UV Irradiation of Aroclor 1254[1,2]

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Although polychlorinated biphenyls (PCB's) have been shown to be widespread, highly persistent environmental contaminants occurring in numerous wildlife specimens and food samples (1,2,3), little is known about their fate in the environment. One proposed mechanism of breakdown is degradation by ultraviolet (uv) radiation from the sun (2). The degradation of PCB's by this means seemed feasible since their structure is similar to many of the chlorinated insecticides which are readily degraded by uv light (4,5,6). To study this possibility, solutions of a commercial PCB mixture (Aroclor 1254, Monsanto Chemical Co.) were irradiated with a laboratory uv lamp and sunlight.

EXPERIMENTAL

A solution of 200 ppm Aroclor 1254 (supplied by Monsanto Chemical Co.) in acetone was prepared and diluted 1:100 (2 ppm) with distilled water, hexane, and benzene. Three ml portions of each solution were placed in quartz cuvettes (Beckman standard 1 cm absorption cells) fitted with teflon caps. The samples, placed at a distance of 14 cm from the light source, were irradiated with a Hanovia Utility Quartz Lamp (100 watt) for 5, 15, 30 and 45 minutes. Control samples of each solvent system were not irradiated. The benzene and hexane samples were concentrated to one ml using a rotary evaporator. The water sample was extracted with two consecutive 10 ml portions of hexane in a separatory funnel. The extract was dried with anhydrous sodium sulfate and concentrated to 1 ml.

Hexane solutions of 1, 10 and 100 ppm in glass stoppered quartz test tubes were exposed to direct sunlight during the month of July and sampled weekly for three weeks.

All samples were analyzed using an F & M Model 810 gas chromatograph equipped with a tritium electron capture detector: carrier gas, 95% argon and 5% methane, 60 ml/min; injector, 200° C; column, 180° C; detector, 200° C. A glass column, 122 cm x 4 mm I.D., packed with 2% SE-30 and 2% QF-1 on Anakrom ABS 70/80 mesh was used.

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RESULTS AND DISCUSSION

Figure 1 represents a typical chromatogram of the unirradiated mixture. For purposes of following the pattern of degradation, only the first 10 major peaks, which represent tetra-, penta- and hexachlorobiphenyls, were examined. The Aroclor 1254 mixture was readily degraded in all three solvent systems but at different rates in each. Tables 1-3 present the percentages of each peak remaining, compared to the unirradiated sample, after varying lengths of irradiation with the Hanovia lamp.

In general, the PCB's degraded fastest in hexane, then water, and slowest in benzene. The fact that some peaks increased in size suggests that the more highly chlorinated PCB's were being dechlorinated to form PCB's with lower molecular weights and shorter retention times. It is also quite evident from the variations between each peak that the PCB's do not all degrade at the same rate.

There are two possible explanations for the effect of solvent on degradation rate. The most obvious is the transmission limit for uv radiation of the solvent. This limit is approximately 190 nm, 210 nm and 280 nm for water, hexane, and benzene, respectively. By comparing the rates in hexane and water to that in benzene, it would appear that the shorter wavelength, higher energy radiation is more effective. The second explanation could be that the solvent participates in the reaction, possibly as a hydrogen donor. In this case, both the reactivity and the polarity of the solvent would be important. One would expect benzene to be a relatively poor hydrogen donor which would explain its slower rate, while hexane and water would be more reactive, thus giving faster rates. The fact that the rate is slower in water than in hexane might be due in part to the relative insolubility of PCB's in water. Even at the low concentration of 2 ppm, it is not known whether PCB's exist in true solution or as a suspension in water.

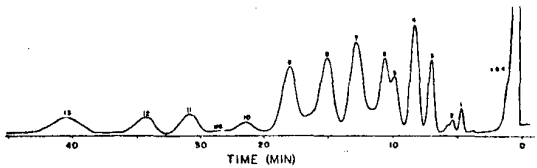

Figure 1. Chromatogram of Aroclor 1254 mixture.

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TABLE 1

Percent of each peak left after irradiation of hexane solutions with uv lamp.

Peak#	Time of Exposure (minutes)		
	5	15	30
1	104%	29%	0
2	275	83	0
3	99	0	0
4	62	0	0
5	0	0	0
6	140	75	0
7	9	0	0
8	28	0	0
9	7	0	0
10	0	0	0

The results of the sunlight (Table 4) and laboratory lamp irradiations agree fairly well except that peak 5 did not appear to degrade as readily. The overall rate of degradation was much slower due to the lower intensity and the lack of short wavelength radiation in sunlight compared to the laboratory lamp. There was a close correlation in the degradation patterns at all three concentrations which suggests the process is not concentration dependant.

From an environmental standpoint, the degradation of PCB's by sunlight is most significant. It should, however, be noted that little is known at this time of the products of the photolytic breakdown of PCB's, thus uv degradation may result in the production of at least transient quantities of more toxic compounds.

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TABLE 2

Percent of each peak left after irradiation of water mixture with uv lamp.

Peak #	Time of Exposure (minutes)			
	5	15	30	45
1	97	20	0	0
2	30	0	0	0
3	121	43	21	10
4	96	45	23	10
5	66	14	0	0
6	80	38	26	15
7	110	78	55	32
8	79	54	35	20
9	75	35	27	10
10	0	0	0	0

TABLE 3

Percent of each peak left after irradiation of benzene solution with uv lamp.

Peak #	Time of exposure (minutes)			
	5	15	30	45
1	104	72	31	55
2	116	48	30	43
3	94	73	57	60
4	96	77	31	55
5	106	61	26	44
6	99	67	43	47
7	75	47	22	15
8	90	68	46	40
9	90	64	45	44
10	106	71	67	63

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TABLE 4

Sunlight Irradiation of Aroclor 1254.

Initial Concentration of Aroclor 1254 in Hexane

	1 ppm			10 ppm			100 ppm		
	% remaining after			% remaining after			% remaining after		
Peak No.	1 week	2 weeks	3 weeks	1 week	2 weeks	3 weeks	1 week	2 weeks	3 weeks
1	97	109	143	65	104	104	85	131	139
2	111	137	161	111	140	180	114	164	184
3	74	76	79	113	94	88	110	110	101
4	83	104	109	127	108	143	92	99	120
5	103	89	87	98	96	94	118	70	63
6	181	211	196	210	206	241	157	205	218
7	58	51	36	68	58	40	68	58	42
8	84	89	75	111	98	90	105	96	80
9	66	47	30	53	44	44	80	56	47
10	62	47	41	49	50	59	80	64	54

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