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Kinetic and Mechanistic Study of Photodechlorination of 2,2′,4,4′-Tetrachlorobiphenyl in Surfactant Solutions

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Polychlorinated biphenyls (PCBs) are worldwide-spread organic contaminants. Their persistence, bioaccumulation and mutagenicity have attracted a great deal of attention to developing new approaches to detoxify PCBs in efficient and environmentally friendly ways (Hutzinger et al., 1974; Sawhney, 1986).

Photodegradation is an important process of PCB decomposition in the environment (Safe et al., 1976; Sawhney, 1986). Photodecay of PCBs in aqueous solution is reported to result in dechlorinated and hydroxylated products (Crosby and Moilanen, 1973; Bunce, 1978). Stepwise formation of dechlorinated congeners is the main degradation pathway during irradiation of PCBs in alkanes and alcohols (Ruzo et al., 1974a, b; Miao et al., 1996, 1999), but methoxylated PCB derivatives were also identified as one of the photoproducts in alcohols (Crosby and Moilanen, 1973; Ruzo et al., 1974a, b; Nordblom and Miller, 1974; Hawarl et al., 1992). Surfactants are effective in enhancing the solubility of PCBs, thus the presence of surfactant micelles in UV-induced photolysis has been shown to improve photodechlorination of PCBs and minimize side reactions such as hydroxyl substitution (Epling et al., 1988; Chu et al., 1998; Shi et al., 1998). Although researchers have studied the photolysis of PCBs dissolved in nonionic surfactant solutions, kinetic information on UV irradiation of PCBs in anionic surfactant solutions has rarely been reported within the scope of our knowledge. The objectives of this study are to investigate the photodecay rates and corresponding quantum yields of 2,2′,4,4′-tetrachlorobiphenyl (2,2′,4,4′CB) in an anionic surfactant solution (sodium dodecylsulfate, SDS) and a nonionic surfactant solution (polyoxyethylene 23 lauryl ether, Brij35), and to evaluate the effectiveness of the two surfactants in enhancing the photodechlorination of PCBs.

Materials and Methods

Both 2,2′,4,4′-tetrachlorobiphenyl and 2,2′,4,4′,6,6′-hexachlorobiphenyl were purchased from AccuStandard Inc (New Haven, CT, USA) with 99% purity. Both SDS and Brij35 were obtained from Sigma-Aldrich Co (St Louis, MO, USA) with 98% purity. The n-Hexane (95% purity) was HPLC grade, and was purchased from Tedia Company Inc (Fairfield, OH, USA); other solvents were analytically pure. All above chemicals were used as they were obtained without further purification.

Surfactant stock solutions were prepared in doubly distilled water at a 4 g/L concentration. 2,2′,4,4′CB-surfactant solutions for photolysis were prepared by addition of 10 mg of pure 2,2′,4,4′CB crystals into a 500 mL bottle containing 400 mL of prepared surfactant solutions, then mixed for 7 days in an orbital shaker. After centrifugation at 10,000 rpms (9837 × g) for 30 minutes, the supernatants of 2,2′,4,4′CB-surfactant solutions were transferred for irradiation. All the solutions were prepared without pH adjustment, aeration, or degassing unless otherwise mentioned. The experiments were performed at room temperature (22 ± 2 °C) and pH 6.65.

Each of the irradiation experiments was conducted in triplicate and accompanied by dark reaction controls run concurrently to the phototransformation assay. All

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2,2′,4,4′CB-surfactant solutions were illuminated by a 254-nm PenRay^{TM} low-pressure mercury lamp (UVP Inc, USA), generating a light intensity of 9.752×10^{-6} Einstein L^{-1} sec^{-1} as estimated by a potassium ferrioxalate chemical actinometer according to Hatchard et al. (1956). Photolyzed compounds and products were extracted into hexane prior to analysis. A 1-mL aliquot was extracted with 4 mL hexane.

The photoproducts were identified by a GC-ECD (Shimadzu GC-14B). The GC-ECD was equipped with a DB-1 capillary column (id×length=0.25mm×30m) (J&W Scientific Inc.). The column temperature of GC was programmed as follows: It was initially held constant at 60 °C for 2 minutes, then raised to 180°C at a rate of 12°C/min, and at a rate of 4°C /min thereafter to 250°C. Finally, it was held constant for 0.5 minutes. The PCB concentrations were calculated by comparing with PCB standards using 2,2′,4,4′,6,6′-hexachlorobiphenyl as the internal standard. The concentration of chloride in photolyzed solutions was measured by using a chloride selective electrode (Orion 96-17). The UV-VIS spectra were measured by using a TU-1901 UV-VIS spectrophotometer (Beijing Purkinje General Instrument, Co.) in 1-cm path-length cells.

Results and Discussion

The UV-VIS spectra changes of 2,2′,4,4′CB dissolved in SDS and Brij35 solutions during irradiation at 254 nm are illustrated in Figure 1. It was found that there was a bathochromic (red) shift of the absorption maxima of the κ band and a subsequent increase of the molar absorptivity of the κ band. According to MacNeil et al. (1976), progressive introduction of ortho chlorine atoms to the Ph-Ph bond resulted in a hipsochromic (blue) shift of κ band and a diminution of ε value, but stepwise chlorine substitution at the para position of biphenyl caused a bathochromic shift of κ band, and vice versa. Thus, the spectral shifts of 2,2′,4,4′CB in surfactant solution during photolysis would imply a possible stepwise dechlorination with preferential removal of the ortho chlorine atoms.

No obvious degradation of 2,2′,4,4′CB was observed in the dark during the experiments. This suggests that degradation due to hydrolysis or biodegradation in the dark is negligible. The gas chromatogram of 2,2′,4,4′CB and its photoproducts in SDS and Brij35 solutions are shown in Figure 2. In Figure 2, only peak 1 (2,2′,4,4′CB) was observed before irradiation. After 20 seconds of irradiation, peak 2 (2,4,4′CB) and peak 3 (4,4′CB) appeared in the photolyzed sample, but the height of peak 1 decreased. It was implied that 2,2′,4,4′CB was degraded by UV irradiation and the photoproducts were 2,4,4′CB and 4,4′CB. As the time increased, the heights of peak 1 and 2 decreased while the height of peak 3 increased. The above results would support stepwise dechlorination—ortho chlorine atoms being preferentially removed,—to be the mechanism of 2,2′,4,4′CB photodegradation in surfactant solutions. This conclusion agreed well with published literature (Epling et al., 1988; Chu et al., 1998).

The concentrations of 2,2′,4,4′CB and its photoproducts are plotted as a function of time in SDS and Brij35 solutions in Figure 3. The initial photolysis reaction should obey a pseudo-first-order kinetics according to Equation 1:

$$C_t = C_0 e^{-kt} \tag{1}$$

where C_t is the concentration of PCBs at time t (mol L^{-1}), C_0 is the initial PCB concentration (mol L^{-1}), and k is the pseudo-first-order rate constant (s^{-1}). To standardize the photolytic efficiency for photodechlorination reactions in surfactant solutions, the quantum yield (Φ) is used according to Equation 2 and can be computed from the slope of a pseudo-first-order plot of Ln(C/C_0) versus irradiation time, shown as Figure 4.

$$\phi = \frac{k}{2.303 I_{o\lambda} \varepsilon_{\lambda} l} \tag{2}$$

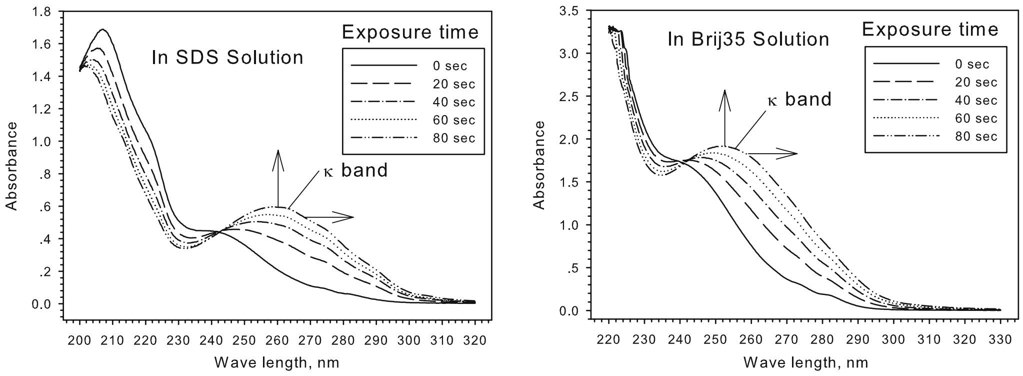

Fig. 1 Spectral changes of samples in SDS and Brij35 solutions during experiments

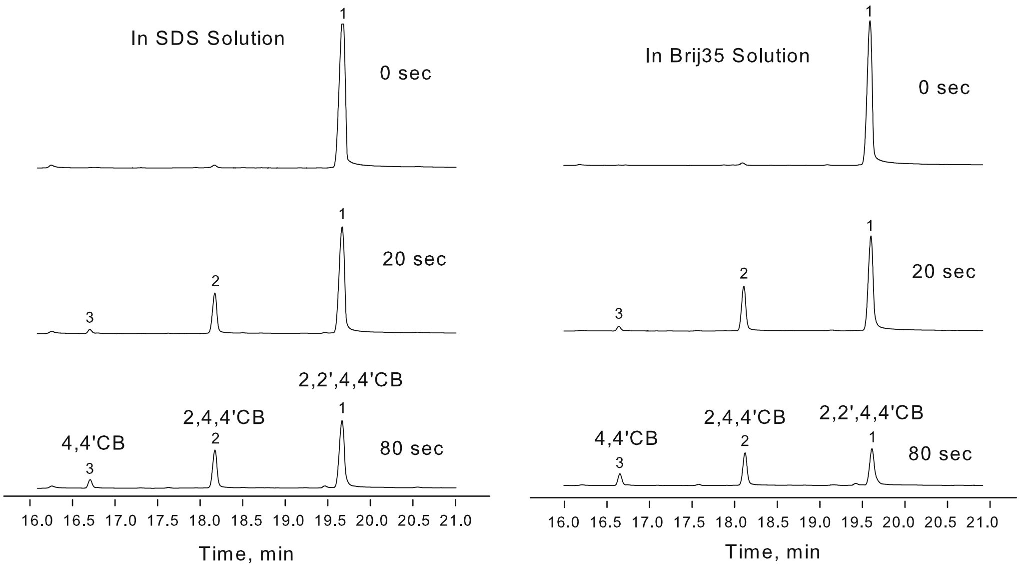

Fig. 2 Gas chromatograms of 2,2′,4,4′CB and its photoproducts in SDS and Brij35 solutions

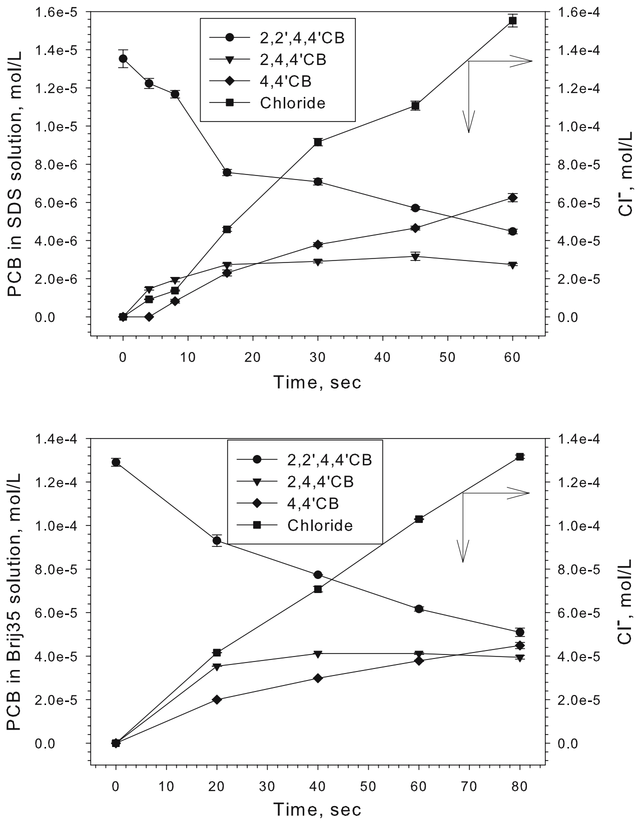

Fig. 3 Concentration of 2,2′,4,4′CB and its photoproducts in SDS and Brij35 solutions

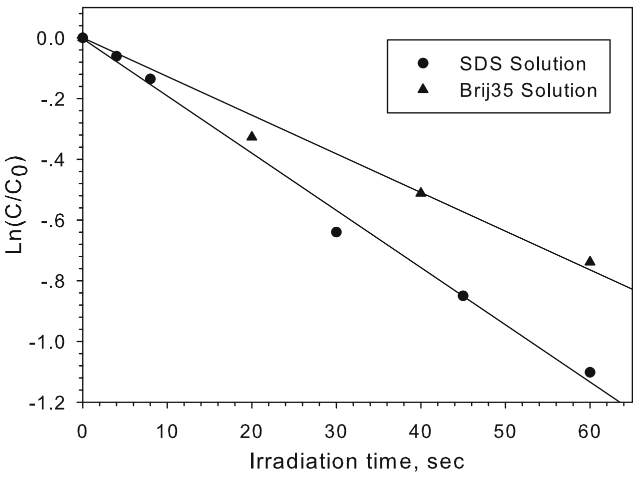

Fig. 4 Pseudo-first-order decay curves of 2,2′,4,4′CB in SDS and Brij35 solutions

where Φ is the quantum yield for the photolysis of 2,2′,4,4′CB molecules (dimensionless), $I_{o\lambda}$ is the intensity of the incident light at wavelength 254 nm (9.752×10^{-6} Einstein L^{-1} s^{-1}), ε_λ is the molar absorptivity of 2,2′,4,4′CB at wavelength 254 nm ($L\ mol^{-1}\ cm^{-1}$), and l is the cell path length (i.e., 1.0 cm). The quantum yields for the initial period of irradiation ($t \leq 60$ sec) calculated by Equation 2 were listed in Table 1. It was observed that the k and Φ values of PCB photodechlorination in the SDS solution were 56.2% and 49.1% greater than those in the Brij35 solution, respectively. It might be implied that both the rate and quantum yield of photolysis were enhanced in SDS solutions relative to those in Brij35 solutions. Surfactants have been proposed for use in soil-washing to enhance the removal of polychlorinated biphenyls from contaminated soils or sediments (Abdul and Gibson, 1991; Jafvert et al., 1995; Chu and So, 2001; Chu and Kwan, 2003). Moreover, the above results show that PCBs in surfactant solutions can be effectively photodegraded. Therefore, surfactant

Table 1 Initial photolysis rates and quantum yields of PCBs

PCB/Solution	ε_λ (L mol^{-1} cm^{-1})	k (s^{-1})	Φ
2,2′,4,4′CB/SDS	9090.9	0.0189	0.0926
2,2′,4,4′CB/Brij35	8675.4	0.0121	0.0621

washing followed by photolysis seems to be a viable technology for remediation of PCB-contaminated soils.

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