

ENVIRONMENTAL PHOTOINCORPORATIONS OF POLYCHLOROBENZENES INTO  
SEVERAL HUMIC MODEL MONOMERS\*

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SUMMARY

Solution phase photoincorporations of six polychlorobenzenes (PCBzs), using UV light centered at 300 nm, into several humic model monomers such as benzoic acid, benzaldehyde, vanillic acid, vanillin, syringic acid, and syringaldehyde were investigated. All PCBzs except hexachlorobenzene gave minor yields of photoproducts formed by the reaction of the polychlorophenyl radicals with the individual humic monomers. In the case of benzoic acid and benzaldehyde, chlorophenylation of the humic model monomers occurred; whereas when monomers having phenolic OH group were present, substituted polychlorodiphenyl ethers were also formed. Furthermore, the irradiation of 1,2,4,5-tetrachlorobenzene solution containing vanillic acid produced, in addition to other photoinduced products, monochloro- and dichloromethoxycarbohydroxydibenzofuran.

Introduction

Polychlorobenzenes (PCBzs), which are anthropogenic chemicals, have been found in almost every aquatic environment worldwide<sup>1-4</sup>. Likewise, natural macromolecules such as humic substances (HSs) including fulvic acids (FAs), humic acids (HAs), and humins occur in almost every aquatic environment<sup>5-8</sup>. It is very likely that water bodies contaminated with PCBzs also contain HSs.

Previously, we reported that during the irradiation ( $\lambda \geq 285$  nm) of solutions of certain

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\*Paper presented at the 3rd International Congress on Environmental Pollution and its Impact on Life in the Mediterranean Region (Istanbul, Sept. 1-4, 1985).

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chlorinated benzenes ( $\text{Cl}_n\text{-Bzs}$ ), viz., 1,3,5- $\text{Cl}_3\text{-Bz}$ <sup>9</sup>, and  $\text{Cl}_4\text{-Bzs}$  and  $\text{Cl}_5\text{-Bz}$ <sup>10</sup> in acetonitrile-water mixtures polychlorobiphenyls (PCBs) with  $2n-1$  and  $2n-2$  Cl atoms together with polychlorophenyl acetonitriles are formed. Most of the photochemically generated and reasonably stable chlorophenyl radicals in natural waters, however, are expected to incorporate into (react with) abundantly available natural organic matter. We, therefore, decided to investigate the photochemical incorporation of PCBzs with FAs or some humic model monomers.

HSs have been reported to sensitize and quench the photolyses of several environmental pollutants;<sup>5,11-14</sup> no report has been published to date on photochemical incorporation of these compounds by HSs. Recently, Choudhry et al. (2) reported that PCBzs containing four, five, and six chlorine substituents react photolytically in  $\text{CH}_3\text{CN-H}_2\text{O}$  in the presence of phenol to produce polychlorinated dibenzofurans (PCDFs) in ca.1% chemical yield. Because of our continuing interest in the photolytic fate of pollutants such as halogenated benzene derivatives in the environment, we undertook further study of photochemically induced reactions of chlorobenzenes with humic type monomers and FAs. The present paper reports our laboratory investigations of the photochemical interactions of six PCBzs with several humic model monomers in aqueous acetonitrile at  $\lambda > 285$  nm.

### Experimental Section

Substrates and Solvents. The sources of PCBzs 1-6 and solvents have been described elsewhere<sup>10</sup>. Benzoic acid (7), benzaldehyde (8), vanillic acid (9), vanillin (10), syringic acid (11), and syringaldehyde (12) were purchased from Aldrich.

Preparation of Solutions. Stock solutions of chlorobenzenes and humic monomers were prepared in acetonitrile. The previously reported method<sup>10</sup> was utilized for the preparation of sample solutions of all PCBzs (1-6) containing each humic model monomers in water-acetonitrile. For the solutions containing humic monomer 7, the ratios of  $\text{H}_2\text{O}:\text{CH}_3\text{CN}$  (v/v) were as follows: 1:1 for PCBzs 1-3; 4:6 for PCBzs 4, 5; and 1:9 for 6 (Table I), whereas in the case of monomer 8, the following ratios of  $\text{H}_2\text{O}:\text{CH}_3\text{CN}$  (v/v) were used: 1:1 for PCBzs 2-5; and 1:9 for 6 (Table II). The photolysis sample solutions of  $\text{Cl}_4\text{-Bz}$  4 containing humic type monomers 9-12 (Table III) were prepared in water-acetonitrile 1:1 (v/v). During the photoinduced reactions of PCBzs with monomer 7 (Table I), concentrations of chlorobenzenes 1-6 were 1.000 mM/L, while each solution contained 5.000 mM/L benzoic acid. Similarly, in the case of benzaldehyde (8), 1.000 mM/L PCBzs 2-6 were used, each solution containing 5.000 mM/L aldehyde 8 (Table II). For the studies on photochemical interactions of 1,2,4,5- $\text{Cl}_4$  Bz (4) with vanillic acid (9), vanillin (10), syringic acid (11) and syringaldehyde (12), concentrations (mM/L) were as follows: 4:1.028, 9:4.934; 4:1.028, 10:5.011; 4:1.112, 11:5.061; and 4:1.075, 12:5.003.

Irradiation Equipment and Experiments. These have been described in detail elsewhere<sup>15,16</sup>.

Extraction Procedures. In the case of irradiation of PCBzs in the presence of humic model monomers, 1.00 mL of  $n$ -hexane containing 0.100 mM/L 4,4'-dichlorobiphenyl as an internal standard (IS) was added to each photolyzed sample as well as the corresponding unphotolyzed samples. The samples were then well shaken and the  $n$ -hexane layer was separated from the  $\text{H}_2\text{O-CH}_3\text{CN}$  layer. The  $n$ -hexane extracts of such samples were treated with ethereal solution of

diazomethane (CH<sub>2</sub>N<sub>2</sub>). After 24 h, a few drops of *n*-nonane were added to the hexane-ether solutions which were then reduced to ca. 0.2 mL with a stream of dry nitrogen.

**Gas Chromatography.** Quantitative analyses of all *n*-hexane extracts were carried out as previously described<sup>10</sup> on a Hewlett-Packard GC equipped with a flame ionization detector. In the case of photolyses of PCBzs 1-6 in solution containing humic model monomers 7-12, the extent of disappearance of the starting PCBz was determined using column A (5% Carbowax 20 M), whereas column C (3% silicone OV 101) was used for the quantitation of the photoinduced products listed in Tables I-III. For the analyses of the samples of Cl<sub>4</sub>-Bzs 3 and 4, column B (10% Carbowax 20 M) was also utilized. GC conditions have been described elsewhere<sup>10</sup>. Tetrachlorobenzenes 3 and 4 are only resolvable on column B<sup>10</sup>.

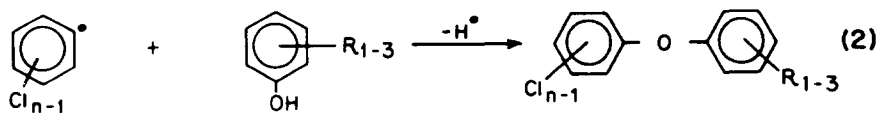
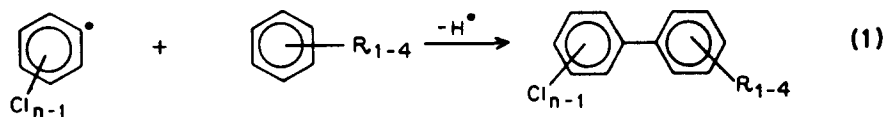
**Gas Chromatography - Mass Spectrometry.** All photoproducts (documented in Tables I, II, and III) were qualitatively characterized on a Hewlett-Packard GC-MS 5894 equipped with a fused silica capillary column coated with CP-SIL 5 (operating conditions of this GC-MS were the same as previously reported<sup>10</sup>).

**Identification of Photoproducts.** Pending the availability of the authentic standards, structures of the photoproducts in Tables I-III were determined by interpretation of GC-MS data.

## Results and Discussion

### Photochemical Interactions with Humic Model Monomers.

Photoreactions of ca. 1 mM/L polychlorobenzenes 1-6 in water-acetonitrile mixtures containing individual compounds 7-12 (approximately 5 mM/L) at λ<sub>max</sub> 300 nm are documented in Tables I-III. These tables include only those products which are formed through the interaction of photolytically generated polychlorophenyl radicals (discussed below) with humic monomers, *viz.* reactions 1 and 2:



where  $n = 3 - 5$  and  $R = \text{COOH}, \text{CHO}, \text{OCH}_3, \text{OH}, \text{etc.}$  For benzoic acid (7) and benzaldehyde (8), Tables I and II also record chemical yields of this type of product. These yields were calculated from the amount of photoconverted starting PCBz; the amount of undecomposed starting chlorobenzene present in a photolyzate being used as an internal standard. For instance, 14.7, 8.2, <2.4, and <2.4% of the decomposed 1,3,5-Cl<sub>3</sub>-Bz (1) is photoconverted into

Table 1. Photochemical Interactions of Polychlorobenzenes (PCBzs) with Benzoic Acid (Z) in Acetonitrile-Water Mixtures.


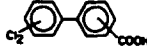

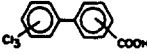








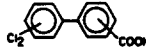
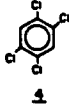


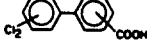

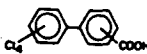
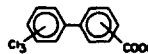

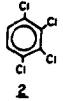
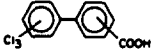
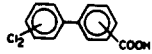
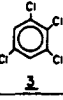
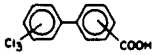
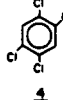
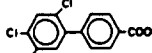
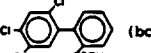
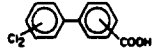
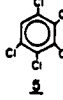
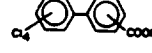
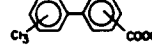
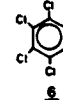
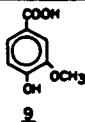
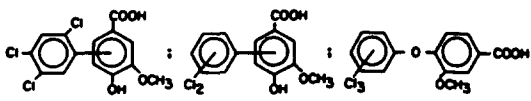
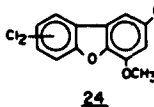
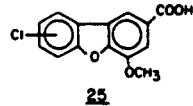
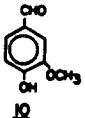
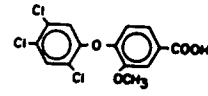
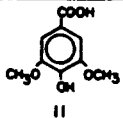
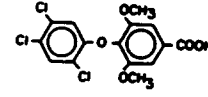
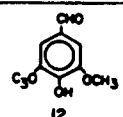
Substrates, PCBzs	Photo-reaction Time, h	Disappearance of Starting PCBz, %	Products, % in parentheses
	16.5	25.6	 (4 isomers) (14.70; 8.15; others <2.40)
	42.0	16.9	 (3 isomers) (1.08; others <0.31) and  (<0.31)
	42.0	79.4	 ;  ;  ;  ;  ;  (1.24; 0.59; others <0.47) and  (6 isomers) (all <0.47)
	9.0	84.3	 ;  (2.10; 2.02) and  (2 isomers) (0.43; <0.34)
	16.5	40.3	 (4 isomers) (all <0.63) and  (<0.63)
	16.5	64.7	---

Table II. Photochemical Interactions of Polychlorobenzenes (PCBzs) with Benzaldehyde (8) in Acetonitrile-Water Mixtures.

Substrate, PCBzs	Photo-reaction Time, h	Disappearance of Starting PCBz, %	Products, % in parentheses
 2	72.0	56.5	 (7 isomers) (0.85; others <0.36) and  (<0.36)
 3	72.0	56.1	 (5 isomers) (0.40; others <0.26)
 4	8.0	44.2	 :  (both <0.32) and  (2 isomers) (both <0.32)
 5	24.0	34.0	 (5 isomers) (all <0.86) and  (0.88)
 6	16.0	29.0	---

four isomers of dichlorophenylbenzoic acid, when the solution of the substrate 1 is exposed for 16.5 h in the presence of monomer 7 (see Table I). Quantitative analytical techniques (see Experimental) failed to separate some components of the photolyzates obtained by the photolyses of Cl<sub>4</sub>-Bz 4 in solutions containing vanillic acid (9), vanillin (10) and syringic acid (11) for 16 h; therefore, the products of these photoreactions were not quantified (Table III). However, the chemical yields of the products documented in Table III were < 1.0%. It should be mentioned that products in which R = COOH and OH were identified as methyl derivatives, diazomethane being used as the methylating agent.

Table III. Photochemical Interactions of 1,2,4,5-Tetrachlorobenzene (4) with some Humic Model Monomers in Acetonitrile-Water Mixtures.

Humic Model Monomers	Photo-reaction Time, h	Disappearance of PCBz, %	Products
 9	16.0	64.3	 (4 isomers);  24 and  25
 10	16.0	37.4	
 11	16.0	31.4	
 12	16.0	82.1	---

Tables I and II indicate that amongst the investigated PCBzs, hexachlorobenzene (6), is unique in not generating products via reaction 1. Recently, Choudhry and Hutzinger<sup>10</sup> reported that Cl<sub>6</sub>-Bz (6) does not yield PBCs contrary to the direct and acetone-sensitized photolyses of PCBzs 2-5 in water-acetonitrile mixtures. Thus pentachlorophenyl radicals produced from 6 appear to be more reactive than tetra-, tri-, and 3,5-dichlorophenyl radicals.

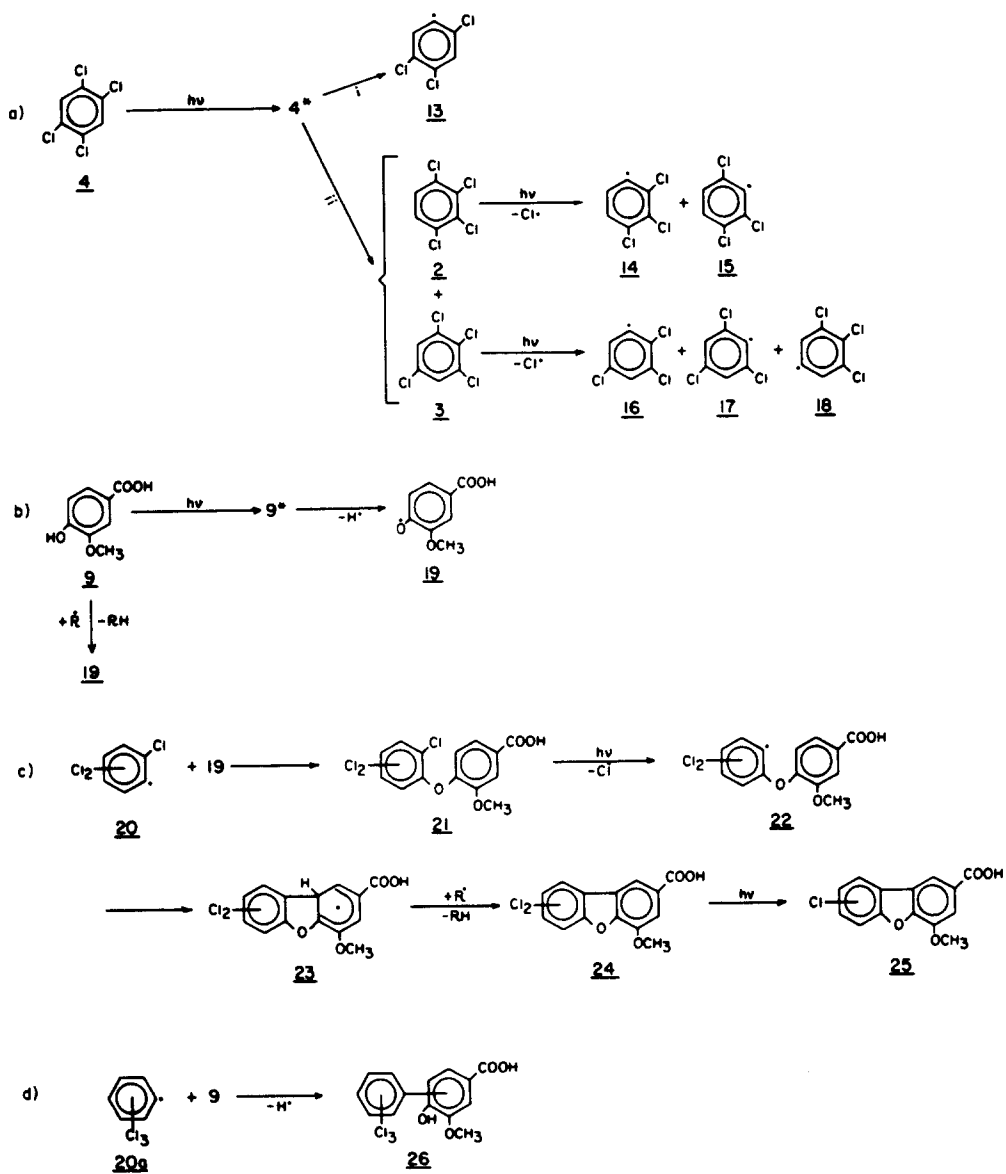
In addition to the products described above (Tables I-III), irradiation of PCBzs 1-5 in the presence of humic model monomers 7-12 yields reductively dechlorinated benzenes as major photoproducts along with minor products including PCBs, photoisomerized PCBzs (except from 5) and polychlorophenyl acetonitriles. No attempt was made to quantify these additional photoproducts. However, complete quantitative data for such photoproducts arising from non-sensitized and acetone-sensitized photoreactions of 1,3,5-Cl<sub>3</sub>-Bz (1)<sup>9</sup> and PCBzs 2-6<sup>10</sup> have recently been published.

The 16-h exposure of Cl<sub>4</sub>-Bz 4 in the presence of vanillic acid (9) leads to the production not only of photoproducts formed through Reactions 1 and 2 but also of mono- and dichlorodibenzofurans having carboxylic and methoxy substituents formed via secondary

photoprocesses (Table III). The photolytically induced reactions of 4 with humic model monomer 9 are suggested in Scheme 1. Photoexcited tetrachlorobenzene 4 undergoes homolytic scission of a C-Cl bond to provide 2,4,5-trichlorophenyl radicals (13) (step a, path i) together with photoisomerization giving rise to the eventual generation of Cl<sub>4</sub>-Bzs 2 and 3 (step a, path ii). Secondary photolyses of these photoisomerized tetrachlorobenzenes then result in the generation of trichlorophenyl radicals 14 and 15 from 2 as well as 16, 17, and 18 from 3 through the homolysis of the appropriate C-Cl bond. The mass spectral detection of trichlorophenylacetonitriles and all expected isomers of heptachlorobiphenyls in the case of photoreactions of Cl<sub>4</sub>-Bzs 2-4 in the presence and absence of acetone as sensitizer in aqueous acetonitrile provides evidence that polychlorophenyl radicals are involved<sup>10</sup>. Further evidence is provided by the detection of such photoproducts in the present studies. Moreover, the photohomolysis of the O-H bond of vanillic acid (9) provides 2-methoxy-4-carbohydroxyphenoxy radicals (19) (step b). In addition, species 19 may be produced through the abstraction of hydrogen atom from the OH group of monomer 9 by free radicals ( $\dot{R}$ ) such as  $\dot{Cl}$ ,  $\dot{C}H_2CN$ , 13-18 and others. Subsequently, 20 (which represents species 13-17) would combine with phenoxy radical 19, to yield trichloro-2'-methoxy-4'-carbohydroxydiphenyl ether 21 containing an o-Cl substituent. The irradiation of ether 21 would produce 2-carbohydroxy-4-methoxydichlorodibenzofuran 24 through the intermediate involvement of diphenylether radicals 22 and  $\sigma$ -complex 23 (see step c). Further, photolysis of 24 would yield monochlorodibenzofuran 25. Alternatively, the product 25 may be generated from the reductively dechlorinated diphenyl ether 21 having a 2-Cl substituent and from the appropriate photoreduced products of Cl<sub>4</sub>-Bz 2-4 and acid 9. It is worth noting that in similar studies Choudhry et al (2) have previously confirmed the intermediacy of 2,4,5-trichlorodiphenyl ether in the photoformation of 2,3-dichlorodibenzofuran from 4 and phenol. The species 18 also likely reacts with 19 to produce 2-methoxy-4-carbohydroxy-3',4',5'-trichlorodiphenyl ether (not shown in Scheme 1); however, this product is not expected to yield 24. Recently, our investigations<sup>15</sup> of the photolysis of tetra- and pentachlorophenols have led us to conclude that phenoxy radicals produced in water-acetonitrile are unable to produce products arising via the phenoxylation of a benzene nucleus. Finally, trichloroarylation of acid 9 by radicals 20a (which represents species 13-18) provides 26 (step d). Whether intermediate 26 having a 2-Cl substituent is also involved in the generation of 24 remains unanswered.

As described in the previous section, because of unavailability of authentic standards, we have been unable to ascribe exact isomeric structures to the photoproducts such as compounds 21 and 24-26 (see Scheme 1). However, the structures, namely, 2,4,5-trichloro-2'-methoxy-4'-carbohydroxydiphenyl ether and 2,4,5-trichloro-2', 6'-dimethoxy-4'-carbohydroxydiphenyl ether were assigned to products formed as a result of photoinduced interaction of Cl<sub>4</sub>-Bz 4 with vanillin (10) and syringic acid (11), respectively, (see Table III). The probability of contributions of radical 13 to Reaction 2 is greater than those of radicals 14-18. Moreover, only one product of this sort was observed in the case of each photoinduced reaction of 4 with 10 and 11. It is noteworthy that in the case of UV exposures of 4 containing syringaldehyde (12) the anticipated photoinduced products are not seen even when 82% of the starting chlorobenzene had disappeared (Table III). Furthermore, during the photochemical interactions of PCBzs 2-5 with benzaldehyde (8) (Table II) as well as

Scheme 1







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