

Photochemistry of Higher Chlorinated PCBs in Cyclohexane

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The degradation pathways of higher polychlorinated biphenyl congeners irradiated at 300 nm were investigated. Ortho dechlorination is an important degradation pathway for congeners bearing one or two such substituents. Steric factors also influence dechlorination at various positions of the more substituted or more reactive ring. Precursors of the toxic congeners 77 and 126, formed upon sunlight irradiation of Aroclor 1254, were identified.

INTRODUCTION

Many publications have dealt with the decomposition pathways of UV-irradiated polychlorinated biphenyls (PCBs) in solution (Bunce et al., 1978; Ruza et al., 1974; Hutzinger et al., 1972; Safe and Hutzinger, 1971). These studies however, were mostly performed with symmetrical and/or lower chlorinated congeners which are not necessarily representative of the generally heavier PCB congeners found in commercial PCB mixtures and in the environment. The main decomposition pathway reported for UV-irradiated PCBs is reductive dechlorination. The monodechlorinated biphenyl radical formed upon homolytic cleavage of a carbon-chlorine bond scavenges a hydrogen atom from the solvent to produce a monodechlorinated PCB congener. It is generally accepted that the more chlorinated PCB congeners are more reactive toward photodechlorination and that ortho chlorines are lost preferentially over meta and para substituents (Zabik, 1983).

In a previous publication (Lépine et al., 1992), the effects of solar irradiation on Aroclor 1254 cyclohexane solutions were reported where, using an isomer-specific chromatographic analysis, formation of large amounts of the very toxic congeners 77 and 126 was observed. The main objective of this study was to elucidate the photodegradation pathways of higher chlorinated PCBs, which are more representative of those found in the environment. Considering the large toxicities of congeners 77 and 126 (Leece et al., 1985), a second objective was to identify their potential precursors to explain the results obtained previously in sunlight-irradiated Aroclor 1254.

EXPERIMENTAL PROCEDURES

Gas Chromatography. A Varian 3500 gas chromatograph equipped with a DB-5 column (30 m × 0.3 mm i.d.) was used. Injections were performed with an on-column injector at 250 °C with helium as the carrier gas. Typically, the temperature program was initially set at 100 °C increased to 150 °C at 20 °C/min, then to 250 °C at 5 °C/min, then to 270 °C at 8 °C/min, and finally to 310 °C at 20 °C/min.

Mass Spectrometry. The detector was a Finnigan ITD 800 interfaced to an IBM XT computer. The scanning mass range was from 100 to 510 amu.

Chemicals. PCB congeners and Aroclor 1254 were purchased from Analab (CT) and were over 99% pure as checked by GC-MS. Cyclohexane was spectrograde and was used without further purification.

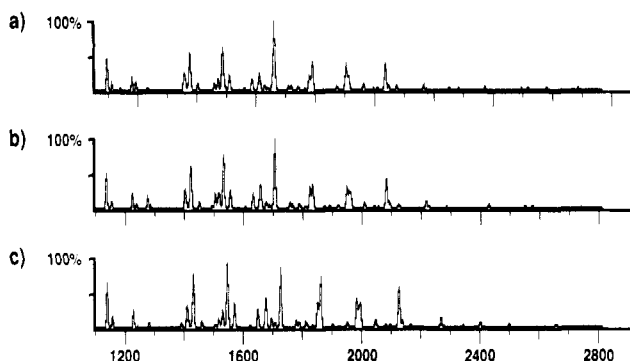


Figure 1. Chromatographic profile of Aroclor 1254 irradiated (a) with sunlight for 55 days or (b) with UV lamps for 10 min. (c) Unirradiated solution.

Sample Preparation and Irradiation. Samples were prepared in triplicate. The concentration of PCBs and Aroclor 1254 in cyclohexane was 4 ppm. Samples were degassed by bubbling with nitrogen for 15 min and placed in 2.2-mL NMR tubes under nitrogen. Samples were irradiated in a Rayonet reactor equipped with three RPR 3000 lamps with maximum emission at 300 nm using a merry-go-round adaptor. After irradiation, 30 ng of deca-chlorobiphenyl was added as internal standard and the solutions were concentrated using a gentle stream of nitrogen. Samples were concentrated in the 30–40 ppm range for pure PCB congeners and in the 300–400 ppm range for Aroclor 1254. Identification of the various dechlorinated PCB congeners was performed using the data of Mullin et al. (1984). The ultraviolet spectra were taken with a Varian DMS 200.

RESULTS AND DISCUSSION

The congeners chosen for this study cover a range of chlorine substituents varying from four to seven. Many of these congeners are present in large amounts in Aroclor 1254. The concentration of these congeners used in the present study was set at 4 ppm, as in the previous Aroclor 1254 experiment. Irradiation conditions at 300 nm were adjusted to reproduce the modifications of the chromatographic profile of the sunlight-irradiated Aroclor 1254 previously reported (Lépine et al., 1992). These modifications were reproduced using an irradiation time of 10 min. Figure 1 shows the similarity of the (a) sunlight- and (b) UV-irradiated Aroclor 1254 with respect to the unirradiated solution (c). Then, to mimic longer sunlight irradiation times and to verify the photostability of the primary photodegradation products, the UV irradiation time was doubled to 20 min. The results of these experiments are presented in Table I. Table II shows the extinction coefficients at 300 nm for these various congeners.

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Table I. Degradation Products of UV-Irradiated PCB Congeners in Cyclohexane

starting material ^a	dest. %	-1Cl, ^b %	% of monodechlorinated products obtained from the starting material through loss of			-2Cl, ^c %	didechlorinated products, ^d %
			<i>o</i> -Cl	<i>m</i> -Cl	<i>p</i> -Cl		
2,2',5,5' (52)	0	ND ^e	ND	ND	ND	ND	ND
3,3',4,4' (77)	1.1	1.1	NR ^f	3,4,4' (37) 83	3,3',4 (35) 17	ND	ND
2,2',4,5,5' (101)	3.3	3.3	2,3',4',5 (70) 25 2,3',4,5 (67) 1	2,2',4,5' (49) 46	2,2',5,5' (52) 28	ND	ND
2,3',4,4',5 (118)	67	60	3,3',4,4' (77) 99.9	2,3',4,4' (66) 0.1	ND	1	3,4,4' (37) 92 3,3',4 (35) 8
2,2',3,4,4',5' (138)	48	29	2,3',4,4',5 (118) 93.1 2,3,3',4,4' (105) 1.2	2,2',4,4',5 (99) 5 2,2',3,4,4' (85) 0.2	2,2',3',4,5 (97) 0.4 2,2',3,4,5' (87) 0.2	18	3,3',4,4' (77) 100
2,2',4,4',5,5' (153)	8.1	6.9	2,3',4,4',5 (118) 28	2,2',4,4',5 (99) 42	2,2',4,5,5' (101) 30	1.2	3,3',4,4' (77) 97 2,3',4',5 (70) 2 2,3',4,5 (67) 1
2,2',3,4,4',5,5' (180)	14	13.2	2,3',4,4',5,5' (167) 38 2,3,3',4,4',5 (157) 0.4	2,2',4,4',5,5' (153) 28.4 2,2',3,4,4',5' (138) 1.2	2,2',3,4',5,5' (146) 36	0.8	3,3',4,4',5 (126) 64 2,3',4,4',5 (118) 13 2,2',4,4',5 (99) 9 2,3',4,5,5' (120) 8 2,2',4,5,5' (101) 7
2,2',3,4,4',5',6 (183)	68.7	55.3	2,2',4,4',5,5' (153) 4.9 2,3,3',4,4',6 (158) 0.1	2,2',4,4',5,6' (154) 92	2,2',3,4',5',6 (149) 2.2 2,2',3,4,5',6 (144) 0.1	13.4	2,2',4,4',6 (100) 72.3 2,2',4,5',6 (103) 21.3 2,2',4,4',5 (99) 5.1 2,2',4,5,5' (101) 0.6 2,2',3,5',6 (95) 0.5 2,3',4,4',6 (119) 0.2

^a Number in parentheses is the corresponding IUPAC number. ^b Percentage of the sum of monodechlorinated products relative to the starting material. ^c Percentage of the sum of didechlorinated products relative to the starting material. ^d Percentage of the sum of didechlorinated products. ^e Not detected. ^f Not relevant.

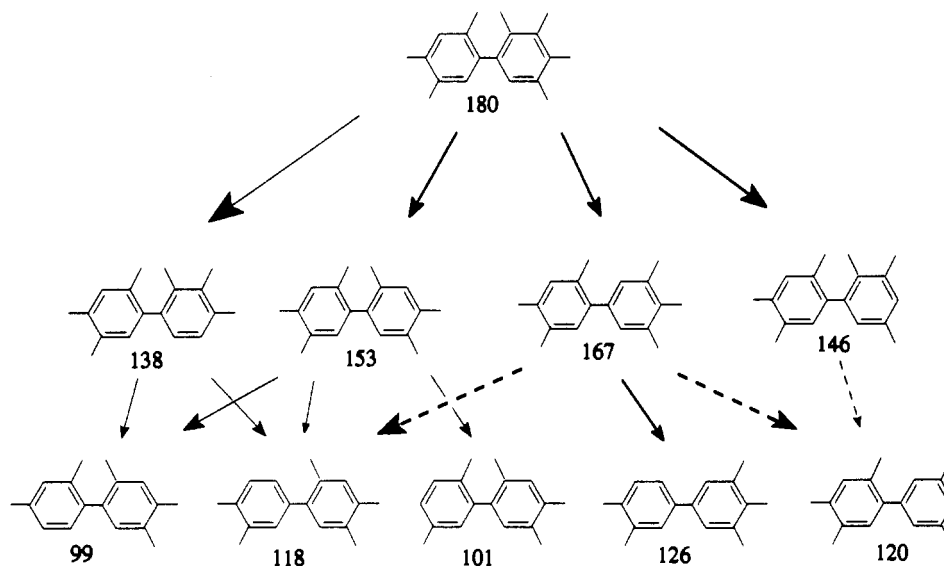


Figure 2. Degradation pathways of congener 180. Dotted arrows are used when the origin of a given congener cannot be formally identified.

Previous studies have demonstrated that, for lower chlorinated PCBs, monoortho- and diortho-substituted congeners were more photolabile than others and that these ortho chlorines are lost preferentially (Zabik, 1983). This increased reactivity of ortho substituents was attributed by Bunce et al. (1978) to the higher triplet energy of monoortho- and diortho-chlorinated congeners which have planar triplets, contrary to the tri- and tetrasubstituted derivatives which have twisted triplets. For lower chlorinated PCBs, monoortho-substituted congeners were found to be more rapidly photodegraded than diortho-substituted congeners because only the loss of the last ortho chlorine would relieve sufficient steric strain from the intermediate. The presence of meta chlorines was

also observed to decrease the reactivity of ortho chlorines, while para chlorines enhanced their reactivity.

Under the reaction conditions used, the 2,2',5,5' congener 52 and the 3,3',4,4' congener 77 were stable. The photostability of congener 77 indicates that if this congener is produced, as observed in the Aroclor 1254 experiment, it will accumulate. In view of the considerable toxicity of this congener, this represents a serious environmental problem. The slight degradation of congener 77 proceeds mostly through loss of a meta chlorine, in agreement with the findings of Ruzo et al. (1972).

The 2,3',4,4',5 congener 118 is largely degraded, and dechlorination, as expected for a monoortho-chlorinated congener (Bunce et al., 1978), proceeds almost exclusively

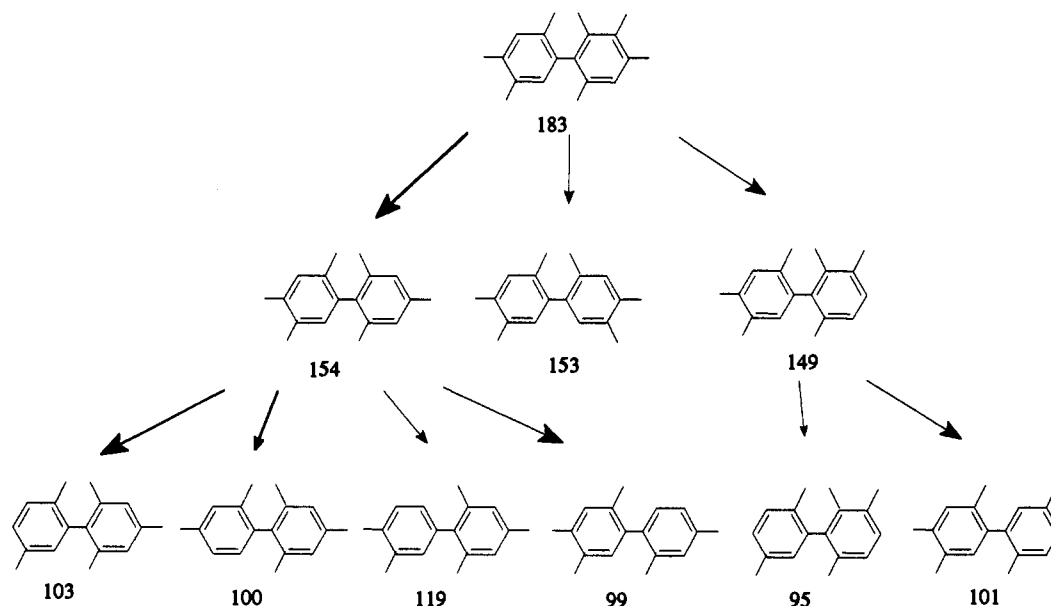


Figure 3. Degradation pathways of congener 183.

Table II. Extinction Coefficient of PCB Congeners at 300 nm in Cyclohexane

congener	extinction coeff ($\times 10^3$), mol/L	congener	extinction coeff ($\times 10^3$), mol/L
77	2.30	153	8.05
101	4.32	180	7.19
118	1.75	183	4.90
138	6.56		

at the ortho position to produce the toxic congener 77. Because congener 118 is very abundant in Aroclor 1254 (Albro et al., 1981), it is certainly a very important precursor of congener 77 in sunlight-irradiated Aroclor 1254.

For the 2,2',4,5,5' congener 101, the very slight degradation observed proceeds evenly at the ortho and para positions and slightly more at the meta position of the more substituted ring. This is probably due to the diminished ortho reactivity caused by the presence of two ortho chlorines and the opposing effects of the meta and para substituents which, in the first case, decreases the efficiency of ortho dechlorination while the latter increases it (Bunce et al., 1978).

The 2,2',3,4,4',5' congener 138 is also appreciably degraded, mostly through loss of the ortho chlorine of its 2,3,4-substituted ring. Both rings share the same number of ortho, meta, and para chlorines, but the steric congestion of the 2,3,4 arrangement probably renders it more reactive, especially at its ortho position, which undergoes the buttressing effect of the adjacent meta chlorine. Loss of the 2-Cl generates congener 118 which, under these reaction conditions, is largely degraded into the toxic congener 77 which is the sole didechlorinated byproduct of 138. Because congener 138 is also very abundant in Aroclor 1254 (Albro et al., 1981), it therefore constitutes another important, albeit indirect, precursor of 77.

The 2,2',4,4',5,5' congener 153 bears the same total number of chlorines and the same number of ortho chlorines as congener 138 but is only slightly degraded. The relative amounts of the various dechlorination products indicate that dechlorination occurs at every position and in the same ratio as for congener 101, which also bears the same 2,4,5 substitution pattern on its most substituted ring and is also little degraded. Ortho dechlorination generates congener 118, which in turn generates congener 77. Congener 153 is relatively abundant in Aroclor 1254

(Albro et al., 1981) and probably also contributes to a small extent to the formation of congener 77 in sunlight-irradiated Aroclor 1254.

The 2,2',3,4,4',5,5' congener 180 is also only slightly degraded and over 99% of the monodechlorinated products arise from dechlorination of its most substituted 2,3,4,5 ring. In contrast with congener 138, which undergoes ortho dechlorination preferentially, dechlorination of congener 180 occurs almost evenly at the 2-, 3-, and 4-positions. The relative deactivation of the ortho chlorine of the 2,3,4,5 ring compared to the 2-Cl of congener 138 could be due to the additional meta substituent which has been shown to deactivate ortho chlorines (Bunce et al., 1978; Zabick, 1983). Steric compression could explain the reactivity at the 3- and 4-positions of congener 180 and the relative stability of the 5-Cl. Dechlorination at the 3-position gives congener 153. As described previously, irradiation of congener 153 generates the congeners 99, 101, and 118, in the ratios described in Table I. In the congener 180 experiment there are three potential precursors of congener 99, namely congeners 137, 138, and 153 (Figure 2). Congener 137 is only present in trace amounts, and Table I shows that production of congener 99 from 138 is very inefficient. Because there are very small amounts of congener 138 produced upon irradiation of congener 180, this leaves only congener 153 as the main precursor of congener 99. Using the ratio of congeners 99, 101, and 118 produced from congener 153, one concludes that in the congener 180 experiment congener 153 is the only precursor of congeners 99 and 101 and it produces about half of the observed amounts of congener 118. This rules out congener 146 as a precursor of congener 101. Most of the remaining amounts of congener 118 can be accounted for by the degradation of congener 138 and possibly, to a lesser extent, by congener 167 degradation. Congeners 146 and 167 are both potential precursors of congener 120. Congener 157 is a potential precursor of congener 126, but the former is present only in very small amounts, which leaves congener 167 as the only important source of congener 126. The fact that congener 126 represents more than 60% of the didechlorinated products reflects the sensitivity of congener 167 toward photodechlorination. Congener 167, like congener 118, bears only one ortho chlorine, a configuration that favors ortho dechlorination over the other substituents as observed for congener 118 and as

noted by Zabick (1983). Thus, the observed formation of the very toxic congener 126 in the sunlight irradiation experiment of Aroclor 1254 can be attributed, at least in part, to the degradation of congener 167. The fact that in this experiment the amounts of 167 did not vary much is explained by its formation from the relatively abundant congener 180.

The 2,2',3,4,4',5',6 congener 183 is largely degraded, and 98% of its monodechlorinated products arise from dechlorination of its most substituted 2,3,4,6 ring. In contrast with all of the other PCB congeners examined in this study, dechlorination occurs almost exclusively at the 3-position. The total lack of reactivity of the ortho chlorines is likely caused by the fact that congener 183 bears three such substituents, a configuration known to inhibit ortho dechlorination (Ruzo et al., 1974). The favored loss of the 3-Cl can again be explained by steric compression factors, this chlorine atom being flanked by two vicinal chlorines. Such an effect has also been invoked by Freeman et al. (1986) to explain the favored loss of the 2-Cl upon UV irradiation of 1,2,3,5-tetrachlorobenzene, a substitution pattern similar to that of the 2,3,4,6-substituted ring of congener 183. Deactivation of ortho chlorines in a congener bearing three such substituents can also be observed in the degradation products of congener 154, itself produced from photodegradation of congener 183. Congener 154 undergoes dechlorination almost exclusively on its 2,4,5 ring in the meta and para positions to produce congeners 103 and 100 in a ratio similar to the one of the dechlorinated products of congener 77. The absence of congener 118 from the degradation products of congener 183 indicates that congeners 99 and 101 are not produced from congener 153 but from congeners 154 and 149, respectively (Figure 3). Congener 149 is also the precursor of congener 95.

All of these results show that dechlorination occurs almost exclusively on the more substituted ring of odd-numbered-substituted congeners as observed by Zabick (1983) for lower chlorinated congeners. The relative reactivity of ortho chlorines vs meta or para substituents is controlled by the substitution pattern of the ring but most importantly by the total number of ortho chlorines in the molecule, ortho dechlorination being dominant for monoortho-substituted congeners such as 118 or 167 and minimal for congeners bearing three ortho chlorines such as congeners 183 and 154.

Because most of congeners presented in Table I along with some primary degradation products share a 2,4,5-substituted ring, the relative reactivity of the other substitution patterns can be compared with respect to the relative amount of the degradation products arising from dechlorination of either ring. The relative reactivity is larger for the 2,3,4,6, 2,3,4, and 2,3,4,5 patterns, similar for the 2,3,6 pattern, and smaller for the 2,4,6, 3,4, and 2,5 patterns. Steric compression factors are certainly, at least in part, responsible for the reactivity of these patterns, especially in the light of the proportions of the degradation products obtained.

CONCLUSION

This study showed that the degradation pathways of higher chlorinated PCB congeners follow the same trend

as those observed for lower chlorinated PCBs. Ortho dechlorination is an important degradation pathway for congeners bearing two or fewer such substituents. Steric compression factors are also important factors controlling the degradation pathways of higher chlorinated PCBs.

The study of the UV-induced dechlorination of higher chlorinated PCB congeners allowed the identification of some important precursors of the toxic congeners 77 and 126 produced upon sunlight irradiation of Aroclor 1254. In the case of congener 77 two of its precursors were found to be congeners 118 and 138, which are very photolabile and present in large amounts in Aroclor 1254. These findings along with the observed photostability of the toxic congener 77 can be an environmental concern.

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