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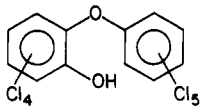
Photochemistry of Polychlorinated Phenoxyphenols. 3. Solvent Effects on the Photochemical Transformations of 3,4,5,6-Tetrachloro-2-(pentachlorophenoxy)phenol

Peter K. Freeman* and Ramanujan Srinivasa

The photochemical transformations of 3,4,5,6-tetrachloro-2-(pentachlorophenoxy)phenol (predioxin, 1) were studied at 300 nm in solvents dibutyl ether, THF, isobutyl alcohol, isopropyl alcohol, methanol, and acetonitrile. The quantum yield for cyclization increases with dielectric constant. The dependence of quantum yield for cyclization upon concentration fits better for an intramolecular electron transfer than an intermolecular one.

Our interest in the photochemical transformations of the perchlorinated phenoxyphenols (predioxin, 1, and meta



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and para isomers) is due to their presence as major contaminants in pentachlorophenol and their ready photoconversions at 300 nm to ether cleavage products, dechlorinated species, and highly toxic polychlorinated dibenzofurans and dibenzodioxins (Freeman and Srinivasa, 1983; Freeman and Jonas, 1984). This report describes some mechanistic features of the cyclization process as revealed by quantum yield dependence upon solvent polarity and substrate concentration.

EXPERIMENTAL SECTION

Materials and Methods. The solvents that were used in the photolysis were purified by distillation except for acetone and methanol, which were of spectrograde and were used as obtained. *m*-Methoxyacetophenone was used as obtained (Aldrich, 99%). Cyclopentanone was freshly distilled prior to its use.

Photolyses. The photolysis of predioxin (1) was carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight 3000-Å Rull lamps. A continuous stream of air was passed into the reactor chamber, and the measured temperature of the chamber during the photolysis was 40 °C. The photolysis samples were placed in quartz tubes (170 mm × 15 mm) attached with Pyrex glass sliding stoppers and degassed through three or four freeze–thaw cycles and sealed in vacuum prior to irradiation. The primary quantum yields of the photoproducts were determined with a cyclopentanone–4-pentenal actinometer. *m*-Methoxyacetophenone was used as the sensitizer.

Product Analysis. The photoproducts were identified by GLC retention times by comparison with those of the known compounds (chlorophenols, chlorobenzenes, 14, 15, and 17) and by mass spectrometry. The free hydroxy compounds formed in the photolysis were converted to their corresponding methyl ethers with diazomethane before the GLC analysis owing to the thermal instability of the former on the column at elevated temperatures. The

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Table I. Molar Extinction Coefficients (ϵ) at λ = 300 nm

compd	cyclohexane concn, M	cyclohexane ϵ	methanol concn, M	methanol ϵ
predioxin (1)	2.016×10^{-4}	2778	0.605×10^{-4}	2793
m-methoxyacetophenone	1.95×10^{-4}	2974	4.74×10^{-4}	2270

product analysis was done on a 5% OV-101–Chromsorb G column at a programmed temperature of 120–250 °C at 10 °C/min with helium as the carrier gas. The response factors for the known compounds were determined by using dodecane as the internal standard. Whenever authentic compounds were unavailable, their response factors were considered as the same as those for known compounds with similar structures. For example, the response factor for the *O*-methyl derivative of octachloro-2-phenoxyphenol, **13a** or **13b**, was considered as the same as that for the *O*-methyl derivative of predioxin (1).

Spectral Analyses. Mass spectral analyses of the photoproducts were done at 70 eV on a Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 gas chromatograph. UV measurements were made on a Varian Cary 118. The UV absorptions of predioxin (1) and *m*-methoxyacetophenone were measured in both nonpolar (cyclohexane) and polar (methanol) solvents. The data in Table I show that the molar extinction coefficient (ϵ) is not very dependent on the solvent polarity.

All of the solvents that were used have light transmission >95% at the irradiation wavelength. Since the predioxin and the sensitizer have absorptions of the same order of magnitude, an excess number of moles of the latter was used in the photolyses in order to ensure its >95% of light absorption.

Photolysis of Predioxin (1) in Solvents of Different Dielectric Constants. A 10.0-mL standard solution of predioxin (1) (0.05 g, 0.1006 mmol) in the respective solvent was prepared. The solutions also contained *m*-methoxyacetophenone (40 mol excess) and dodecane (50 μL). A 5.0-mL sample of each was degassed in quartz tubes by three freeze–pump–thaw cycles and irradiated at 300 nm for 3 h. The results are presented in Table II.

Actinometer. A 10.0-mL solution of cyclopentanone (0.4206 g, 0.5 M) and dodecane (50 μL) in the respective solvent was prepared, and a 5.0-mL sample of each in duplicate was degassed and irradiated simultaneously with the predioxin (1) samples for 3 h.

Diazomethane Treatment. A 0.78 M etherial solution of diazomethane was cautiously added to each of the photolysates at 0–5 °C until the pale yellow color persisted. The excess diazomethane was evaporated under a nitrogen atmosphere and the samples were concentrated to smaller volumes at room temperature before the GLC analysis.

Photolysis of Predioxin (1) in Dibutyl Ether at Various Concentrations. A 10.0-mL dibutyl ether solution containing predioxin (0.4968 g, 1.0 mmol), *m*-methoxyacetophenone (23-fold excess), and dodecane (20 mmol) was prepared. This solution corresponded to 0.1 M predioxin. Four other solutions of different concentrations were prepared from the 0.1 M solution by dilution of the appropriate volume. Two 4.0-mL samples of each were degassed and irradiated at 300 nm for 6 h (Table III). A 25.0-mL solution of cyclopentanone (0.5 M) and dodecane in dibutyl ether was prepared, and three 4.0-mL samples, each containing 4.013 mmol of the ketone, were degassed and irradiated simultaneously with the predioxin samples for 6 h.

RESULTS AND DISCUSSION

Earlier we have described the phototransformations of

Table II. Photolyses of Predioxin (1) in the Presence of *m*-Methoxyacetophenone[a]

photoproduct	*n*-butyl ether mol %[b]	*n*-butyl ether Φ[b,c]	THF mol %	THF Φ	isobutyl alcohol mol %	isobutyl alcohol Φ	2-propanol mol %	2-propanol Φ	methanol mol %	methanol Φ	acetonitrile mol %	acetonitrile Φ
pentachlorophenol	14.6 ± 0.6	0.285 ± 0.012	27.5 ± 0.5	0.536 ± 0.010	2.8 ± 0.1	0.047 ± 0.002	6.1 ± 1.0	0.069 ± 0.011	6.1 ± 2.0	0.069 ± 0.023	4.1 ± 0.2	0.047 ± 0.002
13a	3.5 ± 0.7	0.068 ± 0.014	17.6 ± 0.9	0.343 ± 0.017	0.0		0.0		0.0		0.0	
13b	1.4 ± 0.0	0.027 ± 0.0	4.0 ± 0.5	0.078 ± 0.001	11.3 ± 0.3	0.190 ± 0.005	11.0 ± 0.6	0.125 ± 0.007	8.9 ± 0.5	0.101 ± 0.006	0.0	
14	0.0		0.3 ± 0.3	0.006 ± 0.006	1.9 ± 0.1	0.032 ± 0.007	3.0 ± 0.0	0.034 ± 0.0	0.0		0.2 ± 0.0	0.002 ± 0.0
16	0.0		0.0		0.0		0.0		7.8 ± 2.8	0.089 ± 0.032	0.0	
15	0.0		0.0		3.3 ± 0.0	0.055 ± 0.0	3.0 ± 0.0	0.034 ± 0.0	0.0		0.0	
18a	0.0		1.9 ± 1.8	0.037 ± 0.034	1.2 ± 0.4	0.020 ± 0.007	0.9 ± 0.3	0.010 ± 0.003	0.0		0.0	
17	0.6 ± 0.0	0.012 ± 0.0	0.0		5.2 ± 0.2	0.087 ± 0.003	6.9 ± 0.1	0.079 ± 0.001	46.1 ± 0.8	0.526 ± 0.009	47.9 ± 0.3	0.546 ± 0.003
18b	0.0		0.0		2.4 ± 0.3	0.040 ± 0.005	0.0		0.0		0.0	

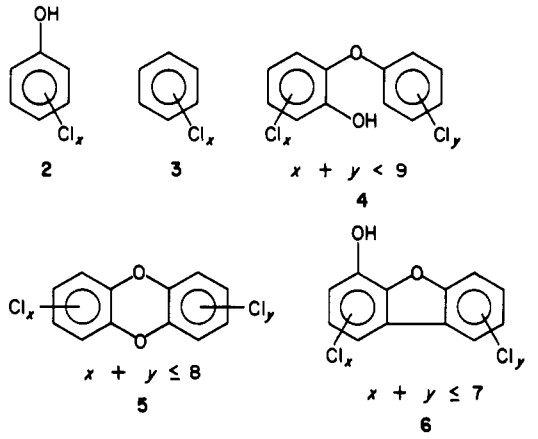
[a] Reaction carried out at 300 nm, 3 h; solvent, 40 mol excess of *m*-methoxyacetophenone. [b] The mole percent and quantum yields are the average and range for two runs. [c] The quantum yields were determined by using a cyclopentanone actinometer in the solvent employed in the run.

Table III. Photolysis of Predioxin (1) at Different Concentrations in Dibutyl Ether[a]

concn of 1, M		photoproducts			
		PCP	13a	13b	17
0.0100	mol %[b]	15.3 ± 2.4	2.1 ● 0.2	2.0 ± 0.5	3.3 ± 0.0
	Φ[b,c]	0.226 ± 0.036	0.031 ± 0.003	0.03 ● 0.007	0.049 ± 0.0
0.0200	mol %	8.7 ± 0.8	1.7 ± 0.2	0.7 ± 0.3	0.2 ± 0.0
	Φ	0.129 ± 0.012	0.025 ± 0.003	0.01 ± 0.004	0.03 ± 0.0
0.0401	mol %	4.3 ± 0.3	1.0 ● 0.0	0.1 ± 0.1	0.1 ± 0.1
	Φ	0.064 ± 0.004	0.015 ± 0.0	0.0015 ● 0.0015	0.0015 ± 0.0015
0.0801	mol %	3.7 ± 0.2	0.7 ± 0.2	trace	trace
	Φ	0.055 ± 0.003	0.01 ± 0.003		

[a] Photolyses carried out at 300 nm for 6 h with 23-fold excess of *m*-methoxyacetophenone. [b] The mole percent and quantum yields are the average and range for two runs. [c] The quantum yields were determined by using cyclopentanone actinometry.

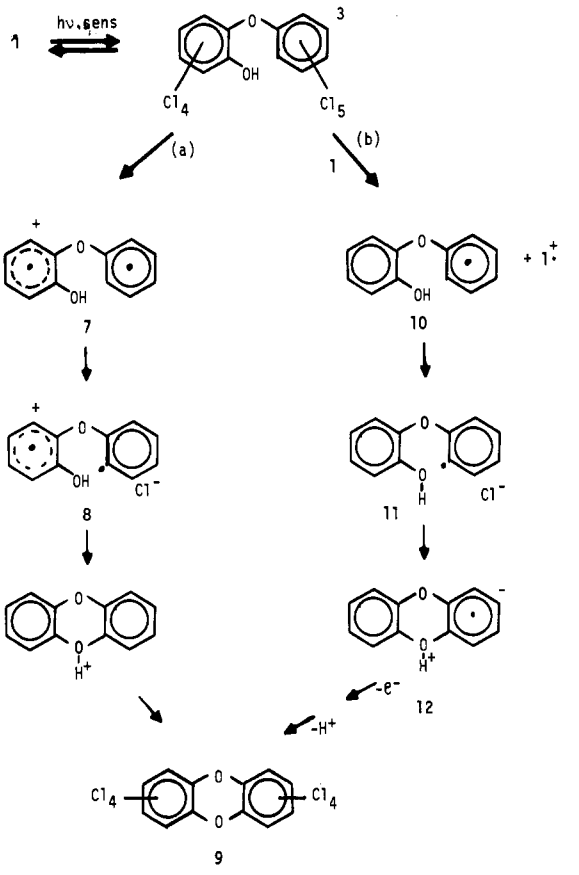
predioxin (1). Three major reaction pathways were observed: (a) ether cleavage leading to polychlorophenols (2)



and polychlorobenzenes (3), (b) reductive dechlorination producing products represented by 4, and (c) cyclization generating polychlorodibenzodioxins (5) and hydroxypolychlorodibenzofurans (6). In the direct irradiations (300 nm, cyclohexane) ether cleavage and reductive dechlorination predominated, while in the sensitized photolyses (acetone or *m*-methoxyacetophenone/cyclohexane) cyclization was a dominant or substantial contributor with evidence of competing ether cleavage and dechlorination (Freeman and Srinivasa, 1983).

The cyclization pathway was enhanced by 81% when a run in acetone was compared with a run in acetone in the presence of the electron transfer reagent triethylamine. Since the C–Cl bond energy should be about 95 kcal/mol (Egger and Cocks, 1983), and the energy of the triplet state is 72 kcal/mol or less, the enhancement of the cyclization process in the presence of an electron transfer reagent suggests radical anion formation from the triplet state followed by C–Cl bond fission and cyclization (Ohashi et al., 1973; Bunce et al., 1975, 1976, 1978; Ruzo et al., 1975; Chitten et al., 1978; Davidson and Goodin, 1981; Grimshaw and deSilva, 1981; Soumillion and deWolf, 1981). Such a process, in the absence of triethylamine, might involve an intramolecular electron transfer (route a, Scheme I) (Okajima et al., 1977; Soumillion and deWolf, 1981; Todesco et al., 1981) or intermolecular electron transfer (route b, Scheme I). In route a radical cation–radical anion 7 is formed, followed by expulsion of chloride ion to form cation diradical 8. The delocalized odd electron density on the hydroxyl oxygen interacts with the ortho radical center to form the conjugate acid of octachlorodioxin, which loses a proton forming 9. Alternatively (route b), intermolecular electron transfer might generate radical anion 10, which could form radical 11, which might cyclize and subsequently lose an electron and a proton to form

Scheme I



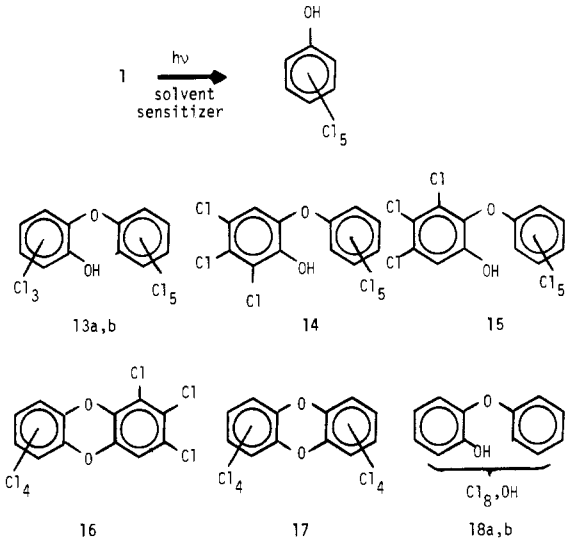
octachlorodibenzodioxin (9).

In either an intra- or intermolecular electron transfer process there is charge creation in the transition state, and cyclization should be sensitive to the polarity of the medium. It seemed important, therefore, to evaluate the dependence of quantum yield upon solvent polarity. A consideration of the phototransformations of predioxin (1) in the presence of sensitizer *m*-methoxyacetophenone in dibutyl ether, THF, isobutyl alcohol, isopropyl alcohol, methanol, and acetonitrile revealed the formation of pentachlorophenol, dechlorinated predioxins **13a**, **13b**, **14**, and **15**, dioxins **16** and **17**, and two dihydroxy species **18a** and **18b** (Scheme II and Table II).

As the dielectric constant is increased from the relatively nonpolar ethers dibutyl ether (ϵ = 3.1) and THF (7.6) to isobutyl alcohol (17.7) and isopropyl alcohol (18.3) to the more polar methyl alcohol (32.6) and acetonitrile (37.5), we view a regular and dramatic increase in the quantum yields of the cyclization products, **16** and **17**. This supports the electron transfer mechanisms outlined in Scheme I.

In order to attempt to uncover whether the process is intramolecular or intermolecular, the dependence of

Scheme II



quantum yield for cyclization upon concentration of predioxin (1) was studied. Reactions were carried out in dibutyl ether at 300 nm, and the results are presented in Table III. Since the intermolecular process is a bimolecular process competing with unimolecular processes, one should observe an increase in cyclization with increasing concentration if this mode is operative. Instead, we see the very low amounts of cyclic product maintained, and at least qualitatively, the intramolecular process emerges as the preferred alternative.

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Enzymatic Degradation of α- and β-Cyclodextrins by *Bacteroides* of the Human Colon

Robert N. Antenucci* and James K. Palmer

Thirty *Bacteroides* strains from the human colon were tested for the ability to degrade cyclodextrins (CDs) in vitro. Twenty-four strains were able to degrade CDs. Cyclodextrinase (CDase) in two of these strains, *Bacteroides ovatus* 3524 and *Bacteroides distasonis* C18-7, has been studied. Organisms were grown on a minimal medium containing CD (0.5%), and CDase activity was assayed by measuring the increase in reducing sugar (as glucose) when CDs were incubated at 37 °C for 4 h with crude enzyme preparations. CDase activity was predominantly cell bound and induced in both organisms by growth on CDs. The products of CD hydrolysis by the crude enzyme preparations from the two strains were sharply different. *B. ovatus* 3524 CDase catalyzed production of glucose only, while the *B. distasonis* C18-7 catalyzed production of a series of maltooligomers. CDase was stable and active under expected conditions of the colon environment (pH 7.0; 37 °C).

Cyclodextrins (CDs) are cyclic oligosacchrides composed of six or more α-1,4-linked glucose units (Radley, 1968). CDs readily form inclusion complexes with various chemicals, often significantly increasing the stability and/or water solubility of the complexed compounds (Saenger, 1981). This complex formation is the basis for recent publications and patents that propose the use of CDs as nutritionally inert stabilizers in various food and pharmaceutical products. For example, CDs stabilize anthocyanin pigments (Yamada et al., 1980), increase water solubility of vitamins A, D, E, and K (Pitha et al., 1981), and stabilize food flavors, unsaturated fatty acids, and vitamin A, as well as a variety of foods including rice, cheese, and noodles (Szejtli, 1981).

In contrast to the considerable information concerning the use and role of CDs in stabilizing various food and food ingredients, the fate of ingested CDs or CD complexes is not clear. CDs are only slowly hydrolyzed by salivary or intestinal amylases (French and McIntire, 1950). This fact has been taken as evidence that CDs are metabolically inert. However, CDs could be fermented by colon anaerobes to yield products (e.g., fatty acids) that are known to have nutritive value.

CD metabolism in rats was investigated by Anderson et al. (1963) through oral administration of [^{14}C]-β-CD to rats

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