PHOTOLYSIS OF α-PHENYLBENZOIN IN MICELLAR SOLUTIONS: FORMATION OF A REARRANGED RADICAL-PAIR COMBINATION PRODUCT

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Summary

During the photolysis of α-phenylbenzoin in micellar solution a thermally unstable product was formed. This coloured product is formed from the interaction of a caged benzoyl and diphenylketyl singlet radical pair. The reaction is strongly influenced by KBr, KI and Cu^{2+}.

1. Introduction

Photochemical α cleavage of benzoin derivatives leads to the generation of radicals capable of initiating polymerization processes [1]. α-Phenylbenzoin (PB) is photochemically cleaved to give benzoyl (B) and diphenylketyl (DK) radicals [2, 3] (Scheme 1).
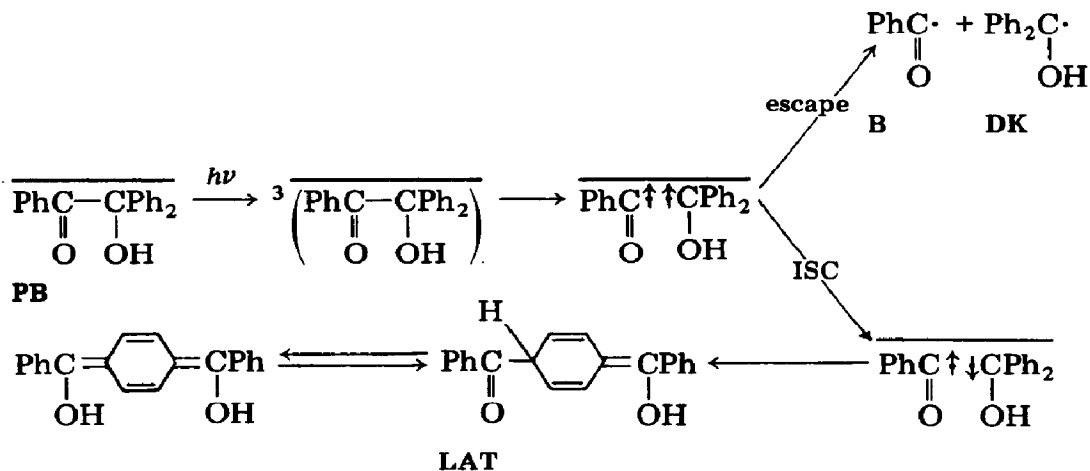
Scheme 1.

The quantum yields of photolysis in the absence of oxygen in acetonitrile, n-hexane and methanol are 0.11, 0.13 and 0.4 respectively [4]. Benzaldehyde, benzil, benzophenone and benzpinacol are the final products of photolysis in homogeneous solutions. The relative distribution of the final products is dependent on the solvent and the concentration [4].

In this work we present the results of the photolysis of PB in micellar solutions of sodium laurylsulphate (SLS) and cetyltrimethylammonium bromide (CTAB). It can be expected that rearranged radical pair combination products (LAT) will also be formed (see Scheme 1). Such compounds were found in the photolysis of benzoin ethers on a silica-gel surface [5] or in the photoinduced reduction of benzophenone in micelles [6].

2. Experimental details

PB was prepared by reacting phenylmagnesium bromide with benzil [2]. SLS (Pierce Chemical Co.) was used as received. CTAB (Lachema) was recrystallized twice from methanol by adding diethyl ether. Doubly distilled water was used for the preparation of the micellar solutions. The micellar solutions of PB were prepared by mixing 0.05 g fine pulverized PB in 50 ml 5×10^{-2} M SLS or CTAB for 5 h at 313 K. The resulting concentration of PB in the solutions was, after filtration, about 1.2×10^{-3} M.

For the photolysis experiments the solutions were placed in quartz cells (10 mm × 10 mm × 40 mm), with necks sealed using silicon resin stoppers, and were bubbled with pure argon for 20 min before irradiation. The light from an XBO 101 (Narva) xenon lamp was filtered using a glass filter which is transparent at 350 nm or longer wavelengths. After a predetermined irradiation time the absorption spectra were measured using a Perkin–Elmer 330 spectrophotometer.

3. Results and discussion

The electronic absorption spectrum of PB in pure ethanol and in a micellar solution of SLS is shown in Fig. 1. The spectra are seen to resemble each other closely. As far as we know there is no detailed interpretation of these spectra available in the recent literature. In deoxybenzoins [7], which are analogous compounds, the long wavelength absorption band belongs to the transition from the lowest excited singlet state ($n\pi^*$ electronic configuration). The phosphorescence spectra of these compounds at 77 K show vibronic structure typical of a transition from the lowest $n\pi^*$ triplet state [7]. We have observed very good agreement between the phosphorescence spectra of PB and benzophenone at 77 K [8]. Most probably the T_1 state of PB also has an $n\pi^*$ electronic configuration (0–0 transition at 434 nm).

In our photolysis experiments PB is excited at the wavelength of the shoulder corresponding to the $S_0 \rightarrow S_{n\pi^*}$ transition. After complete

photolysis of PB in micellar solutions of SLS and CTAB the distribution of the products was 90% benzophenone, 10% benzil and 1% benzhydrol. In contrast to the homogeneous solutions (ethanol and toluene) where the spectral changes during photolysis are obtained only in the absorption region of PB [8], in micellar solutions we observed an increase in absorption in the region 320 - 480 nm with a maximum at 410 nm (Fig. 2(a)). On irradiation, the initially colourless solution turns yellow and blue fluorescence is emitted. The coloured product generated is thermally unstable. It disappears from the solution on standing in the dark at room temperature (Fig. 2(b)). This product quickly vanishes on bubbling the solution with oxygen.

The process of absorbance increase on excitation followed by thermal (dark) decomposition in the closed cell can be repeated several times. After the coloured product reaches its highest absorbance, a prolongation of the photolysis also causes its decomposition. After the thermal reaction, when the absorbance drops to almost zero, the next irradiation raises the absorbance back to the level reached in the previous cycle of irradiation.

Similar behaviour is observed with micellar solutions of CTAB. The thermal reaction in SLS is described by first-order kinetics; the calculated rate constant is $(6 \pm 0.4) \times 10^{-3}$ s^{-1}. In CTAB solution the assumption of first-order reaction kinetics is valid up to the half-decrease in the absorbance, and the rate constant is $(8.8 \pm 0.5) \times 10^{-3}$ s^{-1}.

Adding KBr in a concentration higher than 10^{-2} M to the SLS micellar solution of PB has a great influence on the increase in absorbance at 410 nm (Fig. 3). Under the same irradiation conditions the reaction is faster and the
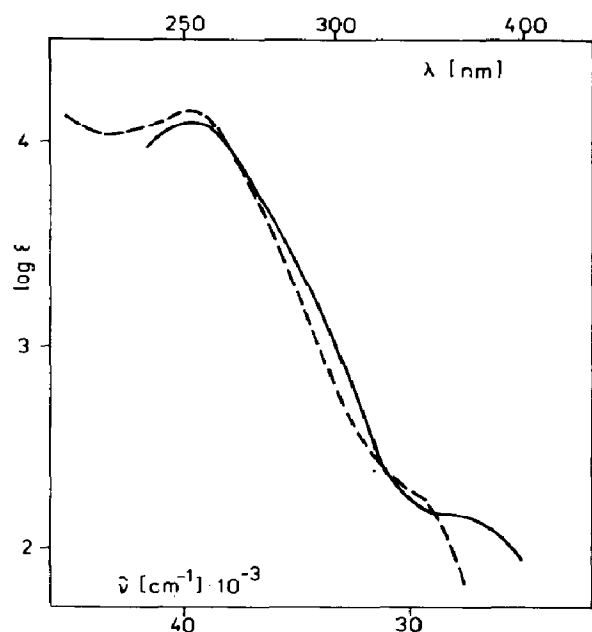

Fig. 1. Electronic absorption spectrum of PB in ethanol (– – –) and in SLS (10^{-3} M) micellar solution (———).
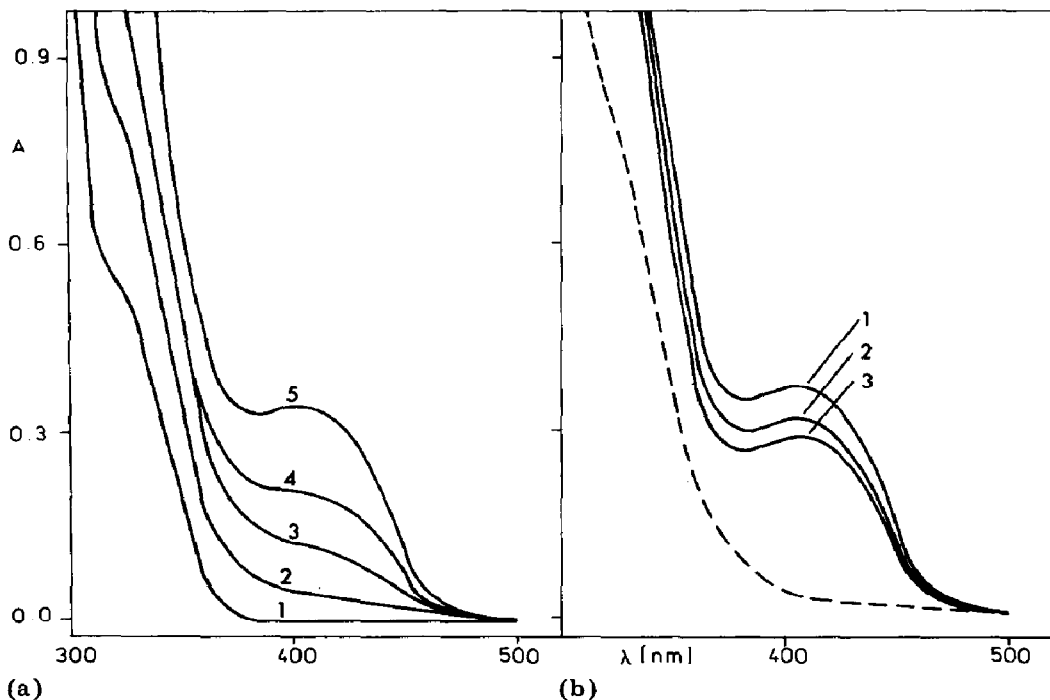
Fig. 2. (a) Increase in absorption during the photolysis of PB in SLS (5×10^{-2} M) micellar solution: curve 1, 0 s; curve 2, 1200 s; curve 3, 1800 s; curve 4, 2400 s; curve 5, 4200 s. (b) Thermal reaction after photolysis of PB in SLS micellar solution: curve 1, 0 s; curve 2, 1800 s; curve 3, 3600 s; – – –, air bubbled.
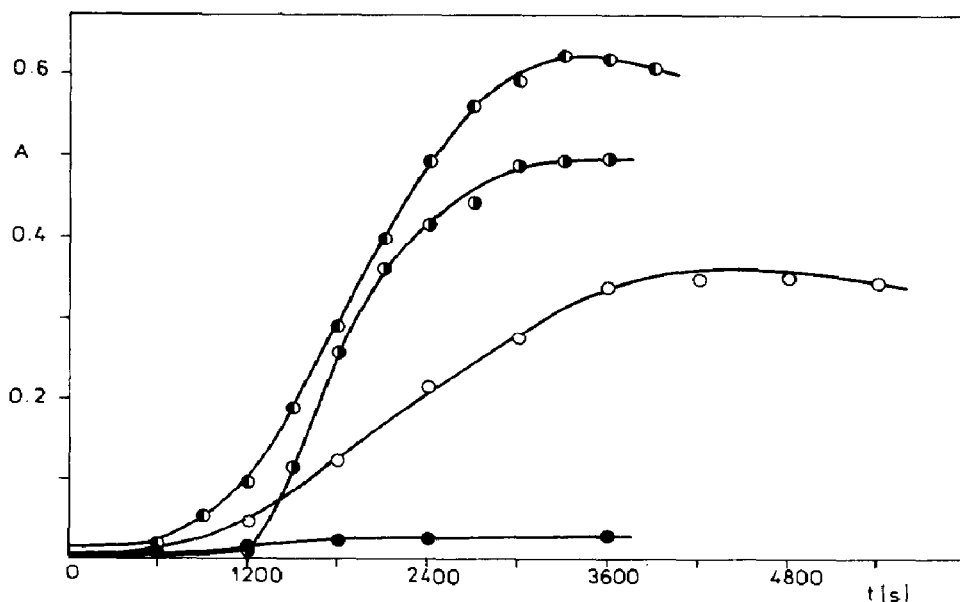

Fig. 3. Increase in absorbance (408 nm) of LAT during photolysis of PB in SLS micellar solution: ○, no additives; ◐, 10^{-2} M KBr; ◑, 10^{-2} M KI; ●, 10^{-2} M CuCl$_2$.

absorbance is twice as large. If KI in the same concentration is added to the SLS solution of PB, irradiation leads to a maximum increase in absorbance by a factor of up to 1.7; a remarkable increase in absorbance is initially detected in this case (Fig. 3). Addition of $CuCl_2$ at a concentration of 10^{-2} M strongly diminishes the increase in absorbance in the spectral region discussed (Fig. 3).

Using results obtained with similar compounds [7 - 11] we believe that PB is dissolved mostly in the hydrophobic inner part of the SLS or CTAB micelles (in our experiments the micellar concentration is about 7×10^{-4} M, and the concentration of dissolved PB in micellar solution and in pure water is about 1.2×10^{-3} M and 1.1×10^{-4} M respectively). On photolysis a triplet radical pair of B and DK radicals is formed, corresponding to Scheme 1 (also see refs. 2 and 3). Reaction between radicals is possible only after an intersystem crossing (ISC) process inside the micelles or after their escape from the micelles. The caged singlet radical pair can react to give the initial compound PB or the combination product LAT formed by para coupling of both radicals. The resulting structure is similar to the products formed in the case of benzophenone photoreduction [6, 12]. The proposed chemical structure for LAT is shown in Scheme 1; this compound is probably in tautomeric equilibrium with the *para*-quinoidal structure.

Adding an electrolyte to the micellar solution generally causes a decrease in critical micelle concentration and an increase in micellar aggregation number which is accompanied by an increase in occupation number of the solubilizate [13]. The influence of KBr and KI at higher concentrations is probably explainable by these effects. An increase in occupation number of PB molecules in micelles increases the fraction of recombined radical pairs, leading to a higher concentration of LAT. In the case of the anionic SLS micelles, the heavy-atom effect of Br^- and I^- on the radical pair ISC process is rather negligible in comparison with homogeneous solutions.

Our results clearly show that the formation of LAT is strongly inhibited by the presence of Cu^{2+}. It is still under discussion whether this process proceeds in the Stern layer or in the hydrophobic interior of the micelle [14]. In relation to the dynamic behaviour of the micellar system, it is quite possible that water and solvated ions penetrate into the micellar interior. Recent experiments confirm such ideas [15].

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