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Formation of Toxic PCB Congeners and PCB-Solvent Adducts in a Sunlight Irradiated Cyclohexane Solution of Aroclor 1254

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The widespread use of polychlorinated biphenyls (PCBs) in a variety of industrial applications along with their remarkable chemical stability have made them ubiquitous contaminants. These substances are found in the environment as the sum of industrial mixtures (Zell et al. 1978). The acute toxicity of these mixtures is relatively low for most animal models. However, some specific PCB congeners that are structurally related to 2,3,7,8-tetrachlorodibenzodioxin (TCDD) have toxicological properties similar to TCDD (Safe et al. 1985). These coplanar congeners, namely the 77, 126 and 169 congeners, according to IUPAC nomenclature, along with their less toxic monoortho-substituted analogs 105, 118, 156, 157, 167 and 189 are even considered a greater threat to terrestrial and marine mammals than polychlorinated dibenzodioxins and dibenzofurans (Kannan et al. 1989). The most toxic congeners 77, 126 and 169 are however present in very small amounts in most industrial PCB mixtures (Albro et al. 1981).

Photodegradation by sunlight is an important decomposition mechanism of polychlorinated biphenyls in the environment (Sawhney 1986). Photodegradation of PCBs proceeds through successive dechlorination of the biphenyl nucleus and thus modify the proportions of the various congeners in a PCB mixture (Herring et al. 1972). The objectives of this work is to study the effects of sunlight on a typical PCB mixture such as Aroclor 1254, in a congener specific approach in order to observe the variations in the levels of these toxic congeners in the irradiated mixture.

MATERIAL AND METHODS

Aroclor 1254 (Lot no. 001) was purchased from Analab. "Spectrograde" cyclohexane was purchased from Anachemia and used without further purification.

Dilute solutions of Aroclor 1254 (4 ppm) in degassed cyclohexane were exposed in NMR tubes to sunlight for a period of 55 days in december and january. Irradiation

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was performed in the Montreal area at 10°C. Analysis was performed with a Varian 3500 equipped with a 30 m DB-5 column (J. & W. Scientific Inc.) (0.3 mm i.d., film thickness 0.25 micron) with helium as carrier gas. GC conditions were initially set at 100°C then to 150°C at 20°C/min, then to 230°C at 2°C/min, then to 250°C at 3°C/min and to 310 at 20°C/min. The mass spectrometer was a Finnigan ITD 800 scanning from 100 to 515 amu. Experiments were performed in triplicate. Identification of the various congeners was performed according to Mullin et al. (1984). Results are presented in Table 1. Peak area are reported as the ratios of the total ion current of a given peak on the sum of the areas of all the peaks of the chromatogram.

RESULTS AND DISCUSSION

The amounts of many higher chlorinated congeners decreased while those of some lower chlorinated congeners increased in agreement with the results reported by others (Herring et al. 1972). Isomer specific analysis indicates that the amounts of the monoortho substituted congeners 189, 156, 157 and 118 decreased considerably while congener 167 increased. Congener 105 which coelutes with other congeners could not be studied. The much more toxic congeners 77 and 126 which were not detected in unirradiated Aroclor 1254, represented 2.5 and 0.43%, respectively, of the irradiated mixture. Congener 169 was not detected in the standard or in the irradiated solution. Considering the large number of congeners present in Aroclor 1254, 2.5% represents a major peak of the chromatogram. The toxicity associated to such amounts of congener 77 is certainly of environmental concern. The amounts of congener 126 are smaller by a factor of six but the toxicity of congener 126 is far greater than the toxicity of congener 77. In terms of Toxic Equivalent Factors (TEF), the acute toxicity of such amounts of congener 126 is equal or larger than the one associated with the production of congener 77 (Safe 1990). Because the acute toxicities of congeners 77 and 126 are an order of magnitude greater than the one of their monoortho-substituted analogs, the overall toxicity of the mixture is likely to increase considerably.

Formation of these toxic planar congeners probably occurred, at least in part, from dechlorination at the ortho position of their monoortho substituted precursors, considering the reported greater reactivity of PCB ortho chlorines toward photodechlorination (Zabik 1983). Thus, the large production of congener 77 probably occurred from orthodechlorination of the very abundant congener 118, which is 43% degraded in irradiated Aroclor 1254.

Table 1. Peak area of selected PCBs congeners in unirradiated and irradiated Aroclor 1254[a]

Isomer number	Number of chlorines	Peak area of congener in Aroclor 1254	Surface area of congener in irradiated Aroclor 1254
52	4	5.0244 [0.13]	4.9000 [0.11]
49	4	1.2219 [0.06]	1.2053 [0.00]
44	4	2.1735 [0.05]	2.1350 [0.07]
(70+76)	4	3.1593 [0.12]	3.2235 [0.43]
95	5	7.1589 [0.21]	6.1741 [0.23]
91	5	1.0015 [0.04]	1.1100 [0.08]
92	5	1.4508 [0.04]	1.5130 [0.01]
89	5	2.3805 [0.08]	2.4044 [0.08]
101	5	8.2793 [0.22]	8.6228 [0.13]
99	5	3.1055 [0.08]	3.4858 [0.27]
97	5	2.4894 [0.08]	2.6914 [0.03]
87	5	4.3689 [0.11]	4.4397 [0.48]
120	5	1.2235 [0.07]	1.5354 [0.26]
77	4	0.0000 [0.00]	2.4938 [0.24]
110	5	8.0700 [0.17]	7.7416 [0.65]
82	5	0.9126 [0.03]	1.0698 [0.09]
(134+144)		1.1515 [0.04]	1.1263 [0.01]
149	6	4.3050 [0.67]	4.3508 [0.12]
118	5	7.3067 [0.64]	4.1251 [0.16]
(132+153)	6	4.8001 [0.33]	5.2195 [0.27]
168	6	2.1077 [0.18]	1.4929 [0.01]
127	5	3.2055 [0.33]	2.1356 [0.12]
141	6	1.1312 [0.01]	0.9842 [0.04]
138	6	6.5541 [0.06]	5.3139 [0.63]
158	6	1.0142 [0.09]	1.1333 [0.04]
126	5	0.0000 [0.00]	0.4354 [0.04]
128	6	1.5967 [0.18]	1.5169 [0.04]
167	6	0.3363 [0.02]	0.3973 [0.01]
156	6	1.0275 [0.02]	0.2722 [0.01]
157	6	0.1937 [0.01]	0.1464 [0.03]

[a] Numbers in bracket are standard deviation

The production of congener 126 could also come from the relatively abundant congener 156 which is 74% degraded. Congener 157 which is 25% degraded is also a potential precursor of congener 126. Congener 167 which is also another potential precursor of congener 126 increased in irradiated Aroclor 1254, which could only indicate that it is produced more rapidly than it is degraded.

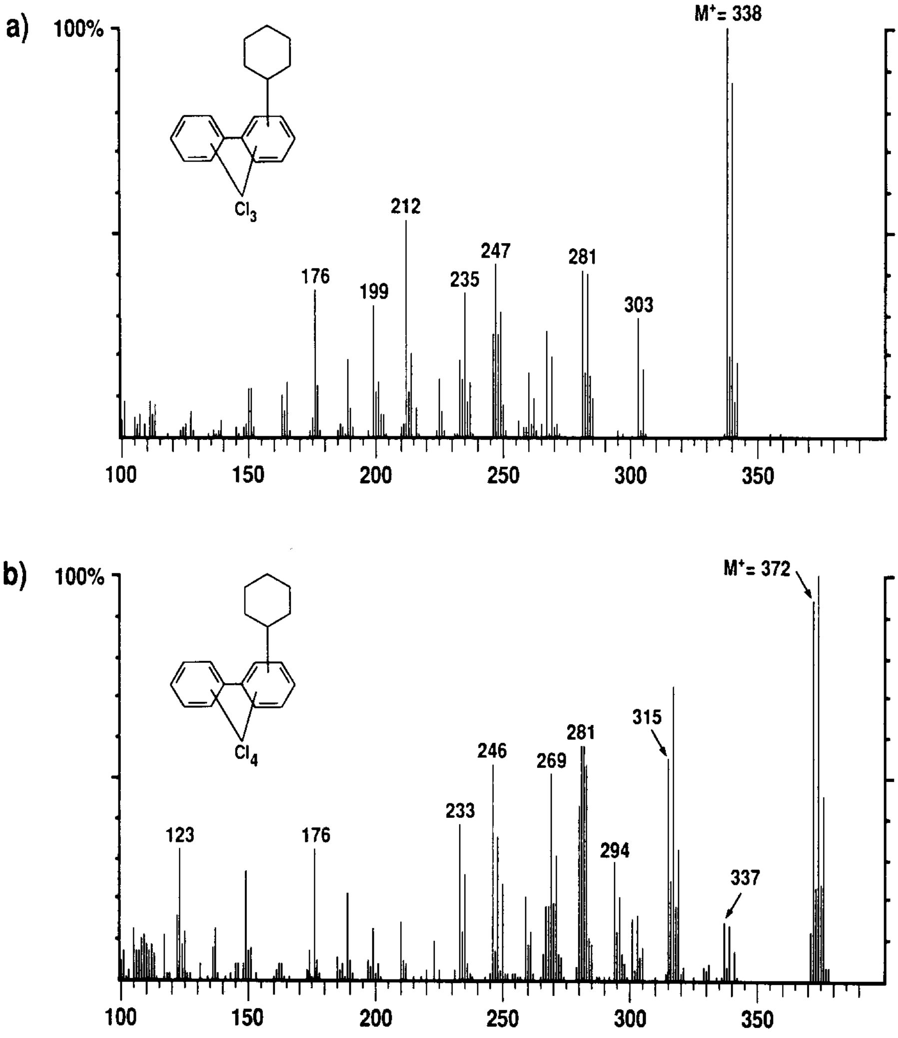

Figure 1. Mass spectra of the tri (a) and tetrachlorinated (b) cyclohexyl-PCBs formed in irradiated Aroclor 1254.

Another type of compounds was also observed in the irradiated Aroclor 1254 cyclohexane solution. These two compounds are cyclohexyl adducts of PCBs bearing three and four chlorine substituents. These compounds both represent 0.6% of the Aroclor mixture. The mass spectra of these compounds are presented in figure 1. Formation of PCB-solvent adducts upon UV irradiation was previously reported in aqueous or methanolic solvents but never, to our knowledge, in saturated aliphatic solvent. Formation of covalent bond between PCBs and non polar substances such as lipid was postulated in a publication dealing with UV irradiated PCBs adsorbed on cultured human cells (Bründl and Buff 1988). Mass spectrometric identification of these cyclohexyl-PCB adducts confirms that aliphatic matrix can indeed form covalent bond with PCBs upon UV irradiation.

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