Short Communication

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## Photolysis of diphenylmercury in micellar solution: effect of micelle size on radical combination reactions

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## 1. Introduction

The increasing pollution of natural water by organic mercury compounds has stimulated considerable interest in the photochemistry of these compounds under model environment conditions. For instance, the inhibition of photosynthesis and growth in phytoplankton communities in the presence of organic mercury compounds has been studied [1]. Decomposition rates in sunlight have been determined for diphenylmercury (DPM) and related compounds [2].

In the presence of hydrocarbons or alcoholic solvents (RH) the photolysis of DPM is known to follow the pattern [2 - 5]

$$C_6H_5{-}Hg{-}C_6H_5 \xrightarrow{\ h\nu\ } 2C_6H_5\cdot + Hg$$

$$C_6H_5\cdot + RH \rightarrow C_6H_6 + R\cdot$$
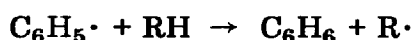
Further reactions, including the evolution of hydrogen subsequent to the formation of excited mercury atoms and radicals, have been reported to occur at considerably slower rates [3, 5].

Although DPM is almost insoluble in water, substantial amounts of it can be solubilized in aqueous media containing amphiphilic compounds which are omnipresent in nature. The photolysis of DPM was therefore studied in aqueous solutions containing sufficient tenside to ensure solubilization in micelles.

## 2. Experimental details

### 2.1. Materials

DPM (Merck, 97% pure) was used as supplied. Solutions of sodium dodecylsulphate (Merck, p. a.), cetyltrimethylammonium bromide (Merck, p. a.) and Brij-35 (polyoxyethylene dodecylether) (Ega, p. a.) were prepared using demineralized water. The tensides were checked with respect to their critical micelle concentrations by the surface tension method. The values agreed with the literature data. *n*-hexane and methanol (Merck, Uvasol) were used without further purification.

### 2.2. Irradiation

$10^{-3}$ M solutions of DPM in $n$-hexane, methanol, 0.1 M sodium dodecyl-sulphate, 0.1 M cetyltrimethylammonium bromide and 0.1 M Brij-35 were irradiated for 15 min at 23 °C using quartz-filtered light from a high pressure mercury lamp. The apparatus used has been described elsewhere [6]. The solutions were deoxygenated by bubbling nitrogen gas (99.996% pure) through them.

### 2.3. Analysis

The irradiated solutions were analysed directly by liquid phase 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 using extinction coefficients. The column material was LiChroprep RP 18 (Merck), and the solvent was aqueous methanol (methanol-to-water ratio of 4).

## 3. Results and discussion

When $10^{-3}$ M nitrogen-saturated solutions of DPM are irradiated benzene is found to be the main product in all cases. No trace of the radical recombination product biphenyl could be detected in $n$-hexane, in methanol and in one micellar solution. The quantum yields were somewhat lower in aerated solutions but had no significant effect on the product yields given in Table 1.

That benzene formation is by far the dominant process is expected on the basis of previous work [3 - 5, 8]. A more interesting observation is that biphenyl production may amount to as much as 1.5% of converted educt in a suitable micellar environment. This cannot be due to an ordinary cage effect [9] as the microfluidity in Brij-35 micelles should be less than that in cetyltrimethylammonium bromide micelles which is known to be less than that in sodium dodecylsulphate micelles [10 - 12]. Consequently, the formation of cage products like biphenyl in cetyltrimethylammonium bromide and sodium dodecylsulphate micelles should be less rather than more probable

TABLE 1

Product yields of the photolysis of diphenylmercury in various solvents

| Solvent | Benzene (%) | Biphenyl (%) | Micellar weight (g $mol^{-1}$) |
|---|---|---|---|
| $n$-hexane | 100 | — | |
| Methanol | 100 | — | |
| 0.1 M Brij-35 | 100 | — | 61700[a] [7] |
| 0.1 M cetyltrimethylammonium bromide | 96 | < 0.5 | 30000 [7] |
| 0.1 M sodium dodecylsulphate | 98 | 1.5 | 17800 [7] |

[a]In 0.4 M NaCl.

than their formation in Brij-35 micelles. However, the data in Table 1 suggest that there is a correlation with micellar weight (or volume since micelle densities should not differ much). This indicates that the hydrophobic effect prevents non-polar radicals like phenyl from diffusing out of the micelle and enhances the re-encounter probability. This "super cage effect" in micelles has already been established in the photolysis of asymmetrically substituted dibenzylketones in solutions containing cetyltrimethylammonium chloride [13]. In this case selective combination of benzyl radicals leads to high yields of the corresponding dibenzyl compounds. However, the effects of micelle size have not been reported, but they are not likely to be significant for benzyl radicals because their reactivity with respect to hydrogen abstraction is negligible compared with that of the phenyl radicals investigated here.

## 4. Conclusion

The photolysis of suitable compounds in micellar solutions offers the possibility of controlling the ratio of radical combination rates to radical abstraction rates by performing the reaction in micelles of suitable size. It follows that the product pattern obtained by the photolysis of pollutants in natural water may depend on the presence of amphiphiles.

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