

Figure 2. Schematic representation of the sequestering effect of micelles on the free radicals produced by photolysis of ACOB. The vapor chromatographic analyses provide a clear experimental demonstration of the increase in regioselectivity which occurs above the cmc.

two \dot{B}) were produced by photolysis and existed for a long enough period of time to combine. Such a situation would require that a second ketone in the same micelle as \dot{A} and \dot{B} absorb light during the lifetime of \dot{A} and \dot{B} . If this were true, an intensity dependence on the formation of AA and BB is expected. No such dependence was found (tenfold intensity decrease). Finally the possibility of scrambling of the starting ketone was shown not to occur under our experimental conditions so that AA and BB can be formed by a pathway involving initial generation of ACOA and BCOB.

As the ratio [ketone]/[micelle] increases, the ratio of [AB]/(AA + BB) decreases (Table I). For example, at fixed [HDTCl] = 0.025 and [ACOB] = 1.6×10^{-4} M and 1×10^{-3} M, the values of AB/(AA + BB) are 98/2 = 49 and 75/25 = 3.0, respectively. At low ratios of ketone to detergent, a significant quantity of the ketone is forced into the aqueous phase and multiple occupancies of a single micelle occur. Both of these effects could lead to a decrease in the ratio of AB/(AA + BB). We are able to show that the major pathway for formation of AA and BB under these conditions is due to photolyses of the ketone dissolved in the aqueous phase by means of the following experiment.

Addition of an efficient free-radical scavenger, which is only soluble in the aqueous phase and is positively charged (so as to be repelled when it approaches a HDTCl micelle), should eliminate significantly the contribution of AA and BB resulting from photolysis in the aqueous phase.¹³ This leads to the expectation that addition of such a radical scavenger will cause the ratio of [AB]/[AA + BB] to increase. Experimentally (Table I), this is precisely what is found to occur: at 0.025 M HDTCl the ratio is 76/(11 + 13) = 3.2 at 0 M CuSO₄ and 98/2 = 49 at 0.01 M CuSO₄. In contrast, concentrations of up to 0.2 M NaCl had little effect on the product ratio.

In conclusion, our results indicate that the generation of two radicals $\dot{A} + \dot{B}$ in a single micelle effectively sequesters these reactive species into a "super hydrophobic cage" in which translational diffusion is dimensionality restricted,¹⁷ and from which escape is improbable. The result is a dramatic enhancement of selectivity in formation of AB relative to AA and BB as compared to homogeneous solution.

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- The ketone was stirred in H₂O for several hours and then the excess ketone was filtered. Photolysis of this solution followed by pentane extraction resulted in formation of a statistical ratio of ethanes in addition to several unidentified products (~20% of products).
- A typical experiment is as follows. The aqueous solution of ketone and HDTCl is prepared and 50 mL of the solution is photolyzed for 30 min with a low-pressure Hg lamp. This solution is diluted with 50 mL of H₂O and extracted with 75 mL of pentane. The pentane was repeatedly extracted with H₂O until it became clear. The pentane was then dried and its volume was reduced to ~0.25 mL. This was analyzed by VPC (1/8 in. \times 6 ft 10% SE-30 on Chrom W, column temperature 190 °C).
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- The number of ketone molecules in a micelle is evaluated by a Poisson distribution.¹² If the aggregation number of HDTCl is assumed to be 100, then at [HDTCl] = 1×10^{-2} and [ketone] = 1×10^{-4} the probability of a micelle having 0, 1, and 2 ketone molecules is 0.32, 0.32, and 0.16, respectively.
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- The photodecarbonylation of dibenzyl ketones probably proceeds in two steps: homolytic α cleavage followed by decarbonylation.¹⁴ The lifetime of the acyl fragment is not known. We plan to measure absolute quantum yields for reaction (eq 1) in micellar systems in order to determine if the efficiency of recombination of ACOB (or ACOB) radicals is enhanced.
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- An alternative explanation might be that the increased viscosity of the micelle interior (~30 cP)¹⁸ prevents diffusion of the initially formed radicals. However, this seems unlikely since a statistical distribution of products is obtained when the unsymmetrical ketone is photolyzed in ethylene glycol (13.8 cP).
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Magnetic Isotope and Magnetic Field Effects on Chemical Reactions. Sunlight and Soap for the Efficient Separation of ¹³C and ¹²C Isotopes

Sir:

The observation of CIDNP¹ is one important manifestation of the effect of electron nuclear hyperfine coupling (HFC) on chemical processes involving diradicaloids.^{2,3} When HFC influences the reactivity of radical pairs (the *magnetic isotope effect* on chemical reactions), it is theoretically possible to enrich magnetic isotopes⁴ relative to nonmagnetic isotopes in photochemical or thermal reactions, and to influence the rates and products of chemical reactions by application of an external magnetic field (the *magnetic field effect* on chemical reactions). As a result of the study of the photolysis of dibenzyl ketone (DBK) employing sunlight and ordinary mercury lamps as excitation sources,⁵ we report that (1) a measurable, but small, ¹³C/¹²C isotope separation occurs in homogeneous (benzene) solution;^{4a} (2) the efficiency of ¹³C/¹²C isotopic

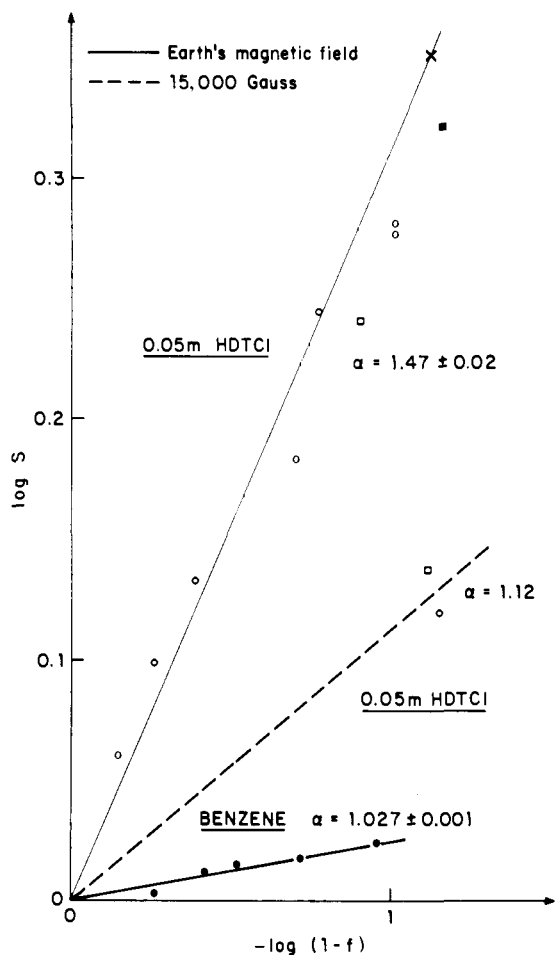
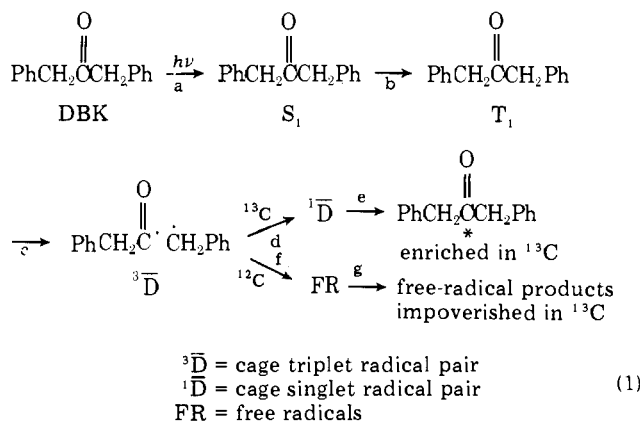


Figure 1. ¹³C content of recovered dibenzyl ketone (DBK). Plot of separation factor, *S*, vs. fraction, *f*, of reacted DBK. The equation $\log S = -\alpha^{-1}(\alpha - 1) \log(1 - f)$ is employed⁸ to determine α . The value of α derived from the slope of a plot of $\log S$ vs. $-\log(1 - f)$ is given in the figure. Only the circled points were used to calculate α . The value of α for the experiment in a magnetic field of 15 000 G is based on a single conversion (~90%). Initial ¹³C content in carbonyl of DBK: ○, 47.6%; ●, 25.4%; □, 22.3%; ×, 1.1% (natural abundance). Light source: Hanovia medium-pressure Hg lamp. ■ indicates sunlight: 47.6% ¹³C in starting ketone.

separation is greatly enhanced in soap solution relative to homogeneous solution; (3) the carbonyl carbon of DBK is specifically and exponentially enriched as photolysis proceeds; (4) an external magnetic field significantly influences the efficiency of ¹³C/¹²C isotopic separation.

Photolysis of DBK in aprotic homogeneous solution at room temperature yields 1,2-diphenylethane and CO quantitatively. This reaction proceeds⁶ via the sequence $S_1 \rightarrow T_1 \rightarrow {}^3\bar{D} \rightarrow \text{FR}$ (eq 1). The quantum yield for loss of DBK is ~0.7. Samples of ¹³C-enriched DBK (specifically enriched at the carbonyl



carbon) were photolyzed in C₆H₆ solution to various conversions by means of a mercury lamp. Mass spectrometric analyses⁷ of the ¹³C/¹²C content of the recovered DBK revealed an increase in the ¹³C/¹²C ratio of recovered DBK.^{4a} We employ Bernstein's formulation⁸ for expressing isotopic enrichments in order to obtain enrichment parameters that are independent of the percent conversion and that allow ready comparison with data in the literature. The quantity *S* is an "overall separation factor" derived from the mass spectrometric values of ¹³C and ¹²C in recovered DBK; the quantity ($\alpha - 1$) represents a single-stage separation factor and represents the ratio of rates (or efficiencies) of reaction of ¹²C relative to ¹³C. The larger the value of α , the larger the ¹³C enrichment of remaining DBK in the recovered material.

Soap solutions (hexadecyltrimethylammonium chloride, 0.05 M) of DBK were photolyzed to various conversions by means of a mercury lamp or by sunlight. Mass spectrometric⁷ analysis of the ¹³C/¹²C content of the recovered DBK showed the ¹³C enrichment to increase as a function of extent of photolysis and to follow Bernstein's formulation (Figure 1). Complementary NMR analysis (satellite method^{9b}) demonstrated that the enrichment occurred in the carbonyl carbon.

In contrast to the results for benzene solution for which $\alpha \sim 1.03$, an α value of ~1.47 (Figure 1) is found for photolysis of DBK in soap solution. Such a value of α is well out of the range of values reported^{9a} for mass isotope effects ($\alpha \sim 1.02$ –1.05). The enrichment specifically involves a *magnetic isotope effect* since the value of α decreases substantially when photolysis is conducted with the sample in the field of a strong magnet (Figure 1). A value of $\alpha \sim 1.47$ implies a "single-stage separation factor" ($\alpha - 1$) of ~0.47 giving a ¹³C enrichment of $\geq 100\%$ if a sample of natural abundance of ¹³C is photolyzed to ~90% conversion. This prediction was confirmed (Figure 1).

What is the mechanistic origin of the ¹³C enrichment, the dramatic enhancement of the ¹³C enrichment in detergent

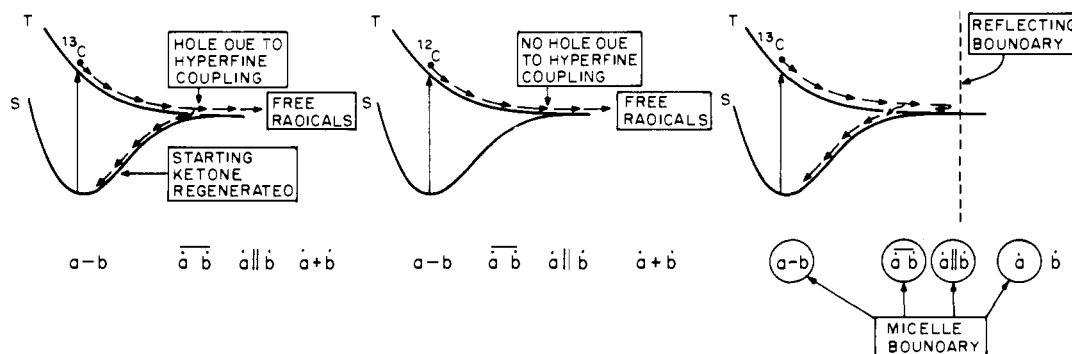


Figure 2. Schematic surface representation of the hyperfine mechanism for ¹³C enrichment of the carbonyl carbon of DBK by photolysis in soap solution. In the figure, *a* represents the PhCH₂CO group, *b* represents the CH₂Ph group, and ¹³C refers to the carbonyl carbon.

solutions, the large magnetic field effect on the ^{13}C enrichment, and the specificity of enrichment at the carbonyl carbon?

The magnitude of the magnetic isotope effect may be computed from the expression P (the probability for formation of DBK from any radical pair), which is available from the theory of CIDNP:^{2,3}

$$P \sim \epsilon \int_0^{\infty} f(t) |C(t)|^2 dt \quad (2)$$

ϵ is the probability that $^1\bar{\text{D}}$ pairs yield DBK, $f(t)$ represents the distribution of lifetimes among radical pairs, and $|C(t)|^2$ is the probability that by time t the radical pair will be in a singlet state. The product $f(t) |C(t)|^2 dt$ may be viewed as the probability that a radical pair formed at $t = 0$ will form $^1\bar{\text{D}}$ at time t .

CIDNP studies of the photolysis of DBK¹⁰ are consistent with the idea that HFC provides an important mechanism for intersystem crossing in $^3\bar{\text{D}}$. The most significant HFC in $^3\bar{\text{D}}$ should be due to the coupling of the odd electron of PhCH_2CO to a ^{13}C nucleus ($a \sim 130$ G).¹¹ Therefore, if ^{13}C HFC operates to control the rate of ISC of $^3\bar{\text{D}}$ to $^1\bar{\text{D}}$, and if $^3\bar{\text{D}}$ pairs possessing no ^{13}C HFC are scavenged or decarbonylate at a rate faster than they convert to $^1\bar{\text{D}}$, as photolysis proceeds $\text{PhCH}_2\text{COCH}_2\text{Ph}$ must become enriched in ^{13}C and the enrichment must occur predominantly at the carbonyl carbon.

The photolysis of DBK in soap solutions produces radical pairs in micelles.¹² The explicit form of $f(t)$ in eq 2 for a radical pair in a micelle favors ^{13}C enrichment (relative to a homogeneous fluid solution) via two factors: (1) the "restricted dimensionality" for diffusional excursions¹³ of a radical pair in the micelle¹⁴ and (2) the high local viscosity¹⁵ of the interior of a micelle. In effect, both of these factors should favor the efficiency of $^3\bar{\text{D}} \rightarrow ^1\bar{\text{D}}$ interconversions by "slowing down" the $^3\bar{\text{D}} \rightarrow \text{FR}$ processes. Further evidence that HFC is operating as the dominant mechanism for ^{13}C enrichment is found in the observation that the single-stage enrichment drops from 0.47 in the earth's magnetic field (~ 0.5 G) to 0.12 in the presence of a strong laboratory magnetic field ($\sim 15\,000$ G).

The mechanics of a HFC induced magnetic isotope separation are shown in Figure 2 in terms of energy surfaces. The crucial postulate is that HFC provides a "hole"¹⁶ on the " ^{13}C triplet surface" which provides access to the DBK (S_0) surface and that no such hole exists on the " ^{12}C triplet surface". A representative point that is put on the T surface (i.e., path a \rightarrow b, eq 1) will follow a trajectory on the T surface which takes it to the "crucial geometries" required for $^3\bar{\text{D}} \rightarrow ^1\bar{\text{D}}$ interconversion. The micelle enhances the probabilities of finding these geometries by providing a "reflecting boundary" for representative points that "overshoot" the hole. DBK, regenerated via path a \rightarrow b \rightarrow c \rightarrow d \rightarrow e must be enriched in ^{13}C , and incorporation of DBK into a micelle must enhance the process, the only question being the exact amount of the enrichment.

The idea of isotopic separation by employing HFC may be applied generally to any reaction involving a singlet-triplet crossing (or touching) along the reaction coordinate and possessing significant HFC at the structure corresponding to the crossing (or touching). Magnetic isotope effects may eventually be employed for the practical separation or enrichment of isotopes and the control of partitioning along reaction pathways involving intersystem crossing. In addition, they provide a novel mechanistic tool which complements CIDNP and which demonstrates the existence of diradicaloids and singlet-triplet crossings (or touchings) along a reaction coordinate.

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A Phosphoranide¹ Anion—Direct Observation of a Tetracoordinated Phosphorane Species

Sir:

Although tetracoordinated tetrahedral phosphonium cations² and tetracoordinated trigonal-bipyramidal (TBP) phosphoranyl radicals³ are well known, the anionic species derivable from the radicals by one-electron reduction, phosphoranide¹ anions, have received scant attention.⁴ We here report the direct observation of such a species.