles, and adsorbed monolayers,<sup>4a</sup> we sought to probe whether a synthetic monolayer of a long-chain hydrocarbon, chemically bonded to the surface of a silica gel support, might produce a micelle "model" which could subsequently be altered systematically to find the optimum "position" for the "reflecting boundary" for highest isotopic enrichment. We prepared such a surface by the reaction of trichlorododecylsilane with silica gel,<sup>5</sup> giving rise to a surface which is a permanently bonded, rather than adsorbed, hydrocarbon monolayer. Adsorption of DBK onto this surface<sup>7</sup> followed by irradiation<sup>8</sup> gave rise to the same products observed in previous solution studies of DBK. The recovered DBK, as in Turro's reports, was found<sup>9</sup> to be enriched in <sup>13</sup>C! The results of a series of irradiations are shown in Figure 1. As Turro has noted, the use of  $\alpha$ , the "single-stage separation factor",<sup>10</sup> is a convenient way to describe the efficiency of enrichment, where the larger the value of  $\alpha$ , the larger the efficiency of <sup>13</sup>C enrichment. The value of  $\alpha$  is obtained by noting that the slope of  $\log S$  vs.  $-\log(1-f)$  equals  $(\alpha - 1)/\alpha$ . Figure 1 leads to a value of 1.66 for  $\alpha$  in our study, which may be compared with the value of 1.47 found<sup>1a,c</sup> in micelles<sup>11</sup> and the value of 1.03 for solution photolysis.<sup>1a</sup>

(5) The "RP-silica gel" was prepared by using the procedure of Berendsen<sup>6</sup> with Merck Silica Gel 40, trichlorododecylsilane, and catalytic chlorotrimethylsilane to give a product which was found to be 11.17% carbon, indicating a very high surface coverage.

(6) (a) Berendsen, G. E.; Galan, L. *J. Liq. Chromatogr.* **1978**, *1*, 561. (b) Berendsen, G. E. "Preparation and Characterization of Well-Defined Chemically Bonded Stationary Phases for High Pressure Liquid Chromatography"; Delft University Press: Delft, Netherlands, 1980.

(7) Typically, a slurry was prepared of a solution of 1.0 g of DBK in ca. 100 mL of 3:1 pentane/ether and 10 g of the RP-silica gel. The solvent was removed in vacuo to give the dry, free-flowing solid which was used in the irradiations.

(8) Irradiating dibenzyl ketone with naturally abundant <sup>13</sup>C by using a 450-W medium-pressure Hanovia lamp, under a nitrogen atmosphere, through Pyrex.

(9) The DBK was isolated by high-performance-low-pressure LC on Merck silica gel 40, eluting with ether/pentane. The extent of enrichment was determined by GC/MS analysis.

(10) Bernstein, R. B. *J. Phys. Chem.* **1952**, *56*, 893; *Science* **1957**, *126*, 119.

Thus, the synthetic monolayer surface seems to be quite analogous to a micelle in providing an artificial "reflecting boundary" which leads to an enhanced magnetic isotope effect over solution photolysis. We feel that it is unlikely that the dodecyl system and conditions reported here will be found to be the optimum environment for enrichment and hope that by varying the degree of crowding of the surface and/or length of the hydrocarbon chain, we will find significantly higher enrichment factors are possible. Work along these lines is currently in progress.

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(11) For simplicity the previous assumption<sup>1a</sup> that all enrichment occurred at one carbon was maintained in our work.

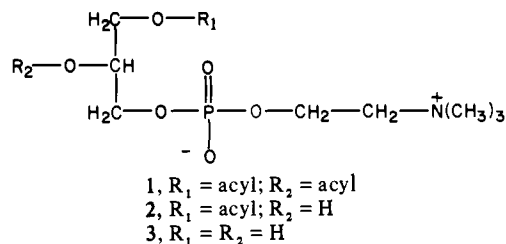
### Quadrupolar <sup>13</sup>C-<sup>14</sup>N Couplings and <sup>14</sup>N Relaxations in Aggregated and Nonaggregated Choline Phospholipids

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Quadrupolar relaxation ( $T_1$ ) of nitrogen-14 (spin 1, positive quadrupole moment) is greatly dependent on the symmetry of substitution around the nitrogen nucleus,<sup>1,2</sup> and  $T_1$ , in turn, affects the resonance of directly bonded nuclei with a spin  $1/2$ .<sup>3</sup> Hence, <sup>14</sup>N  $T_1$  and the quadrupolar <sup>13</sup>C-<sup>14</sup>N couplings ( $J_{CN}$ ) are sensitive to changes in the nitrogen environment. In the present study, we show that carbon-nitrogen couplings and quadrupolar <sup>14</sup>N relaxations of phosphatidylcholine (1; PC) are dependent on the



solvent, but that the magnitude of <sup>14</sup>N  $T_1$  and  $J_{CN}$  is not so much the result of phospholipid-solvent interactions than it is a consequence of aggregation or, better, nonaggregation of the PC species in a given medium.

In the absence of quadrupolar relaxation, nuclei of spin  $1/2$  coupled to nuclei of spin 1 produce simple multiplets.<sup>4</sup> Quadrupolar relaxation, however, modulates the line shape of the spin  $1/2$  nucleus (e.g., <sup>13</sup>C) when random transition occurs between states 0 and  $\pm 1$  according to

$$\eta = 10\pi T_1 J_{CN} \quad (1)$$

with  $\eta$  being a dimensionless parameter. Pople<sup>4</sup> has previously calculated theoretical line shapes for conditions  $\eta^2 = 10^n$  ( $n = 0$ ,

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