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Aqueous Solubilities and Transformations of Tetrahalogenated Benzenes and Effects of Aquatic Fulvic Acids

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INTRODUCTION

The fate of organic pollutants in the environment is largely dependant on their physical and chemical properties (Mackay et al. 1985). For example, halogenated benzenes show quite different properties depending on the number and the position of the attached halogen atoms to the benzene ring. 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB) has the least aqueous solubility and largest toxicity among its isomeric compounds. 1,2,4,5-TeCB is used as a raw material for 2,4,5-T herbicides, and at elevated temperature it can produce the highly toxic 2,3,7,8-TcDD (Hay 1982). Many of the previous studies on halogenated benzenes have been focused on their photochemistry in an organic solvent system (Anisimov et al. 1985; Crosby and Hamadmad 1971; Freeman et al. 1986; Hutzinger and Choudhry 1984; Nakada et al. 1983).

Studies of halogenated benzenes in aqueous conditions without photochemical effect are rare. Recently, aqueous solubility enhancement of hydrophobic organic pollutants by humic substances was studied (Chiou et al. 1986). Aqueous solubility enhancement did not occur with all test compounds. Partition-like interactions between solute and cosolute were suggested for the increase of aqueous solubilities. In this paper, we investigated the transformation of the three most symmetrical tetrahalogenated (fluoro, chloro, bromo) benzenes in absence of the photo effect. Solute and solvent interactions, and influence of aquatic fulvic acids (FA) on aqueous solubilities and transformation of the three tetrachlorobenzenes and 1,2,4,5-TeBB were studied.

MATERIALS AND METHODS

Three tetrachlorobenzenes, 1,2,4,5-tetrafluorobenzene (1,2,4,5-TeFB), and 1,2,4,5-tetrabromobenzene (1,2,4,5-TeBB) compounds were purchased from Aldrich Chemical Co. Their purities were higher than 98%, and they were used without further treatment. Pure water was prepared by Millipore water purification system. Nanograde quality

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Send reprint request to Professor F.Y. Saleh at the above address of n-hexane was used for extraction. Highly purified aquatic FA was purchased from U.S. Geological Survey in Denver, Colorado.

In the solubility and effects of FA experiments, 50 mL solutions of 0, 20, 40, 60, and 80 mg/L FA in water were prepared, and 50 mg of 1,2,4,5-TeCB was added into each of the five solutions. Samples were vigorously stirred for 24 hours. After equilibration of the solute and solvent, the samples were filtered through a 0.45 μm glass fiber filter followed by extraction with n-hexane. A 5 μL of n-hexane extract was injected into a Tracor 560 GC with Ni^{63} electron capture detector (GC-ECD). The same procedures were applied to 1,2,3,4-TeCB, 1,2,3,5-TeCB, and 1,2,4,5-TeBB compound. Standards of pure compounds were prepared in n-hexane.

In transformation test, 150 mg of each 1,2,4,5-TeFB, 1,2,4,5-TeCB, and 1,2,4,5-TeBB was added into 250 mL of pure water in brown conical flask. The flasks were tightly sealed, and were vigorously stirred on a magnetic stirrer under dark conditions for 24 hours. The samples were then filtered, extracted, and injected into GC-ECD. The same procedures were applied to samples dissolved in n-hexane instead of water.

For the electron spin resonance (ESR) study, two 2 mL portions of 1% aquatic FA in alkaline water (pH 12.5) were prepared as a reference and sample, and enough amount of 1,2,4,5-TeCB was added into the one of aqueous FA solution. Reference and sample solutions of FA were stirred on the magnetic stirrer. 100 μL of aqueous solutions were sampled for ESR measurement at time intervals from reference and sample solutions. The total radical concentrations of FA were monitored by Varian 4502 ESR spectroscopy. The same procedures were applied to 1,2,4,5-TeBB.

RESULTS AND DISCUSSION

Table I shows the properties of five test compounds. The most symmetric 1,2,4,5-Tetrahalogenated benzenes showed the largest hydrophobicity in their isomeric groups. This large hydrophobicity is related with the higher toxicity of these compounds. The experimental aqueous solubilities of the four test compounds in pure water are also shown in Table I. The experimental results are in good agreement with the predicted values (Yalkowsky 1980). The effect of FA on aqueous solubilities of four tetrahalogenated benzenes were investigated. Figure 1 shows the aqueous solubilities of the four test compounds and the effects of FA on solubilities. No significant changes were observed in three TeCB isomers. But, 1,2,4,5-TeCB showed a slight tendency of increase in

Table I. Properties of Five Test Compounds

	1245-TeFB	1245-TeCB	1235-TeCB	1234-TeCB	1245-TeBB
Molecular weight^a	150.07	215.89	215.89	215.89	393.72
Boiling point (°C)^a	90	243	246	254	-
Melting point (°C)^a	4	140	52	46	180
Solubility (mg/L)^b	-	0.54	3.58	4.12	0.044
Solubility (mg/L)^c	-	0.56±0.02	2.79±0.14	3.27±0.02	0.040±0.004
Ph-X energy (Kcal/mol)^d	116	90	90	90	72
Ph-X distance (nm)^d	13	17	17	17	18.5

a: Aldrich, 1989; b: Yalkowsky, 1980; c: This study; d: Lowry and Richardson, 1981.

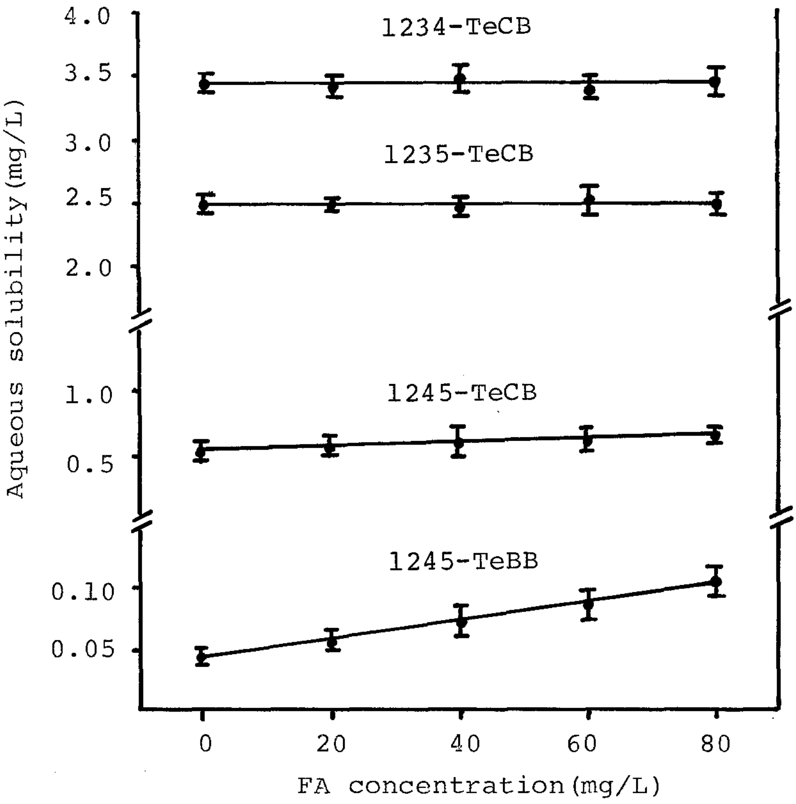

Figure 1 Aqueous solubilities of four tetrahalogenated benzenes in presence of aquatic FA

aqueous solubilities. 1,2,3,4- and 1,2,3,5-TeCB compound is more polar, and has a lower melting point than 1,2,4,5-TeCB leading to good association with water. An obvious tendency of aqueous solubility enhancement is observed in 1,2,4,5-TeBB compound. The solubilities were steadily increased with increase of FA concentration. Aqueous solubilities of 1,2,4,5-TeBB relative to hydrophobicity of 1,2,4,5-TeBB relative to 1,2,4,5-TeCB leads larger partitioning with FA, and results larger aqueous solubility enhancement.

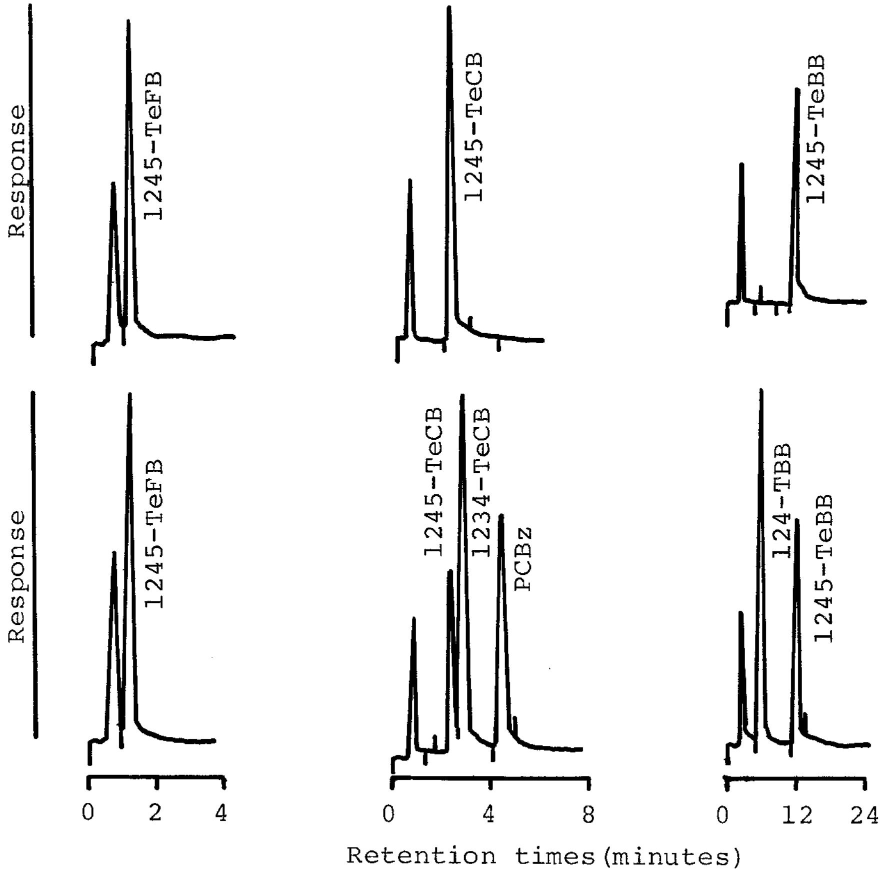

Figure 2 GC-ECD chromatograms of 1,2,4,5-TeFB(left), 1,2,4,5-TeCB(center), and 1,2,4,5-TeBB(right) in n-hexane(upper) and in water(lower)

Figure 2 shows typical gas chromatograms of three 1,2,4,5-tetrahalogenated benzenes in n-hexane and in water, respectively. 1,2,4,5-TeFB showed no differences between the chromatograms in n-hexane and in water. Solvent effect based on solute and solvent molecular interactions seems not large enough to initiate any bond cleavages. This is due to the strong bond energies between carbon and fluorine atoms. The 1,2,4,5-TeCB showed additional peaks besides the parent peak in the aqueous conditions. The additional peaks were identified as 1,2,3,4-TeCB and Pentachlorobenzene (PCBz), respectively. Confirmation was made by comparison of GC retention times and GC-MS spectra. In aqueous solution of 1,2,4,5-TeCB, the hydrophobic interactions are expected to be large. The considerably high melting point of 1,2,4,5-TeCB indicates large entropy changes when solubilized in water. Cleavage of the carbon and chlorine bond is likely to occur in 1,2,4,5-TeCB due to the larger hydrophobic interactions and larger entropy changes. Chlorinated benzene radicals and chlorines formed by carbon and chlorine bond cleavage can be the subject of rearrangement or recombination of radicals to form 1,2,3,4-TeCB and PCBz (Nakada et al. 1979). The production of 1,2,3,4-TeCB or PCBz is dependent on the available intermediate aryl radicals and chlorine atoms. In aqueous condition, 1,2,4,5-TeBB showed 1,2,4-tribromobenzene (1,2,4-TBB) as a major transformation product. Lack of bromine atom rearrangement or increased bromine compound seems related to the reactivity of the bromine atom. Compared to the chlorine, the atomic size of bromine is large, and electron affinity is small. On the other hand, the bond energy between carbon and bromine in 1,2,4,5-TeBB is much weaker than that of 1,2,4,5-TeCB. As a result, cleavage of carbon and bromine is much favorable, but recombination is unfavorable in case of 1,2,4,5-TeBB.

In ESR study, the free radical populations in aqueous FA were monitored to investigate the radical mechanism. The disappearance of radicals of FA was slightly accelerated in presence of 1,2,4,5-TeCB. However, in presence of 1,2,4,5-TeBB, the disappearance of radicals in FA showed no significant differences. Figure 3 shows the results. The 1,2,4,5-TeCB can produce smaller size radical species than 1,2,4,5-TeBB. 1,2,4,5-TeCB aryl radicals or chlorine atoms can penetrate into FA molecules more easily, and can react more effectively with radicals on FA. On the other hand, larger size and weaker electronegativity of radical species from 1,2,4,5-TeBB compound results in smaller reactivity. The radicals in FA seem not effectively consumed by 1,2,4,5-TeBB aryl radicals or bromine atoms.

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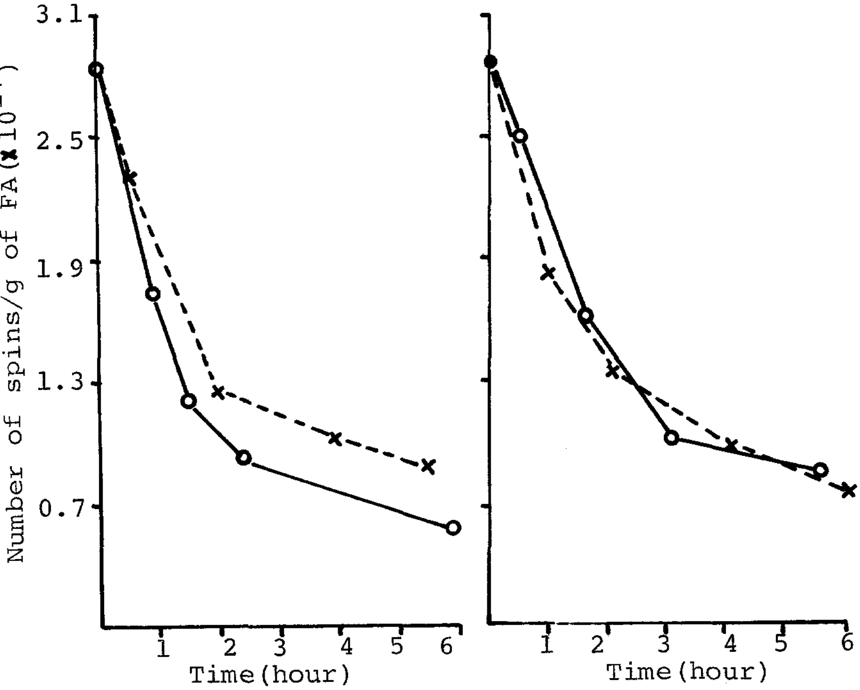

Figure 3 Disappearance of free radicals in 1% aquatic FA(pH 12.5) in presence of 1,2,4,5-TeCB(left) and 1,2,4,5-TeBB(right). Reference FA(dotted line) and presence of halogenated benzenes(solid line).

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