

Short Communication

Photohydrolysis of *m*-methoxybenzylacetates in micellar solutions: substitution of organic solvents

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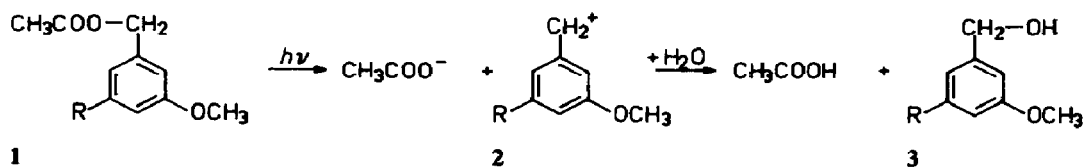
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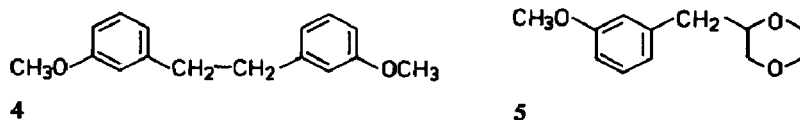
1. Introduction

Amphiphilic substances are known to influence the rate constants and selectivity of chemical [1 - 3] and photochemical [4 - 8] reactions because of the peculiar heterogeneous, *i.e.* micellar, structure of solutions containing amphiphiles at concentrations exceeding the critical micelle concentration. Also, the possibility of replacing organic solvents by aqueous micellar solutions is a practical advantage that merits consideration. Both features of micellar solutions will be illustrated here by comparing the quantum yields of the photohydrolysis of *m*-methoxybenzylacetates in aqueous amphiphile solutions and in organic solvent mixtures.

The photohydrolysis reaction



(a, R ≡ H; b, R ≡ OCH₃) was investigated by Zimmerman and coworkers [9, 10] and was carried out in 1:1 water:dioxane mixtures because of the low solubility of these compounds in water. The photohydrolysis of 1a was reported to yield the byproducts 4 (3,3'-dimethoxydibenzyl) and 5 (3-methoxybenzyldioxane)



which indicate homolytic cleavage of 1a as a side reaction; 1b underwent photohydrolysis in a clean reaction without byproducts yielding 3b via the benzyl cation 2b. In the present study the photohydrolyses of these compounds were investigated in cationic, anionic and non-ionic micelles, and for comparison in three dioxane-water mixtures.

2. Experimental details

2.1. Materials

3,5-dimethoxybenzylacetate 1b and 3-methoxybenzylacetate 1a were prepared as described elsewhere [9]. Dioxane (Merck, p.a.) was used as supplied. Methanol for liquid chromatography was distilled once before use. Sodium dodecylsulphate (Merck, p.a.) and Brij-35 (polyoxyethylene dodecylether (Ega, p.a.)) were tested with respect to their critical micelle concentrations by the surface tension method. As no anomalies with respect to the literature data [11] were obtained, the substances were used without further purification. Micellar solutions were prepared using demineralized water.

2.2. Irradiations

10^{-3} M solutions of 1a and 1b in mixtures of dioxane and demineralized water as well as in 0.1 M aqueous solutions of the amphiphiles were irradiated for 20 min at 30 °C in an apparatus which has been described elsewhere [12] using quartz-filtered light from a high pressure mercury lamp. The solutions were deoxygenated by bubbling nitrogen gas (99.996% pure) through them.

2.3. Analysis

The irradiated solutions were analysed directly by liquid chromatography using Miniprep LC equipment (ISA-Jobin-Yvon) fitted with a Spectrochrom M UV absorption detector (Gilson). The educt and product peaks were identified by comparison with standard samples, and the peak integrals were corrected by extinction coefficients. The column material was LiChroprep RP 18 (Merck) and the solvent was a 4:1 methanol:water mixture.

The optical transmission values of the solvents were measured on an Acta M VII spectrophotometer (Beckman).

3. Results

When 10^{-3} M solutions of 1a and 1b in water:dioxane mixtures (1:1 by volume) were irradiated, results agreeing with the previous work of Zimmerman and Sandel [9] were obtained. About half of 1a underwent the photohydrolysis reaction to 3a by heterolytic fission. Of the byproducts, the dioxane addition product 5 appeared as a liquid chromatographic peak. The formation of the radical combination product 4 was suppressed at the concentration used. 1b was hydrolysed to more than 90%. These experiments were repeated in other water:dioxane mixtures (3:1 and 1:3) as well as in 0.1 M aqueous solutions of the three surfactants sodium dodecylsulphate, cetyltrimethylammonium bromide and Brij-35.

In the case of 1a the type and the relative amounts of the byproducts varied from solvent to solvent. In the dioxane-rich solvent mixture the dioxane adduct yield was slightly higher than in the 1:1 mixture, whereas in the water-rich mixture it was suppressed to 10% of its value in the 1:1 mix-

ture. In addition, another byproduct which differed in its liquid chromatographic retention time was formed (probably 3-methoxytoluene produced by reaction of the benzyl radicals with water (see ref. 13)) which was not identified. The yield of benzyl alcohol did not vary significantly. This behaviour was also observed in the three amphiphile solutions in which different byproducts were formed (probably by reaction of the benzyl radicals with the amphiphiles). Again the radical combination product 4 was not observed because of the isolation of the micellar-solubilized educt molecules. Obviously the ratio of homolytic splitting to photohydrolysis was not affected by the solvents used. In the case of 1b only negligible amounts of byproducts were detected. A clean photohydrolysis to the corresponding alcohol was observed.

The results in terms of relative quantum yields are summarized in Table 1. These were determined by measuring the integrals of the peaks of the hydrolysis products in the liquid chromatogram after irradiating each sample for 6 min. (Absolute quantum yields for photohydrolysis products in 1:1 water:dioxane mixtures are known to be about 10% [9].) The relative quantum yield values for the consumption of the educts agree closely with the results for ϕ_1 and ϕ_2 given in Table 1. In all cases the formation of the product peaks followed zero-order kinetics.

TABLE 1

Relative quantum yields ϕ_1 and ϕ_2 of the photohydrolysis of 3-methoxybenzylacetate and 3,5-dimethoxybenzylacetate respectively in various solvents

	<i>Dioxane:water</i>			<i>0.1 M sodium dodecyl-sulphate</i>	<i>0.1 M cetyl-trimethyl-ammonium bromide</i>	<i>0.1 M Brij-35</i>
	<i>1:3</i>	<i>1:1</i>	<i>3:1</i>			
ϕ_1	0.96	0.67	0.51	0.95	1	0.86
ϕ_2	0.97	0.50	0.37	1	0.99	0.85
Transmission of solvent (%)						
At 248 nm	23.6	8.4	6.5	86.2	75.9	46.6
At 254 nm	47.0	28.6	20.4	86.6	76.4	51.2

4. Discussion

The results show clearly that it is not necessary to carry out photohydrolyses of 1a and 1b in organic solvents for reasons of solubility. The quantum yields in aqueous micellar solutions are even somewhat higher. No special "micellar catalysis" effect need be invoked to explain this result. It is simply a consequence of the more efficient use of the light quanta in the aqueous systems which absorb less of the effective wavelengths (254 and 248 nm) of the high pressure mercury lamp (see Table 1).

Zimmerman and Sandel [9] could not decide whether the ratio of the homolytic to the heterolytic cleavage rates for 1a is determined by the competition of these reactions in the excited singlet state or by the competition of singlet heterolysis with intersystem crossing followed by homolysis in the excited triplet state. Also, mechanistic studies on related systems [13] could not rule out the involvement of one of the excited states in both reactions. Since it is known that the bromide counter-ions of cetyltrimethylammonium micelles interact with micellarly solubilized excited molecules [14, 15], we expect an enhancement of intersystem crossing rates in these micelles compared with the other solvents. Therefore the competition of singlet and triplet reactions should be reflected in a marked difference between the heterolysis quantum yields obtained in cetyltrimethylammonium bromide and in sodium dodecylsulphate micelles which contradicts the results (see Table 1). Therefore the competition of homolysis and heterolysis in the same excited state is more likely.

5. Conclusion

Photohydrolysis reactions of substances which are poorly soluble in water can be performed in aqueous micellar solutions. The advantages over organic solvents (dioxane, acetonitrile and alcohols) include fewer health risks because of the high vapour pressures of the organic solvents, better use of the excitation light because of the greater optical transmission of the micellar solutions and possible control of side reactions.

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