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Magnetic and Micellar Effects on Photoreactions. 2. Magnetic Isotope Effects on Quantum Yields and Magnetic Field Effects on Separation Efficiency. Correlation of ^{13}C-Enrichment Parameters with Quantum Yield Measurements

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Abstract: The quantum yields (Φ) and ^{13}C isotopic enrichment parameters (α) for photolysis of dibenzyl ketone in aqueous detergent solution have been measured as a function of applied magnetic field and isotopic substitution. A quantitative correlation is shown to exist between the magnitude of α and quantum yield data. The mechanism of ^{13}C enrichment and the magnetic field effects are discussed and shown to be mechanistically related.

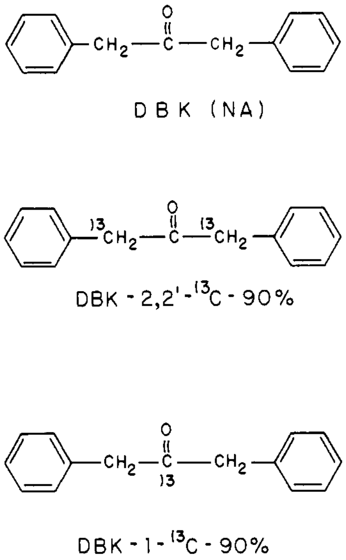
Introduction

In the preceeding paper,[1] evidence was reported which demonstrated that incomplete photolysis of dibenzyl ketone (DBK) in micelle solution results in ^{13}C enrichment of the residual, unconverted DBK and of the minor product, 1-phenyl-4′-methylacetophenone (PMAP). It was shown that the efficiency of the ^{13}C enrichment may be expressed quantitatively in terms of α, a single-stage isotopic separation factor[2] that may be computed from experimental measurements of the extent of conversion and of the $^{13}C/^{12}C$ contents in the initial and residual DBK. From determination of α under various conditions it was established that the efficiency of ^{13}C enrichment was substantially greater for photolysis in aqueous detergent solution than in homogeneous solution. In this paper we report measurements of the quantum yields for disappearance of DBK and for the appearance of products as a function of environment (homogeneous vs. detergent solution), isotopic substitution, and applied laboratory magnetic fields.[3] The isotopic separation parameter α is shown to be related to quantum yield measurements and thereby to provide a link between measurement of ^{13}C enrichment efficiency and measurable photochemical parameters.

Results

Absolute Quantum Yield Measurements. The absolute quantum yields for disappearance of DBK and for the appearance of 1,2-diphenylethane (DPE) were measured at room temperature for benzene and aqueous hexadecyltrimethylammonium chloride (HDTCl) solutions (above the cmc) and are summarized in Table I. The structures and abbreviated names of the dibenzyl ketones employed in this study are shown in Chart I. In all cases, solutions were deaerated by nitrogen purging. In benzene solvent, both the measured quantum yield of DBK (natural abundance, NA) disappearance ($\Phi_{-DBK}{}^{12C} = 0.72 \pm 0.12$) and the measured quantum yield for DBK-*1*-^{13}C (90% isotope incorporation) disappearance ($\Phi_{-DBK}{}^{13C} = 0.70 \pm 0.12$) are substantial but experimentally less than unity. Strikingly, the corresponding quantum yields are much lower for photolysis in aqueous 0.05 M HDTCl solution: $\Phi_{-DBK}{}^{12C} = 0.30 \pm 0.01$ and $\Phi_{-DBK}{}^{13C} = 0.22 \pm 0.01$. The quantum yield for *disappearance* of DBK (NA) is experimentally indistinguishable in the earth's magnetic field ($\Phi_{-DBK}{}^{12C} = 0.30 \pm 0.01$) or in a strong applied laboratory field of 15000 G ($\Phi_{-DBK}{}^{12C} = 0.32 \pm 0.03$). However, the quantum yields for disappearance of DBK-*1*-^{13}C (90%) in the earth's field ($\Phi_{-DBK}{}^{13C} = 0.22 \pm 0.01$) and in a strong magnetic field ($\Phi_{-DBK}{}^{13C} = 0.28 \pm 0.03$) are experimentaly distinct.

Chart I. Abbreviations for Structures Investigated



DBK (NA)

DBK-2,2′-^{13}C-90%

DBK-1-^{13}C-90%

The absolute quantum yield for the disappearance of DBK in aqueous HDTCl solution is equal to the sum of the absolute quantum yields for appearance of PMAP and DPE under all conditions involving the absence of radical scavengers. Although the quantum yield for appearance of PMAP is low, it is higher for DBK-*1*-^{13}C (90%) than for DBK (NA): $\Phi_{PMAP}{}^{12C} = 0.060 \pm 0.005$ and $\Phi_{PMAP}{}^{13C} = 0.074 \pm 0.007$, respectively.

Relative Quantum Yield Measurements. The isotopic separation parameter α has been related quantitatively[4] to the quantum yields for disappearance of DBK, according to eq 1. In this equation

$$\alpha^{\Phi} = \frac{\text{rate of disappearance of } ^{12}\text{C ketone}}{\text{rate of disappearance of } ^{13}\text{C ketone}} = \frac{\Phi_{-DBK}{}^{12C}}{\Phi_{-DBK}{}^{13C}} \quad (1)$$

$\Phi_{-DBK}{}^{12C}$ refers to the quantum yield for disappearance of DBK

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Table I. Quantum Yields for Photolysis of Dibenzyl Ketone at Room Temperature

ketone	solvent	$\Phi_{-\mathrm{DBK}}{}^{^{13}\mathrm{C}}$ [a]	$\Phi_{-\mathrm{DBK}}{}^{^{13}\mathrm{C}}$ [a]	α^{Φ} [d]	α^{MS} [e]
DBK-NA	benzene	0.72 ± 0.12	0.70 ± 0.12[b]	1.04 ± 0.05	1.03 ± 0.01
DBK-*1*-^{13}C (90%)	0.05 M HDTCl (0.5 G)	0.30 ± 0.01	0.22 ± 0.01[b]	1.37 ± 0.03	1.35 ± 0.03
DBK-*1*-^{13}C (90%)	0.05 M HDTCl (300 G)	0.375 ± 0.03	0.245 ± 0.03[b]	1.53 ± 0.04	1.47 ± 0.04
DBK-*1*-^{13}C (90%)	0.05 M HDTCl (14 000 G)	0.32 ± 0.03	0.28 ± 0.03[b]	1.16 ± 0.04	1.16 ± 0.03
DBK-*2,2'*-$^{13}C_2$ (90%)	0.05 M HDTCl (0.5 G)	0.30 ± 0.01	0.25 ± 0.01[c]	1.20 ± 0.03	1.18 ± 0.04

[a] The quantum yield of the disappearance of DBK was calculated on the basis of the disappearance of valerophenone whose disappearance quantum yield is reported to be 1.0 in *tert*-butyl alcohol. The ODs at 313 nm of DBK in benzene, HDTCl, and valerophenone in *tert*-butyl alcohol were measured to be 0.60, 0.41, and 0.50, respectively (c 0.005 M, $l = 1$ cm). The data presented are slightly different from the previously reported data which were based on the assumption that the ODs of DBK and valerophenone are identical at 313 nm. [b] Computed for 100% ^{13}C at the carbonyl carbon. [c] Computed for 100% ^{13}C at the α,α'-carbons. [d] α^{Φ} values are determined by quantum yield measurements according to eq 1. [e] α^{MS} values are determined by mass spectrometric analysis according to eq 7 in the preceding paper.

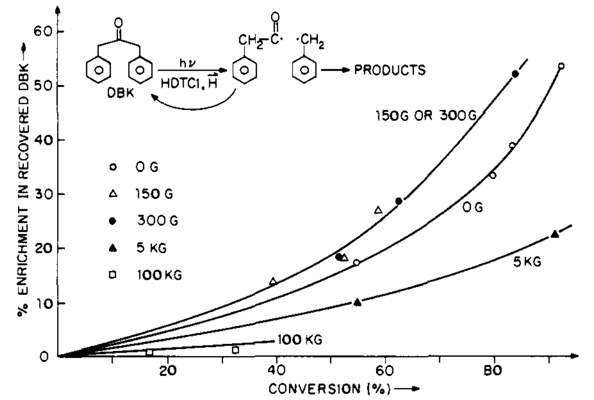


Figure 1. The percent ^{13}C enrichment at a single carbon atom of dibenzyl ketone as a function of conversion at various magnetic fields. The percent enrichment is computed from mass spectrometric data as described in the preceding paper.

containing only ^{12}C atoms (i.e., DBK-NA, to a good approximation), and $\Phi_{-\mathrm{DBK}}{}^{^{13}\mathrm{C}}$ refers to the quantum yield for disappearance of a ^{13}C-enriched DBK (e.g., DBK-*1*-^{13}C (90%) and DBK-*2,2'*-$^{13}C_2$ (90%)), the calculated values being adjusted to represent 100% ^{13}C. For example, if the ratio of quantum yields for disappearance of DBK-NA and DBK-*1*-^{13}C are measured, then the proper correlation of α^{Φ} and $^{12}\Phi/^{13}\Phi$ will refer to ^{13}C enrichment specifically at the 1-position. The isotopic enrichment factor can also be measured by mass spectrometric analysis for ^{13}C. The α^{MS} determined in this manner can then be compared to α^{Φ} determined by quantum yield measurements.

The values of α^{MS} and α^{Φ} are listed in Table I. It is found that there is excellent agreement between the absolute values found by the two independent methods. It should be noted that as used here α refers to enrichment at a single carbon atom.[1]

Isotopic Enrichment Efficiency as a Function of Applied Magnetic Fields. The percent enrichment in recovered DBK (mass spectral analysis) at various fields is shown in Figure 1. Note that, for a given percent conversion, the enrichment is maximal at low fields (~150–300 G) and nearly negligible at very high fields (100 000 G). The parameter α was determined for samples of DBK subjected to varying magnetic fields by mass spectrometric analysis (α^{MS}) of the ^{13}C content of the recovered residual DBK and by measurement of $^{12}\Phi/^{13}\Phi$ as a function of magnetic field strength (α^{Φ}). The results are summarized in Figure 2 by a plot of α^{MS} and of α^{Φ} as a function of magnetic field. From Figure 2, an excellent agreement of the value of α measured by the two methods is apparent.

Comparison of the Photolysis of DBK in Micellar and Homogeneous Solution. A working chemical mechanism for interpretation of the data in Table I and Figure 1 is given in Scheme I. The general outline of the established photochemistry of DBK in homogeneous solution[5] is assumed to apply for photolysis in micelles: photoexcitation of the n,π* state of DBK leads to S_1(n,π*) which then undergoes efficient intersystem crossing (ISC) to T_1 (n,π*). The latter undergoes α cleavage to produce a triplet radical pair $C_6H_5CH_2\dot{C}O\ \dot{C}H_2C_6H_5$ (^{3}D). The quantum yield for net disappearance of DBK ($\Phi_{-\mathrm{DBK}}$) in benzene solution (0.72) is substantial. The fraction (0.28) of photoexcited DBK molecules which do not undergo net reaction (1) may have undergone α cleavage to form radical pairs which then recombine before decarbonylation or (2) may have undergone some molecular radiationless process from S_1 or T_1 to S_0. From the very short lifetime of T_1 (τ_T derived from quenching studies) it has been concluded that every molecule which reaches T_1 undergoes α cleavage.[6]

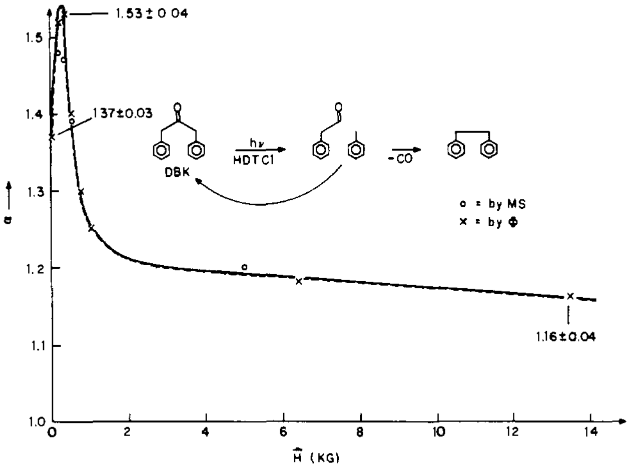
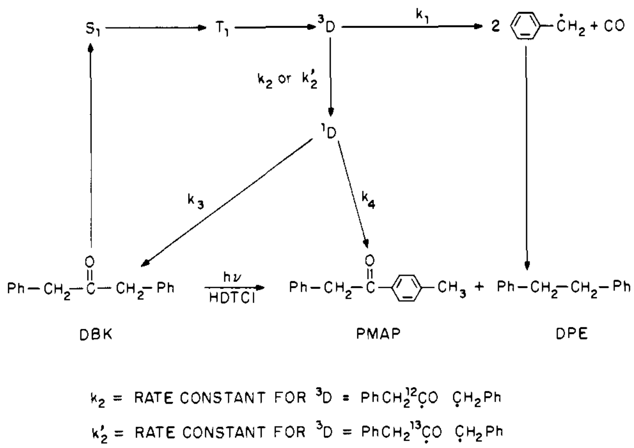


Figure 2. Variation of α as a function of applied laboratory field.

Scheme I. Working Mechanism for the Photolysis of DBK



k_2 = RATE CONSTANT FOR ^{3}D = $\mathrm{PhCH_2{}^{12}\dot{C}O\ \dot{C}H_2Ph}$

k'_2 = RATE CONSTANT FOR ^{3}D = $\mathrm{PhCH_2{}^{13}\dot{C}O\ \dot{C}H_2Ph}$

The substantially lower quantum yield for disappearance of DBK in micellar solution may be associated with a more efficient recombination of $C_6H_5CH_2\dot{C}O\ \dot{C}H_2C_6H_5$ produced by α cleavage or by the occurrence of a novel radiationless molecular deactivation process. Since the magnitude of the cage effect for reactions of radical pairs has been shown to increase substantially in micellar solution relative to homogeneous solution,[7] we propose that the

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(5) Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6076.

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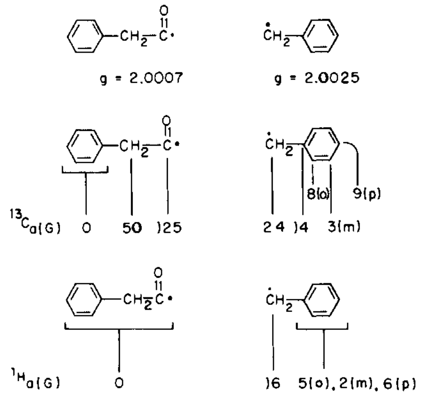

Figure 3. Relevant magnetic parameters for the $PhCH_2\dot{C}O$ $\dot{C}H_2Ph$ radical pair. The values for ^{13}C hyperfine coupling in the $\cdot CH_2Ph$ radical are computed from measured proton hyperfine coupling constant according to the procedure given by: Karplus, M.; Fraenkel, G. K. *J. Chem. Phys.* **1961**, *35*, 1312. The other values are derived from direct ESR measurements in the literature.[9]

lowering of $\Phi_{\text{-DBK}}$ for micellar relative to benzene photolysis is mainly due to an increase in the efficiency of *cage* recombination of geminate $C_6H_5CH_2\dot{C}O$ $\dot{C}H_2C_6H_5$ radical pairs.

With the postulate that spin-correlated geminate radical pairs generated in micelles undergo relatively efficient cage recombination, we are in a position to understand the origin of the magnetic effects on Φ and α that are given in Table I.

Magnetic Effects on Φ and α. Consider the situation for photolysis of DBK in the earth's field (~0.5 G). Under these conditions all three triplet sublevels (T_+, T_-, and T_0) are strongly mixed by molecular tumbling, and each can undergo hyperfine-induced (hfi) ISC to a singlet radical pair (^1D in Scheme I) when the radicals have separated in space to a distance sufficient to cause the exchange interaction to become less than the hyperfine interaction.[8] Under these conditions the rate of ISC from ^3D to ^1D will depend in detail on the hfi experienced by each radical center in the pair.[6] Figure 3 lists the appropriate ^1H and ^{13}C values of *a*, the hyperfine coupling constant,[9] for the $C_6H_5CH_2\dot{C}O$ $\dot{C}H_2C_6H_5$ radical pair. By far, the largest value of *a* occurs for ^{13}C hfi ISC of the carbonyl carbon atom of $C_6H_5CH_2\dot{C}O$. Thus, triplet radical pairs (^3D) that happen to possess a ^{13}C atom at the carbonyl carbon of the $C_6H_5CH_2CO$ fragment will experience the most rapid hfi ISC to singlet radical pairs (^1D) that possess a ^{13}C atom at the carbonyl carbon of the $C_6H_5CH_2\dot{C}O$ fragment. Since ^1D produced by ISC can regenerate DBK by cage combination, the latter will be enriched in ^{13}C at the carbonyl carbon if an "escape" pathway is available for ^3D that possess a ^{12}C atom at the carbonyl carbon. In fact, the decarbonylation step $C_6H_5CH_2\dot{C}O \rightarrow C_6H_5\dot{C}H_2 + CO$ provides the required escape pathway. In the *limiting case* one could imagine *all* of the ^3D containing ^{13}C at the carbonyl carbon recombining to regenerate DBK while *all* of the ^3D containing ^{12}C at the carbonyl carbon undergoes decarbonylation! Experimentally, α is a measure of the degree to which this limit is approached.

Of course, when one starts with natural abundance (NA) DBK *all* ^{13}C atoms that possess significant hfi ISC will participate in the ISC of ^3D to ^1D; however, the major ^{13}C hfi ISC are seen from Figure 3 to derive from only three carbon atoms of the radical pair:[9] the carbonyl carbon (a = 125 G) and the methylene carbon (a = 50 G) of the $C_6H_5CH_2\dot{C}O$ fragment and the methylene carbon (a = 25 G) of the $C_6H_5\dot{C}H_2$ fragment.

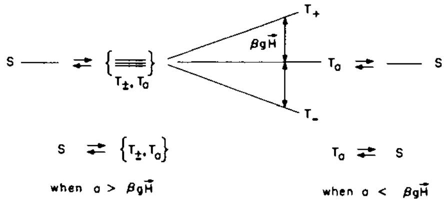

Figure 4. Zeeman splitting of the triplet (T_+, T_-, T_0) sublevels of a radical pair when the exchange interaction is weaker than the hyperfine coupling $J < a$. When a is much greater than the Zeeman splitting, all three triplet levels can undergo hyperfine induced intersystem crossing to the degenerate singlet. When a is much less than the Zeeman splitting, T_+ and T_-, but not T_0, are inhibited from undergoing hyperfine induced intersystem crossing. At sufficiently high fields, intersystem crossing may be determined by the difference in g factors of the radical pair and not the hyperfine interactions.

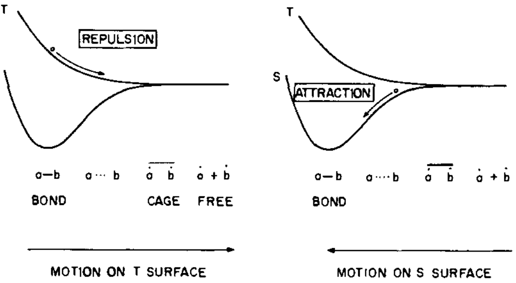

Figure 5. Schematic representation of a representative point on a repulsive triplet surface (motion spontaneous to the right) and of a representative point on an attractive singlet surface (motion spontaneous to the left).

The results given in Table I and in Figures 1 and 2 provide compelling support for the postulate that ^{13}C hyperfine coupling can be a major factor in determining the rate of ISC of triplet $C_6H_5CH_2\dot{C}O$ $\dot{C}H_2C_6H_5$ radical pairs in micellar solution. From the quantum yield data at 0.5 G, the *decrease* in $\Phi_{\text{-DBK}}$ with ^{13}C substitution at the C-1 or the C-2,C-2' carbons (relative to $\Phi_{\text{-DBK}}$ for DBK-NA) is consistent with more efficient ISC in ^{13}C enriched radical pairs. Furthermore, the quantum yield for DBK-*1*-^{13}C is lower than that for DBK-*2,2'*-$^{13}C_2$, a result consistent with the larger hfi ISC of the carbonyl carbon relative to the methylene carbons in the $C_6H_5CH_2\dot{C}O$ $\dot{C}H_2C_6H_5$ radical pair. Finally, the variation of $\Phi_{\text{-DBK}}$ with variation in applied field is further confirmation that magnetic effects are operating to determine the magnitude of the quantum yields.

The detailed pattern of α as a function of applied field provides perhaps the most impressive evidence that a magnetic isotope effect[8] is operating to determine the ^{13}C enrichment. The observation of a *maximum* value of α at fields of ~200–300 G is qualitatively understood in terms of competing Zeeman inhibition of ^1H hfi ISC and ^{13}C hfi ISC of radical pairs (Figure 4). Since a for ^1H hfi ISC is smaller than a for ^{13}C hfi ISC, smaller values of the applied field (~10–100 G) suffice to "quench" ^1H hfi ISC from the T_+ and T_- levels of the radical pair than are needed (200–300 G) to "quench" ^{13}C hfi ISC. Of course, the T_+ and T_- levels eventually undergo ISC by some mechanism(s) that does not involve hfi ISC, but DBK that is regenerated by such pathways will *not* be enriched in ^{13}C. At still higher fields (>500 G), the T_+ and T_- levels are substantially inhibited from ISC, and the value of α decreases to a value even lower than that found in the earth's feild.

According to CIDNP theory,[8] at sufficiently high magnetic fields, ISC will become Zeeman induced if Δg for the radical pair is large enough (Figure 4). Indeed, at 100 000 G the measured value of α is 1.03, i.e., comparable to the value in homogeneous solution. This result is understood if it is assumed that in fields of 100 000 G, T_+ and T_- ISC to S, induced by hfi ISC, is completely ineffective, and T_0 to S ISC occurs, not by a hfi mechanism

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(8) For a discussion of magnetic field and magnetic isotope effects on reactions of radical pairs, see: (a) Atkins, P. W.; Lambert, T. P. *Ann. Rep. Chem. Soc. A* **1975**, 67; (b) Sagdeev, R. Z.; Salikhov, K. M.; Molin, Y. M. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 297; (c) Buchachenko, A. L. *Ibid.* **1976**, *45* 3751; Lawler, R. G.; Evans, G. T. *Ind. Chim. Belge* **1971**, *36*, 1087; (d) Atkins, P. *Chem. Br.* **1976**, 214; (e) Buchachenko, A. L. *Russ. J. Phys. Chem. (Engl. Transl.)* **1977**, *51*, 1445; (f) Buchachenko, A. L. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 761. For reviews of the theory of CIDNP, see: (f) Kaptein, R. *Adv. Free-Radical Chem.* **1975**, *5*, 381; (g) Closs, G. *Proc. Int. Congr. Pure Appl. Chem.* **1971**, *4*, 19; (h) Firth, P. G.; McLauchlan, K. A. *Annu. Rep. Prog. Chem., Sect. A: Phys. Inorg. Chem.* **1975**, 378.

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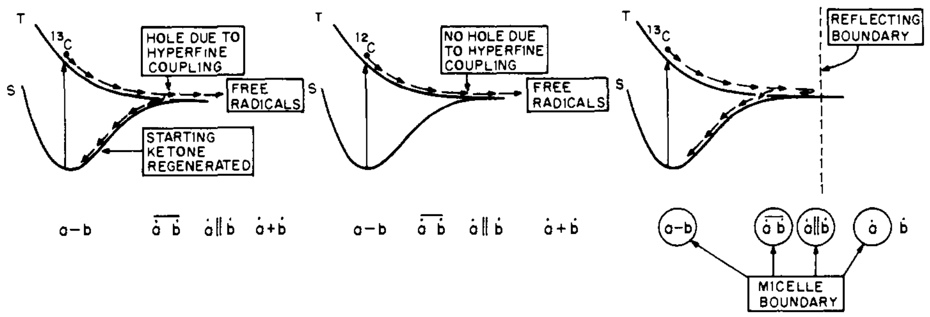

Figure 6. Schematic representation of the basis of the ^{13}C isotopic enrichment and the special role of micelles. In this figure, a represents the PhCH$_2$CO fragment and b represents the CH$_2$Ph fragment.

but rather by a Zeeman mechanism.

Origin of the Magnification of Magnetic Effects by Micelles. The expectation that photolysis of DBK should lead to progressive ^{13}C enrichment in the residual, unconverted DBK is a natural consequence of the radical pair theory of CIDNP.[8] The remarkable efficiency of ^{13}C enrichment when photolysis is conducted in micellar solution is not immediately obvious. According to CIDNP theory,[8] the efficiency of cage reaction of a correlated triplet radical pair will depend on (1) the probability that a triplet radical pair formed at $t = 0$ will be a singlet radical pair before the radical pair is irreversibly destroyed and (2) the probability that the singlet radical pair, once formed, will undergo cage reaction.

Schematically, the general idea behind the enrichment experiment may be understood by using a very simple description of the behavior of molecules on a dissociative triplet surface which possess a bonding singlet surface of lower energy. Figure 5 (left) shows a representative point moving along a dissociative triplet surface. The triplet surface is repulsive for all nuclear geometries corresponding to the *molecular* structure; i.e., in the triplet state the energy of the molecule decreases as bond a–b increases in length. We say that in the triplet state the representative point moves spontaneously to the right. Eventually, the bond breaks, a· and b· are produced, and the further separation of the a and b nuclei does not lead to a further lowering of the energy of the system. Suppose that the radical pair a·,b· can experience a mechanism that allows the representative point to "jump" to the singlet surface; once on the singlet surface the point will move spontaneously "to the left"; i.e., the a–b bond will reform.

The key idea behind the magnetic isotope method for separation of ^{13}C from ^{12}C by photolysis of DBK is the postulate that ^{13}C hyperfine coupling provides the radical pairs (a = PhCH$_2\dot{C}$O, b = Ph$\dot{C}$H$_2$) possessing ^{13}C with a mechanism by which the representative point can jump from the triplet surface to the singlet surface when the point is in a region for which the singlet and triplet states are degenerate. Since this mechanism is unavailable to radical pairs that possess only ^{12}C nuclei, the representative points for these molecules will not be able to make the jump from the triplet surface to the singlet surface by way of a ^{13}C hfi mechanism. In effect, ^{13}C electron hyperfine coupling provides a "hole" in the triplet surface through which the ^{13}C-containing triplet radical pair can jump to the singlet surface, i.e., undergo intersystem crossing from a triplet radical pair to a singlet radical pair.

From this simple picture the role of micelles may be viewed as providing a restricted volume of space that prevents irreversible diffusive escape of the radical from the micellar cages for long periods of time. From experimental data, it is expected that C$_6$H$_5$CH$_2\dot{C}$O and C$_6$H$_5\dot{C}$H$_2$ will remain geminate and will be contained in the micelle in which they are formed for (1–10) × 10^{-6} s. This time period may be compared with estimates[10] of $\sim 10^{-10}$ s for radical pair escape from solvent cages of nonviscous homogeneous solvents such as benzene or $\sim 10^{-8}$ s in viscous homogeneous solvents such as glycerol. Experimentally, the value of α is not very different for photolysis of DBK in benzene (α = 1.04) which has a viscosity of 0.6 cP at 25 °C or cyclohexanol (α = 1.08) which has a viscosity of 60 cP at 25 °C. The "microscopic viscosity" experienced by solutes in HDTCl micelles has been determined to be ~30–40 cP.[11] Thus, the value of α for photolysis of DBK in HDTCl micelles ($\alpha \approx 1.4$–1.5) is too large to be explained on the basis of viscosity effects alone.

We propose an explanation of the special role of micelles in terms of the restricted volume of space that is imposed upon solutes that are dissolved in micelle aggregates. The explanation may be couched in terms of potential energy surfaces as shown in Figure 6. The reaction coordinate represents the breaking of the OC–CH$_2$ bond. As the OC–CH$_2$ bond breaks, the representative point "slides" down the electronically repulsive triplet surface. When the bond is broken, the triplet surface becomes essentially degenerate with the ground-state singlet surface. A magnetic interaction is required before the representative point can make a "jump" from the T surface to the S surface. Such a jump can be induced by hyperfine interaction only when the point is far to the right, i.e., when the triplet and singlet are nearly degenerate and $J < a$. The "jump" from T to S requires a "hole" in the T surface through which the point may fall.

The role of the micelle may be viewed as providing a boundary which "reflects" the representative point back toward the hyperfine-induced hole after an "overshoot" has occurred. Thus, diffusive escape is temporarily thwarted, and a ^{13}C-containing molecule receives extra chances to find a hole which allows return to ground-state DBK. Eventually, of course, escape by decarbonylation will take place if neither diffusive escape nor bond formation occurs.

Summary

The quantum yields for disappearance of DBK in micellar solution are subject to both magnetic field and magnetic isotope effects. The observed ^{13}C enrichment in recovered unconverted DBK is shown to result from a ^{13}C magnetic isotope effect which operates to enhance ISC of triplet C$_6$H$_5$CH$_2\dot{C}$O $\dot{C}$H$_2$C$_6$H$_5$ radical pairs. The efficiency of enrichment, measured in terms of α, is subject to magnetic field effects because of Zeeman interactions which modify the hfi ISC of the radical pairs.

The remarkable ability of micelles to magnify magnetic effects is attributed to a felicitous confluence of the dynamics of molecular mechanics which must occur in a restricted space and the dynamics of hyperfine-induced intersystem crossing in radical pairs. The correctness of these qualitative features has been confirmed by a recent quantitative theory which explicitly takes into account the restricted volume of space accessible to a radical pair in a micelle aggregate.[12]

The relationship between α (for a single atom) and the measured ^{13}C/^{12}C content in recovered DBK at various conversions is shown in Figure 7 which displays a family of curves for different values of α, ranging from α = 1.05 to 20. From Table I and Figure 2 we note that values of $\alpha \approx 1.5$ are experimentally realizable.

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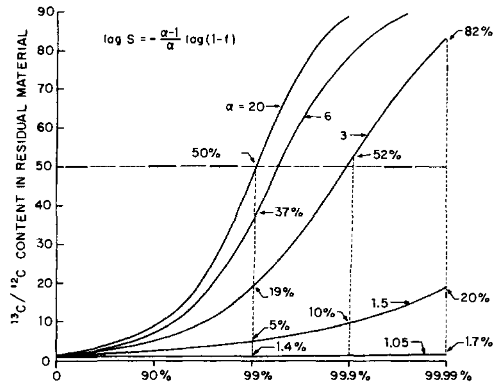

Figure 7. Computed $^{13}C/^{12}C$ content (at a single atom) in recovered residual DBK at various fractions of conversion. The curves are generated from the indicated formula (see preceding paper for a discussion).

However, there is no theoretical basis to prevent experimental α values from approaching much larger magnitudes. A goal of future research will be to design experimental strategies that will produce substantially larger values of α.

Experimental Section

Dibenzyl Ketone and Isotopically Labeled Dibenzyl Ketone. Dibenzyl ketone (Aldrich) was sublimed at 10^{-1} torr (bath temperature ca. 40 °C) to yield colorless crystals that were stored at 0 °C under nitrogen. The preparations of dibenzyl-*1*-^{13}C (90%) ketone and dibenzyl-*2,2'*-$^{13}C_2$ (90%) ketone were described in the preceding paper.[1]

Solvents and Detergents. Water was doubly distilled (first distillation from $KMnO_4$); benzene (Fisher, "spectroanalyzed"), cyclohexane (Fisher, "spectroanalyzed"), dodecane (Aldrich, 99%), and cyclohexanol (Fisher, reagent grade) were used without further purification. Hexadecyltrimethylammonium chloride (HDTCl, Eastman Co.) was recrystallized from ethanol and dried subsequently at 10^{-2} torr at room temperature.

Preparation of Samples for Analysis. VPC/MS Analyses. For VPC/MS analysis, an aqueous, deoxygenated solution containing 0.005 M DBK mixtures of known ^{13}C content and 0.05 M HDTCl were photolyzed to 40–90% conversion (1000-W, high-pressure, Hg lamp, Pyrex filter). Products were extracted from the photolysis mixtures with CH_2Cl_2 or Et_2O, and the organic layer was analyzed by VPC (to determine the extent of conversion) and by VPC/MS (to determine ^{13}C content).

Quantum Yield Measurements. A "merry-go-round" set up immersed into a thermostated bath was used. A medium-pressure, Hanovia, Hg lamp was employed as the light source; 313-nm light was selected, and aqueous K_2CrO_4 (2.6 mm) and Corning 7-54 filters were used. For absolute quantum yield measurements a valerophenone/*tert*-butyl alcohol standard ($\Phi = 1.0$)[12] was used. Sample solutions of calibrated volume and 0.005 M DBK (in 0.05 M detergent or organic solvent) were placed in quartz tubes, deoxygenated by nitrogen bubbling (for 5 min), and then stoppered tightly. The photolysis mixtures (typically 10–20% conversion) were extracted with calibrated volumes of CH_2Cl_2 or Et_2O (containing an internal standard, typically hexadecane) and then subjected to quantitative analysis by VPC analysis.

Data Treatment. The calculation of α from mass spectrometric measurements was described in the preceeding paper.[1]

Calculation of α from Quantum Yield Data. The quantum yield ratio (R) for disappearance of DBK relative to DBK-*1*-^{13}C (90%) was determined by quantitative VPC analysis. The values of α^{Φ} were calculated by the formula $\alpha^{\Phi} = 0.9R/(1 - 0.1R)$ which allows α to refer to DBK containing 100% ^{13}C at the 1-carbon. An analogous method was employed for determining α^{Φ} by comparing the quantum yields for disappearance of DBK and DBK-*2,2'*-$^{13}C_2$ (90%).

Experiments with Variable Laboratory Magnetic Fields. Magnetic field experiments were performed with an Alpha Scientific, Inc., Model 4500 4-in., adjustable-gap electromagnet. Calibrations were made with a Bell Model 640 gaussmeter. Fields employed were in the range of 0 G to 16 kG (depending upon gap width). The high-field experiment (at 100 kG) was performed at the Francis Bitter National Magnet Laboratory, MIT. For the preparative photolyses, samples of aqueous, deoxygenated detergent solutions of DBK mixtures of known degree of ^{13}C labeling were placed into a quartz tube (as described above) and positioned into the center of the gap of the electromagnet. A specific magnetic field was produced by applying a calibrated current (generally the magnitude of the applied field was confirmed by measurement with a gaussmeter). The agitated solution was irradiated with a 450-W Oriel xenon lamp for appropriate amounts of time. Samples were drawn and analyzed (as described above) for chemical conversion and ^{13}C enrichment.

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