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# PHOTOCHEMISTRY OF HALOGENATED BENZENE DERIVATIVES: PART VII. PHOTOINCORPORATIONS OF POLYCHLOROBENZENES WITH HUMIC MODEL MONOMERS IN AQUEOUS ACETONITRILE SOLUTIONS

GHULAM GHAUS CHOUDHRY,* JUST ANTON VAN DEN BROECKE,†
G. R. BARRIE WEBSTER and OTTO HUTZINGER‡
Pesticide Research Laboratory, Department of Soil Science, University of Manitoba, Winnipeg, Canada R3T 2N2; †Laboratory of Environmental and Toxicological Chemistry, University of Amsterdam, 1018 WV Amsterdam, The Netherlands; and ‡Department of Ecological Chemistry and Geochemistry, University of Bayreuth, D-8580 Bayreuth, F.R.G.

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**Abstract**—Aqueous acetonitrile solution-phase photoincorporations of six polychlorobenzenes (PCBzs) into some humic model monomers such as benzoic acid, benzaldehyde, vanillic acid, vanillin, syringic acid and syringaldehyde were investigated using UV light centered at 300 nm. All the PCBzs studied except hexachlorobenzene yielded photoproducts by the reaction of the polychlorophenyl radicals with the individual humic monomers. Chlorophenylation of humic model monomers occurred in the case of benzoic acid and benzaldehyde; substituted polychlorodiphenyl ethers were also formed when monomers containing a phenolic OH group were present. Furthermore, the irradiation of 1,2,4,5-tetrachlorobenzene in solution in the presence of vanillic acid produced monochloro- and dichloromethoxydibenzofuran carboxylic acids in addition to the other photoincorporated products.

**Keywords**—Photoincorporations Polychlorobenzenes Humic model monomers Substituted polychlorinated biphenyls Substituted polychlorodiphenyl ethers Substituted polychlorinated dibenzofurans

## INTRODUCTION

Polychlorobenzenes (PCBzs), compounds of anthropogenic origin, have been found in almost every aquatic environment worldwide [1–4], as have natural macromolecules such as humic substances including fulvic acids, humic acids and humins [5–8].

Previously, we reported that photoproducts such as polychlorobiphenyls (PCBs) with $2n-1$ and $2n-2$ Cl atoms are formed during the irradiation ($\lambda > 285$ nm) of solutions of chlorinated benzenes ($Cl_n$=Bzs), viz., 1,3,5-$Cl_3$-Bz [9], and $Cl_4$-Bzs and $Cl_5$-Bz [10] in acetonitrile-water. It appears reasonable to expect that when relatively stable chlorophenyl radicals are photochemically generated in natural waters they may react with the abundantly available natural organic matter. In view of the complex nature of humic substances [5–8] it was preferable for us to first investigate these types of reactions with humic model monomers.

Humic substances (fulvic acids, humic acids and humins) are complex materials; more than 150 compounds in three major classes—aliphatics, substituted benzenes and polycyclic aromatic hydrocarbons—have been reported as products obtained through chemical degradation and physical separation techniques (see Table III in ref. 5). The second class of the approximately 80 humic monomers includes benzene (poly) carboxylic acids, vanillin, vanillic acid, syringaldehyde, syringic acid and several other benzene derivatives [5–7]. We therefore decided to include some of these monomeric degradation products in our studies of the photoincorporation of PCBzs into humic monomers.

As cited in the recent protocol guidelines for the investigations of photochemical fate of pesticides in water, air and soils [11], the levels of pes-

*To whom correspondence may be addressed.
For part VI in this series of articles, see ref. 18.

ticides (and environmental pollutants) in aquatic systems recommended for the evaluation of kinetics frequently do not permit the observation, isolation and identification of the photoproducts arising from the test chemicals. For instance, the use of two sunlight actinometers, namely, *p*-nitroanisole (7.9 $\mu$M)/pyridine and *p*-nitroacetophenone (20 $\mu$M)/pyridine in water (both developed and evaluated by Dulin and Mill [12]), has been frequently noted in the literature [11]. The photoproducts, however, have not been reported for either of these chemical actinometers. Similarly, Choudhry and Webster [13; Choudhry and Webster, manuscript submitted for publication] were not able to observe any photoproduct arising from polychlorinated dibenzo-*p*-dioxins (PCDDs) (approximate 1 $\mu$M levels) in aqueous acetonitrile during studies of the kinetics and quantum yields of these pollutants. According to the above-mentioned guidelines [11], it is necessary, however, that as many as possible of the laboratory degradation products be qualitatively and quantitatively identified, even though they may not be present at detectable levels in actual field studies, so that a mechanism of the degradation of a pollutant can be established. For this purpose, the solubility of the test pesticide (environmental chemical) in water may need to be increased several-fold, using larger volumes of the cosolvent, e.g., $CH_3CN$, up to 50% (v/v). In view of the guidelines and our previous experience (see ref. 18, and preceding articles of this series), we have used increased proportions of cosolvent as required.

Humic substances have been reported to sensitize and quench the photolysis of several environmental pollutants [5,14–17]; however, no report has been published to date on the photochemical incorporation of these compounds with humic macromolecules. Recently, Choudhry et al. [2] reported that PCBzs containing four, five and six chlorine substituents react photolytically in $CH_3CN$-$H_2O$ in the presence of phenol to produce polychlorinated dibenzofurans (PCDFs) in an approximate 1% chemical yield. Because of our continuing interest in the environmental photolytic fate of chlorinated aromatic pollutants [18], we undertook further study of photochemically induced reactions of chlorobenzenes with humic-type monomers. This article reports our laboratory investigations of the photointeraction of six PCBzs with selected humic model monomers in aqueous acetonitrile at wavelengths typically used in environmental photochemistry.

## METHODS

### *Substrates and solvents*

The source of PCBzs *1* through *6* and solvents have been described elsewhere [10]. 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 [10] was utilized for the preparation of sample solutions of all PCBzs (*1* to *6*) containing each humic model monomer in water-acetonitrile. For the solutions containing humic monomer *7*, the $H_2O$:$CH_3CN$ ratios (v/v) were as follows: 1:1 for PCBzs *1* to *3*, 4:6 for PCBzs *4* and *5* and 1:9 for PCBz *6* (Table 1). In the case of monomer *8*, the following $H_2O$:$CH_3CN$ ratios (v/v) were used: 1:1 for PCBzs *2* to *5* and 1:9 for PCBz *6* (Table 2). The photolysis sample solutions of $Cl_4$-Bz *4* containing humic monomers *9* to *12* (Table 3) were prepared in 1:1 (v/v) $H_2O$:$CH_3CN$. During the photoinduced reactions of PCBzs with monomer *7* (Table 1), the concentrations of chlorobenzenes *1* to *6* were 1.00 mM and each solution contained 5.00 mM benzoic acid. Similarly, in the case of benzaldehyde (*8*), 1.00 mM solutions of PCBzs *2* to *6* were used, each solution containing 5.00 mM aldehyde *8* (Table 2). For the studies on the photochemical interactions of 1,2,4,5-$Cl_4$-Bz (*4*) with vanillic acid (*9*), vanillin (*10*), syringic acid (*11*) and syringaldehyde (*12*), the concentrations (mM) were as follows: *4*: 1.03 and *9*: 4.93; *4*: 1.03 and *10*: 5.01; *4*: 1.11 and *11*: 5.06; *4*: 1.08 and *12*: 5.00 (Table 3).

### *Ultraviolet spectra*

UV spectral data for 1,3,5-$Cl_3$-Bz (*1*) and humic model monomers *7* to *12*, documented in Table 4, were recorded on a Cary-14 double-beam spectrophotometer. Previously reported data for PCBzs *2* to *6* were also recorded on this instrument (Table 4) [2].

### *Irradiation equipment and experiments*

Photolyses were carried out in Pyrex tubes (2.0 ml sample solution) utilizing a previously described [19] Rayonet Photochemical Reactor equipped with a merry-go-round apparatus. The Reactor was equipped with 16 RPR 3,000-Å lamps hav-

ing an energy output of 90% between 290 and 310 nm. The emission maximum of these lamps occurred at about 300 nm; the flux density was approximately 0.525 mW/cm$^2$. Samples were not deaerated prior to photolysis. It should be noted that Pyrex transmits less than 1% of radiations below 290 nm [19].

*Extraction procedures.* For the irradiation of PCBzs in the presence of humic model monomers, 1.00 ml *n*-hexane containing 0.100 mM 4,4′-dichlorobiphenyl as an internal standard was added to each photolyzed sample as well as to the corresponding unphotolyzed samples. The samples were then shaken well and the *n*-hexane layer separated from the $H_2O$-$CH_3CN$ layer. The *n*-hexane extracts of the samples were treated with an etheric solution of diazomethane ($CH_2N_2$). After 24 h, a few drops of *n*-nonane was added as a keeper to the hexane-ether solutions, which were then reduced to approximately 0.2 ml under a stream of dry nitrogen.

*Gas chromatography.* Quantitative analyses of all *n*-hexane extracts were carried out as previously described [10] on a Hewlett-Packard GC equipped with a flame ionization detector. For photolyses of PCBzs *1* to *6* in solutions containing humic model monomers *7* to *12*, the extent of disappearance of the initial PCBz was determined using column A (5% Carbowax 20 M); column C (3% silicone OV 101) was used for the quantitation of the photoincorporated products listed in Tables 1 and 2. The products (Tables 1 and 2) were quantified by previously described techniques [2,9,10,18,19] that used the amount of undecomposed initial PCBz present in a photolyzate. The chemical yields of these photoproducts were calculated from the amount of phototransformed initial chlorobenzene. For the analyses of the $Cl_4$-Bz *3* and *4* samples, column B (10% Carbowax 20 M) was also used. GC conditions have been described elsewhere [10]. Tetrachlorobenzenes *3* and *4* are only resolvable on column B [10].

*Gas chromatography–Mass spectrometry.* All photoproducts (documented in Tables 1, 2 and 3) 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 as reported previously [10]).

*Identification of photoproducts*

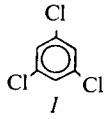
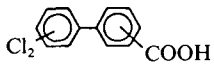
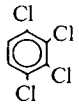
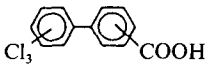
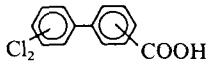
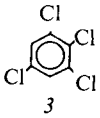
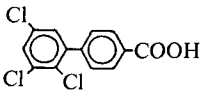
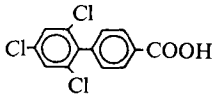
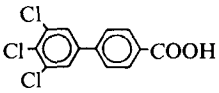
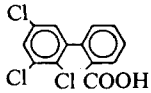
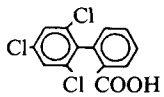
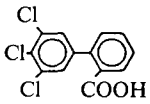
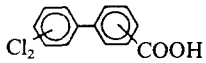
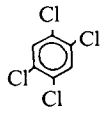
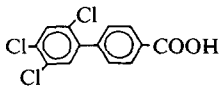
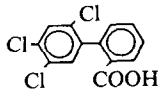
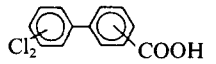
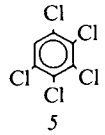
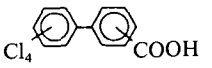
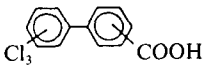
Pending the availability of authentic standards, structures of the photoproducts in Tables 1 to 3 were determined by interpretation of GC-MS data. The mass spectra of all chlorinated photoproducts (Tables 1 to 3) showed fragments (m/e) formed through the loss of 1 Cl, 2 Cl, and so on, atom(s) from the parent molecular ions ($M^{+\cdot}$). In these mass spectra, the ion clusters for $M^{+\cdot}$ and fragments containing Cl had relative abundances characteristic of the correct number of Cl atoms [20]. Moreover, the mass spectra of the methylated derivatives of the polychlorophenylbenzoic acid photoproducts arising through the photoincorporations of PCBzs *1* to *5* into humic monomers *7* and *8* (Tables 1 and 2 showed m/e values such as M-31 (M-$OCH_3$) and M-59 (M-$COOCH_3$)) confirmed the presence of $COOCH_3$ groups in these derivatized compounds. The M-31 and M-59 fragments were also present in the spectra of the photoproducts recorded in Table 3. Likewise, in addition to the above-described features, the mass spectra of the polychlorodiphenyl ether products containing $OCH_3$ and $COOCH_3$ (after methylation) substituents and those of the methyl ester of the dibenzofuran carboxylic acid *24* and *25* (documented in Table 3) revealed fragments with m/e values of M-63, indicative of the loss of COCl groups from the parent molecular ion.

## RESULTS AND DISCUSSION

The photoreactions of approximate 1 mM concentrations of polychlorobenzenes *1* to *6* in water-acetonitrile mixtures containing individual compounds *7* to *12* (approximately 5 mM) at $\lambda_{max}$ of 300 nm are documented in Tables 1 to 3. The tables include only those products formed through the incorporation of photolytically generated polychlorophenyl radicals (discussed below) into humic monomers, viz., Reactions 1 and 2 (Fig. 1), where $n = 3$–5 and R = COOH, CHO, $OCH_3$, OH, and so on.

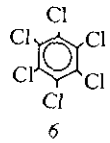
For benzoic acid (*7*) and benzaldehyde (*8*), Tables 1 and 2 also record chemical yields calculated on the basis of photoconverted initial PCBz. For instance, 14.7, 8.2, less than 2.4 and less than 2.4% of the decomposed 1,3,5-$Cl_3$-Bz (*1*) was photoconverted into four isomers of dichlorophenylbenzoic acid when the solution of substrate *1* was exposed for 16.5 h in the presence of monomer *7* (see Table 1). Quantitative analytical techniques (see Methods) failed to separate some components of the photolyzates obtained by the photolyses of $Cl_4$-Bz *4* in solutions containing vanillic acid (*9*), vanillin (*10*) and syringic acid (*11*) for 16 h; therefore, the products of these

Table 1. Photochemical interactions of polychlorobenzenes (PCBzs) with benzoic acid (*7*) in acetonitrile-water mixtures

| Substrate (PCBz) | Photoreaction time (h) | Disappearance of initial PCBz (%) | Product[a] |
|---|---|---|---|
|  *1* | 16.5 | 25.6 |  (4 isomers: 14.7; 8.15; others <2.40) |
|  *2* | 42.0 | 16.9 |  (3 isomers: 1.08; others <0.31)<br>  (<0.31) |
|  *3* | 42.0 | 79.4 |   <br>    <br>  (1.24; 0.59; others <0.47)<br>  (6 isomers: all <0.47) |
|  *4* | 9.0 | 84.3 |   (2.10; 2.02)<br>  (2 isomers: 0.43; <0.34) |
|  *5* | 16.5 | 40.3 |  (4 isomers: all <0.63)<br>  (<0.63) |

*continued*

Table 1. (continued)

| Substrate (PCBz) | Photoreaction time (h) | Disappearance of initial PCBz (%) | Product[a] |
|---|---|---|---|
|  6 | 16.5 | 64.7 | — |

The $CH_3CN:H_2O$ ratios (v/v) were 1:1 for PCBzs *1* to *3* and 3:2 for PCBzs *4* and *5*, whereas for hexachlorobenzene (*6*), $CH_3CN:H_2O$ (9:1) was the solvent system. Concentrations of PCBzs *1* to *6* were 1.00 mM, and each sample solution contained 5.00 mM humic monomer *7*.

[a]Number of isomers, if any, and their percentages of total product given in parentheses.

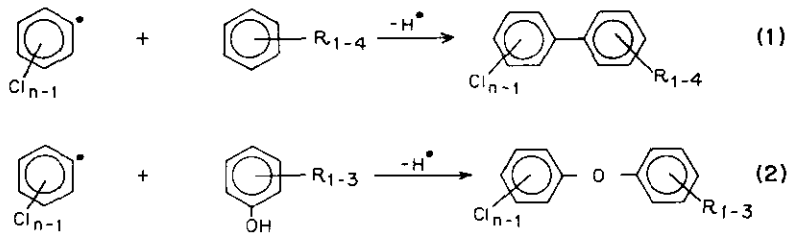



Fig. 1. Reactions by which photolytically generated polychlorophenyl radicals are incorporated into humic monomers.

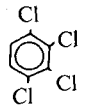
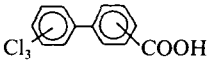
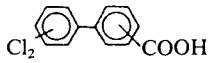
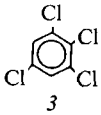
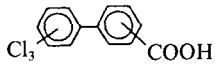
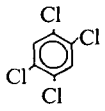
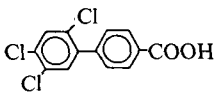
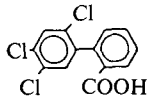
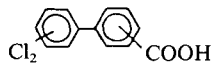
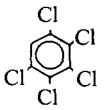
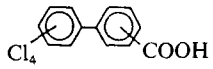
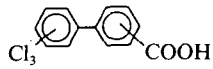
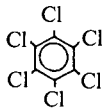
photoreactions were not quantified (Table 3). However, the chemical yields of the products documented in Table 3 were less than 1.0%. It should be mentioned that products in which R = COOH and OH were identified as methyl derivatives; diazomethane was used as the methylating agent.

Tables 1 and 2 indicate that among the PCBzs investigated, hexachlorobenzene (*6*) was unique in not generating products via Reaction 1. Recently, Choudhry and Hutzinger [10] reported that $Cl_6$-Bz (*6*) *does not yield PCBs, contrary to the direct* and acetone-sensitized photolyses of PCBzs *2* to *5* in water-acetonitrile mixtures.

In addition to the products described above (Tables 1 to 3), irradiation of PCBzs *1* to *5* in the presence of humic model monomers *7* to *12* yielded reductively dechlorinated benzenes as the 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 nonsensitized and acetone-sensitized photoreactions of 1,3,5-$Cl_3$-Bz (*1*) [9] and PCBzs *2* to *6* [10] have been published previously.

The 16-h exposure of $Cl_4$-Bz *4* in the presence of vanillic acid (*9*) led to the production not only of photoproducts formed through Reactions 1 and 2 (Fig. 1) but also of mono- and dichlorodibenzofurans having carboxylic and methoxy substituents formed via secondary photoprocesses (Table 3). The photolytically induced reactions of *4* with humic model monomer *9* are suggested in Fig. 2. Photoexcited tetrachlorobenzene *4* undergoes homolytic scissure of a C-Cl bond, which produces 2,4,5-trichlorophenyl radicals (*13*) (step a, path i), together with photoisomerization to eventually generate $Cl_4$-Bzs *2* and *3* (step a, path ii). Secondary photolyses of these photoisomerized tetrachlorobenzenes generate trichlorophenyl radicals *14* and *15* from *2* and *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 $Cl_4$-Bzs *2* to *4* in the presence and absence of acetone as a sensitizer in aqueous acetonitrile is

Table 2. Photochemical interactions of polychlorobenzenes (PCBzs) with benzaldehyde (*8*) in acetonitrile-water mixtures

| Substrate (PCBz) | Photoreaction time (h) | Disappearance of initial PCBz (%) | Product[a] |
|---|---|---|---|
|  *2* | 72.0 | 56.5 |  (7 isomers: 0.85; others <0.36)<br>  (<0.36) |
|  *3* | 72.0 | 56.1 |  (5 isomers: 0.40; others <0.26) |
|  *4* | 8.0 | 44.2 |   (both <0.32)<br>  (2 isomers: both <0.32) |
|  *5* | 24.0 | 34.0 |  (5 isomers: all <0.86)<br>  (0.88) |
|  *6* | 16.0 | 29.0 | — |

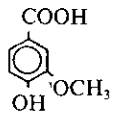
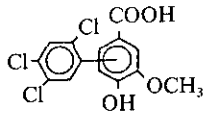
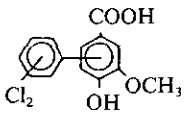
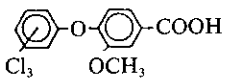
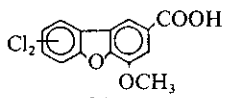
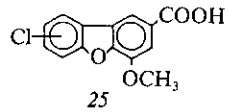
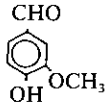
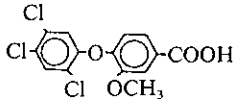
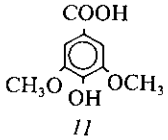
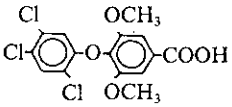
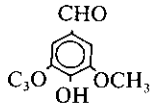
For PCBzs *2* to *5*, $CH_3CN$:$H_2O$ (1:1, v/v) was used as the solvent system and for substrate *6*, the solvent system was 9:1 $CH_3CN$:$H_2O$. Concentrations of PCBzs *2* to *6* were 1.00 mM, and each sample solution contained 5.00 mM humic monomer *8*.

[a]Number of isomers, if any, and their percentages of total product given in parentheses.

evidence that polychlorophenyl radicals are involved [10]. 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*) produces 2-methoxy-4-carbohydroxyphenoxy radicals (*19*) (Fig. 2, step b; see below). In addition, species *19* may be produced when the hydrogen atom is abstracted from the OH group of monomer *9* by free radicals (·R) such as ·Cl, $\cdot CH_2CN$, *13* to *18* and others. Subsequently, *20* (which represents species *13* to *17*) would combine with phenoxy radical *19* to yield trichloro-4′-carbohydroxy-2′-methoxydiphenyl ether *21*, containing an *o*-Cl substituent. The irradiation of ether *21* would produce 2-carbohydroxy-

Table 3. Photochemical interactions of 1,2,4,5-tetrachlorobenzene (*4*) with some humic model monomers in acetonitrile-water mixtures

| Humic model monomer | Photoreaction time (h) | Disappearance of PCBz *4* (%) | Product |
|---|---|---|---|
|  *9* | 16.0 | 64.3 |    (4 isomers)  *24*  *25* |
|  *10* | 16.0 | 37.4 |  |
|  *11* | 16.0 | 31.4 |  |
|  *12* | 16.0 | 82.1 | — |

The $CH_3CN$:$H_2O$ ratio (v/v) for the solvent system was 1:1. Concentrations (mM) of the chlorobenzene *4* and humic monomers *9* to *12* were as follows: *4*: 1.03 and *9*: 4.93; *4*: 1.03 and *10*: 5.01; *4*: 1.11 and *11*: 5.06; *4*: 1.08 and *12*: 5.00.

dichloro-4-methoxydibenzofuran (*24*) through the intermediate involvement of diphenylether radicals *22* and $\sigma$-complex *23* (Fig. 2, 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 $Cl_4$-Bzs *2* to *4* and acid *9*.

It is worth noting that, in similar studies,

Table 4. Ultraviolet[a] spectra of polychlorobenzenes[b] and humic model monomers[c] in acetonitrile

| No. | Compound | $\lambda_{max}$ (log $\epsilon_{max}$)[d] | $\epsilon_{300}$ |
|---|---|---|---|
| *1* | 1,3,5-$Cl_3$-Bz[e] | 203 (4.64)<br>219 (4.10)<br>264 (2.21)<br>272 (2.33)<br>279 (2.23) | 5.0 |
| *2* | 1,2,3,4-$Cl_4$-Bz | 277 (2.47)<br>286 (2.39) | 7.2 |
| *3* | 1,2,3,5-$Cl_4$-Bz | 279 (2.47)<br>288 (2.40) | 84.2 |
| *4* | 1,2,4,5-$Cl_4$-Bz | 282 (2.90)<br>291 (2.89) | 35.5 |
| *5* | $Cl_5$-Bz | 284 (2.53)<br>293 (2.51) | 123 |
| *6* | $Cl_6$-Bz | 288 (2.53)<br>298 (2.43) | 270 |
| *7* | Benzoic acid | 225 (4.06)<br>271 (2.92)<br>278 (2.81) | <0.4 |
| *8* | Benzaldehyde | 225 (4.01)<br>271 (2.93)<br>278 (2.86) | 24 |
| *9* | Vanillic acid | 205 (4.28)<br>215 (0.99)<br>257 (4.02)<br>277 (3.67) | 2,322 |
| *10* | Vanillin | 202 (4.17)<br>225 (4.26)<br>272 (4.08)<br>303 (4.00)<br>356 (2.38) | 9,600 |
| *11* | Syringic acid | 217 (4.46)<br>271 (4.06) | 2,196 |
| *12* | Syringaldehyde | 206 (4.24)<br>225 (4.21)<br>299 (4.06) | 11,577 |

[a]Recorded on Cary-14 double-beam spectrophotometer.
[b]Data for PCBzs *2* to *6* from ref. 2.
[c]Present work.
[d]$\lambda$ in nm and log $\epsilon_{max}$ in L $mol^{-1}$ $cm^{-1}$.
[e]Solvent was methanol.

Choudhry et al. [2] confirmed that 2,4,5-trichlorodiphenyl ether is an intermediate in the photoformation of 2,3-dichlorodibenzofuran from *4* and phenol. Species *18* also probably reacts with *19* to produce 4-carbohydroxy-2-methoxy-3′,4′,5′-trichlorodiphenyl ether (not shown in Fig. 2); however, this product is not expected to yield *24*. Our recent investigations [19] of the photolysis of tetra- and pentachlorophenols led us to conclude that phenoxy radicals produced through the photohomolysis of the OH group and by other free-radical processes in water-acetonitrile will not generate products arising from the phenoxylation of a benzene nucleus. Finally, trichloroarylation of acid *9* by radicals *20a* (which represent species *13* to *18*) produces *26* (Fig. 2, step d). Whether intermediate *26*, having a 2-Cl substituent, is also involved in the generation of *24* remains unknown.

As mentioned previously, because authentic standards are unavailable, we have been unable to

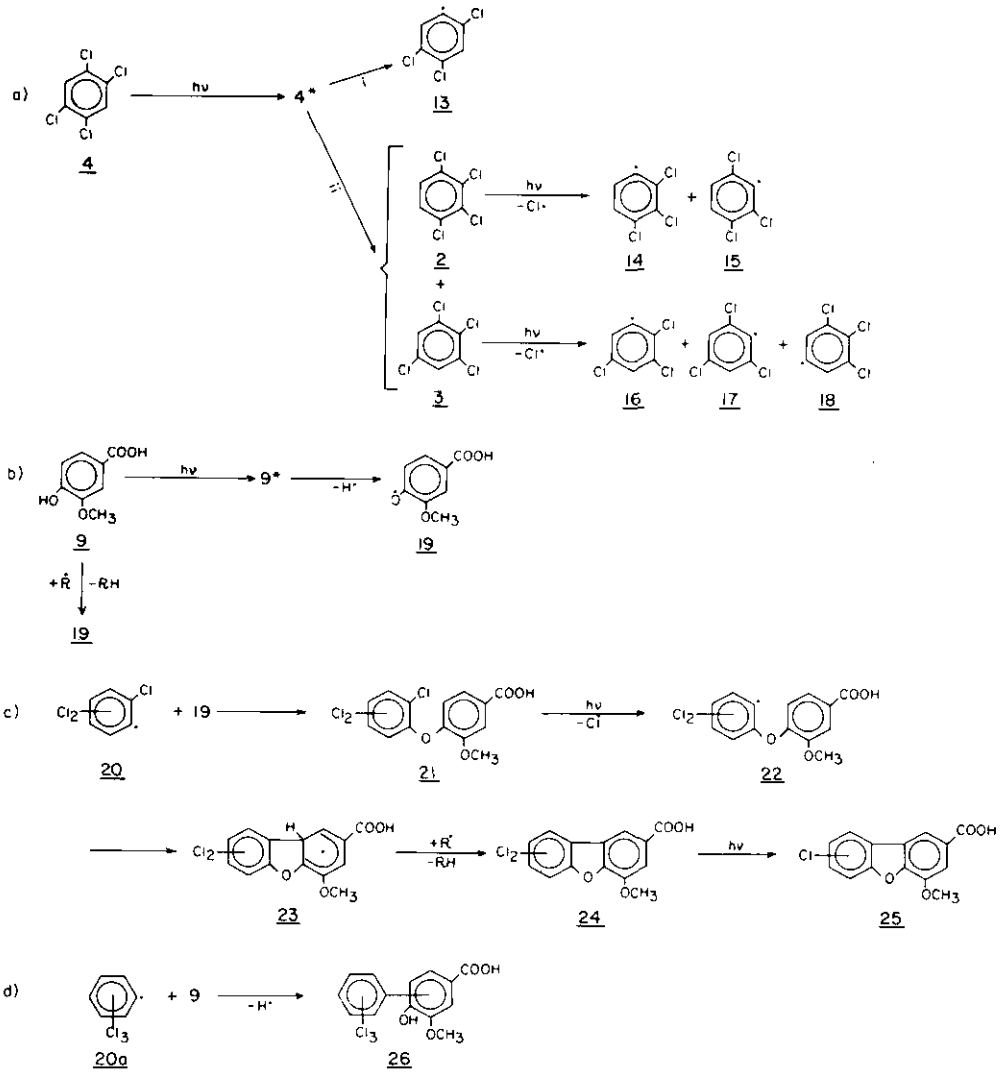


Fig. 2. Mechanism of photoincorporation of $Cl_4$-Bz *4* into humic model monomer *9*.

ascribe exact isomeric structures to the photoproducts, such as compounds *21* and *24* to *26* (see Fig. 2). However, the structures 2,4,5-trichloro-4'-carbohydroxy-2'methoxydiphenyl ether and 2,4,5-trichloro-4'-carbohydroxy-2',6'-dimethoxydiphenyl ether were assigned to products formed in the photoinduced interaction of $Cl_4$-Bz *4* with vanillin (*10*) and syringic acid (*11*), respectively (see Table 3). The probability of radical *13*'s contributing to Reaction 2 (Fig. 1) is greater than those of radicals *14* to *18*. Moreover, only one product of this sort was observed for 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 were not seen even when 82% of the initial chlorobenzene had disappeared (Table 3). Furthermore, during the photoincorporations of PCBzs *2* to *5* into benzaldehyde (*8*) (Table 2) as well as of *4* into vanillin (*10*) (Table 3), the aldehydic group on the nucleus of humic monomers and/or those of the photoproducts were photooxidized into carboxylic acid groups. Choudhry et al. [19] elsewhere reported such photooxidations of halogenated benzaldehydes.

During the photochemical interactions of 1,2,

3,4-$Cl_4$-Bz (*4*) with monomers *7* and *8*, 2,4,5-trichloro-4′-carbohydroxybiphenyl and 2,4,5-trichloro-2′-carbohydroxybiphenyl (the structures assigned above) were noticed (Tables 1 and 2, respectively), indicating that σ-complexes *27* and *28* (Fig. 3)—formed through the attack of intermediate radicals *13* (from *4*) on the *para* and *ortho* positions, respectively, of the nucleus of the monomers—are involved to a larger extent. Unlike the *meta* (with respect to R) isomer, the unpaired electron on species *27* and *28* is delocalized over the substituent of the monomer, so that extra stabilization is imparted to these σ-complexes. The same appears to occur in the case of the reaction of radicals *16* and *17* produced from PCBz *3* (see Table 1).

The frequent formation of dichlorophenylbenzoic acids from the photoincorporations of $Cl_4$-Bz *2* to *4* into *7* and *8* can partly be attributed to the photodegradation of the trichlorophenylbenzoic acid photoproduct and to the reaction of the product trichlorobenzenes with the monomers.

Although in the presence of acetone as a triplet sensitizer (0.553 mM) the photodegradation of 1,2,4,5-$Cl_4$-Bz (*4*) (1.112 mM) is accelerated twofold [10], the photoconversion of *4* (1.0 mM) is approximately three times slower when 5.0 mM vanillic acid (*9*) is present in the system (compare the results given in Table 3 with those in Table 2 of ref. 10). However, Table 4 indicates that the molar extinction coefficients at 300 nm ($\epsilon_{300}$) of $Cl_4$-Bz *4* and humic monomer *9* are 35.5 and 2,322 L $mol^{-1}$ $cm^{-1}$, revealing that the observed retardation of the rate of photolysis of *4* by *9* may be due to light screening rather than to quenching of the excited molecules of *4* by the ground-state molecules of *9*. Furthermore, the values of $\epsilon_{300}$ for the humic monomers *7* to *10* are in the following order: benzoic acid (*7*) < benzaldehyde (*8*) and vanillic acid (*9*) < vanillin (*10*) (Table 4), whereas the extent of degradation of 1,2,4,5-$Cl_4$-Bz (*4*) is in the opposite sequence (Tables 1 to 3). Finally, the $\epsilon_{300}$ value for syringic acid (*11*) is smaller than that of syringaldehyde (*12*), but the extent of the photoconversion of *4* in the presence of these monomers increases from *11* to *12*.

It is interesting that the yield of photoincorporated products for 1,3,5-$Cl_3$-Bz (*1*) is as much as 23%. Thus, the extent of the photoincorporation reaction is sizable for some chlorinated aromatic pollutant species. The quantity of photoproducts is clearly not dependent solely upon the rate of photolysis of the PCBz. For example, 1,2,4- and 1,3,5-$Cl_3$-Bz had equal photolysis rates in 1:1 $H_2O$:$CH_3CN$ [9], but only the latter compound yielded a chlorobiphenyl product (2,3′,4,5′-6-$Cl_5$-BP). Moreover, the photoreaction of these two PCBzs in methanol did not produce pentachlorobiphenyls at all; in this case the former PCBz degrades three times faster than the latter [9]. A similar observation was made for tetra- through hexachlorobenzenes [10]. This and other work [9,10] indicates that the relative stabilities of the photogenerated polychlorophenyl radicals may be more significant than the photolysis rates.

Finally, it should be remembered that the above-described experiments on the photoincorporations of PCBzs into humic model monomers were carried out using an approximate 1 mM solution of the PCBzs containing about 5 mM monomers (see Tables 1 to 3). It is apparent that the concentrations of the humic model monomers as well as of the pollutants used in the present studies were considerably higher than would be found in most natural water bodies; therefore the yields of the products resulting from the photoincorporation reactions of PCBzs with humic monomers (cf. Reactions 1 and 2, Fig. 1) are probably higher than would be encountered in natural waters. In other words, there is no doubt that such photoincorporations will be dependent upon the concentrations of the substrates; however, such dependency will become less significant when natural occurring acetone is present [10].

## ENVIRONMENTALLY SIGNIFICANT CONCLUSIONS

Although the structures of the photoincorporated products of PCBzs with humic model monomers, viz., benzaldehyde, benzoic acid, vanillin, vanillic acid, syringaldehyde and syringic acid (documented in Tables 1 to 3) have been assigned

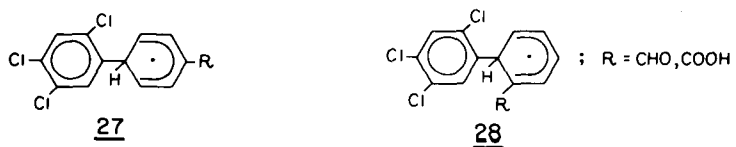



Fig. 3. Structures of σ-complexes *27* and *28*.

based on GC-MS data and are therefore tentative, the photoincorporation of PCBzs into the humic monomers investigated appears to occur through intermediate polychlorophenyl radicals. These relatively long-lived intermediate radicals, produced from PCBzs in the aqueous environments and possessing characteristics similar to those of $H_2O$-$CH_3CN$ mixtures, are likely to interact with the free-radical centers of humic substances, such as fulvic acids, humic acids and humins. It is noteworthy that humic macromolecules are known to possess free-radical characteristics, having $10^{17}$ to $10^{18}$ spins/g [5,7,21]. However, PCBzs may sorb onto humic substances and the light absorption spectra of the resulting complexes may differ from those of unbound (free) chlorobenzenes, whereby the nature of photoproducts and rates perhaps will change. Finally, radical species from PCBzs may also react with other substituted benzenes derived from humic substances and lignins [5–8].

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