RESEARCH NOTE

SOLVENT SENSITIVITY OF TYPE II PHOTOREACTIONS OF KETONES AS A DEVICE TO PROBE SOLUTE LOCATION IN MICELLES

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Abstract—The solvent sensitivity of the Type II reaction is employed as a device to investigate the properties of detergent solutions. The quantum yield for Type II reaction and the ratio of cleavage to cyclization are used as specific monitors of local solvent properties of micelles. Our results indicate that the average position of phenyl alkyl ketones is either on the micelle surface or in the Stern layer. The absence of significant residence time of the excited ketone in the aqueous phase is confirmed by the lack of quenching of Type II reaction by Eu^{3+} in micellar solutions.
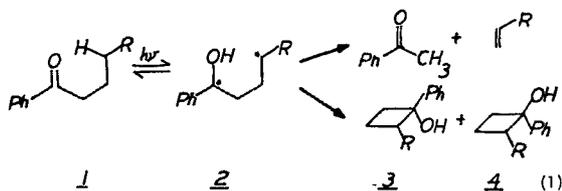
INTRODUCTION

The emission properties of electronically excited organic molecules have been extensively employed as a means of probing microenvironmental structural and dynamic properties of detergent solutions and biological membranes (Edelman and McClure, 1968; Fendler and Fendler 1975; Hautala et al., 1974). We report here an example of the use of photochemical properties of electronically excited organic molecules to deduce the location of molecules solubilized in micelles.

The Type II photoreactions (cleavage and cyclization, Eq. 1) of aryl alkyl ketones are known to be solvent dependent (Wagner, 1971). Both the quantum

yield of reaction 1 and the ratio of cyclobutanols **3** and **4** are sensitive to solvent. For example, the quantum yield for Type II reaction of **1** (R = CH₃) increases from a few tenths in benzene solvent to 1.0 in t-butanol (Wagner, 1972). At the same time in going from benzene to t-butanol the ratio of **3/4** increases from 4.0 to 2.0, respectively (Wagner, 1972). Both effects are explained in terms of the effect of hydrogen bonding of the diradical intermediate **2** (R = CH₃). Formation of a hydrogen bond between **2** and solvent favors formation of products by cleavage and cyclization relative to reversion of the diradical to **1** (Wagner, 1972). The same hydrogen bonding influences the ratio of **3/4**. In a general way, increas-

ing solvent polarity is expected to parallel the influence of hydrogen bonding on the reaction quantum yield and cyclization ratio of **3/4**. The sensitivity of the quantum yield of Type II reaction and the cyclization ratio to hydrogen bonding polarity is the basis for the use of this photoreaction as a probe for the site location of aryl alkyl ketones in micelles.

Valerophenone (**1**, R = CH₃) and octanophenone (**1**, R = (CH₂)₃CH₃) were employed as probe molecules and hexadecyl tetramethyl ammonium chloride (HTAC) was employed as the detergent from which micelles were formed. Benzene and t-butanol were employed as reference non-polar and polar, hydrogen bonding solvents, respectively.

MATERIALS AND METHODS

Valerophenone (Aldrich) was purified by preparative vapor phase chromatography on an SE-30 column followed by vacuum distillation. Octanophenone (Aldrich) was passed through acid washed alumina and then distilled under reduced pressure. Chlorine gas was bubbled through benzene (Fisher, spectra analyzed) under the irradiation of a medium pressure mercury lamp for 30 min. The resulting benzene photostate was washed with aqueous solutions of Na_2CO_3, $NaHCO_3$ and water in that order. After drying with molecular sieves, the benzene was distilled from P_2O_5 and stored over sodium.

Redistilled water and t-butanol (Fisher, Certified) was used. HTAC (Eastman) was washed with dry ether (3X) and recrystallized from acetone-ether (5X). Degassed samples (five freeze-pump-thaw cycles at 10^{-3} mm) were irradiated in parallel with a merry-go-round apparatus (Moses, 1969) equipped with a 450 W Hanovia medium pressure mercury lamp. A 2 M potassium chromate in 5% aqueous potassium carbonate was used as a filter. The extent of reaction 1 and cyclobutanol ratio were monitored by quantitative v.p.c. analysis on a 4% QF-1 mixed 1% Carbowax 20 M column (chromosorb Q support). Benzyl methyl ketone and valerophenone were added after irradiation as internal standards for valerophenone and octanophenone, respectively. Acetophenone was identified by

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Table 1. Quantum yields, trans/cis ratios and solvent
effects of Type II processes.

Ketone*	Solvent	Φ†	3/4‡
$PhCO(CH_2)_3CH_3$	t-BuOH	1.00	1.5
$PhCO(CH_2)_3CH_3$	C_6H_6	0.33	3.6
$PhCO(CH_2)_3CH_3$	HTAC (0.05 M)	1.06	1.9
$PhCO(CH_2)_6CH_3$	t-BuOH	1.00	1.1
$PhCO(CH_2)_6CH_3$	C_6H_6	0.29	4.7
$PhCO(CH_2)_6CH_3$	HTAC (0.05 M)	0.71	1.2

* Concentration of valerophenone = 0.01 M; concentration of octanophenone = 5 mM.

† Quantum yields for total disappearance of ketones are relative to valerophenone in t-BuOH which is assumed to be 1.00. Estimated error limits are ± 10%.

‡ That valerophenone is completely associated with micelles was established by the observation that the OD at 325 nm and 340 nm due to the ketone in pure water solutions is negligible. At 0.05 M detergent the OD was found to be 0.2 (325 nm) and 0.1 (340 nm).

comparison of v.p.c. co-injections. Cyclobutanols were isolated from preparative v.p.c. with the same type of column used in quantitative analysis and identified by their characteristic spectra: IR (3600 cm^{-1}, hydroxy group), mass spectrum (m/e, M-18, M-28 and 120 peaks, characteristics of 1-phenyl cyclobutanol) and NMR (doublet methyl peaks at δ 0.5 and δ 1.1 for 3 and 4, respectively for $R = CH_3$; multiplet alkyl peaks at δ 0.5 ~ 1 and δ 0.7 ~ 1.3 for 3 and 4, respectively for $R = (CH_2)_3CH_3$).

RESULTS AND DISCUSSION

The results of our studies on quantum yields and cyclobutanol ratios are summarized in Table 1. It is evident that the values of Φ (Type II reaction) and the ratio of 3/4 in micellar solution are more similar to those found for photolyses in t-butanol than in benzene.

In order to determine whether significant amounts of our ketone probes are solubilized in the aqueous phase, quenching experiments by Eu^{3+} were performed. The triplet states of aromatic ketones are quenched effectively by Eu^{3+} (Heller and Wasserman, 1965; Wagner and Schott, 1968). Our quenching experiments are summarized in Table 2. Addition of 5 mM Eu^{3+} (as $EuCl_3$) to an aqueous solution of valerophenone causes a substantial reduction of the quantum yield of the Type II reaction. In contrast, the Type II reaction of valerophenone in 0.05 M HTAC solutions is not quenched by 5 mM Eu^{3+}.

The observation that the values of the quantum yield of Type II reaction and of the ratio 3/4 in micellar solution are similar to those in t-butanol and are not similar to those in benzene allows the conclusion that the ketone is not solubilized exclusively in the hydrocarbon core of the micelle. In terms of a static model this may be interpreted to mean that the average position of the excited ketone is either in the Stern layer or on the surface of the micelle. In terms of a dynamic model this means that the excited ketone is capable of spending sufficient time in the Stern layer or micelle surface to enjoy the hydrogen bonding offered by water molecules in these regions of the micelle. Whichever model is preferred, our results exclude the possibilities that the ketones spend significant portions of time in the aqueous phase (lack of quenching of Type II reaction by Eu^{3+}) and that they are "locked" into the hydrocarbon core of the micelle (quantum yields and cyclization data).

The observation that Type II reaction of valerophenone is more efficient in detergent solution than that for octanophenone is consistent with a less polar "average" environment for the latter. This is to be expected from the greater hydrophobic character induced by the longer alkyl chain. Finally, it should be noted that the 3/4 ratio is comparable for valerophenone and for octanophenone. This result suggests that although the quantum yield and 3/4 ratio are both solvent polarity dependent, the latter is less so and tends to reach a "saturation value" (high solvent polarity limit) more rapidly than does valerophenone.

In conclusion, our results suggest that solvent sensitive photoreactions, like solvent sensitive absorption or emission, can serve as useful probes of the chemical environments of probe molecules dissolved in micellar solutions. Extensions of this work to other solvent sensitive reactions and to bilayer and membrane systems (McDaniel et al., 1976) are apparent.

Table 2. Quenching of acetophenone formation from excited valerophenone* by Eu^{3+}.

Solvent	(Eu^{3+}), M	Rel. $\Phi_{Acetophenone}$
HTAC (0.05M)	0.00	1.00
HTAC (0.05M)	0.005	1.02
H_2O	0.00	1.00
H_2O	0.005	0.62

* Concentrations of valerophenone = 0.01 M.

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