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(12) P.C.R. Inc., Gainesville, Fla. 32602. CF_3OF is an extremely reactive and toxic gas, and proper safety precautions should be followed in its use.

(13) The stereochemistry of adduct **2** was not determined but the preferred loss of the elements of $HOCF_3$ to give **3** coupled with precedence for cis addition of CF_3OF to alkenes (Barton, D. H. R.; Hesse, R. H.; Jackman, G. P.; Ogunkoya, L.; Pechet, M. M. *J. Chem. Soc., Perkin Trans 1* **1974,** 739) led us to prefer a geometry in which the F and OCF_3 moities are cis to each other.

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Magnetic and Micellar Effects on Photoreactions. Micellar Cage and Magnetic Isotope Effects on Quantum Yields. Correlation of ^{13}C Enrichment Parameters with Quantum Yield Measurements

Sir:

The photoinduced homolytic α-cleavage reaction of dibenzyl ketone (DBK) produces a geminate triplet radical pair[1] whose reactivity has been shown to be significantly influenced by micellar[2] and magnetic[3] effects (Scheme I). The products derived from the initial $PhCH_2\ COCH_2Ph$ triplet radical pair (^3D) may be classified as geminate (spin-correlated) products which form in a cage process or as free-radical (spin-uncorrelated) products which form after (complete) diffusional separation of the initially formed radical pair. The remarkable ^{13}C enrichment discovered in recovered DBK after partial photolysis in micellar solution was interpreted in terms of an enhanced cage effect of radical pairs in a micelle and a magnetic isotope (^{13}C) effect.[4,5] Both of the latter operate on the reactivity of ^3D by influencing the rate of triplet-singlet crossing via nuclear-electronic hyperfine interaction to yield a singlet radical pair, ^1D, which is presumed to undergo efficient recombination to regenerate DBK. The enhanced cage effects of radical pairs in micelles predicts (1) a decreased quantum yield for disappearance of DBK and appearance of 1,2-diphenylethane (DPE) in hexadecyltrimethylammonium chloride (HDTCl) micelles (Φ_{-DBK}^{HDTCl} and Φ_{DPE}^{HDTCl}) relative to the quantum yields in homogeneous benzene solution ($\Phi_{-DBK}^{benzene}$ and $\Phi_{DPE}^{benzene}$). The magnetic isotope effect concept allows the further extraordinary predictions:[5] (2) the quantum yield for disappearance of DBK and appearance of DPE will be significantly less for a ketone enriched in ^{13}C in the carbonyl carbon; (3) the quantum yield for disappearance of DBK and appearance of DPE will be influenced by the application of an external laboratory magnetic field on the sample during photolysis; (4) the quantum yields for cage reactions will be magnetic field dependent; (5) the magnitude of α, predicted by Bernstein's formula[6] (^{13}C enrichment as a function of percent conversion) is directly related to the value of α derived from quantum yield measurements. In a sufficiently strong magnetic field (provided by a laboratory magnet), intersystem crossing will no longer be determined by hyperfine interactions, but by (isotope independent) differences in g factors of the radicals of ^3D. In this limit, differences in the behavior of DBK that are due to magnetic isotope effects will vanish; i.e., α will decrease to unity.

The absolute quantum yields for total disappearance of DBK and for the appearance of DPE were measured in benzene and in HDTCl solutions. Ratios of these quantum yields were also measured independently and with a higher precision than was possible for the absolute quantum yields. Finally, the influence of added $CuCl_2$ (specific scavenger of free radicals in the aqueous phase) and of laboratory magnetic fields on Φ_{-DBK}^{HDTCl} and Φ_{DPE}^{HDTCl} were obtained. The results are shown in Table I. The notations $^{12}\Phi$ and $^{13}\Phi$ refer to quantum yield measurements of DBK containing 99% ^{12}C and 90% ^{13}C, respectively, in the carbonyl carbon. The values in Table I are adjusted to represent quantum yields of DBK containing 100% ^{12}C and

Scheme I. Pathways for Photolysis of DBK in Micellar Solution

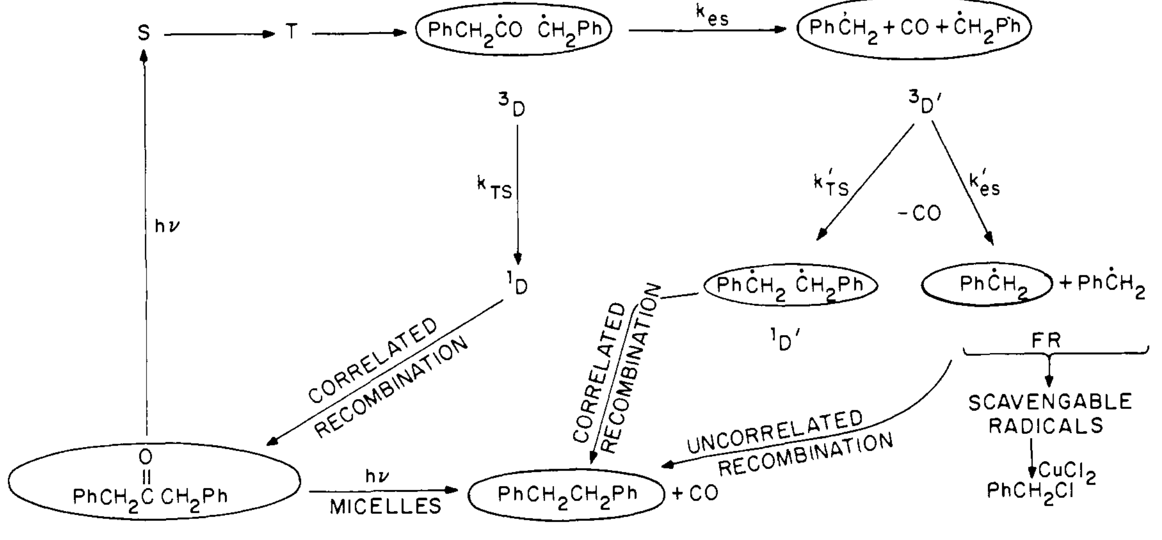

Table I. Quantum Yields, Quantum Yield Ratios, and α Values for the Photolysis of $PhCH_2COCH_2Ph$ in Benzene and HDTCl

conditions	${}^{12}\Phi^{a}$	${}^{13}\Phi^{a}$	${}^{12}\Phi(Cu^{2+})^{b}$ −DBK	${}^{12}\Phi(Cu^{2+})^{b}$ +DPE	${}^{12}\Phi/{}^{13}\Phi^{c}$	Bernstein's α^{d} for ${}^{13}C$ enrichment
benzene (0.5 G)[e]	0.87 ± 0.12	0.84 ± 0.12			1.04 ± 0.05	1.03 ± 0.01
HDTCl (0.5 G)[e]	0.24 ± 0.03	0.17 ± 0.02	0.24 ± 0.01	0.06 ± 0.002	1.41 ± 0.07	1.41 ± 0.05
HDTCl (14 400 G)	0.25 ± 0.03	0.22 ± 0.03	0.24 ± 0.01	0.04 ± 0.005	1.15 ± 0.01	1.16 ± 0.05

[a] Quantum yield for disappearance of DBK is equal to the quantum yield for formation of DPE in these experiments. The accuracy of the absolute quantum yields is subject to ~10% error owing to systematic but difficult corrections caused by new absorptions of products, changes in absorption from solvent effects, etc. [b] The quantum yield for disappearance of DBK is not influenced by Cu^{2+} in the concentration range studied. The quantum yield for the appearance of DPE is decreased sharply when $[Cu^{2+}] \sim 10^{-4}$–10^{-3} M. Above 10^{-3} M the yield of DPE reaches the limiting value listed above. [c] Samples containing 99% carbon-12 and samples containing 90% carbon-13 in the carbonyl carbon of DBK were irradiated (313 nm) with the same number of quanta. ${}^{12}\Phi/{}^{13}\Phi$ was calculated from the formation of DPE (VPC analysis) and correlated to represent quantum yields for DBK containing 100% carbon-12 and 100% carbon-13, respectively. [d] Calculated from the enrichment of DBK in ${}^{13}C$ as a function of conversion. See ref 6. [e] Earth's magnetic field.

100% ${}^{13}C$, respectively, in the carbonyl carbon.

The data in Table I completely corroborates the expected reduction of quantum yield of reaction in micellar solution. The ratio of ${}^{12}\Phi_{-DBK}^{benzene}/{}^{12}\Phi_{-DBK}^{HDTCl}$ is 3.6; thus, the net efficiency of photoreaction is severely inhibited in micellar solution relative to homogeneous solution. The addition of an efficient water-soluble free-radical scavenger of the same charge as the surface of HDTCl micelles can be employed to determine the extent of exit of radicals from the micellar phase into the aqueous phase. From Table I it is seen that, although the quantum yield for disappearance of DBK is unaffected by addition of $CuCl_2$, the quantum yield for formation of $PhCH_2CH_2Ph$ is drastically reduced. We interpret these results to mean that "cage" recombination of $PhCH_2\dot{C}O\ \dot{C}H_2Ph$ radicals is much faster than exit of these radicals from the micelle so that Cu^{2+} does not scavenge these radicals. However, decarbonylation can compete with recombination of these radical pairs (vide infra). *After* decarbonylation (to produce two $Ph\dot{C}H_2$ radicals in a micelle cage), the exit of $Ph\dot{C}H_2$ radicals from the micelle competes effectively with radical-pair recombination to yield DPE, since a substantial decrease in the quantum yield of formation of DPE is found in the presence of aqueous Cu^{2+} scavenger.[7] In this case, *exit* from the micelle provides a mechanism for "escape" which competes with geminate recombination.

Predictions 2 and 3 are also confirmed by the data in Table I. The ratio of ${}^{12}\Phi/{}^{13}\Phi$ is ~1.4 in micellar solutions but only ~1.0 in benzene solution. This result allows the conclusion that micellar recombination of $Ph\dot{C}H_2\ {}^{13}\dot{C}OCH_2Ph$ radicals is significantly more efficient than micellar recombination of $Ph\dot{C}H_2\ {}^{12}\dot{C}OCH_2Ph$ radicals. As expected from prediction 3, the quantum yield for reaction of DBK-${}^{13}C$ is increased by the application of a magnetic field; i.e., the efficiency of recombination of $Ph\dot{C}H_2\ \dot{C}OCH_2Ph$ radicals is reduced significantly by the application of an external magnetic field.[8] This result is consistent with the inhibition of intersystem crossing of $T_{\pm}$ levels of the radical pair due to Zeeman splitting.[9]

A striking confirmation of prediction 4 is provided by the observation that the quantum yield for the scavengeable $Ph\dot{C}H_2$ radicals dramatically increases when a magnetic[8] field is applied during photolysis. This result is expected theoretically because $T_{\pm} \rightarrow S$ intersystem crossing is inhibited in a magnetic field; thus application of a laboratory field will enhance the efficiency of exit of $Ph\dot{C}H_2$ radicals from the micelle relative to cage recombination.

Finally, to test prediction 5, the results of ${}^{13}C$ enrichment experiments must be correlated with quantum yield data. It is possible to identify the quantum yield ratio ${}^{12}\Phi_{-DBK}/{}^{13}\Phi_{-DBK}$ with Bernstein's[6] isotopic ${}^{13}C$ enrichment parameter α, where the latter is a measure of the isotopic rate constant ratio for a unimolecular reaction:

$$\alpha \equiv {}^{12}\Phi_{-DBK}/{}^{13}\Phi_{-DBK} = \frac{{}^{13}k_{TS} + {}^{13}k_{es}}{{}^{12}k_{TS} + {}^{12}k_{es}} \qquad (1)$$

We assume that k_{es} is an isotope independent unimolecular rate constant for "escape" of a spin-correlated radical pair by decarbonylation or exit into the aqueous phase. If this interpretation is correct, then the value of ${}^{12}\Phi_{-DBK}/{}^{13}\Phi_{-DBK}$ should be equal to α. From Table I it is seen that the agreement between ${}^{12}\Phi_{-DBK}/{}^{13}\Phi_{-DBK}$ and α is excellent. A stringent test of the correlation of α and ${}^{12}\Phi_{-DBK}/{}^{13}\Phi_{-DBK}$ is the prediction that both should decrease correspondingly when photolysis is conducted in a strong magnetic field. From Table I it is seen that both parameters decrease by exactly the same extent upon proceeding from a field of ~0 G (earth's field) to a laboratory field of ~15 000 G.

If the rate of the "escape" process can be estimated, a value of k_{TS} for hyperfine induced intersystem crossing of the radical pair $PhCH_2\dot{C}O\ \dot{C}H_2Ph$ in a micelle may be evaluated. The rate constant of decarbonylation[1,10] of $PhCH_2\dot{C}O$ radicals (k_{-CO}) has been determined to be $\sim 10^{8}\ s^{-1}$ at room temperature in homogeneous solvents. This value is much higher than the value for escape of $Ph\dot{C}H_2$ radicals from HDTCl micelles which should be[11] in the range of $\sim 10^{5}\ s^{-1}$. If we identify k_{es} with k_{-CO} from eq 1, we estimate k_{TS} to be $\sim 10^{8}\ s^{-1}$.

From a simple model, the rate of intersystem crossing in ${}^{3}D$ is also expected to be influenced by an external magnetic field via a term that is proportional[8] to ΔgH which represents the intersystem crossing rate due to the difference in precessional rates of the electron spin vectors due to different g factors (Δg) of the individual radicals in a magnetic field of strength of H. The value[12] of Δg for $PhCH_2\dot{C}O\ \dot{C}H_2Ph$ radical pair is $\sim 2 \times 10^{-3}$. This value of Δg corresponds to a rate of intersystem crossing of $\sim 10^{8}\ s^{-1}$ in a laboratory field of 10 000 G and a rate of $\sim 10^{9}\ s^{-1}$ in a laboratory field of 100 000 G. From our estimate of a hyperfine determined value of $k_{TS} \sim 10^{8}\ s^{-1}$ for ${}^{3}D$ at low fields, we expect that in a "very strong" laboratory field the ΔgH term will determine the magnitude of k_{TS}. In this case, the distinction between DBK-${}^{12}C$ and DBK-${}^{13}C$ which is due to a nuclear isotope effect is removed and the two isotopic ketones should behave equivalently. Indeed, in a field of 100 000 G the value of α (isotopic enrichment) falls to 1.03 ± 0.02; i.e., the very strong external field has effectively surpressed the large difference in behavior of the isotopic ketones.

In summary, a number of exceptional effects on the quantum yields for cage reaction and product formation have been found for the photolysis of DBK in HDTCl micellar solutions. All or these effects may be qualitatively understood in terms of Scheme I and the concepts of a micelle cage for radical pairs, the magnetic isotope effect on intersystem crossing in radical pairs, and the magnetic field effect on intersystem crossing in radical pairs.

Acknowledgments. The authors are grateful to various members of the Columbia community for their generous loans of equipment that was vital to the measurements for derivation of the data in Table I, i.e., Professor S. J. Lippard (loan of a variable field magnet); Professor T. J. Katz (loan of a minigrator); Professors G. Flynn (loan of a Varian-Aerograph VPC); Professor B. P. Dailey (loan of the space beside a supercon magnet); and Professor S. Hartmann (loan of a Hall gauss meter). We especially thank Professor R. Bernstein for enlightening discussions and variable advice concerning the relationship of α to quantum yield data. The assistance of Mr. Chao Chung in identifying the products of Cu^{2+} scavenging and of Dr. Ming-Fea Chow and Mr. Gregory Weed in refining some data in Table I is gratefully noted. We thank the Francis Bitter National Magnet Laboratory at the Massachusetts Institute of Technology for access to and use of a 100 000 G magnet. Support of this work by tha National Science Foundation and the Department of Energy is gratefully acknowledged. B.K. thanks the Swiss National Science Foundation for a Postdoctoral Fellowship.

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(7) In a previous publication[2] it was noted that micelles inhibited cross coupling of radicals produced by photolysis of asymmetrical ketones. The low yield of cross coupling was due not only to an enhanced "cage" effect due to sequestering of the geminate radical pair by micelles, but also to scavenging by O_2; i.e., since the systems were air saturated, escaping radicals were trapped by O_2 in the aqueous phase. In the present work, the systems were deoxygenated by N_2 purging before photolysis.

(8) The onset of significant external magnetic field effects on α occurs at relatively low magnetic fields (<1000 G). A detailed report of the magnetic field dependence of α will be reported in due course.

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Additions and Corrections

Crystal and Molecular Structure of the Free Base Porphyrin, Mesoporphyrin IX Dimethyl Ester [*J. Am. Chem. Soc.*, **97**, 5363 (1975)].

By ROBERT G. LITTLE and JAMES A. IBERS,* Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

On p 5365 structures for **1** and **2** should be interchanged. In Table VI the coefficient *A* for the least-squares planes 1 through 6 should be multiplied by 10. A corrected Table VII is given below. The transannular separations for the title compound are no longer significantly different from those in other free base porphyrins. Thus the discussion of these differences, both in this paper and in Caughey, W. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6639-6645, is no longer applicable.

Table VII. Transannular Distances (Å) in Three Free-Base Porphyrins

Atoms	OEP[a]	Porphine[b]	MP-IX DME[c]
HN(1)-HN(3)	2.36 (4)	2.41 (4)	2.28 (10)
N(1)-N(3)	4.195	4.112	4.181
N(2)-N(4)	4.052	4.058	4.060
N(1)-N(2)	2.917	2.886	2.894
N(2)-N(3)	2.916	2.889	2.937
N(3)-N(4)	2.917	2.901	2.893
N(4)-N(1)	2.916	2.879	2.932
C(5)-C(15)	6.841	6.853	6.859
C(10)-C(20)	6.844	6.834	6.811
C(5)-C(10)	4.828	4.814	4.815
C(10)-C(15)	4.849	4.862	4.844
C(15)-C(20)	4.828	4.822	4.825
C(20)-C(5)	4.849	4.860	4.848

[a] Reference 13, the errors on the C-C and N-N distances are ±0.002 Å. [b] Reference 11, estimated errors ±0.007 Å. [c] This work, estimated errors ±0.004 Å.

Ion-Solvent Interaction. Effects of Added Polar Compounds on the Conductances of Several Alkali Metal Salts in 2-Butanone at 25 °C [*J. Am. Chem. Soc.*, **101**, 328 (1979)].

By M. D. JACKSON and W. R. GILKERSON,* Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.

Page 333: The scale on the abscissa of Figure 6 is incorrect, as well as one point having been added inadvertently. The correct Figure 6 is below.

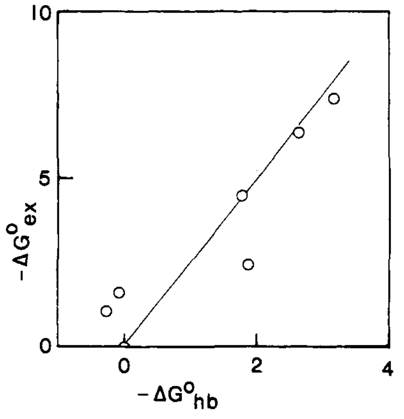

Figure 6. The free energy of exchange, ΔG°_{ex}, for the displacement of THF by ligand on lithium cation as a function of ΔG°_{HB}, the free energy of hydrogen-bond formation of the ligand with *p*-fluorophenol, both in kcal mol^{-1}.

Specific Inclusion Catalysis by β-Cyclodextrin in the One-Step Preparation of Vitamin K_1 or K_2 Analogues [*J. Am. Chem. Soc.*, **101**, 1019 (1979)].

By IWAO TABUSHI,* KAZUO YAMAMURA, KAHEE FUJITA, and HIROMU KAWAKUBO, Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan.