the cycloadduct **12** in yields ranging from 47% to 89%. For selected physical and spectral data of the adducts, see Table VII.

**Epoxidation of the *N*-Phenylmaleimide Adducts. (3a$\alpha$,4$\alpha$,5$\alpha$,8$\alpha$,8a$\alpha$,9$\alpha$,9a$\alpha$)-3a,4,5,6,7,8,9,9a-Octahydro-10-[(4-methoxyphenyl)methylene]-2-phenyl-4a,8a-epoxy-4,9:5,8-dimethano-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (13-OMe).** To a solution of **12**-OMe (50 mg, 0.1 mmol) in dry dichloromethane (10 mL) at 0 °C was added MCPBA (0.039 g) in dry dichloromethane (10 mL). The reaction mixture was stirred at 0 °C for 4 h and washed with 5% sodium thiosulfate solution (3 × 25 mL), saturated sodium bicarbonate solution (4 × 25 mL), and water (25 mL). The organic layer was dried, filtered, and concentrated to give a pale yellow residue. Purification by radial chromatography (silica gel, 1-mm plate, 30% ethyl acetate in petroleum ether) gave 0.052 g (99%) of the epoxide as a white powder: mp 245–246 °C; IR ($CHCl_3$, cm$^{-1}$) 3030, 3000, 2990, 2940, 1770, 1710, 1605, 1510, 1385, 1295, 1250, 1190, 1035, 885, 830, 690, 660; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.38–7.32 (m, 3 H), 7.15 (d, $J$ = 9 Hz, 2 H), 6.99–6.96 (m, 2 H), 6.81 (d, $J$ = 9 Hz, 2 H), 6.10 (s, 1 H), 4.29 (s, 1 H), 3.78 (s, 3 H), 3.62 (s, 3 H), 2.94 (s, 2 H), 1.90 (d, $J$ = 9 Hz, 1 H), 1.81–1.70 (m, 3 H), 0.84 (d, $J$ = 9 Hz, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm) 176.34, 176.04, 158.76, 137.69, 131.55, 129.10, 129.05, 128.71, 126.46, 119.82, 113.94, 57.59, 57.38, 55.20, 51.77, 46.66, 46.53, 46.15, 40.78, 40.68, 37.51, 26.58, 26.44; MS $m/z$ ($M^+$) calcd 439.1783, obsd 439.1819.

**Prototypical Cycloaddition of 11 with Dimethyl Acetylenedicarboxylate.** A solution of **11** (0.4 mmol) and dimethyl acetylenedicarboxylate (74 $\mu$L, 0.6 mmol) in dry benzene (10 mL) was evacuated and flushed with nitrogen several times. The reaction mixture was warmed to 60–65 °C and stirred for 1–3 days under nitrogen. Evaporation of the solvent provided oily residues, which were purified by MPLC on silica gel (elution with 20–25% ethyl acetate in petroleum ether) to afford cycloadducts **14** along with the corresponding epoxides **15**. Yields range from 52% to 69%.

**Prototypical Cycloaddition of 11 with Benzyne.** A solution of **11** (0.4 mmol) in dry dimethoxyethane (5 mL) was warmed to reflux under a nitrogen atmosphere. Solutions of anthranilic acid (66 mg, 0.5 mmol) in dimethoxyethane (5 mL) and isoamyl nitrite (90 $\mu$L, 0.7 mmol) in dimethoxyethane (5 mL) were added dropwise, simultaneously from separate addition funnels. After addition was complete, the reaction mixture was stirred at reflux for 1–3 h. Removal of the solvent followed by chromatography on silica gel (elution with 1–2% ethyl acetate in petroleum ether) gave cycloadducts **16** in yields of 27–78% overall.

**Prototypical Epoxidation of 16.** To a cold (0 °C) bicarbonate-buffered solution of **16** (0.06–0.27 mmol) in dichloromethane (5–10 mL) was added 1.5 equiv of MCPBA in a single portion. The reaction mixture was stirred at this temperature for 4 h, washed with 5% sodium thiosulfate (4 × 25 mL) and saturated sodium bicarbonate solutions (3 × 25 mL), dried, filtered, and concentrated to give nearly pure epoxides. Column chromatography on silica gel (elution with 2–5% ethyl acetate in petroleum ether) gave pure samples of **17**. Yields ranged from 41% to 76%.

**Prototypical Cycloaddition of 11 with (*Z*)-1,2-Bis(phenylsulfonyl)ethylene.** A solution of **11** (0.20 mmol) and the disulfone (300 mg, 1.0 mmol) in dry dichloromethane (2 mL) was pressurized to 90 000 psi for 3–7 days. Removal of the solvent followed by MPLC purification on silica gel (elution with 35–40% ethyl acetate in petroleum ether) gave adducts **18** and **19**. Small amounts of adducts arising from the *trans*-disulfone isomer were detected but were not characterized.

**Acknowledgment**. Financial support from the National Cancer Institute (Grant CA-12115) is gratefully acknowledged. We thank Professor Rolf Gleiter (Heidelberg) for his eager willingness to record the PE data and carry out the associated molecular orbital calculations.

**Supplementary Material Available:** Spectral and analytical data for compounds of type **12–15** and **17–19** (21 pages). Ordering information is given on any current masthead page.

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# Studies of the Antenna Effect in Polymer Molecules. 23. Photosensitized Dechlorination of 2,2′,3,3′,6,6′-Hexachlorobiphenyl Solubilized in an Aqueous Solution of Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene)

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*Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.* *Received June 5, 1990*

**Abstract:** Photodechlorination of 2,2′,3,3′,6,6′-hexachlorobiphenyl (HCB) solubilized in an aqueous solution of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) was studied with use of solar-simulated radiation. The reaction was found to be photosensitized by the naphthalene antenna units present in the copolymer. Studies performed in a low molecular weight model system have shown that dechlorination of HCB may occur via an exciplex intermediate. Exciplex formation in the system is efficient because of the high local concentration of HCB in proximity to the naphthalene polymeric units.

## Introduction

In previous papers in this series, it has been shown that novel antenna polyelectrolytes commonly referred to as "photozymes" behave as efficient photocatalysts.[1-9] In aqueous solutions these polymers adopt a pseudomicellar conformation that results in the formation of hydrophobic microdomains that are capable of solubilizing sparingly water-soluble organic compounds. Aromatic chromophores such as naphthalene, anthracene, phenanthrene, or carbazole incorporated in the polymer chain absorb light from the near-UV–visible spectral region. Excitation energy may then be used to induce photochemical reactions involving molecules solubilized within the polymer. It has been shown that the

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polymers photosensitized the unimolecular photolysis of 2-undecanone[1] as well as the bimolecular oxidation of polynuclear aromatic compounds (PNA)[2] or styrene.[9]

Polychlorinated biphenyls (PCBs) have been widely used by industrialized nations, mainly as dielectric and cooling fluids, with excellent performance. Unfortunately, they are also recognized as almost universally distributed pollutants that are generally considered to be resistant to environmental degradation. Studies of bacterial degradation on mixtures of commercially used PCBs in aerobic conditions have shown that the process is generally more efficient for mono- and dichlorobiphenyls than it is for highly chlorinated components.[10,11] Also, bacterial attack on chlorinated biphenyls has been shown to be stereospecific.[12-14] Dechlorination occurs primarily from the meta and para positions. The bacterial strains *Alcaligenes eutrophus* H 850 have been shown to be effective in the degradation of a mixture of PCBs under aerobic conditions.[15,16]

Photochemical dechlorination has been suggested as a possible alternative method of decomposition of PCBs under environmental conditions.[17-19] The efficiency of the process is, however, limited due to the low absorption of PCBs in the solar spectral region[20] (as a result of their low extinction coefficients and low concentrations in water) and because the dechlorination reaction that involves hydrogen abstraction from water is very slow, even during irradiation with highly energetic light at $\lambda = 254$ nm.[21]

Photozymes may provide an ideal way to increase the efficiency of the photochemical reaction of PCBs under environmental conditions. This paper reports studies of the photosensitized dechlorination of 2,2′,3,3′,6,6′-hexachlorobiphenyl (HCB) solubilized in an aqueous solution of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN). In order to gain better insight into the mechanism of the process, only one isomer was used instead of commercial mixtures of PCBs.

## Experimental Section

**Materials.** Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) was synthesized and purified according to the method previously described.[1]

2,2′,3,3′,6,6′-Hexachlorobiphenyl (99%) and other PCB congeners (all obtained from Chem Sources Inc.) were used as received. Naphthalene (N, Aldrich 99+% Gold Label) was recrystallized three times from spectral-grade methanol.

2,2-Di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH, Aldrich, 98%) was used without further purification.

Sodium sulfate (BDH, ACS reagent grade) and Florisil (Aldrich, 60–100 mesh, reagent grade) were activated, stored at 130 °C, and used without purification.

Dichloromethane (Caledon, ACS reagent grade), hexane (Caledon, ACS reagent grade), isooctane (Aldrich, HPLC grade), and acetone (Caledon, spectrograde) were used without further purification. Distilled water was deionized by use of a Millipore Milli-Q water purification system.

**Procedures. Solubilization of HCB.** Solubilization of HCB in aqueous polymer solutions (2 g $dm^{-3}$) was achieved by slowly injecting microliter quantities of probe ($1 \times 10^{-3}$ M) dissolved in acetone in milliliter quantities of polymer solution. The mixture was shaken for 5 min and equilibrated in the dark for 2–4 h.

Solar-simulated irradiations were performed by using an apparatus described in detail elsewhere.[22]

Irradiations with monochromatic light at $\lambda = 280$ nm were carried out with a deep-UV constant-intensity control system (Optical Associates Model 780). The incident light intensity was determined by using a ferrioxalate actinometer; $I_0 = 6.87 \times 10^{-7}$ einstein $dm^{-3}\ s^{-1}$.[23]

**Gas Chromatographic Analysis.** Quantitative and qualitative analyses of the systems studied were carried out with use of a Hewlett-Packard 5890 gas chromatograph equipped with both flame ionization (FID) and electron capture detectors (ECD) and Hewlett-Packard HP-5 capillary column (25 m, 0.2-mm inside diameter, 0.11-μm film thickness). The HP-5 liquid phase is 5% diphenyl- and 95% dimethylpolysilane. The chromatographic conditions were as follows: split injection (10:1 ratio), injection port at 220 °C, FID detector at 270 °C, ECD detector at 300 °C, column temperature from 120 to 240 °C at a rate of 2 °C/min. Helium (Linde, ECD grade) was used as the carrier gas. Flow rate was adjusted to 1.77 mL/min.

Samples for the analysis were prepared as follows. Isooctane (1 mL) was added to the aqueous polymer solution (100 mL) containing solubilized HCB. The resulting solution was extracted in triplicate with dichloromethane (15 mL). The extracts were dried with sodium sulfate, then concentrated to 1 mL, and subsequently passed through a miniature (20-cm-long) Florisil column eluted with hexane. The resulting solution was concentrated (to 1 mL) and analyzed.

Peak identifications were based on matching retention times of the components of the analyzed mixture to known standard compounds (biphenyl, 2-chlorobiphenyl, 2,2′-dichlorobiphenyl, 2,2′,3,3′-tetrachlorobiphenyl, 2,2′,6,6′-tetrachlorobiphenyl, and 2,2′,3,3′,6,6′-hexachlorobiphenyl) as well as by comparison to the published relative retention indices.[24]

Concentrations of the substrate and products were determined by use of a calibration performed by injecting a mixture of known composition and defined concentration and determining the respective peak area.

**Gas Chromatography–Mass Spectra Measurements.** The GC–MS spectra of the irradiated samples were measured with use of a Hewlett-Packard 5890 gas chromatograph interfaced with a VG70-250S mass spectrometer (chemical ionization).

**Ultraviolet Spectra Measurements.** UV absorption spectra of the samples were measured with use of a Hewlett-Packard 8451A diode-array spectrophotometer.

**Fluorescence Spectra Measurements.** Steady-state fluorescence spectra of the samples were recorded at room temperature and at 77 K on a Spex Fluorolog-2 fluorescence spectrometer.

## Results and Discussion

**Photochemical Reactions of HCB Solubilized in Aqueous Solutions of PSSS-VN.** Accurate determination of the solubility of chlorinated biphenyls in water is complicated by their strong absorption on the surface of the measuring vessels. On the basis of data in the literature,[25] the solubility of HCB in water is estimated to be $\sim 2.2 \times 10^{-8}$ mol $dm^{-3}$. The solubility of HCB increases considerably, however, in the presence of PSSS-VN. The amount of the HCB that could be dissolved in aqueous solutions of PSSS-VN increases steadily with increase in polymer concentration. This is due to the solubilization of the compound in the hydrophobic microdomains created within the polymeric chain due to the clustering of hydrophobic naphthalene units in contact with water. By use of a method described previously,[9] the distribution coefficient for HCB between the polymeric pseudophase and water was estimated to be $(7.6 \pm 0.5) \times 10^4$. The distribution coefficient ($K$) was defined as the ratio of the weight fraction of

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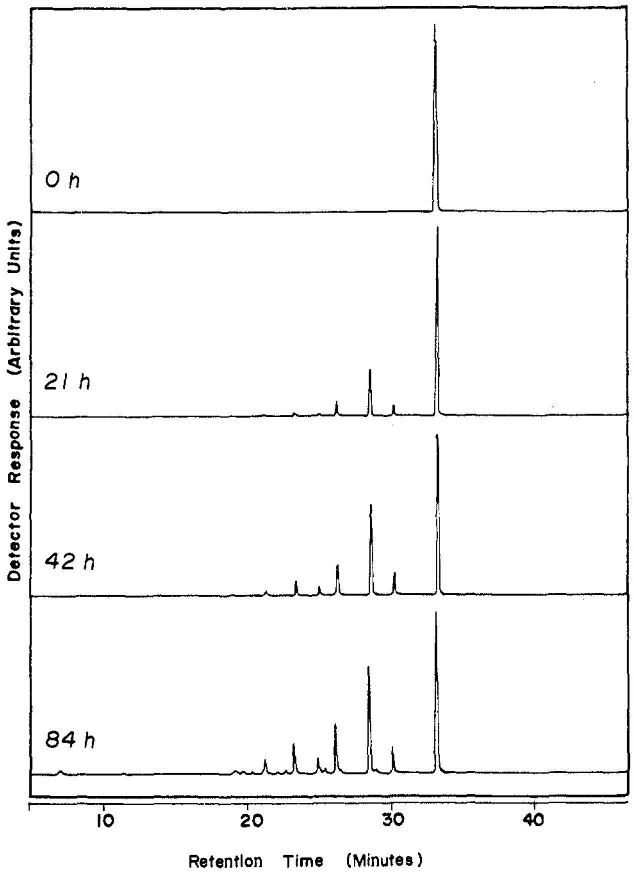

Figure 1. GC traces for HCB before and after irradiation in aqueous solutions of PSSS-VN with solar-simulated radiation for 21, 42, and 82 h. All chromatograms were normalized. An electron-capture detector was used. GC conditions are given in text.

Table I. Composition of the Reaction Mixture Obtained after Irradiation of 2,2',3,3',6,6'-Hexachlorobiphenyl Solubilized in an Aqueous Solution of PSSS-VN[a]

| PCB congener | retention time (min) | congener distrib (mol %) |
|---|---|---|
| biphenyl | 5.09 | 4.8 |
| 2,6-dichlorobiphenyl | 10.14 | 1.5 |
| 2,2'-dichlorobiphenyl | 10.38 | 3.5 |
| 2,3-dichlorobiphenyl | 13.98 | 1.3 |
| 2,2',5-trichlorobiphenyl | 16.31 | 1.2 |
| 2,2',3-trichlorobiphenyl | 18.06 | 1.2 |
| 2,2',5,6'-tetrachlorobiphenyl | 21.31 | 0.7 |
| 2,2',3,6-tetrachlorobiphenyl | 22.31 | 1.0 |
| 2,2',5,5'-tetrachlorobiphenyl | 23.42 | 2.0 |
| 2,2',3,5'-tetrachlorobiphenyl | 25.07 | 0.6 |
| 2,2',3,6,6'-pentachlorobiphenyl | 26.40 | 4.4 |
| 2,2',3,5',6-pentachlorobiphenyl | 28.83 | 13.7 |
| 2,2',3,3',6-pentachlorobiphenyl | 30.56 | 2.2 |
| 2,2',3,3',6,6'-hexachlorobiphenyl | 33.66 | 61.9 |

[a] Twenty-four hours at $\lambda = 280$ nm.

HCB in the polymeric pseudophase ($\chi_{HCB}^{p}$) to the weight fraction of HCB in water ($\chi_{HCB}^{aq}$): $K = \chi_{HCB}^{p}/\chi_{HCB}^{aq}$. As was shown previously, the fact that the molecules of the probe are solubilized in a limited volume in the polymeric pseudophase results in its high local concentration.[26] This may facilitate the photochemical reactions of the probe in the system.

Irradiation of aqueous solutions of PSSS-VN containing solubilized HCB was performed with monochromatic light at 280 nm and with solar-simulated radiation in a nitrogen atmosphere. Photochemical reactions were followed by GC analysis. Figure 1 shows the GC traces obtained for the system before and after irradiation with solar-simulated radiation. Dechlorination of HCB was evident from a simple visual inspection of the chromatograms of the irradiated samples. GC patterns obtained for the samples irradiated with monochromatic light ($\lambda = 280$ nm) were similar to those obtained for the systems irradiated with solar-simulated radiation. The appearance of peaks characterized by shorter retention times indicates the formation of new compounds containing less chlorine atoms per molecule than the starting material, HCB.[24] By use of GC traces of known model compounds, literature data,[24] and GC–mass spectra, it was possible to identify the major products formed during irradiation. Table I presents the composition of the reaction mixture obtained after 24 h of irradiation of HCB (50 ppm) solubilized in aqueous solution of PSSS-VN ($c_{pol} = 2$ g dm$^{-3}$) with monochromatic light at $\lambda = 280$ nm. On the basis of product analysis, it can be concluded that the photoreaction consists of dechlorination of HCB. It has been observed that the reaction initiated with solar radiation results in the formation of similar major products. Table II presents the composition of the reaction mixture formed during irradiation of HCB (1.6 ppm) in aqueous solution of PSSS-VN with solar light for different periods of time. The content of HCB decreases considerably during the reaction, and the reaction mixture becomes subsequently richer in the less chlorinated biphenyls. Figure 2 illustrates the dependence of the HCB conversion on the irradiation

Table II. Composition of the Reaction Mixture Obtained after Solor-Simulated Irradiation of 2,2',3,3',6,6'-Hexachlorobiphenyl Solubilized in an Aqueous Solution of PSSS-VN

| PCB congener | retention time (min) | congener distrib (mol %) at irrad time (h) 21 | 42 | 84 |
|---|---|---|---|---|
| 2-monochlorobiphenyl | 7.63 | 0.0 | 0.0 | 15.1 |
| 2,2',6-trichlorobiphenyl | 15.90 | 0.0 | 0.0 | 0.6 |
| 2,2',5-trichlorobiphenyl | 16.80 | 0.0 | 0.5 | 0.6 |
| 2,2',3-trichlorobiphenyl | 18.99 | 0.0 | 0.0 | 0.5 |
| 2,2',6,6'-tetrachlorobiphenyl | 19.22 | 0.0 | 0.2 | 0.6 |
| 2,3',5-trichlorobiphenyl | 19.73 | 0.2 | 0.7 | 0.9 |
| 2,2',5,6'-tetrachlorobiphenyl | 21.31 | 0.7 | 2.6 | 4.3 |
| 2,2',3,6-tetrachlorobiphenyl | 22.31 | 0.1 | 0.2 | 0.3 |
| 2,2',3,6'-tetrachlorobiphenyl | 22.88 | 0.0 | 0.4 | 0.6 |
| 2,2',5,5'-tetrachlorobiphenyl | 23.42 | 1.5 | 4.8 | 6.3 |
| 2,2',3,5'-tetrachlorobiphenyl | 25.07 | 0.6 | 2.6 | 3.2 |
| 2,2',3,6,6'-pentachlorobiphenyl | 26.40 | 6.2 | 9.6 | 11.3 |
| 2,2',3,5',6-pentachlorobiphenyl | 28.83 | 17.8 | 26.2 | 20.5 |
| 2,2',3,3',6-pentachlorobiphenyl | 30.56 | 4.4 | 7.3 | 5.8 |
| 2,2',3,3',6,6'-hexachlorobiphenyl | 33.66 | 68.5 | 44.9 | 29.4 |

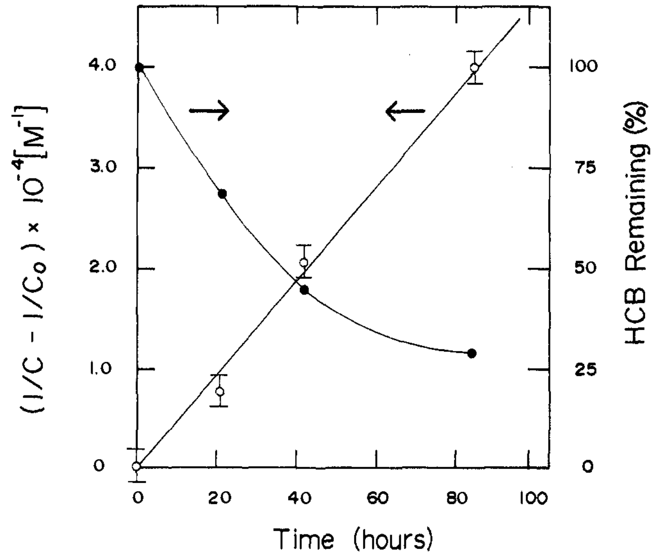

Figure 2. Plot of the changes in HCB concentration versus irradiation time according to the second-order kinetic equation ($1/c - 1/c_0$, where $c$ and $c_0$ are the concentrations of HCB at irradiation times $t = t$ and $t = 0$, and dependence of HCB concentration on irradiation time.

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**Table III.** Composition of the Reaction Mixture Obtained after Solar-Simulated Irradiation of 2,2′,3,3′,6,6′-Hexachlorobiphenyl Solubilized in an Aqueous Solution of PSSS-VN before and after Degassing

| PCB congener | retention time (min) | congener distrib (mol %) | | |
|---|---|---|---|---|
| | | before | $N_2$ | $O_2$ |
| 2-monochlorobiphenyl | 7.63 | 8.1 | 0.0 | 0.0 |
| 2,2′,5-trichlorobiphenyl | 16.80 | 0.2 | 0.0 | 0.4 |
| 2,3′,5-trichlorobiphenyl | 20.39 | 0.2 | 0.2 | 0.4 |
| 2,2′,5,6′-tetrachlorobiphenyl | 21.31 | 0.5 | 0.7 | 0.5 |
| 2,2′,3,6-tetrachlorobiphenyl | 22.31 | 0.0 | 0.1 | 0.0 |
| 2,2′,5,5′-tetrachlorobiphenyl | 23.42 | 0.7 | 1.5 | 0.5 |
| 2,2′,3,5′-tetrachlorobiphenyl | 25.07 | 0.4 | 0.6 | 0.3 |
| 2,2′,3,6,6′-pentachlorobiphenyl | 26.40 | 4.5 | 6.2 | 4.2 |
| 2,2′,3,5′,6-pentachlorobiphenyl | 28.83 | 12.0 | 17.8 | 10.2 |
| 2,2′,3,3′,6-pentachlorobiphenyl | 30.56 | 3.2 | 4.4 | 2.6 |
| 2,2′,3,3′,6,6′-hexachlorobiphenyl | 33.66 | 70.2 | 68.5 | 80.9 |

**Table IV.** Composition of the Reaction Mixtures Obtained after Solar-Simulated Irradiation of 2,2′,3,3′,6,6′-Hexachlorobiphenyl Solubilized in Various Solvents[a]

| PCB congener | retention time (min) | congener distrib (mol %) | | |
|---|---|---|---|---|
| | | PSSS-VN(aq) | hexane | water |
| 2,2′,6,6′-tetrachlorobiphenyl | 19.22 | 0.0 | 0.5 | 0.0 |
| 2,3′,5-trichlorobiphenyl | 19.77 | 0.2 | 0.0 | 0.2 |
| 2,2′,5,6′-tetrachlorobiphenyl | 21.31 | 0.7 | 1.9 | 0.0 |
| 2,2′,3,6-tetrachlorobiphenyl | 22.31 | 0.1 | 0.0 | 0.1 |
| 2,2′,5,5′-tetrachlorobiphenyl | 23.42 | 1.5 | 1.0 | 0.0 |
| 2,2′,3,5′-tetrachlorobiphenyl | 25.07 | 0.6 | 0.1 | 0.0 |
| 2,2′,3,6,6′-pentachlorobiphenyl | 26.40 | 6.2 | 12.1 | 1.9 |
| 2,2′,3,5′,6-pentachlorobiphenyl | 28.83 | 17.8 | 18.6 | 0.8 |
| 2,2′,3,3′,6-pentachlorobiphenyl | 30.56 | 4.4 | 0.3 | 0.2 |
| 2,2′,3,3′,6,6′-hexachlorobiphenyl | 33.66 | 68.5 | 65.5 | 96.8 |

[a] Key: irradiation time, 21 h; starting concentration of HCB solubilized in PSSS-VN, $4.4 \times 10^{-6}$ M; hexane, $4.4 \times 10^{-6}$ M; water, $2.2 \times 10^{-8}$ M.

time as well as the fit of the experimental data to the second-order kinetic equation. It can be noticed that the fit is reasonably good, which indicates that the observed reaction is a second-order process.

The rate (as well as extent) of dechlorination is considerably influenced by the presence of oxygen and also by the type of reaction medium. Table III shows the results of irradiating the aqueous solutions of PSSS-VN containing solubilized HCB in air atmosphere (no degassing), saturated with nitrogen, and saturated with oxygen. In each case, dechlorination is the major photoreaction. The presence of oxygen inhibits photodechlorination. This can be explained by taking into account the fact that the process is photosensitized by the naphthalene polymeric chromophores and is less efficient when these chromophores are deactivated by oxygen. (The incident light is almost exclusively absorbed by the naphthalene antenna chromophores present in the polymer due to their high concentration and considerably higher extinction coefficients in this spectral region.) The other factor that might explain the inhibiting action of oxygen is the possibility that the reaction occurs with the formation of an intermediate that may be deactivated by oxygen.

Table IV presents the product distribution determined after irradiation of HCB in hexane, in water, and in the aqueous solution of PSSS-VN for 21 h in an oxygen-free atmosphere with solar-simulated radiation. The total concentrations of HCB in the aqueous polymer solution and in hexane were the same and equal to $4.4 \times 10^{-6}$ M. The water solution was saturated with HCB; the resulting HCB concentration was approximately $2.2 \times 10^{-8}$ M. Irradiation of the HCB in these media results in its dechlorination. The process is only slightly less efficient in the aqueous polymer solution than in hexane and very inefficient in water. One of the reasons for the variation in efficiency is the difference in the concentration of HCB. The other reason may be the difference in physical properties of the medium. Of these, the most important seems to be the ability of the medium to donate hydrogen. During dechlorination, the chlorine atom in the HCB molecule is replaced by hydrogen, which is most likely abstracted from the solvent molecules. In the polymer solutions, both water and polymer molecules can be considered as a source of hydrogen.

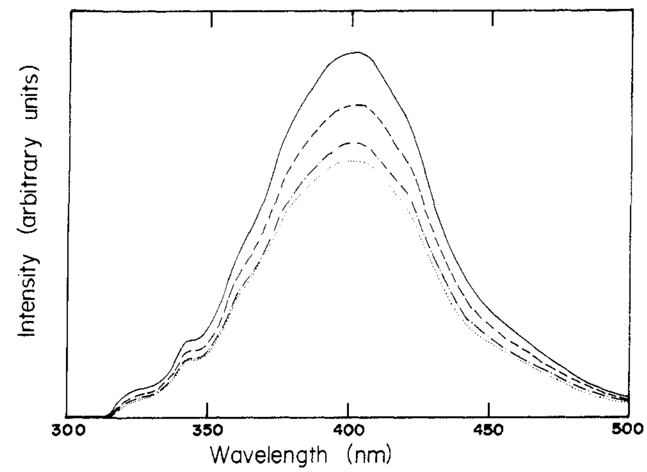

**Figure 3.** Steady-state fluorescence spectra of PSSS-VN in aqueous solution in the absence (—) and in the presence of HCB at various concentrations: $2.8 \times 10^{-5}$ M (---); $8.3 \times 10^{-5}$ M (-·-); $1.7 \times 10^{-4}$ M (···) ($\lambda_{ex}$ = 280 nm).

It was observed that HCB solubilized in aqueous solutions of PSSS-VN quenches fluorescence of the naphthalene polymeric chromophores (Figure 3). The process is quite efficient, and its occurrence confirms the hypothesis that HCB is trapped inside hydrophobic polymeric microdomains. It is difficult, however, to elucidate the mechanism of this process in the complicated polymeric system. For this reason, a low molecular weight model system was studied.

**Studies of the Mechanism of Naphthalene-Photosensitized Dechlorination of HCB.** Irradiation of the mixture of naphthalene ($c = 6.8 \times 10^{-4}$ M) and HCB ($c = 5 \times 10^{-6}$ M) in hexane solution with solar-simulated radiation and with monochromatic light at 280 nm also results in the dechlorination of HCB. The GC pattern of the irradiated mixture shows that the major products formed are the same types as those for HCB irradiated in the aqueous polymer solution. The reaction occurs with free-radical formation as was shown by monitoring the consumption of free-radical scavenger DPPH during the irradiation of the naphthalene and HCB mixture in the presence of DPPH. This observation is in agreement with the generally accepted mechanism of photodechlorination of chlorinated aromatics involving dissociation of the C–Cl bond with the formation of $Cl^{\bullet}$ radicals. It was postulated that the reaction takes place in the excited triplet state of the molecule.[18,19] It should be noted, however, that the energy required for the direct dissociation of the C–Cl bond in chlorinated aromatic is about 87 kcal $mol^{-1}$.[27] This is well above the energy of the triplet level of HCB, which is about 62 kcal $mol^{-1}$.[20,28] The occurrence of the process can be thermodynamically possible, considering that the actual reaction is not a unimolecular photolysis of HCB but rather a bimolecular process involving interaction between an excited molecule of HCB and solvent. This results in the formation of pentachlorobiphenyl (PeCB) and a molecule of RCl, where R denotes a radical formed from the solvent due to hydrogen abstraction:

$$HCB^{*} + RH \rightarrow PeCB + RCl \qquad (1)$$

The energy barrier for such a process should be substantially different from that for the unimolecular dissociation of a C–Cl bond in aromatics. The above mechanism cannot be justified, however, at the present time because of the lack of thermodynamic parameters characterizing the reactants.

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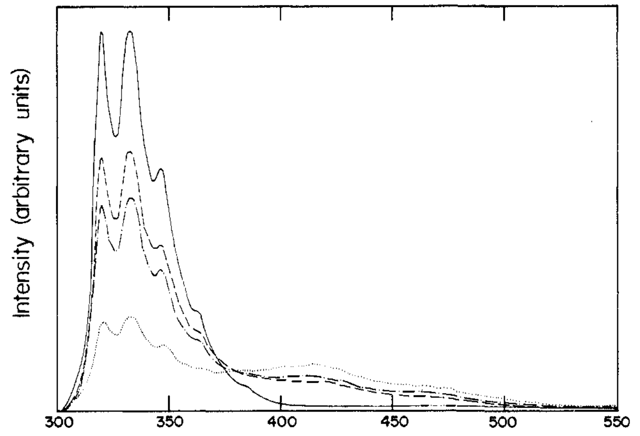

**Figure 4.** Steady-state fluorescence spectra of naphthalene in hexane solution in the absence (—) and in the presence of HCB at various concentrations: $2.8 \times 10^{-5}$ M (---); $8.3 \times 10^{-5}$ M (-•-); $1.7 \times 10^{-4}$ M (···) ($\lambda_{ex}$ = 280 nm).

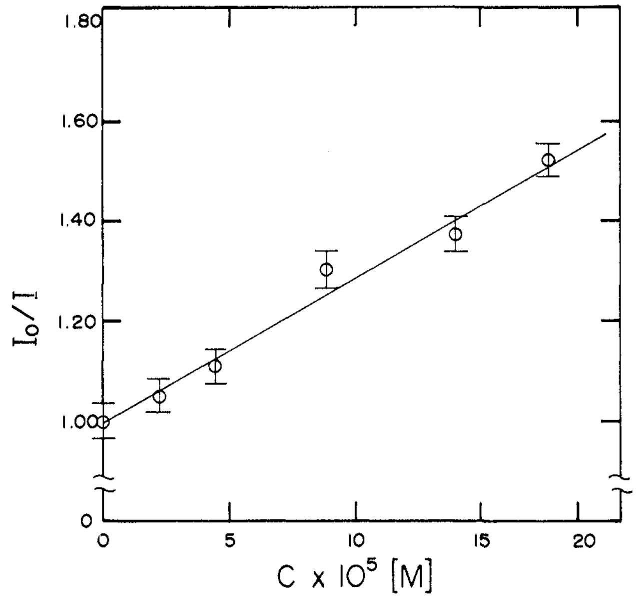

**Figure 5.** Stern–Volmer plot of the ratio of naphthalene fluorescence intensities ($I_0/I$) in the absence ($I_0$) and in the presence of quencher ($I$) versus concentration of HCB.

The other possibility, which should be considered in order to explain photosensitized dechlorination of HCB, involves the existence of some type of complex formation. Measurements of the steady-state fluorescence spectra of naphthalene in the absence and in the presence of HCB in hexane solution show two interesting features of the system (Figure 4). In the presence of HCB, the fluorescence intensity of naphthalene decreases and a broad, structureless emission band appears in the long-wavelength spectral region ($\lambda_{max}$ = 415 nm). Stern–Volmer analysis of the quenching data (Figure 5) gives the bimolecular rate constant $k_q = (2.9 \pm 0.1) \times 10^{10}$ M$^{-1}$ s$^{-1}$. This value is close to the diffusion-controlled rate constant for a bimolecular process in hexane at 20 °C.[29] It is difficult to explain such a high value of $k_q$ solely in terms of singlet–singlet energy transfer. On the basis of the absorption and emission spectra of HCB in hexane, the energy level for HCB in its first excited singlet state was determined to be ~95 ± 3 kcal mol$^{-1}$. The energy level for naphthalene in its first excited singlet state is about 92 kcal mol$^{-1}$.[29]

It can be observed that the intensity of the long-wavelength fluorescence band increases steadily with an increase in HCB concentration. The two-component spectra display an isoemissive point at $\lambda$ = 382 nm, characteristic of stoichiometric complex formation. The absorption and excitation spectra of the mixture do not show any new bands, only those characteristic of the components of the mixture. This indicates that there is no specific interaction between the molecules in the ground state and makes it reasonable to postulate that exciplex formation between naphthalene and HCB occurs. This is in agreement with the observation of a red shift in the fluorescence maximum and a decrease in intensity in the fluorescence band assigned to the exciplex in more polar solvents such as methanol ($\lambda_{max}$ = 422 nm) as well as with increase in the fluorescence intensity at low temperatures due to the decrease of exciplex dissociation. The probability of complex formation between HCB and naphthalene in the excited singlet state is considerably higher than in the ground state because the polarizability ($\alpha$) of naphthalene in the excited singlet state is considerably higher than in the ground state ($\Delta\alpha = 11.32 \times 10^{-24}$ cm$^3$).[30]

**Table V.** Position of the Exciplex Maximum and Properties of the Solvents Used in the Experiments

| solvent | $\tilde{\nu}$ (cm$^{-1}$) | $\eta$ | $\epsilon$ |
|---|---|---|---|
| hexane | 24096 | 1.375 | 1.89 |
| methanol | 23697 | 1.331 | 32.70 |

The red shift of the maximum of the fluorescence band observed when the solvent polarity increases can be related to the dipole moment, $\mu$, of the exciplex as follows[31-33]

$$\tilde{\nu}_s = \tilde{\nu}_g - \frac{\mu_c^2}{hca^3}\left[2\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) - \left(\frac{n^2 - 1}{2n^2 + 1}\right)\right] \tag{2}$$

where $\tilde{\nu}_2$ and $\tilde{\nu}_g$ are the wavelengths of the exciplex fluorescence maxima in solution and in the gas phase, respectively, $\epsilon$ is the dielectric constant, $n$ is the refractive index, and $a$ is the radius of equivalent sphere occupied by the complex. Using the experimental data for the exciplex fluorescence maximum in hexane and methanol solution (Table V) and assuming the value of 4.5 Å for the parameter $a$, the dipole moment for naphthalene–HCB complex was determined to be ~3.2 ± 0.2 D.

We suggest that the quenching of the fluorescence of naphthalene by HCB can be explained by exciplex formation followed by electron transfer from naphthalene to HCB. Electron transfer can be possible if $\Delta G$ of the process is negative. The free energy for electron transfer in nonpolar solvents can be calculated from the Rehm–Weller equation[34]

$$\Delta G_{ex} = E_D{}^{ox} - E_A{}^{red} - E_S + C \tag{3}$$

where $E_D{}^{ox}$ and $E_A{}^{red}$ are the oxidation potential of donor and reduction potential of accepter, respectively, $E_S$ is the energy of the excited singlet state of donor, and $C$ is an electrostatic correction term. Taking the literature data for the oxidation potential for naphthalene ($E_D{}^{ox}$ = 1.6 eV),[35] the reduction potential for HCB ($E_A{}^{red}$ = −2.18 eV),[36] and the energy of the excited singlet state for naphthalene ($E_S$ = 3.99 eV)[36] and assuming the value for electrostatic term $C$ = 0.1, the free energy for the electron transfer from naphthalene to HCB in hexane ($\Delta G$) was found to be equal to −0.11 eV. This indicates that electron transfer from naphthalene to the HCB molecule can occur. The process should result in the formation of the naphthalene radical cation and HCB radical anion. The HCB radical anion can expel a Cl$^\bullet$ radical or Cl$^-$ anion,

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which might explain the observed dechlorination of HCB.

On the basis of the experimental data presented above, the following reaction scheme can be proposed to describe naphthalene-sensitized photodechlorination of HCB

$$^1N_0 + h\nu \rightarrow {}^1N^* \tag{4}$$

$$^1N^* \rightarrow {}^1N_0 + h\nu' \tag{5}$$

$$^1N^* \rightarrow {}^1N_0 \tag{6}$$

$$^1N^* \rightarrow {}^3N^* \tag{7}$$

$$^1N^* + {}^1HCB_0 \rightarrow ({}^1N^*\ HCB) \rightarrow N^{\bullet+} + HCB^{\bullet-} \tag{8}$$

$$HCB^{\bullet-} + RH \rightarrow PeCB + Cl^{\bullet}(Cl^-) + R^{\bullet} \tag{9}$$

where $^1N_0$, $^1N^*$, and $^3N^*$ represent the naphthalene molecule in the ground, excited singlet, and excited triplet states, respectively, $^1HCB_0$ is the molecule of HCB in ground state, ($^1N^*$ HCB) stands for naphthalene–HCB exciplex, $N^{\bullet+}$ is the naphthalene radical cation and $HCB^{\bullet-}$ is the HCB radical anion, and RH is the solvent molecule acting as the hydrogen donor.

The compounds formed as a result of dechlorination of HCB (i.e., pentachlorobiphenyl, tetrachlorobiphenyl, etc.) are also expected to form exciplexes with naphthalene and act as electron acceptors. This was experimentally shown for 2,2′,3,3′-tetrachlorobiphenyl. It is therefore reasonable to postulate that the same reaction scheme proposed above is also valid for each chlorinated biphenyl formed in the system and can thus explain their stepwise dechlorination.

The above mechanism could be fully accepted if the radical intermediate could be detected and identified. The naphthalene radical cation has a distinct absorption spectrum that differs considerably from that of naphthalene.[32] An attempt to detect the presence of this intermediate by flash photolysis was undertaken but was unsuccessful, probably because of its short lifetime (<1 μs)[37] and limitations of the apparatus used.

It should be noted that while the mechanism proposed previously seems reasonable for the naphthalene-sensitized dechlorination of HCB, in the case of direct photolysis of HCB in an organic solvent as well as in an aqueous solution of PSSS-VN, the participation of the HCB excimer might also be of some importance. Due to steric factors, HCB cannot form a fully overlapped excimer. It can, however, form two types of partly overlapped excimers, characterized by two different geometries.[38] The creation of HCB excimer in the polymeric pseudophase is highly probable because of the high local concentration of the solubilized compound.

## Conclusions

Irradiation of aqueous solutions of PSSS-VN containing solubilized HCB with solar-simulated radiation in an oxygen-free atmosphere results in dechlorination of HCB. On the basis of the model studies performed with use of a low molecular weight system, the mechanism of dechlorination of HCB involving a naphthalene–HCB exciplex intermediate followed by electron transfer has been proposed. Electron transfer generates the HCB radical anion, which then can easily expel a chlorine radical (or anion). This sequence can be repeated by chlorinated biphenyl compounds containing fewer chlorine atoms formed in the reaction. This could explain the step by step dechlorination of HCB that should ultimately result in the formation of a nonchlorinated biphenyl.

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**Registry No.** HCB, 38411-22-2; (SSS)(VN) (copolymer), 115468-37-6; naphthalene, 91-20-3.

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# Regiospecific Synthesis of Polysubstituted Naphthalenes and Iodoacylnaphthoquinones via Zirconocene Complexes of Naphthalynes

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**Abstract:** Zirconocene complexes of substituted naphthalynes have been generated in situ and trapped with nitriles to form azametallacycles with excellent regiochemical control. These compounds can be converted into ketones, α-iodo ketones, and iodoacylnaphthoquinones with experimentally simple procedures.

Natural products that contain aromatic and/or quinoid structures are of great medicinal importance.[3] The requirement for efficient routes to these molecules has spurred an intensive effort to develop general methods for the regiospecific preparation of highly substituted aromatic systems.[4] Despite such efforts, a need for more efficient and flexible routes to many types of aromatic molecules still exists. In this paper, we describe a general route to highly substituted naphthalenes and iodoacylnaphthoquinones via intermediate zirconocene complexes of naphthalynes.

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