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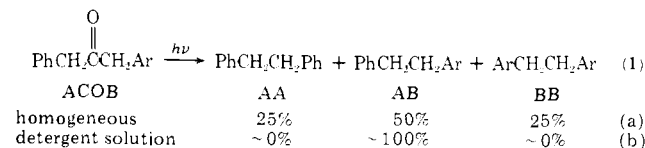
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Photoreactions in Detergent Solutions. Enhancement of Regioselectivity Resulting from the Reduced Dimensionality of Substrates Sequestered in a Micelle

Sir:

Below the critical micelle concentration (cmc), detergents exist mainly as monomers in aqueous solution,¹ whereas at higher concentration (above the cmc) these amphiphiles aggregate to form globular micelles that are characterized by a hydrocarbon-like interior ("inside"), a hydrophilic, highly polar and ionic surface ("boundary"), and an aqueous exterior ("outside"). For example, the conventional model² of hexadecyltrimethylammonium chloride (HDTCl) indicates that above the cmc this detergent becomes organized to form (roughly spherical) micelles consisting of 50–70 monomers. Micelles can be employed to organize organic substrates in detergent solutions. The influence of organizational aspects of micelles has provide information on numerous micellar catalyses,³ photophysical⁴ and photochemical^{5,6} processes. It is also possible to reverse the strategy and use photophysical and photochemical information to deduce the structural and dynamic properties of micelles. We report here a study of the influence of micelle formation on the selectivity of a photoreaction. Our results provide information on the dynamics of organic solutes in micellar systems and indicate a means of enhancing reaction selectivity by taking advantage of the "reduction of dimensionality" enforced upon hydrophobic reagents that are sequestered into a micellar environment.

The photodecarbonylation of dibenzyl ketones in homogeneous fluid solution occurs via a free-radical mechanism in which coupling products (1,2-diarylethanes) are produced in quantitative yield.⁷ For an asymmetric dibenzyl ketone (ACOB) the coupling products AA, AB, and BB are formed in yields of 25, 50, and 25%, precisely the ratio expected for statistical, nonselective coupling of the free radicals \dot{A} and \dot{B} produced by photodecarbonylation (eq 1a).



Irradiation of (*p*-tolyl)benzyl ketone (ACOB) in benzene,⁷ or in water,⁸ yields a statistical mixture of coupling products (eq 1, Ar = *p*-CH₃C₆H₄). Addition of HDTCl to aqueous solutions of ACOB causes a remarkable effect on the product mixture (Table I).⁹ The yield of AB relative to AA + BB is a dramatic function of added HDTCl (Figure 1). Since the ratio of AB/(AA + BB) shows marked increases only above a concentration of HDTCl that is 10⁻³ M (the reported cmc of

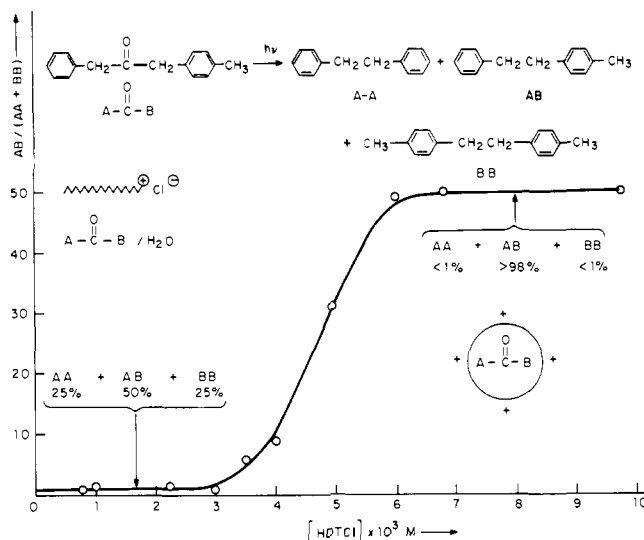


Figure 1. Variation on the ratio of the asymmetric coupling product (AB) to the sum of the symmetric coupling products (AA + BB) as a function of detergent concentration. The ketone concentration was fixed at 4×10^{-4} M.

Table I. Ratio of AB/[AA + BB] as a Function of Ketone and Detergent Concentration

[HDTCl] ^a	[ACOB] ^b	ketone/micelle ^c	AB/[AA + BB]
1×10^{-3}	4.4×10^{-4}	44	1.4
5×10^{-3}	4.4×10^{-4}	9	6.7
1×10^{-2}	4.4×10^{-4}	4	~50
2.5×10^{-2}	1.6×10^{-4}	0.6	~50
2.5×10^{-2}	5.8×10^{-4}	2.4	3.8
2.5×10^{-2}	1.2×10^{-3}	4.8	2.5
2.5×10^{-2}	7.4×10^{-4}	2.9	3.2
2.5×10^{-2}	7.4×10^{-4}	2.9	~50 ^d

^a Hexadecyltrimethylammonium chloride. ^b (*p*-tolyl)benzyl ketone.

^c The mean number of ketone molecules per micelle, calculated on the assumption that the aggregation number of HDTCL = 100.

^d Solutions contain 0.01 M CuSO₄.

this detergent),¹⁰ we conclude that the selectivity is micellar in origin. Above the cmc, the quantum yield for reaction in detergent solution is $\sim 1/3$ for that in benzene solution.

By controlling the ratio of ketone to detergent (above the cmc), situations may be created so that micelles contain zero, one, or more ketone molecules.¹¹ Photolysis leads to generation of $\dot{A} + \dot{B}$ within a single micelle.¹³ In homogeneous solution \dot{A} and \dot{B} diffuse apart to become "free" radicals, but, when they are both produced in a single micelle, they are sequestered in a special environmental "cage" (Figure 2). Since \dot{A} and \dot{B} are hydrophobic they are effectively confined to the "reduced dimension" of space defined by the hydrophobic portion of the micelle, i.e., its "inside". In order for products of the type AA or BB to form, two \dot{A} or two \dot{B} radicals must diffuse together. Several mechanisms for formation of AA and BB are therefore possible. For example, \dot{A} and \dot{B} may diffuse out of their original "cage", and enter the aqueous phase. Formation of AA and BB may occur by reaction of radicals in the aqueous phase or by penetration by \dot{A} or \dot{B} of the boundary of a micelle containing a radical of the same type. Collisions between micelles also provide a mechanism for generation of AA and BB, but such a mechanism is unlikely to be effective since the common exterior charge causes repulsion between micelles and in addition only collisions between micelles both of which happen to contain \dot{A} and \dot{B} can cause the scrambling.¹⁵

The occurrence of two or more ketones in a single micelle would enhance the formation of AA and BB, only if two \dot{A} (or

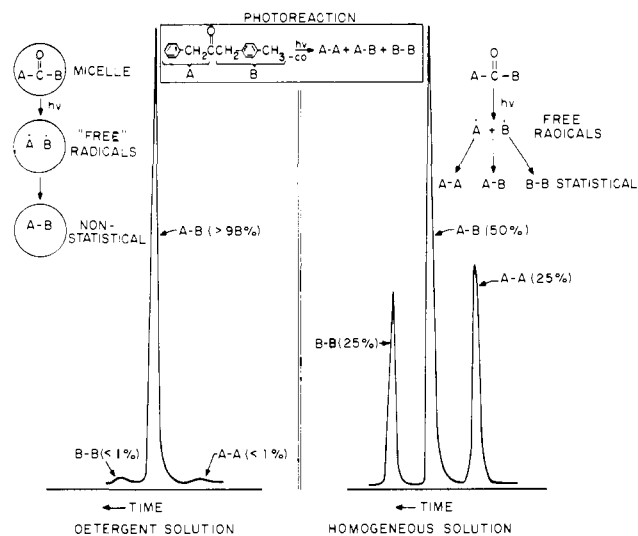


Figure 2. Schematic representation of the sequestering effect of micelles on the free radicals produced by photolysis of ACOB. The vapor chromatographic analyses provide a clear experimental demonstration of the increase in regioselectivity which occurs above the cmc.

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. X 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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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