

Photodechlorination of Polychlorobenzene Congeners in Surfactant Micelle Solutions

Wei Chu and Chad T. Jafvert*

School of Civil Engineering, Purdue University, 1284 Civil Engineering Building, West Lafayette, Indiana 47907

Photochemical reactions of polychlorobenzene congeners in aqueous solutions containing surfactant micelles have been investigated. All photolysis experiments were performed with a Rayonet RPR-100 merry-go-round photo-reactor utilizing 253.7-nm monochromatic ultraviolet (UV) lamps. Photoreduction through photodechlorination was shown to be the main decay pathway in which lesser chlorinated congeners and benzene were formed as intermediates. Final products included H^+ and Cl^- in approximately stoichiometric amounts. In addition, some minor pathways were observed including photochlorination (the reverse reaction), photoisomerization, and finally photohydrolysis, through which phenol was formed. The quantum yield for the decay of hexachlorobenzene was found to be about an order of magnitude greater in micellar solutions than in water alone. Several hydrogen sources were investigated with sodium borohydride shown to be a promising rate enhancer at elevated concentrations.

Introduction

Surfactant solutions have been shown to be effective in desorbing hydrophobic organic pollutants from soil (1-4) and independently have been shown to act as catalysts in photochemical decay reactions of chlorinated organic compounds (5, 6). As a consequence, utilization of surfactants as solubilizing agents to remove contaminants from soils followed by photolytic destruction may prove to be a promising soil remediation strategy through which the surfactants may be recovered and/or recycled. Several recent papers (e.g., refs 7-10) have examined in some detail the distribution of nonpolar compounds between surfactant micelles and soil particles. Information regarding photochemical reactions of environmentally relevant chemicals in surfactant solutions, on the other hand, is very limited. Hence, in this study we have examined the photodechlorination of polychlorobenzene (PCB) congeners (generally starting with hexachlorobenzene) in aqueous solutions containing selected surfactants and report on reaction pathways, decay rates, and quantum yields.

Numerous investigators have shown that photodechlorination of aryl chlorides occurs. However, low efficiency and side reactions often impede the rates of these dechlorination processes whether they occur naturally or through artificial means. Zepp *et al.* (11) have demonstrated that among all potential degradation routes in natural water, direct photolysis by sunlight is either not possible or represents only a minor pathway for most compounds. Direct photodechlorination of PCBs under sunlight in aqueous solutions, for example, has quantum yields as low as 0.0003 (12). Zepp and Cline (13) have suggested the long half-lives and/or low quantum yields of dechlorination reactions might be caused by naturally occurring humic substances, which inhibit free radical

chain reactions. Oxygen molecules also quench the triplet state, retarding free radical reactions. Sorption to natural particles further decreases photolysis rates to almost insignificant levels (14). Additionally, Epline and Florio (15) have observed side reactions in the photolysis of chlorobenzenes that result in the formation of chlorophenols and chlorobiphenyls, while photolysis of PCBs was shown to give rise to more toxic dibenzofuran compounds.

To become viable as a remediation tool, the photolysis process must be modified to enhance photodegradation rates and minimize side reactions. This possibly may be accomplished through variation in (i) solvent (e.g., micellar, organic, or pure water phases) (5, 11), (ii) sensitizing agent (16), and/or (iii) hydrogen source (electron donor) (12, 17). Three major benefits possibly may be achieved through the addition of surfactants. These include the following: (i) the ability to separate the contaminants from the optically impervious media, (ii) the ability to increase the quantum yield, and (iii) the attenuation of side reactions (i.e., production of dimers) or quenching reactions.

Materials and Experimental Methods

Chemicals. All chemicals were reagent grade except for the surfactants and solvents. All solvents (isooctane, acetonitrile, and acetone) were HPLC grade, used without further purification, and purchased from Fisher, Maill-inkrodt, or Aldrich. All solutions were made with distilled water, prepared by distilling deionized water that contained 0.01 M $KMnO_4$ and 0.01 M KOH added to the still to oxidize any organic impurities.

Due to the negative charge present on most soils, application of surfactants in proposed soil washing schemes is largely restricted to neutral and anionic types. Some physical and chemical characteristics of those surfactants chosen for this study are shown in Table 1 (18).

The chlorobenzenes listed in Table 2 were purchased from Aldrich and used without further purification. The molar absorptivities, $\epsilon_{p,\lambda}$, at 253.7 nm for compounds of interest are reported also in Table 2 (19-23).

Methods. All photochemical experiments were conducted in a darkroom outfitted with red lights. All experiments were carried out in 5-mL cylindrical quartz cuvettes placed in a RPR-100 Rayonet photochemical reactor equipped with a merry-go-round apparatus (Southern New England Ultraviolet). Light sources were two 253.7-nm phosphor-coated low-pressure mercury lamps (Rayonet). The light intensity to which each tube was exposed was determined from separate tubes containing the chemical actinometer, potassium ferrioxalate (24). The zero-order decay product, $Fe(C_2O_4)_2^{2-}$, was determined spectrophotometrically upon $Fe(II)$ complexation with 1,10-phenanthroline. The intensity of incident UV light was generally around 3.0×10^{-6} Einstein $L^{-1} s^{-1}$.

In each experiment, 5-mL aqueous solutions each containing identical concentrations of a single chloro-substituted benzene (often HCB), a surfactant, and

* To whom correspondence should be addressed. Phone: (317)-494-2196.

Table 1. Physical and Chemical Characteristics of Selected Surfactants

product name	type ^a	chemical formula and/or name	FW ^c	cmc (M) ^b	aggr. no. ^b
Tween 20	N	polyoxyethylene (20) sorbitan monolaurate	1227		
Tween 80	N	polyoxyethylene (20) sorbitan monooleate	1310	9.9 × 10 ⁻⁶	
Brij 35	N	C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₂₃ OH polyoxyethylene(23) lauryl ether	1200	43 × 10 ⁻⁶ (35 °C)	40 (25 °C)
Brij 58	N	C ₁₆ H ₃₃ (OCH ₂ CH ₂) ₂₀ OH polyoxyethylene(20) cetyl ether	1124		
dodecyl sulfate	A	CH ₃ (CH ₂) ₁₁ OSO ₃ Na	288	8.4 × 10 ⁻³	71 (23 °C)

^a N, nonionic surfactant; A, anionic surfactant. ^b Source: Fendler and Fendler (18). ^c FW, formula weight.

Table 2. Molar Absorptivities of Compounds Examined

compound	abbrv	molar absorptivity at 253.7 nm (M ⁻¹ cm ⁻¹)	ref (of molar absorptivity)	GC-ECD retention time ^a
Chlorinated Benzenes				
monochlorobenzene	MCB	138	<i>b,c</i>	NA
1,3-dichlorobenzene	1,3-DCB	1066	<i>b</i>	10.58 ± 0.05
1,4-dichlorobenzene	1,4-DCB	144	<i>b</i>	10.92 ± 0.05
1,2-dichlorobenzene	1,2-DCB	140	<i>b,c</i>	12.02 ± 0.05
1,3,5-trichlorobenzene	1,3,5-TCB	123	<i>b</i>	17.67 ± 0.05
1,2,4-trichlorobenzene	1,2,4-TCB	144	<i>b</i>	20.47 ± 0.05
1,2,3-trichlorobenzene	1,2,3-TCB	84	<i>b</i>	22.70 ± 0.05
1,2,3,5-tetrachlorobenzene	1,2,3,5-TeCB	140	<i>f</i>	30.22 ± 0.05
1,2,4,5-tetrachlorobenzene	1,2,4,5-TeCB	124	<i>b</i>	30.36 ± 0.05
1,2,3,4-tetrachlorobenzene	1,2,3,4-TeCB	280	<i>f</i>	33.47 ± 0.05
pentachlorobenzene	PeCB	850	<i>a,e</i>	40.85 ± 0.05
hexachlorobenzene	HCB	2782	<i>a</i>	46.93 ± 0.05
Others				
benzene		212	<i>b-d</i>	NA
acetone		11	<i>b</i>	NA
aniline		1375	<i>c</i>	NA
triethylamine	TEA	30	<i>a</i>	NA
sodium borohydride	SBH	≈0	<i>a</i>	NA

^a This study. ^b Simons (19). ^c Lang (20). ^d Friedel and Orchin (21). ^e Parke (22). ^f Conrad-Billroth (23).

possibly an additive (e.g., quencher, sensitizer, or hydrogen source) were irradiated in the photoreactor. Tubes were removed as a function of time with the concentration at zero time determined from an unexposed sample. The initial concentration of each chloro-substituted benzene was chosen so that the calculated solubility in each surfactant solution was not exceeded (9). 1,2,4-TCB was chosen as a starting material for final product analysis because it was found to be a predominant reaction intermediate (from HCB), and a much higher initial concentration could be used with it than with the more highly substituted chlorobenzenes.

Generally, polychlorobenzenes were quantified with a Hewlett Packard 5890 Series II GC equipped with a splitless injector, an electron capture detector (ECD), an integrator, and a 28 m × 0.323 mm DB-5 column (film thickness of 0.25 μm) subsequent to extraction into isooctane. Sample retention times and areas were compared to those of analytical standards. To chromatographically separate all the substitution benzenes, the temperature was ramped from 50 °C (for 2 min) to 110 °C (for 1 min) at a rate of 2 °C/min, to 150 °C (for 1 min) at a rate of 4 °C/min, and to 250 °C (for 15 min) at a rate of 15 °C/min, resulting in the retention times reported in Table 2. To avoid the formation of emulsions in the extraction step, 4 mL of each illuminated sample was pipetted into a 25-mL test tube, diluted with approximately 10 mL of distilled water, and carefully overlaid with 2 mL of isooctane. Tubes were outfitted with Teflon-lined caps and were gently agitated just slightly off vertical with a twist-action shaker in the dark at 20 °C for 24 h. With this method, the extraction efficiency of each compound was determined to be greater than 95%.

Analysis of monochlorobenzene, benzene, and phenol was accomplished by HPLC with a Micromeritics 750 LC pump, a Rheodyne injector (with a 200 μL loop), an Adsorbosphere HS C18 column (Alltech), a Knauer UV/Vis detector at 210 nm, and an integrator. The mobile phase was 70% or 40% (v/v) acetonitrile in water depending on the hydrophobicity of the specific compound being monitored. A Dionex 2000i/SP ion chromatograph equipped with an Ion Pac AS4A column (4 mm) and conductivity detector was used to determine chloride ion concentrations of the aqueous samples (containing surfactants). The eluant was 2.8 mM NaHCO₃ and 2.3 mM Na₂CO₃ buffer.

Most products were confirmed by GC-MS analysis with a Finnigan MAT 800 mass spectrometer and HP 5890A GC equipped with the same length and diameter DB-5 column as that used for product quantification. Mass spectra were compared to those of standards.

Initial decay rates of polychlorobenzenes were determined from the integrated first-order decay expression:

$$P_t = P_0 e^{-k_p t} \quad (1)$$

where P_0 and P_t are the concentration of the parent chlorine-substituted benzene at time zero and t (M), respectively, and k_p is the first-order decay rate constant (s⁻¹). The quantum yields for photolysis under the monochromatic light source were calculated by (25)

$$\Phi_p = \frac{k_p}{2.303 I_{\lambda,0} \epsilon_{p,\lambda} l} \quad (2)$$

where Φ_p is the quantum yield, $I_{\lambda,0}$ is intensity of the incident light at 253.7 nm (Einstein L⁻¹ s⁻¹), $\epsilon_{p,\lambda}$ is the

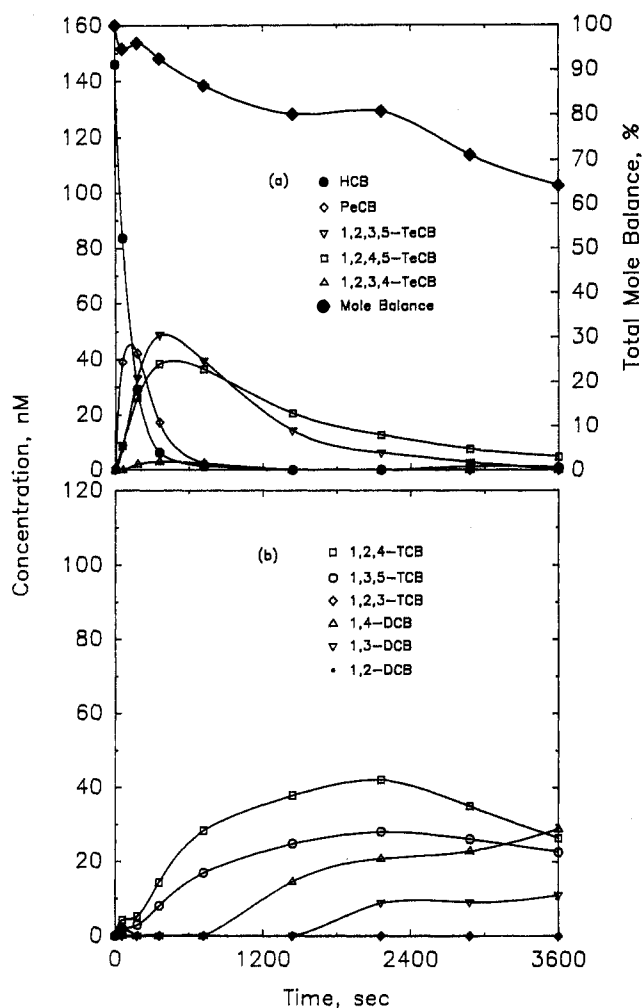


Figure 1. Photodechlorination of HCB and its decayed homologues within 4.5×10^{-4} M Brij 58 surfactant micelles at 253.7 nm. (Lines only indicate trends in the data.)

molar absorptivity at 253.7 nm ($L \text{ mol}^{-1} \text{ cm}^{-1}$), and l is the cell path length (cm).

Results and Discussion

Photodechlorination. HCB was irradiated in solutions containing one of the five different surfactants shown in Table 1. A representative decay chronicle of HCB and its products, solubilized with 4.5×10^{-4} M Brij 58, is shown in Figure 1. Figure 2 indicates that the initial decay is first order in HCB concentration. At this Brij 58 concentration, virtually all HCB is contained within micelles. The appearance of significant concentrations of PeCB and all tetra-, tri-, and dichlorobenzenes demonstrates the main overall reaction occurring is photoreduction, resulting specifically in photodechlorination.

All major chlorinated products were confirmed by GC-MS. An HCB-saturated 5.0×10^{-4} M Brij 58 solution was illuminated for 10 min and back-extracted into isoctane concentrating 40-fold. Of those products shown in Figure 1, only 1,2-DCB and 1,2,3,4-TeCB, which are minor products (detected in this sample by the ECD at less than 40 ppb), were not evident by GC-MS. No biphenyl, dibenzofuran, or other chlorine-containing compounds were detected by GC-MS, and no additional peaks appeared on ECD chromatographs.

Photolysis of 2.8×10^{-8} M HCB in distilled water is characterized by an initial lag stage ($\Phi = 0.0043$), followed

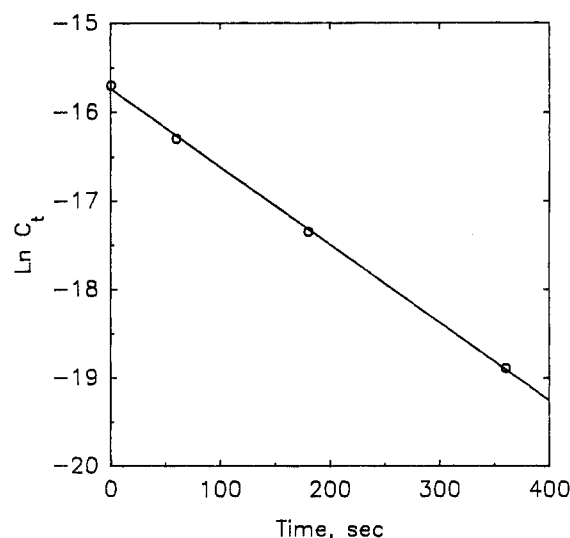


Figure 2. First-order decay of 1.5×10^{-7} M HCB within 4.5×10^{-4} M Brij 58 surfactant micelles at 253.7 nm. The slope of $8.0 \times 10^{-3} \text{ s}^{-1}$ resulted from a light intensity of $3.7 \times 10^{-6} \text{ Einstein s}^{-1} \text{ L}^{-1}$. This intensity results from two lamps within the photoreactor.

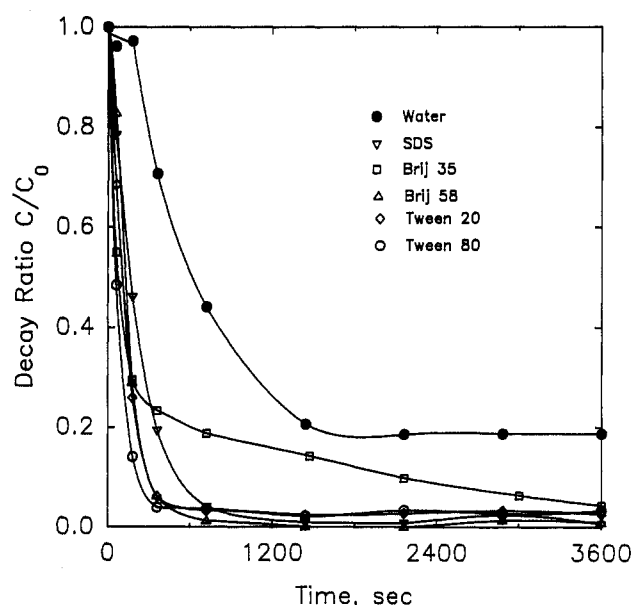


Figure 3. Photodechlorination of HCB in solutions containing various surfactants. In all cases, the light intensity is approximately $3.0 \times 10^{-6} \text{ Einstein s}^{-1} \text{ L}^{-1}$. A lag phase was observed for distilled water samples.

by a more rapid apparent first-order decay ($\Phi = 0.058$) (see Figure 3). The lag phase may result from the initial near-zero concentrations of free radicals and/or hydrogen sources. Additionally, at such low HCB concentrations (limited by solubility), the chance of photochemically produced reactant-new radical encounter is low. The O-H bond in water (119 kcal/mol) is usually too strong to donate a hydrogen to an aryl radical; however, in this case, water seems to be the only hydrogen source available.

Figure 3 also shows that no lag phase was observed for all surfactant solutions (see Table 3 for experimental conditions). As no classical hydrogen sources were added, either impurities in the commercial surfactant or the surfactants themselves must be acting as hydrogen sources. In surfactant solutions, initial HCB photoreduction always appeared to be first order. This was further shown in Brij 58 solutions from an initial rate study in which the initial HCB concentration was varied by over 1 order of mag-

Table 3. Quantum Yields of Hexachlorobenzene Photoreduction in Surfactant Solutions

solution	surfactant concn (M)	HCB concn (M)	TEA concn (M)	light intensity ^a (Einstein L ⁻¹ s ⁻¹)	quantum yield ^b	decay rate ^b (s ⁻¹)
distilled water		2.82 × 10 ⁻⁸		3.3 × 10 ⁻⁶	0.058	0.0012
dodecylsulfate	8.67 × 10 ⁻³	1.89 × 10 ⁻⁷		2.4 × 10 ⁻⁶	0.29	0.0045
Brij 35	4.17 × 10 ⁻⁴	1.64 × 10 ⁻⁷		3.3 × 10 ⁻⁶	0.32	0.0066
Brij 58	4.49 × 10 ⁻⁴	1.01 × 10 ⁻⁷		3.7 × 10 ⁻⁶	0.37	0.0087
Tween 20	8.87 × 10 ⁻⁵	1.34 × 10 ⁻⁷		2.4 × 10 ⁻⁶	0.50	0.0076
Tween 80	7.64 × 10 ⁻⁵	1.45 × 10 ⁻⁷		3.7 × 10 ⁻⁶	0.51	0.0121
Tween 80 with TEA	7.64 × 10 ⁻⁵	1.24 × 10 ⁻⁷	2.00 × 10 ⁻⁶	4.4 × 10 ⁻⁶	0.54	0.0150

^a The intensity of light was determined with the ferrioxalate chemical actinometer. ^b Quantum yields and decay rates were determined at 253.7 nm in the Rayonet merry-go-round reactor.

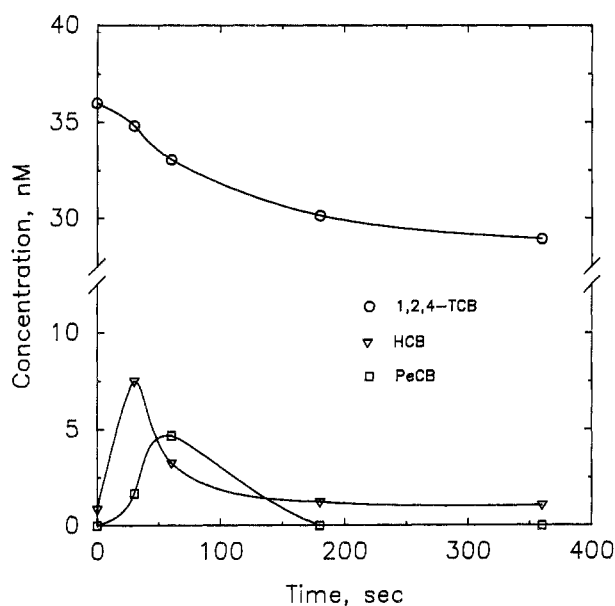
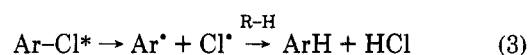


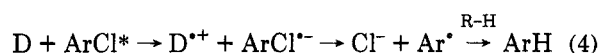
Figure 4. Decay of 1,2,4-TCB within 7.6 × 10⁻⁵ M Tween 80 solutions at 253.7 nm giving rise to some traces of HCB and PeCB as photochlorination products.

nitude (8.8 × 10⁻⁹ M to 3.3 × 10⁻⁷ M). After about 80–95% removal, however, the decay rate generally declines. Several possible explanations may account for this, including the following: (i) a substrate such as the hydrogen source may be near depletion, (ii) the photoproducts may significantly absorb light, acting as an internal light filter, (iii) photoproducts may act as quenchers, and (iv) the reaction may be reversible. Regarding iv, reaction reversibility was substantiated in some of our individual experiments, which showed that the photolysis of 1,3-DCB and 1,2,4-TCB gave rise to trace amounts of HCB and PeCB. Additionally, inhibition due to H⁺ accumulation will occur. These experiments will be discussed in detail later. Quantum yields were determined for HCB loss from the initial decay data shown in Figure 3. The results indicate that the quantum yield at 253.7 nm increases from 0.058 without surfactant to 0.29, 0.32, 0.37, 0.50, and 0.51 in the presence of SDS, Brij 35, Brij 58, Tween 20, and Tween 80, respectively (see Table 3 for experimental conditions).

The lower rate in DS solutions may be an effect of micellar charge. Photodechlorination of aryl halides in the presence of a hydrogen source and/or an electron donor may occur through two separate pathways or mechanisms, both resulting in the formation of an Ar–H bond from the Ar–Cl bond. The mechanisms are as follows: (i) C–Cl bond photolytic cleavage followed by radical scavenging

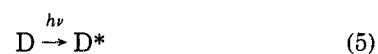


and (ii) an electron transfer process to a donor followed by decay of the radical anion

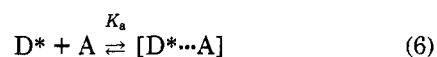


where in the latter case, the excited-state electron transfer between the donor (D) and the acceptor (A) involves five steps, as outlined by Whiten *et al.* (6):

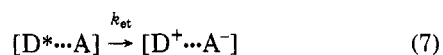
irradiation



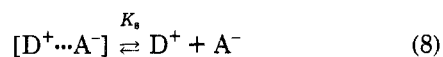
approach



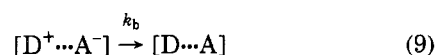
electron transfer



separation



decay



Presumably, the electron transfer process may be retarded by the negative charge on the micellar surface, which may expel the ArCl⁻ radical, an important intermediate in the latter mechanism.

Reaction Reversibility. As previously mentioned, evidence of reaction reversibility, resulting in photochlorination, was confirmed in some individual experiments. The photodecay of 3.6 × 10⁻⁸ M 1,2,4-TCB in the presence of 2.0 × 10⁻⁶ M triethylamine (TEA) resulted in maximum concentrations of 4.7 × 10⁻⁹ M PeCB and 7.5 × 10⁻⁹ M HCB (see Figure 4). Detector sensitivity likely precluded determination of tetrachloro compounds. In another experiment, upon illumination of 1.0 × 10⁻⁷ M HCB in 4.5 × 10⁻⁴ M Brij 58 solutions, trace amounts (≈10⁻⁹–10⁻¹⁰ M) of HCB reappear at 48 and 60 min after no detectable amounts at 24 and 36 min (see Figure 1).

Because the rate of photodecay increases with increasing chlorine substitution on the ring, the reverse reaction was only evident at low HCB (and PeCB) concentrations; at high concentrations, the forward reaction dominates.

Table 4. Photoisomerization Products Detected within Brij 58 Solutions at 253.7 nm

initial isomer	isomers formed upon illumination
1,3-DCB	1,2-DCB; 1,4-DCB
1,4-DCB	1,3-DCB
1,2-DCB	1,3-DCB; 1,4-DCB
1,3,5-TCB	1,2,4-TCB
1,2,4-TCB	1,2,3-TCB; 1,3,5-TCB
1,2,3-TCB	1,3,5-TCB; 1,2,4-TCB
1,2,3,5-TeCB	none
1,2,4,5-TeCB	none
1,2,3,4-TeCB	none

Table 5. Decay Quantum Yields of Polychlorinated Benzenes in Solutions of Brij 58 at 253.7 nm^a

compound	first-order photodecay rate (s ⁻¹)	quantum yield
1,3-DCB	1.40 × 10 ⁻³	0.053
1,4-DCB	1.34 × 10 ⁻³	0.35
1,2-DCB	1.35 × 10 ⁻³	0.37
1,3,5-TCB	1.07 × 10 ⁻³	0.33
1,2,4-TCB	1.21 × 10 ⁻³	0.32
1,2,3-TCB	1.10 × 10 ⁻³	0.50
1,2,3,5-TeCB	2.67 × 10 ⁻³	0.72
1,2,4,5-TeCB	1.88 × 10 ⁻³	0.58
1,2,3,4-TeCB	5.24 × 10 ⁻³	0.71
PeCB	1.47 × 10 ⁻²	0.66
HCB	1.44 × 10 ⁻²	0.40

^a Light intensity = 8.8 × 10⁻⁶ Einstein L⁻¹ s⁻¹ at 253.7 nm within the Rayonet merry-go-round photoreactor. Initial solutions were saturated with the respective di-, tri-, or tetrachlorobenzene in 5.00 × 10⁻⁴ M Brij 58.

Photodechlorination in Tween 80 solutions, under those conditions in which the most rapid rate was achieved, resulted in almost an oscillating profile of HCB at low concentration (around 3–4 × 10⁻⁹ M). Clearly, extensive scavenging of chlorine radicals by the aromatic rings occurs prior to ultimate ring cleavage.

Photoisomerization. Another minor pathway observed was photoisomerization. During the illumination of those compounds listed in Table 4, their structural isomers and other decay products were monitored. Isomers listed are those for which the concentration increased after irradiation times of 1–3 min. Direct photolysis in 5.0 × 10⁻⁴ M solutions of Brij 58 resulted in photoisomer products for all the dichloro- and trichlorobenzenes and no measurable isomers for any of the tetrachlorobenzenes. The latter observation may result from the more rapid decay rates of the TeCBs compared to the DCBs and TCBs. Quantum yields were calculated from the initial decay rates of the parent compounds in these experiments. This information along with quantum yields for PeCB and HCB are provided in Table 5.

It should be noted that all tri-, di-, and monochloro-substituted benzenes have lower micelle-water partition coefficients such that a major fraction of each of these species will reside in the water phase as opposed to the micellar pseudophase at the surfactant concentrations employed in these experiments. Hence, these reported quantum yields likely result from the summation of the reactions in each phase, with the reaction of the water-soluble fraction gaining significance as the partition coefficient decreases.

Final Products. Upon illumination of 4.5 × 10⁻⁵ M 1,2,4-TCB containing 9.8 × 10⁻⁴ M Brij 58, the chloride ion concentration increased from 9.4 × 10⁻⁷ to 1.1 × 10⁻⁴

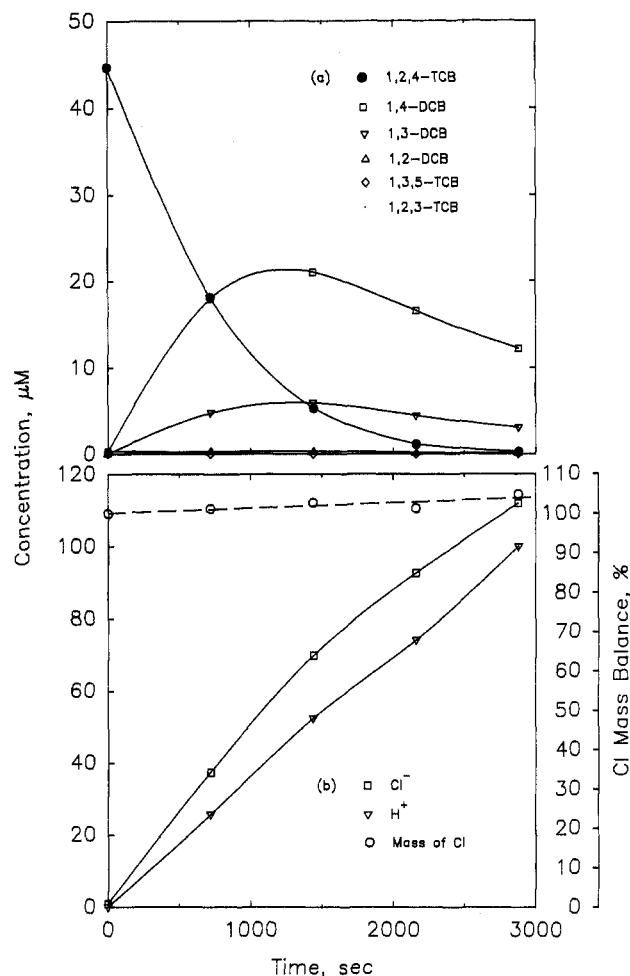


Figure 5. Photodecay of (a) 1,2,4-TCB within 9.8 × 10⁻⁴ M Brij 58 solutions at 253.7 nm and its decayed homologues and (b) the formation of the final products H⁺ and Cl⁻. The mass balance on chlorine (accounted for by all TCBs, DCBs, and Cl⁻) indicates a nearly perfect recovery.

M within 48 min. During the same time period, the pH of the reaction mixture decreased from 6.9 to 4.0. Assuming close to unity activity coefficients to calculate proton ion concentrations and assuming no buffer capacity, we find that chloride and proton ion concentrations are almost perfectly matched as a function of time (see Figure 5). Additionally, a total mass balance on chlorine (Cl⁻ and polychlorobenzene species) is balanced to within 4% of the initial 1,2,4-TCB chlorine content at each measurement time. This concurs with the absence of additional chlorinated products as observed by GC-MS and GC-ECD other than chlorobenzenes. The absence of biphenyl or chlorinated biphenyls as products is likely due to the compartmentalization effect of micelles, isolating radical aryl groups from other aryl groups, and reducing PCB formation from that known to occur in nonmicellar systems. With the main final product shown to be Cl⁻ (and H⁺, presumably from the hydrogen donor), complete dehalogenation at longer time periods is most likely assured.

Illumination of 1.9 × 10⁻⁴ M monochlorobenzene (MCB) in 8.5 × 10⁻³ M Brij 58 solutions ($\Phi = 0.83$) gave rise to phenol as a product with little to no measurable benzene produced over time. Phenol was also confirmed as a product of HCB decay in Brij 58 solutions by GC-MS. Hence, photohydrolysis occurs if no proper hydrogen source is present in the system. On the other hand, in the

presence of 5.0×10^{-3} M TEA, the decay of MCB ($\Phi = 0.49$) gave both phenol and benzene as final products in a ratio of approximately 1:10, indicating that, when an appropriate hydrogen source is present, a competition between photohydrolysis and photoreduction occurs.

Benzene itself was found to further decay. In the absence of a hydrogen source, the observed quantum yield was 0.28 at a concentration of 4.3×10^{-5} M benzene in 8.5×10^{-3} M Brij 58. Although products of benzene decay were not measured, other researchers have indicated the direct photoreaction of benzene in water results in aldehydes, organic acids, and CO_2 (26).

Hydrogen Sources. Selected chemicals were tested for their ability to act as hydrogen sources. These included triethylamine (TEA), 1,3-phenylenediamine (1,3-PDA), aniline, acetone, and sodium borohydride. Irradiation of 3.5×10^{-7} M HCB in 1.5×10^{-4} M Tween 80 solutions in the presence of 1.0×10^{-4} M of each of the five hydrogen sources resulted in no significant increase in the decay rate. Similar results were obtained when 5.0×10^{-4} M Brij 58 was used in place of Tween 80. Here, observed initial quantum yields were 0.27, 0.29, 0.32, 0.34, 0.36, and 0.38 for 1,3-PDA, sodium borohydride, TEA, the blank, aniline, and acetone, respectively. This observation is not surprising if chemical distribution again is considered. The affinity each of these H-donors has for the micellar core is considerably less than that for water. Hence, isolation of HCB within the micellar core away from these species in the water phase would lead to no enhancement if the reaction of free radical intermediates with other sources is more rapid than diffusion from the micelle to the water phase.

Although no appreciable effect on HCB decay was observed in these experiments, this (10^{-4} M) and lower concentrations of H-donors altered product distribution in a couple of ways. First, addition of the aromatic hydrogen sources (1,3-PDA and aniline) under these conditions resulted in an increasing mass of chloro-substituted benzene rings, by as much as 20%, shortly after initiating irradiation even without accounting for monochlorobenzene, phenol, and benzene, which are not detectable with the ECD at the applied initial dose of HCB (3.5×10^{-7} M). Hence, this increase in mass of chlorinated benzene rings indicates that these aromatic H-donors or their decay products participate in photochlorination. Second, the addition of 2×10^{-6} M TEA to a 7.6×10^{-5} M Tween 80 solution resulted in either a change in the overall decay pathway or the TEA significantly increased the rate of tri- and dichlorobenzene decay, as no TCBs or DCBs were detected. Note that these compounds will reside predominately in the water phase with TEA. Hence, the decay of these more water-soluble compounds is likely enhanced such that their rate of decay is greater than their rate of formation.

If we increase TEA to 5×10^{-3} M, the observed quantum yield for HCB decreases to 0.015. However, at this concentration, TEA may act as a chemical filter, absorbing most of the incident light. The absorbance ratio ($\epsilon_{\text{TEA}}C_{\text{TEA}}/\epsilon_{\text{HCB}}C_{\text{HCB}}$), where ϵ_{HCB} (at 253.7 nm) is $2782 \text{ M}^{-1} \text{ cm}^{-1}$ and ϵ_{TEA} is $29.8 \text{ M}^{-1} \text{ cm}^{-1}$, is calculated to be 306. Additionally, TEA itself may act as a free radical quencher (27), explaining the quite variable dechlorination rates observed by Epline *et al.* for difference PCB congeners in 0.05 M TEA (12).

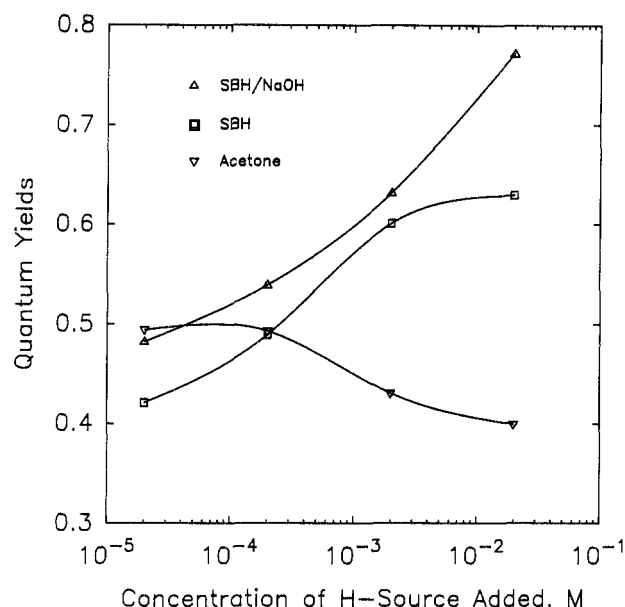


Figure 6. Quantum yield for the photodecay of HCB within 4.0×10^{-4} M Brij 58 solutions at 253.7 nm as a function of hydrogen source concentration. Sodium borohydride shows a positive effect at high concentration, especially in basic solutions.

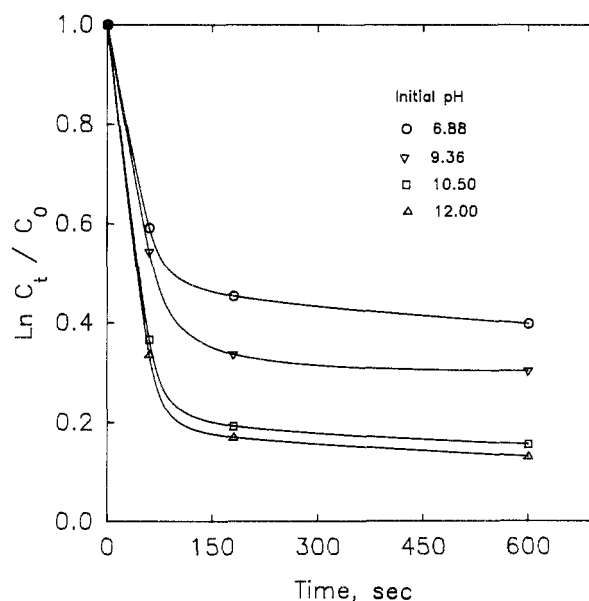


Figure 7. Photodechlorination rate (and extent of reaction) of HCB within 4.6×10^{-4} M Brij 58 solutions at 253.7 nm at difference initial pH values.

Alternatively, higher concentrations of SBH resulted in a distinctive increase in the quantum yield of HCB decay, as shown in Figure 6. Compared with 88% decay without SBH ($\Phi = 0.49$) after 2 min of irradiation, about 94% was decayed with 2.0×10^{-2} M SBH present ($\Phi = 0.63$). A slightly higher efficiency was further achieved when the stock SBH solution was prepared in 2% NaOH: This improved the fraction removed in 2 min of irradiation to 97% ($\Phi = 0.77$).

Although, the initial HCB decay was found to be relatively independent of hydrogen ion concentration, one of the final reaction products is H^+ . Hence, at the higher pH values, this product is consumed by OH^- , possibly decreasing the rate of the back-reaction resulting in an apparent increase in the forward rate. This hypothesis is consistent with the data in Figure 7 that indicate that,

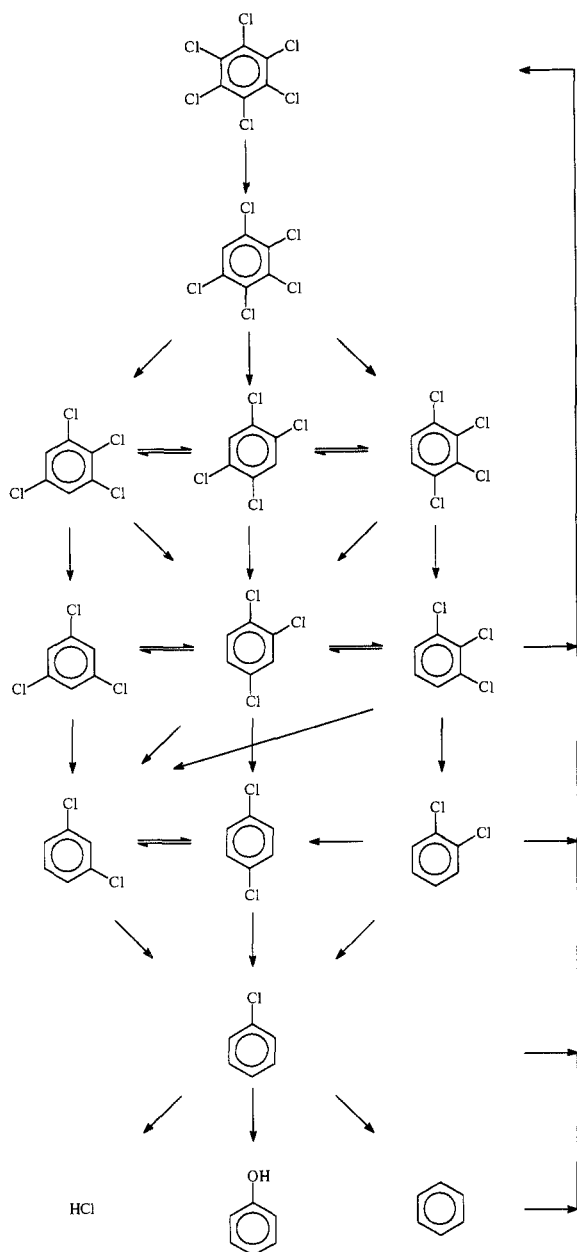


Figure 8. Photoreaction pathways of polychlorobenzenes in Brij 58 solutions at 253.7 nm. Pathways indicated include photodechlorination, photochlorination, photoisomerization, and photohydrolysis reactions.

while the initial decay rate of 1.7×10^{-7} M HCB in 4.6×10^{-4} M Brij 58 solutions is largely invariant with pH, progression of the reaction is hindered at the lower pH values. The instability of SBH in water under acidic conditions may result in the slightly increased initial rate of decay at the higher pH values (see Figure 6).

Contrary to the small catalytic effect of acetone at low concentrations, inhibition was observed at higher concentrations as shown in Figure 6. As with TEA, high concentrations of acetone may act as a chemical filter. The molar absorptivity of acetone at 253.7 nm is $11 \text{ M}^{-1} \text{ cm}^{-1}$; about 250 times lower than that of HCB ($2782 \text{ M}^{-1} \text{ cm}^{-1}$). However, at 10^{-3} M acetone (compare to 3.0×10^{-8} M of HCB), the light absorbed by acetone is not negligible.

Conclusions

We have reported on results of HCB photodegradation utilizing four nonionic and one anionic surfactant. The

initial quantum yield for HCB decay increased from 0.058 in distilled water (after an initial lag phase) to 0.29, 0.32, 0.37, 0.50, and 0.51 in the presence of SDS, Brij 35, Brij 58, Tween 20, and Tween 80, respectively. The photo-products—pentachlorobenzene, all tetra-, tri-, and dichlorobenzenes, monochlorobenzene, benzene, phenol, H⁺, and Cl⁻—were observed. Clearly, the overall photochemical kinetic process or mechanism leading to these products is complex. In addition to the main reductive pathway of photodechlorination, at least three minor pathways exist within the reacting system. They include photochlorination, photohydrolysis, and photoisomerization. With initial rate studies, we have shown that all the dechlorination steps indicated with arrows in Figure 8 occur in Brij 58 micellar solutions. Note that all possible reactions were not observed during these initial rate studies; however, inclusion of the observed photoisomerization reactions suggests that all possible products may occur for each compound, albeit at minor concentrations.

The addition of H sources, specifically SBH, further enhanced the photodechlorination rates. It is apparent that the decay quantum yield depends on the concentration and the molar absorptivity of each H source and the affinity of the H source and reacting species for the micellar phase.

Clearly, some potential exists for future application of this process in soil restoration. In ongoing studies to be reported on soon, we additionally have shown that the photoreduction of HCB and Aroclor mixtures, either extracted from sediment with surfactant or spiked into solutions containing surfactant-extracted humic material, was found to occur at rates, under some conditions, comparable to those reported herein.

Acknowledgments

Support for this project was provided through a grant from the Purdue Research Foundation. The authors would like to acknowledge Richard Larson (University of Illinois) and Richard Zepp (U.S. EPA, Athens, GA) for the helpful suggestions and comments which they graciously provided throughout this study and to give special thanks to Karen Marley (University of Illinois) who performed the GC-MS analysis on our samples.

Literature Cited

- (1) Jafvert, C. T., Rogers, J. E., Eds. *Biological Remediation of Contaminated Sediments, with special emphasis on the Great Lakes*; EPA/600/9-91/001; Jan 1991.
- (2) Wayt, H. J.; Wilson, D. J. *Sep. Sci. Technol.* **1989**, *24*, 905-937.
- (3) Vigon, B. W.; Rubin, A. J. *J. Water Pollut. Control Fed.* **1989**, *61*, 1233-1240.
- (4) Clark, A. N.; Mutch, R. D.; Wilson, D. J.; Oma, K. H. *Water Sci. Technol.* **1992**, *26*, 127-135.
- (5) Freeman, P. K.; Hatlevig, S. A. Preprint Extended Abstract, Presented at the American Chemical Society Annual Meeting, Division of Environmental Chemistry, San Francisco, CA, Apr 5-10, 1992; *Preprint of Extended Abstracts*, pp 272-275.
- (6) Whiten, D. G.; Russell, J. C.; Schmehl, R. H. *Tetrahedron* **1982**, *38*, 2455-2487.
- (7) Jafvert, C. T. *Environ. Sci. Technol.* **1991**, *25*, 1039-1045.
- (8) Kile, D. E.; Chiou, C. T. *Environ. Sci. Technol.* **1989**, *23*, 832.
- (9) Jafvert, C. T.; Heath, J. K.; Hoof, P. L. V. *Water Res.* **1994**, *28*, 1009-1017.
- (10) Jafvert, C. T.; Heath, J. K. *Environ. Sci. Technol.* **1991**, *25*, 1031-1038.

- (11) Zepp, R. G.; Wolfe, N. L.; Gordon, J. A.; Baughman, G. L. *Environ. Sci. Technol.* **1975**, *9*, 1144-1149.
- (12) Epline, G. A.; Florio, E. M.; Bourque, A. J.; Qian, X. H.; Stuart, J. D. *Environ. Sci. Technol.* **1988**, *22*, 952-956.
- (13) Zepp, R. G.; Cline, D. M. *Environ. Sci. Technol.* **1977**, *11*, 359-366.
- (14) Hutala, R. R.; Zepp, R. G. *Surfactants Effect on Pesticide Photochemistry in Water and Soil*; EPA-600/3-78-060; U.S. EPA: Washington, DC, 1978.
- (15) Epline, G. A.; Florio, E. M. *J. Chem. Soc. Perkin Trans. 1* **1988**, 703-706.
- (16) Hawari, J.; Demeter, A.; Greer, C.; Samson, R. *Chemosphere* **1991**, *22*, 1161-1174.
- (17) Freeman, P. K.; Ramnath, N. *J. Org. Chem.* **1991**, *56*, 3646-3651.
- (18) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.
- (19) Simons, W. W. *The Sadtler Handbook of Ultraviolet Spectra*; Sadtler Research Laboratories: Philadelphia, PA, 1979.
- (20) Lang, L. *Absorption Spectra in the Ultraviolet and Visible Region*; Hungarian Academy of Sciences: Budapest, 1959.
- (21) Friedel, R. A.; Orchin, M. *Ultraviolet Spectra of Aromated Compounds*; Wiley: New York, 1951.
- (22) Parke, D. V. *Biochem. J.* **1960**, *74*, 5-8.
- (23) Conrad-Billroth, H. *Z. Phys. Chem.* **1932**, *19*, 76-83.
- (24) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London* **1956**, *235A*, 518-536.
- (25) Choudhry, G. G.; Webster, G. R. *Photochemistry of Environmental Aquatic System*; Cooper, W. J., Zika, R. G., Eds.; American Chemical Society: Washington, DC, 1987; pp 61-73.
- (26) Bolton, J. R.; Cater, S. R. *Aquatic and Surface Photochemistry*; Helz, G. R., Zepp, R. G., Crosby, D. G., Eds.; CRC Press Inc.: Boca Raton, FL, 1994; pp 480-481.
- (27) Loudon, G. M. *Organic Chemistry*, 2nd ed.; Benjamin/Cummings Publishing Co., Inc.: Menlo Park, CA, 1988; pp 159-161.

Received for review June 27, 1994. Accepted August 15, 1994.*

* Abstract published in *Advance ACS Abstracts*, September 15, 1994.