THE SOLUBILITIES OF TWENTY-ONE CHLOROBIPHENYLS IN WATER

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Commercial PCB preparations consist of complicated mixtures of chlorobiphenyls with different chlorine content and their isomers. The composition of these technical products has only recently been established [1-8].

A knowledge of the solubilities of PCB components is necessary for experiments involving individual isomers and may also be useful for the evaluation of PCB distribution in natural waters.

Considerable differences in the solubilities of chlorobiphenyls with different numbers of chlorination as well as positional isomers were indicated by change in the GC peak pattern of Aroclor 1254 re-extracted from aqueous solutions with hexane[7] Solubilities of five mono-and dichlorobiphenyls also vary widely[8].

We wish to present the results of our study on the solubilities of twenty-one chlorobiphenyls in water. Most of the compounds investigated are major components of commercial PCB preparations. Since water soluble humic substances were recently reported to act as carriers for lipophylic compounds including pollutants[9, 10] the solubility of 4, 4'-dichlorobiphenyl in aqueous extracts of humic acid was also measured. The solubility of this compound was also determined in the presence of different concentrations of Tween 80. Aroclor preparations have an increased solubility in water in the presence of solubilizers[11] and the presence of the biologically relatively inert Tween 80 (e.g. 2% Tween 80 in nutrient solution showed no measurable growth inhibition in a number of microorganisms [12]) may allow the use of higher concentrations of chlorobiphenyl in many experiments.

EXPERIMENTAL

Instrumentation. Gas chromatography (GC) was carried out on a Varian 1800 instrument using a glass column (5 ft. x 2 mm i.d.) packed with 1.5% XE-60 on Anakrom Q operated at temperatures of 160-190°C depending on the compound. Carrier gas was nitrogen at a flow rate of 30 ml/min. Injector and electron capture detector were kept at 220°C.

Chemicals. Chlorobiphenyls (99% pure) were either Syntherized or obtained from Analabs Inc. (North Haven, Conn., U.S.A.). Humic acid was purchased from Aldrich Chem. Co. (Milwaukee, Wisc., U.S.A.).

Methods. An example for the determination of the solubility of one chlorobiphenyl in water is given below.

A hexane solution of the chlorobiphenyl (1 mg) was pipetted into a 300 ml Erlenmeyer flask and the solvent evaporated to give a thin film of the compound. Water (100 ml) was added, the flask sealed with parafilm and the mixture shaken at 30°C for 10 days. After this time the aqueous suspension was allowed to equilibrate at 22-24°C for 3 hr. Contact of aqueous chlorobiphenyl solution with glass was kept to a minimum after this step because of the known adsorption effects[13]. An aliquot (10 ml) was drawn using a syringe carrying a small filter compartment and immediately

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extracted with hexane (2 x 10 ml). The hexane extract was concentrated to 10 ml and 2 μl samples were injected into the gas chromatograph. Quantitative evaluation was carried out by measuring the peak height using calibration curve of known amounts of chlorobiphenyl standard in hexane. Sampling and analyses were carried out in duplicate.

RESULTS AND DISCUSSION

In view of the problems with adsorption and low solubility, the experiments were not designed to give solubility data as absolute physical constants but were intended to yield comparable values of reasonable accuracy for biological experiments.

The data for twenty-one chlorobiphenyls in water are shown in Table 1.

TABLE 1

Solubility of chlorobiphenyls in water

Compound	Solubility (mg)	Solubility (ppm)
Monochlorobiphenyls		
2-	6.0	5.8
3-	3.35	3.6
4-	1.20	1.17
Dichlorobiphenyls		
2, 4-	1.40	1.40
2, 2'-	1.56	1.44
2, 4'-	1.90	1.85
4, 4'-	0.08	0.07
Trichlorobiphenyls		
2, 4, 4'-	0.085	0.085
3, 4, 2'-	0.075	0.080
Tetrachlorobiphenyls		
2, 2', 5, 5'-	0.046	0.046
2, 3, 2', 3'-	0.037	0.030
2, 3, 2', 5'-	0.170	0.170
2, 4, 2', 4'-	0.070	0.065
2, 4, 3', 4'-	0.055	0.060
2, 5, 3', 4'-	0.041	0.041
3, 4, 3', 4'-	0.175	0.175
Pentachlorobiphenyls		
2, 3, 4, 2', 5'-	0.021	0.023
2, 4, 5, 2', 5'-	0.035	0.028
Hexachlorobiphenyl		
2, 2', 4, 4', 5, 5'-	0.0088	0.0088
Octachlorobiphenyl		
2, 3, 4, 5, 2', 3', 4', 5'-	0.0068	0.0072
Decachlorobiphenyl	0.015	0.015
4, 4'-Dichlorobiphenyl		
+ Tween 10 0.1%	6.2	5.5
+ Tween 80 1%	10.0	10.0
+ Humic acid extract	0.075	0.06

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ACKNOWLEDGMENTS

We thank Dr. Freed for supplying data prior to publication. P.R.W. expresses his gratitude to the "Deutsche Forschungsgeminschaft" for financial support. Part of this work was carried out while O. H. was on leave at the Bayerische Landesanstalt. This author would like to thank the "Deutsche Akademische Austauschdients" for the invitation to Germany and financial aid.

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PROGRESS REPORTS ON PCB ISOMERS

By: Michael Bolgar

Given the toxicity and persistence of the widely dispersed polychlorinated biphenyls (PCB's) it seems logical that the U.S. Interdepartmental Taskforce on PCB's in their 181-page May 1972 Report (Com-72-10419) would include as part of their recommendation (page 18) the following additional studies, (italics are ours):

1. *Toxicological evaluation of a select number of representative, purified PCB isomers as well as purified trace contaminants such as the chlorinated dibenzofurans.*

2. Definitive mammalian elaboration of the kinetics, absorption, distribution, metabolism, and excretion of the technical PCBs as well as *a number of key isomers and the chlorinated dibenzofurans.*

3. Elaboration of the subcellular and intracellular actions of the technical PCBs as well as *a number of representative isomers and chlorinated dibenzofurans.*

4. More definitive epidemiological studies of the PCBs with both more representative population sampling and standardization on the basis of lipid content of the tissues.

In our list of biphenyls and 50 isomers of the 209 possible chlorobiphenyls we included a great number of the major components present in the commercial mixtures. For

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instance, Willis and Addison[1] report that the major components of Aroclor 1221 accounting for 92.3 weight per cent are biphenyl, 2-Cl, 4-Cl, 2, 2'-Cl_2, 2, 4'-Cl_2 (all available from Analabs stock). From Sissons and Welti's[2] list of the major components of the more important Aroclor 1254 (we list more than half). Methods have been developed[3] to recover PCB's present in waste and river water and to increase detectability by perchlorinating the samples sensitizing them to electron-capture detection by gas chromatography[4].

We have made the tools available (polyurethane foam plugs and perchlorination kits).

Assembled below is data of melting points taken of our pure isomers and taken from the literature. This list reveals interesting features of configuration/physical property corelation.

MELTING POINTS OF POLYCHLORINATED BIPHENYLS

Chlorine Position	*Melting Points*
Mono	
2-Cl	32.0-32.5°C
3-Cl	Oil
4-Cl	75.5-77.0°C
Di	
2, 3-Cl_2	Oil (Lit. 27.7-28.2°C)
2, 4-Cl_2	Oil (Lit. 24-25°C)
2, 5-Cl_2	Oil (Lit. 22-23°C)
2, 6-Cl_2	34-35°C
3, 4-Cl_2	47-48°C
3, 5-Cl_2	Oil (Lit. 31-32°C)
2, 2'-Cl_2	60-61°C
3, 3'-Cl_2	25-26°C
4, 4'-Cl_2	148-149°C
2, 3'-Cl_2	Lit. Oil
2, 4'-Cl_2	42.5-43.5°C
3, 4'-Cl_2	Lit. Oil
Tri	
2, 3, 4-Cl_3	101-102°C
2, 3, 5-Cl_3	Lit. 41°C
2, 3, 6,-Cl_3	58-60°C
2, 4, 5-Cl_3	76-78°C
2, 4, 6-Cl_3	62.0-63.5°C
2, 3, 2'-Cl_3	Lit. 28-29°C
2, 3, 4'-Cl_3	Lit. 73°C
2, 4, 4'-Cl_3	57.0-57.5°C
2, 5, 2'Cl_3	43-44°C
2, 5, 3'-Cl_3	40.0-40.5°C
2, 5, 4'-Cl_3	63.5-64.5°C
3, 4, 2'-Cl_3	60.0-60.5°C
3, 4, 4'-Cl_3	Lit. 87-88°C
3, 5, 2'-Cl_3	Lit. 58°C
3, 5, 4'-Cl_3	Lit. 88°C

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MELTING POINTS OF POLYCHLORINATED BIPHENYLS

Chlorine Position	*Melting Points*
Hepta	
2, 3, 4, 5, 6, 2′ 5′-Cl_7	147-150°C
2, 3, 4, 5, 6, 3′, 4′-Cl_7	Lit. 116-118°C
2, 3, 4, 5, 2′, 3′, 4′-Cl_7	Lit. 134.5-135.5°C
2, 3, 4, 5, 2′ 3′ 6′-Cl_7	Lit. 130.5-130.7°C
2, 3, 4, 5, 2′ 4′ 5′-Cl_7	Lit. 109-110°C
2, 3, 4, 5, 2′ 4′ 6′-Cl_7	Lit. 152-153°C
2, 3, 4, 5, 3′ 4′ 5′-Cl_7	Lit. 162-163°C
Octa	
2, 3, 4, 5, 2′ 3′ 4′ 5′-Cl_8	158-159°C
2, 3, 4, 6, 2′ 3′ 4′ 6′-Cl_8	Lit. 132°C
2, 3, 5, 6, 2′ 3′ 5′ 6′-Cl_8	161-162°C
Nona	
2, 3, 4, 5, 6, 2′ 3′ 4′ 5′-Cl_9	204.5-206.5°C
Deca	
2, 3, 4, 5, 6, 2′ 3′ 4′ 5′ 6′-Cl_{10}	300-310°C (sublimes)

All melting Points taken on a Fischer-Johns melting point stage.

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MELTING POINTS OF POLYCHLORINATED BIPHENYLS

Chlorine Position	*Melting Points*
Tetra	
2, 3, 4, 5-Cl_4	91.5-92.5°C
2, 3, 5, 6-Cl_4	77.0-77.5°C
2, 3, 4, 4'-Cl_4	Lit. 141-142°C
2, 4, 5, 4'-Cl_4	Lit. 125°C
2, 3, 2' 3'-Cl_4	119.5-121.5°C
2, 3, 2' 5'-Cl_4	46.5-47.0°C
2, 4, 2' 4'-Cl_4	41-42°C
2, 4, 2' 5'-Cl_4	64-66°C
2, 4, 3' 4'-Cl_4	127-128°C
2, 5, 2' 5'-Cl_4	86-87°C
2, 5, 3' 4'-Cl_4	104-107°C
2, 6, 2', 6'-Cl_4	190-200°C (sublimes)
3, 4, 3', 4'-Cl_4	182-184°C
3, 5, 3', 5'-Cl_4	Lit. 164°C
Penta	
2, 3, 4, 5, 6,-Cl_5	123-125°C
2, 3, 4, 5, 4'-Cl_5	Lit. 98-99°C
2, 3, 4, 2', 5'-Cl_5	111.5-113.0°C
2, 3, 4, 3' 4'-Cl_5	Lit. 101-105°C
2, 3, 6, 2' 5'-Cl_5	97-98°C
2, 4, 5, 2' 3'-Cl_5	81-82°C
2, 4, 5, 2' 5'-Cl_5	76.5-77.5°C
2, 4, 5, 3' 4'-Cl_5	Lit. 105-107°C
Hexa	
2, 3, 4, 5, 6, 2'-Cl_6	Lit. 134-137°C
2, 3, 4, 5, 6, 3'-Cl_6	Lit. 97-100°C
2, 3, 4, 5, 6, 4'-Cl_6	Lit. 160-165°C
2, 3, 4, 5, 2' 4'-Cl_6	Lit. 77-78°C
2, 3, 4, 5, 2' 5'-Cl_6	89-91°C
2, 3, 5, 6, 2' 5'-Cl_6	100-101°C
2, 3, 4, 2' 3' 4'-Cl_6	155-8°C
2, 3, 4, 2' 4' 5'-Cl_6	78.5-80.0°C
2, 3, 5, 2' 3' 5'-Cl_6	Lit. 128-129°C
2, 3, 6, 2' 3' 6'-Cl_6	115-117°C
2, 3, 6, 2' 4' 5'-Cl_6	Lit. Oil
2, 4, 5, 2' 4' 5'-Cl_6	102-104°C
2, 4, 5, 2' 4' 6'-Cl_6	Lit. Oil
2, 4, 6, 2' 4' 6'-Cl_6	113.5-114.5°C
3, 4, 5, 3', 4' 5'-Cl_6	Lit. 198

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MELTING POINTS OF POLYCHLORINATED BIPHENYLS

Chlorine Position	*Melting Points*
Hepta	
2, 3, 4, 5, 6, 2′ 5′-Cl_7	147-150°C
2, 3, 4, 5, 6, 3′, 4′-Cl_7	Lit. 116-118°C
2, 3, 4, 5, 2′, 3′, 4′-Cl_7	Lit. 134.5-135.5°C
2, 3, 4, 5, 2′ 3′ 6′-Cl_7	Lit. 130.5-130.7°C
2, 3, 4, 5, 2′ 4′ 5′-Cl_7	Lit. 109-110°C
2, 3, 4, 5, 2′ 4′ 6′-Cl_7	Lit. 152-153°C
2, 3, 4, 5, 3′ 4′ 5′-Cl_7	Lit. 162-163°C
Octa	
2, 3, 4, 5, 2′ 3′ 4′ 5′-Cl_8	158-159°C
2, 3, 4, 6, 2′ 3′ 4′ 6′-Cl_8	Lit. 132°C
2, 3, 5, 6, 2′ 3′ 5′ 6′-Cl_8	161-162°C
Nona	
2, 3, 4, 5, 6, 2′ 3′ 4′ 5′-Cl_9	204.5-206.5°C
Deca	
2, 3, 4, 5, 6, 2′ 3′ 4′ 5′ 6′-Cl_{10}	300-310°C (sublimes)

All melting Points taken on a Fischer-Johns melting point stage.

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