Photolysis of Environmentally Important PCBs

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Polychlorobiphenyls (PCBs) are halogenated aromatic environmentally persistent organic pollutants that are very resistant to chemical decomposition or microbial biodegradation and have been linked to a variety of adverse health effects[1]. Most of the 209 possible PCB congeners have low direct toxicity with the exception of the non-ortho substituted (coplanar) PCBs and to some extent the mono-ortho substituted compounds [1]. Large amounts of these compounds are now stored in old transformers and landfills or have escaped into the environment. The most common approach to the destruction of PCB mixtures is incineration. This must be done carefully, however, since even more toxic oxygenated byproducts such as polychlorinated dibenzo-p-dioxins and dibenzofurans can be formed.

Photodegradation is an attractive mechanism for the decomposition of PCBs. Photodecomposition has been reported as an important decomposition mechanism for PCBs in the environment [7]. Sworzyn and Ackerman have reported that photodecomposition of PCBs at a wavelength greater than 290 nm is possible on an industrial scale in terms of cost-benefit and effectiveness[3]. Most PCB congeners do not absorb light strongly above 300 nm, however, and their direct photolysis generally occurs with very low quantum efficiency. Sensitizers and other additives have been used to enhance the photodegradation reactions. These photodegradation reactions generally involve dechlorination of the biphenyl rings [4]. These dechlorination reactions have been reported to proceed by the loss of the chlorine in the order of ortho > para > meta [5]. Additionally, Lepine, Milot, and Vincent[6] have reported the photodegradation of a common commercial mixture of PCBs (Aroclor 1254) under natural sunlight led to the decrease in many of the highly chlorinated PCB species but unfortunately led to an increase in the concentrations of the highly toxic PCBs 77 and 126.

PCBs are very lipophilic compounds that can be easily concentrated and removed from aqueous environmental samples by hydrophobic stationary phases such as octadecylsilylated silica gel (C_{18}). We explored the photolysis of individual, environmentally important PCB congeners that were trapped and concentrated on C_{18} particles. Employing an alkyl alcohol as a sensitizer, efficient dechlorination of PCBs were observed. The products formed, however were often the more toxic coplanar PCBs which then only slowly decomposed to less toxic monochlorobiphenyls and biphenyl. Photolysis reactions must be allowed to proceed until the more photo-stable and more toxic coplanar PCBs are allowed to decompose. These results also suggest that naturally occurring photolysis (which is believed to be very slow due to the poor quantum efficiencies of PCBs in sunlight) will eventually lead to much higher concentrations of the very toxic coplanar PCBs than now is currently found in the environment.

EXPERIMENTAL

Materials and Equipment

The photolysis experiments were performed with a Hewlett Packard (HP) 1090 HPLC system equipped with quartz column (2 mm id, 8 mm od x 250 mm) which was packed with octadecylsilylated silica gel (ODS, particle size: 15 micrometer, 330 m^2/g). The eluents were monitored by UV detector (245 nm) on an HP diode array detector. The column temperature was controlled at 21°C by immersing the column in a water bath together with the UV lamp (450 W, ACE-HANOVIA photochemical, full spectrum mercury arc, medium pressure). The HPLC analysis of the recovered products was performed on a second HP 1090 (MeOH as eluent) equipped with a diode array UV detector (monitoring with 235 nm and 260 nm) or a Waters system with a Model 600E system controller and Model 994 programmable photodiode array detector with Millennium software. An ODS column (Cosmosil C_{18}, 4.6 mm, 150 mm, Nacalai Tesque) was used for the product analysis.

Photolysis of PCBs on ODS

A 5 µL PCB solution (0.1 or 0.2 w/v%) in dioxane was injected and pumped into the quartz column with 2-propanol/H_2O (9/1) at a flow rate of 0.1 ml/min. The mobile phase was pumped for a half of the retention time of the substrate PCB (t_R/2), then the pump was stopped and UV lamp was turned on and the sample was photolyzed in a similar manner as described previously. After 0, 3, 5, 10, 15, or 30 minutes irradiation time, the UV lamp was turned off and the pump was started. The eluent was collected for 10 or 15 min (1.0 ml or 1.5 ml, respectively). A portion of the collected fraction (20 or 30 microliter injection, respectively) was analyzed by HPLC. The identification and quantitation of the products were carried out based on the retention time, area, and comparison with the results of authentic samples. PCB-80 was also photolyzed in the presence of 0.02 M diisopropylethylamine.

RESULTS and DISCUSSION

In this study, we have shown that the highly lipophilic PCBs can be trapped from aqueous solutions by passing them through a very common hydrophobic support (C_{18}). The PCBs on C_{18} can then be efficiently photo degraded by dechlorination of the biphenyl nucleus.

Photolysis studies were conducted on several environmentally important PCB congeners and some of the major photodecomposition products. These included one di-ortho PCB (PCB-153), two mono-ortho PCBs (PCB-105; and PCB-118), and several of the highly toxic coplanar PCBs (including PCB-169, PCB-127, PCB-126, PCB-77, PCB-79, and PCB-80). Several of the smaller decomposition products were also examined for products and rates. These include PCB-11, PCB-13, PCB-15, PCB-35, PCB-36, and PCB-37.

It can be deceiving to determine pathways of the photolysis reactions by merely looking at the products that are found in the milieu after set reaction times. This is because some major products may photo degrade very quickly to form lower chlorinated species and therefore be found in only minor amounts while a minor pathway may lead to a stable product which could be found in higher amounts. We have therefore performed photolysis on several PCBs and looked at relative rates of the decomposition of the parent PCB and determined the major products of the reaction. The products found from photodecomposition at very early stages should more accurately reflect the distribution of the primary products due to a decrease in the effects from

secondary reactions.

Three dichloro-PCBs were examined. PCB-11 (3,3') and PCB-15 (4,4'), which both only have one possible product from photo dechlorination, had similar rates while PCB-13 (3,4'), which has two possible dechlorination products, had a decomposition rate that was roughly double the other two PCBs. This is interesting and could reflect the greater stability of isomers with greater structural symmetry *(vide infra)*. Three trichloro-PCBs were also photolyzed. These were PCB-35 (3,3',4-), PCB-36 (3,3',5-), and PCB-37 (3,4,4'-). The decomposition of PCB-36 was much slower than the others, as indicated by much greater amounts remaining. The other two trichloro-PCBs (35 and 37) had similar rates of photodecomposition , with PCB-37 having a slightly higher rate of dechlorination. This was indicated in the time dependence of the product ratio [35]/[37] in the decomposition of PCB-77, which showed an increase with increased reaction times. The photo degradation of the trichlorobiphenyls mainly resulted in the loss of a meta-chlorine. The ratio of reactivity (m-/p-), however, was 10/1 in the case of PCB-37 producing PCB-15 as a major product and PCB-13 as a minor product but was 5/1 in the decomposition of PCB-35 to PCB-13 as a major product and PCB-11 as the minor product. This indicates that more symmetrical isomers tend to be formed even as byproducts.

The tetrachloro-PCBs showed their greatest spread in photodecomposition rates. PCB-80 showed the slowest rate of decomposition of all the PCBs examined. However, the half life of PCB-80 under the conditions employed is still about 10 min, indicating that a 100 min photolysis can effect 99.9% decomposition since the present system is efficient. The decomposition rate of PCB-77 was slower than that of PCB-79. The slower decomposition of PCB-77 than PCB-79 is also supported by a decreasing ratios of [79]/[77] during the decomposition of PCB-126. PCB-77 produced PCB-35 as the major product, while PCB-79 produced PCB-36. It is interesting to note that the removal of the para-chlorine substituent dominated the decomposition of tetrachlorobiphenyls. This was in contrast to the preferential removal of meta-chlorine substituents that was seen in the trichlorobiphenyls. Although the amount of PCB-35 detected was not predominant, the presence of a large amount of PCB-13 at 15 min could indicate that the major decomposition route of PCB-77 is through PCB-35. PCB-35 seems to be more stable than PCB-37, but it can easily undergo photolysis under these conditions and could be overlooked if not carefully traced. It is interesting to note that the major product from the photolysis of PCB-79 was not only the loss of the para chlorine (which is in agreement to the reported order of Lepine *et al.*[5]) but a chlorine that had an adjacent chlorine.

Lepine[5] also reported that in mixtures of PCBs, ortho chlorines tended to be lost at the fastest rate which was found in the photodecomposition of both the penta and hexa-PCBs. PCB-105 (2,3,3',4,4') and PCB-118 (2,3'4,4',5-) both had very fast rates of photodecomposition in which the ortho chlorines were lost preferentially. The non-ortho substituted PCBs 126 (3,3'4,4'5) and 127 (3,3',4,5,5') had slower photolysis rates. For both of these PCBs, the middle para chlorine was lost first. PCB-105 and PCB-118 decompose through PCB-77, PCB-35, then PCB-13. The presence of a large amount of PCB-13 indicates the major intermediacy of PCB-35, in spite of its low comparable content with PCB-37. Both PCB-127 and PCB-126 indicated the loss of para-chlorine. However the ratios of the loss of para-against meta- for PCB-127 was (p-/m-) = *ca.* 20/1 against *ca.* 3/1 from PCB-126. Here again, the symmetrical PCB-77 was produced in a significant amount in spite of the presence of the two pairs of neighboring chlorines on this isomer.

Two hexachloro-PCBs were also photolyzed. PCB-153 (2,2',3,3'5,5') is a major component of Aroclor 1260 which has two ortho chlorines. This PCB showed very fast photo

dechlorination at the ortho position. The coplanar PCB-169 (3,3',4,4'5,5') also photo degraded at a high rate in which the para chlorine was preferentially lost.

These data have allowed us to propose the major routes of photodecomposition of the two environmentally important hexachloro-PCBs (PCB-153 and 169). PCB-153 (Scheme 1) appears to first lose an ortho chlorine to form PCB-118. The second ortho chlorine is then lost to form the very toxic coplanar PCB-77. This very toxic PCB then can further decompose to form mostly PCB-35 (loss of para Cl) and some PCB-37 (loss of meta Cl). PCB-35 then again loses mostly the meta chlorine to form PCB-13 (which then further degrades to eventually form biphenyl). The photodecomposition of PCB-169 (Scheme 2) is also of great interest. These data indicate that the para chlorines are preferentially lost to form PCB-127 then PCB-80. The photo-degradation of PCB-80 is then subsequent losses of meta chlorines to form PCB 36 then PCB-11, then PCB-2, and finally biphenyl.

Lepine and Masse [4] have previously reported that dechlorination proceeded in the order of ortho>para>meta. In this study, the photolysis of PCB-153, PCB-118, and PCB-105 indicate that dechlorination in the ortho position is favored. In PCB-169, PCB-127, and PCB-126 (all which have 2 meta and one para chlorine adjacent to each other) the para chlorine is preferentially lost. However, in PCBs with only one meta and one para chlorine adjacent, the meta chlorine was preferentially replaced for PCB-37, and PCB-35.

Several rules can be found for the decomposition pathway with the following priority. If two of these factors are met, the reaction tends to produce a dominant product.

1. In all cases, the ring with the greatest degree of chlorination is the primary ring where the dechlorination occurs.
2. Ortho-chlorine substituents and para chlorine substituents that have two adjacent chlorines were preferentially lost in coplanar (non-ortho-substituted) PCBs.
3. Chlorine substituents having neighboring chlorines are replaced more easily than isolated chlorines.
4. Para-chlorine substituents were lost preferentially from coplanar hexa-, penta- or tetrachlorobiphenyls, while meta-chlorine was lost preferentially from trichlorobiphenyls.
5. More symmetrical isomers tend to be formed more easily, and are more stable.

The results indicate that steric congestion and structural symmetry are major factors in determining reactivity. The addition of amine accelerated the decomposition considerably. The effect of amines on rates and pathways of photodecomposition on hydrophobic surfaces should be further studied.

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Scheme 1
Major Routes For The
Decomposition of PCB-153
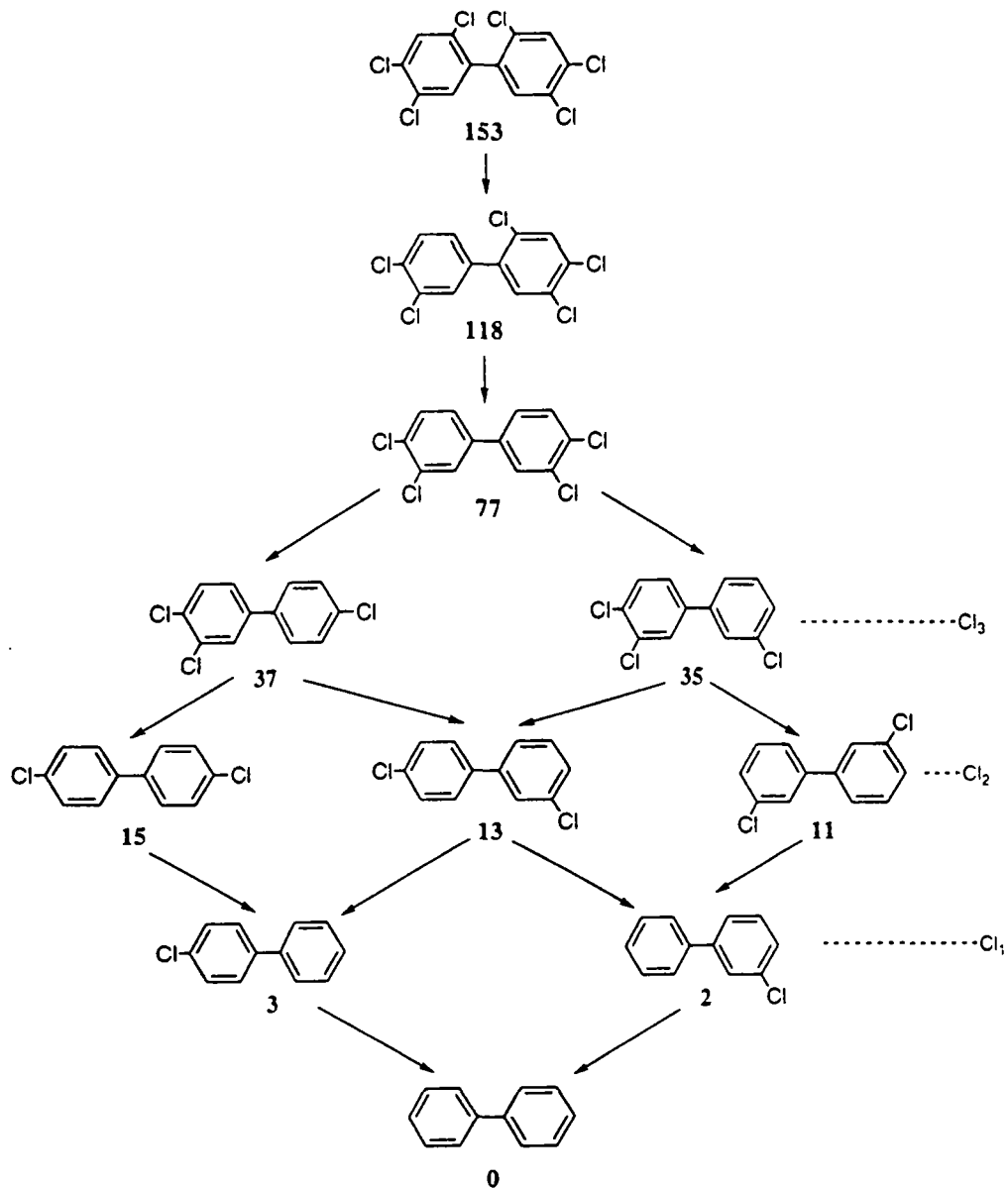
Scheme 2
Major Routes For The
Decomposition of
PCB-169