AQUEOUS SOLUBILITY AND OCTANOL-WATER PARTITION COEFFICIENT OF 3,3',4,4'-TETRACHLOROAZOBENZENE

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INTRODUCTION

3,3',4,4'-tetrachloroazobenzene (TCAB) is known as a toxic substance which has a similar structure and toxicity as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Environmental occurrence of TCAB may be due to application of 3,4-dichloroaniline (3,4-DCA) derived pesticides, due to their bio-transformation of 3,4-DCA[1,2] or due to photolysis of 3,4-DCA[3]. Because of the concern regarding possible health and environmental effects, it may be important to understand the state of pollution by TCAB. Physico-chemical properties are the important parameters for understanding of the behavior of the compound in the environment or in the body of organisms. Especially the aqueous solubility and the water-octanol partition coefficient are fundamental information, although they have not been reported. In this paper, we report the result of measurement of these parameters. The measurement of TCAB was made by GC/HRMS using ^{13}C labelled TCAB as an internal standard[4].

EXPERIMENTAL

Preparation of TCAB and ^{13}C labelled TCAB
Native TCAB and ^{13}C labelled TCAB have been synthesized in our laboratory[4,5]. Their purities are estimated to be more than 99 % by HPLC determination.

Measurement of aqueous solubility of TCAB
The solubility of TCAB in water was determined by adding 1 mg of native TCAB to 1 L of pure water. TCAB powder was added in 1 L of water in glass beaker covered with aluminium foil. The same three sets (S-1, S-2 and S-3) and a set without TCAB (S-control) were prepared. They were left stirring by a magnetic stirrer in a dark room regulated at 20 ° C. An aliquot of solution (about 100 mL) was sampled 0, 3, 7, 22 days. The solution was filtered with a glass filter (0.3 µm pore size, Ø 47 mm, ADVANTEC), and then centrifuged at 2,000 rpm for 15 hours. 100 mL of water sample was exactly collected from middle layer of the solution.
100 mL of water sample was put in a separatory funnel, and 10 ng of ^{13}C labelled TCAB was spiked. The solution was extracted 4 times with hexane using 100 mL at each time. The combined hexane extracts were dried by passing through a layer of anhydrous sodium

sulfate in a glass funnel. The solution was reduced to about 3 mL on a rotary evaporator under reduced pressure. The concentrate was transferred to a 10 mL of centrifuge tube with hexane and the solvent was removed by purging with a nitrogen gas stream. The concentrate was redissolved in 100 µL of toluene.

Octanol-water partition coefficient of TCAB

Preparation of TCAB saturated water: The TCAB saturated water was prepared by same way as described above.

Partitioning of TCAB between octanol and water: 400 mL of saturated water of TCAB and 4 mL of octanol were mixed well in a separatory funnel. The same three sets (P-1, P-2 and P-3) and a set without TCAB (P-control) were prepared. They were left in a dark room regulated at 20 °C for 7 days. Octanol and water solution were analyzed TCAB respectively.

Extraction TCAB from water solution: 1 ng of ^{13}C labelled TCAB was added to 300 mL of water solution in a separatory funnel. The solution was extracted 4 times with hexane using 30 mL at each time. The combined hexane extracts were dried and reduced its volume to about 3 mL. The concentrate was transferred to a 10 mL of centrifuge tube with hexane and the solvent was purged with a nitrogen stream. The concentrate was dissolved in 100 µL of toluene.

TCAB in octanol solution: 30 ng of ^{13}C labelled TCAB (300 µL, methanol solution) was added to 3 mL of octanol solution in a 10 mL of centrifuge tube.

Quantification of TCAB

TCAB was analyzed on a Hewlett Packard 5890 series II gas chromatograph, equipped with a PTE-5 capillary column (25 m × 0.25 mm i.d., 0.25 µm film thickness, Spelco) and connected to a JEOL JMS SX-102A high resolution mass spectrometer. GC/MS operating conditions were: GC column temp. = programmed from 140 °C (1 min.) to 260 °C (10 mins.) at a rate of 20 °C/min., ionization mode = EI, monitoring mass (*m/z*) = 144.9606 and 146.9584, for native TCAB, 150.9803 and 152.9773 for ^{13}C labelled TACB.

RESULTS AND DISCUSSION

Aqueous solubility of TCAB

The time course of TCAB concentration in water was shown in figure 1. TCAB concentrations in water were fluctuating on the third day, but the cause of this phenomenon is not understood. The variation was not due to the measurement by a GC/MS, because the results of two measurements were close to each other. The three values (S-1,2 and 3) were converging to one value as days went by and settled down to 0.159 µg/L (SD = 0.0165) on the 22th day. This is the first report on the aqueous solubility of TCAB.

Aqueous solubility of related compounds have been reported for tetrachlorodibenzo-*p*-dioxin (TCDD), tetrachloro-dibenzofuran (TCDF) and tetrachlorobiphenyl (TCB). The aqueous solubility of 2,3,7,8-TCDD at 25 °C was reported as 0.00791 µg/L[6] and 0.2 µg/L[7], the former being considered more reliable. TCAB is a compound sparingly soluble in water like 2,3,7,8-TCDD but one may say that TCAB is more soluble than TCDD in water.

Octanol-water partition coefficient of TCAB

This physico-chemical property also have not been reported for TCAB. From the

Figure 1 The time course of TCAB concentration (μg/L) in water.

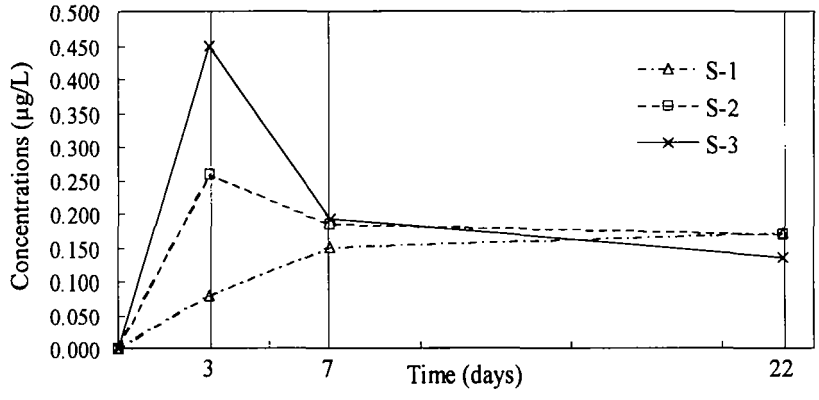

Table 2 Concentrations (μg/L) of TCAB in water and octanol, and octanol-water partition coefficient.

	Concentration (μg/L) of TCAB in octanol (A)	Concentration (μg/L) of TCAB in water (B)	Log Kow[a]
P-control	nd[b]	nd[c]	
P-1	142	0.000408	5.54
P-2	176	0.000436	5.61
P-3	160	0.000569	5.45
Mean			5.53
SD[d]			0.0555

a: octanol-water partition coefficient
nd = not detected
detection limit = b: 50 μg/L, c: 0.0003 μg/L
d: standard deviation

experiment, octanol-water partition coefficient of TCAB was estimated to be 5.53 (table 2). This value is also similar to the related compounds. Kaiser (1983)[8] has reported that the log Kow of 2,3,7,8-TCDD, 1,2,3,4-TCDD and 1,3,6,8-TCDD are all 5.50.
5.53 of log Kow of TCAB is showing that this compound is lipophilic and water-insoluble, similarly to TCDD.

ENV

Organochlorine compounds such as PCBs, DDTs, HCHs, PCDDs, PCDFs, Chlordanes and Drins are known as a ubiquitous pollutants and health hazards as they remain persistently in the environment and ingested through foods. Residue level of these compounds in fish and animals is related to their physico-chemical characters: low water solubility and high octanol-water partition coefficient tend to cause high bio-accumulation. These physico-chemical properties of TCAB are similar to the above compounds and they may suggest the possibility of bio-accumulation similarly as TCDD. Environmental levels of TCAB is, however, not known probably due to the difficulty in analyzing at ultra trace level. Further study will be necessary for this compound, if we consider that TCAB is a toxic compound and it is still discharge into the environment as an impurity of DCA related herbicides.

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