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(13) Note that in ref 8 detachment of a CH_2 was achieved in solution phase photolysis, but irradiation was carried out in a medium which served as an effective trap.

(14) Products which would correspond to such a cleavage reaction (e.g., eq 5) were in no case positively identified. A limit to the extent of their formation was estimated from the limits of the analytical method.

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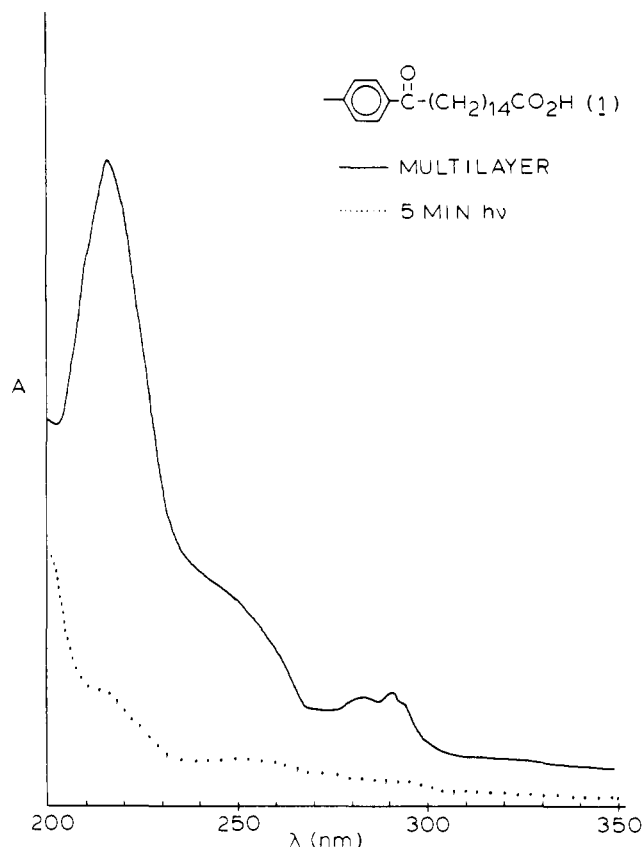
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Figure 1. Absorption spectrum of surfactant ketone **1** in an assembly consisting of 12 layers of 1:1 ketone **1**-arachidic acid: solid line, ketone before irradiation; dotted line, spectrum after 5-min irradiation at 290 nm.

Ketone Photoreactivity as a Probe of the Microenvironment: Photochemistry of the Surfactant Ketone 16-Oxo-16-*p*-tolylhexadecanoic Acid in Monolayers, Micelles, and Solution[1]

Sir:

There has been considerable recent interest in the structure and properties of organized media such as micelles, lipid vesicles, bilayers, and monolayers which are formed by the self-organization of amphipathic molecules.[2-5] A number of techniques have been used as structural probes including fluorescence and other photophysical phenomena.[6-10] Our own work in this area has focused on several photochemical reactions occurring in monolayer films, deposited monolayer assembles, and micelles.[11-13] Most of our previous studies have involved relatively polar chromophores which occupy hydrophilic sites. Recently we have investigated a number of surfactant molecules having a potentially reactive chromophore in a more hydrophobic region. In the present paper we report an investigation of the photoreactivity of the surfactant ketone 16-oxo-16-*p*-tolylhexadecanoic acid (**1**) in monolayer assemblies, anionic micelles, and solution. The results indicate that the microenvironment can produce striking changes in reactivity. Thus we find the characteristic solution process—the type II photoelimination—is effectively eliminated in the highly condensed monolayer assemblies but enhanced compared with hydrocarbon solution in the more fluid micelles.

Ketone **1** was synthesized by Friedel-Crafts reaction of toluene with the acid chloride of methyl hydrogenhexadecanedioate, followed by saponification of the methyl ester to a white solid, mp 95-96 °C. Surface pressure-area isotherms of ketone **1** were obtained by spreading 10 μL of a 5×10^{-3} M chloroform solution of the ketone on a clean water surface ($CdCl_2 \cdot NaHCO_3$) in a circular trough,[14] and then reducing the area of the film by means of a mobile barrier while recording the pressure and area of the film. Films composed of pure **1** were characterized by gradual increases in surface pressure on compression, followed by collapse at relatively low pressure ($\sim$10-15 dyn/cm). In contrast, an equimolar mixture of **1** and arachidic acid ($CH_3(CH_2)_{18}CO_2H$) provided a film

which gave a rapid increase in surface pressure at a molecular area of $\sim$20 $Å^2$/molecule and no collapse at less than 30 dyn/cm. This behavior is typical of a "condensed" fatty acid monolayer.

Monolayer assemblies were easily constructed from the mixture of **1** and arachidic acid by the usual techniques.[6,13] Quartz slides were employed as a support for the assemblies in order that the subsequent reactions of the ketone could be followed by UV spectroscopy.

Generally multilayer assemblies consisting of 12–16 total layers were used in this study. These assemblies gave good UV spectra from which the photoreaction could be easily monitored. Irradiation of the assemblies at 254 or 290 nm resulted in rapid bleaching of the long wavelength absorption (Figure 1). That the observed reaction involves destruction of the carbonyl chromophore was verified by IR spectroscopy. The surface of an aluminum slide was rendered hydrophobic with a thin coating of paraffin and coated with 100 layers of a 1:1 ketone–arachidic acid mixture. A reflectance attachment was used to measure and record the IR spectrum from the slide. The aromatic carbonyl peak (1680 cm^{-1}) and carboxylate carbonyl peak (1540 cm^{-1}) were easily detected and upon irradiation of the assembly the aromatic carbonyl peak was observed to diminish in intensity relative to the carboxylate peak until it could no longer be resolved from the baseline.

Gas chromatographic analysis was employed to determine if volatile products such as *p*-methylacetophenone (from type II cleavage), tolualdehyde (from α cleavage), or toluene (from α cleavage followed by decarbonylation) were formed during the reaction. Irradiation was carried out at 254 nm in a closed quartz cell containing a monolayer assembly and a small amount of hexane to dissolve any volatile materials released from the assembly upon photolysis. Several assemblies were

irradiated sequentially using the same cell and bath in order to increase the concentration of products. The hexane solution was then analyzed by flame ionization gas chromatography at the highest practicable sensitivity. Products were identified by comparison of their retention times with those of authentic samples and yields were calculated relative to an internal hydrocarbon standard added after completion of the irradiation. p-Methylacetophenone was formed in very low yield ($\sim$0.2%) along with other unidentified low-yield products. p-Tolualdehyde was not formed within the limits of detection by this method. The lowest quantity of a product in the hexane bath which could be detected was determined in a separate experiment to be $\sim$10^{-11} mol. Since toluene would not have been cleanly separated from hexane in this experiment, an alternative method of analysis was devised. In this method several slides were irradiated simultaneously in a closed quartz cell and the atmosphere inside the cell after the reaction was sampled with a 5-mL gas-tight syringe. No volatile products at all were detected by gas chromatographic analysis of this sample. Again, control experiments indicated that even low level production of volatile materials would have been detected.[15]

The quantum yield for ketone disappearance in the assemblies upon irradiation at 290 nm was determined to be 0.06. Considering the 0.2% yield of p-methylacetophenone, the quantum efficiency for the type II process, ϕ_{II}, can be estimated to be $\sim$10^{-4}.[16] In comparison, the type II process was found to be the predominant reaction of 1 upon photolysis in degassed benzene solution giving p-methylacetophenone as the only detectable volatile product with $\phi_{II} = 0.2$, a value comparable with those reported for similar aromatic ketones in hydrocarbon solution.[17,18]

It is clear from comparison of the quantum yields in solution and assemblies that the type II fragmentation is severely restricted in the monolayer environment. The type II process can only occur if an excited ketone can assume a conformation which allows abstraction of a γ-hydrogen atom through a cyclic six-membered transition state.[16] The effective termination of this fragmentation in the monolayer environment indicates that the close molecular packing indicated by the 20-Å^2 cross-sectional area results in an externally imposed conformational immobility of the hydrocarbon chains and implies that the hydrophobic region of monolayer assemblies is essentially solid-like, rather than being fluid. The complete lack of type I (α) cleavage products is also reasonable in view of this picture since any radicals formed by α cleavage would have a "cage" of extreme lifetime to facilitate recombination. The present study provides an interesting comparison with results obtained by Guillet and co-workers on the type II photoelimination in polymers, crystals, and melts.[19,20] In the former it has been found that type II reactivity is low below the glass transition temperature of the polymer, presumably because the decrease in motion of the polymer chains precludes assumption of the required conformation.[19,20] Similarly, in crystalline 7-tridecanone no type I or II products are formed but in melted crystals reactivity similar to that in solution occurs.[21] Taken together these results indicate that the sensitivity of the type II reaction to environmental factors provides a useful probe for determining the amount of conformational rigidity in various media.

Ketone 1 can also be incorporated into anionic micellar solution where a somewhat related organized environment might be anticipated. Relatively stable micellar solutions of 1 (0.001 M) in sodium dodecylsulfate (SDS) (0.024 M) containing 0.1 M NaCl were obtained by sonication of the aqueous mixture.[22,23] Irradiation of freshly prepared degassed micellar solutions of 1–SDS led to production of p-methylacetophenone as the only volatile product detectable by gas chromatography. In contrast to the monolayer assemblies the quantum yield in

micellar solution was determined to be 0.8 or four times the benzene solution value. The contrast between photobehavior of 1 in monolayer assemblies and micelles indicates that the reduction in the type II process efficiency in the former is not due simply to incorporation into an organized environment. The high value for the type II process for 1 in micelles is reasonable in view of much recent evidence indicating that the hydrocarbon chains in micelles are disordered and the microviscosity in the hydrocarbon portion is not especially high.[24] The value for ϕ_{II} for 1 in SDS micelles is similar to that obtained for octanophenone by Turro et al.[25] in cationic micelles. In this study it was concluded that the increase over the benzene solution values for ϕ_{II} for octanophenone and valerophenone was most consistent with the ketones not being solubilized exclusively in the hydrocarbon core but spending at least some time either in the Stern layer or on the surface of the micelle.[25] A similar interpretation of the present results would imply that the fourteen carbon polymethylene chain in 1 is mostly bent such that both ends lie near the micellar surface.[26] This may not be unreasonable in view of the high surface:volume ratio in micelles which strongly favors surface sites for even very weakly surface-active molecules.[27] The contrast in reactivity of 1 in micelles, monolayers, and solution suggests that it and related surfactant ketones may be useful probes for environmental studies of other organized media.

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Geometry of Transition States Involving Allylic Hydrogen Abstraction Elucidated by Isotope Effect Studies

Sir:

The symmetry of the transition state in the abstraction of hydrogen from thiols by a variety of free-radical species has been assessed by Pryor and Kneipp[1] through estimates of the magnitude of the primary kinetic deuterium isotope effect over a range of temperatures. Wiberg and Motell,[2] moreover, have established both the linearity of the hydrogen transfer between carbon and chlorine and the symmetry of the transition state in the conversion of methane to methyl chloride by measurement of k_H/k_D as a function of temperature, i.e., measurement of A_H/A_D and $[\Delta E_a]_D^H$. We have now obtained, through measurement of the temperature dependence of k_H/k_D,[3] evidence supporting the occurrence of nonlinear hydrogen abstraction by radicals, a case in point being the abstraction of allylic hydrogen by alkoxy radicals.

The widely accepted mechanism of allylic acetoxylation of olefins[4] with *tert*-butyl peracetate calls for the rate-determining abstraction of allylic hydrogen by *tert*-butoxy radicals. Consequently, it can be assumed that the kinetic isotope effect for reaction of $C_6H_5CHDCH=CH_2$ (**1**) would be indicative of the structural features of the prevailing transition state. This isotope effect at a single temperature has been reported by Denny.[5] We have now measured k_H/k_D for this reaction at a series of temperatures over a range of 90 °C. The results listed in Table I verify the complete temperature independence of k_H/k_D in this reaction; that is to say, $[\Delta E_a]_D^H = 0$ and $A_H/A_D = 2.90$ for allylic hydrogen abstraction by *tert*-butoxyl radical from **1**. There seems very little possibility, moreover, that the appearance of temperature independence of k_H/k_D is a consequence of a fortuitous loss of H and D product radicals via some side reaction occurring at such variable relative rates that at every temperature the product ratio is selectively adjusted to the constant value. The fact that the yields of product, based on the amount of *tert*-butyl peracetate consumed, were in all cases very high ($\geq 85\%$), with no significant amounts of side product evident from the GLC analysis, also militates against this possibility.

It has been previously shown[6] that reaction processes involving nonlinear hydrogen transfer (a bent transition state), characterized by a single rate-determining step,[7] exhibit a temperature-independent isotope effect which is greater than the theoretical maximum,[8] $A_H/A_D = 1.2$, for linear transfer. These criteria for a bent transition state,[6] where the angle of H transfer between the reaction centers is considerably less than 180°, are clearly fulfilled in the allylic acetoxylation of **1** and presumably most olefins undergoing this rate-determined

Table I. Temperature Dependence of the Primary Deuterium Isotope Effect in the Reaction of **1**[a] with *tert*-Butyl Peracetate[b]

reaction temp, °C	hours at heat	product (H/D) isotope ratio[c]	k_H/k_D
25.0	24.0[d]	0.3410 ± 0.0023	2.93
70.50	35.5	0.3516 ± 0.0036	2.84
79.59	30.25	0.3339 ± 0.0012	2.99
90.48	25.00	0.3530 ± 0.0021	2.83
99.42	12.25	0.3418 ± 0.0014	2.93
114.95	2.00	0.3566 ± 0.0034	2.81
temperature range ≡ 90			av ≡ 2.90 ± 0.06

[a] $PhCHDCH=CH_2$ (**1**) was prepared by the copper-catalyzed coupling of vinylmagnesium bromide and C_6H_5CHDCl. The isotope content at C_3 was determined using chemical ionization mass spectrometric and high resolution NMR methods. This method of synthesis was shown by GLC, NMR, and high resolution chemical ionization mass spectroscopy to yield a product (**1**) which was completely free of any contaminants such as the isomeric 1-phenylpropene and was completely deuterated (>99%) in the α position. [b] In each run ~*100* mg of **1** were charged into a heavy-walled tube along with 1.0 mg of CuBr, *90* mg of 40.8% *tert*-butyl peracetate in benzene, and 0.75 mL of dry acetonitrile. Each tube was degassed in a series of freeze-pump-thaw cycles and sealed at $<10^{-3}$-mm pressure. The sealed tubes were then inserted in a thermostatically controlled bath for a period of hours required to bring about nearly complete decomposition of the perester. The product, worked up in the usual manner, consisted predominantly (~90%) of the cinnamyl isomer and was freed of all residual solvent and starting material by gas chromatography. For purposes of the isotope ratio determinations the (unseparated) isomer composition of the product was introduced directly into the inlet system of the mass spectrometer. [c] Determined by the high precision isotope ratio method described by H. Kwart and J. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976). A minimum of 20 000 mass spectral determinations are averaged in each of the recorded values of the isotope ratio. [d] This result was obtained with photoactivation which has been claimed[4] to produce the identical reaction process.

H-transfer process. A simplistic representation of this conclusion is displayed in Figure 1.

This is intended to illustrate how a *tert*-butoxy radical with one of its p orbitals imbedded in the π orbital of the olefin in the form of a π or charge-transfer complex can effect an angular transfer of the allylic hydrogen by utilizing the orthogonal p orbital to complete a five-membered cyclic transition state. When radical attack occurs at a C–H bond, we can expect that the major interaction is with the HOMO, namely the σ orbital. The SOMO of the oxygen radical is lowered in energy by virtue of the oxygen being complexed with the olefinic orbitals. Its interaction with the HOMO of the adjacent C–H can be expected to be greatly beneficiated[9-11] thereby in the resulting pericyclic process. In this picture the role of the double bond in facilitating allylic hydrogen abstraction is not merely involved with lowering the energy of the resulting carbon free radical, which is the textbook explanation of the allylic abstraction process; it also provides a kinetic pathway acting to lower the activation energy of the process. Further appreciation of the significance of this factor is to be gained by comparing these results supporting a bent transition state of allylic H abstraction with the results referenced above demonstrating that a temperature-dependent zero-point energy determined k_H/k_D is observed in the usual case of linear H abstraction from a nonallylic reaction site (for example, in the chlorination of methane[2]).

A similar conclusion has been reached by Walling and Zavitsas,[12] who realized that, while the relative rate constant for H abstraction from *cis*-and *trans*-4-methyl-2-pentane was independent of the source of the *tert*-butoxy radical, the unhindered trans olefin underwent this H-transfer reaction with