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**REDUCTIVE DECHLORINATION OF POLYCHLORINATED BIPHENYLS BY  
ZERO-VALENT IRON IN SUBCRITICAL WATER**

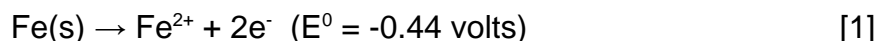
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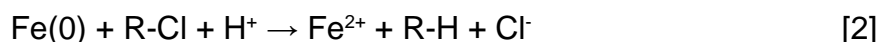
**Introduction**

Polychlorinated biphenyls (PCBs) are a group of chemicals comprising of 209 congeners ranging from mono- to decachlorobiphenyl that are very persistent to degradation and hazardous to the biosphere<sup>1</sup>. Manufactured by subjecting technical biphenyl to chlorine, commercial PCBs typically come with a mixture of many congeners and are categorized by the amount of chlorine by weight present in the PCB mixture. Polychlorinated biphenyls were used in transformers, capacitors, inks, and pesticide formulations. Between 1929 and 1972, United States produced about 560 million kg of PCBs, about half the world's total PCB production. It is estimated that about 400 million kg of the global PCBs are dispersed into the geo-, aqua-, atmo-, and biosphere, with the majority of them being concentrated in the geosphere because of their low volatility, low solubility in water, and high affinity for particulates<sup>2</sup>.

Under the Toxic Substance Control Act (TSCA), the most widely accepted method for remediation of PCBs is by using specialty incinerators that are capable of reaching a temperature of 1200 °C<sup>2</sup>. Despite its high efficacy, pyrolysis of PCBs is expensive and may produce undesirable by-products such as polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) due to incomplete combustion<sup>3</sup>. Several new remediation techniques for PCB are currently under development including bioremediation,  $\gamma$ -radiolysis, and dechlorination using zero-valent metals and other chemical reagents<sup>3-8</sup>. Elemental iron is a reducing agent via the following reaction,



By direct contact with iron it was demonstrated that halocarbons such as trichloroethylene can be dechlorinated to hydrocarbons and chloride ions<sup>3,7</sup>. The reductive dechlorination process follows as:



Though this reaction is kinetically very slow under ambient temperature and pressure, the kinetics can be enhanced by the use of palladized iron<sup>9-11</sup>.

Recent reports indicate that super-heated water is capable of extracting organic pollutants including PCBs from solid matrices<sup>12-16</sup>. A recent publication by Chuang and coworkers indicates that complete reductive dechlorination of PCBs to biphenyl by Fe(0) is possible in the presence of superheated (400°C) water vapor<sup>8</sup>. Subcritical water extraction (SWE) refers to extractions that are performed under conditions that are below the critical temperature ( $T_c$ ) and pressure ( $P_c$ ) of water ( $T_c$ = 373.99 °C,  $P_c$ = 22.064 Mpa). Presently, reports that incorporate SWE and off- or on-line reduction of halocarbons as a remediation technology are not available in the literature. We report in this paper the preliminary findings of dechlorination of Aroclor 1260 with zero-valent iron in subcritical water.

## **Experimental**

### Chemicals and Instruments

Electrolytic iron powder (100 Mesh), HPLC grade acetone, HPLC grade n-hexanes, and HPLC grade water were obtained from Fisher Scientific (Fair Lawn, NJ). Aroclor 1260 standards (2000 ppm in methanol), BZ #54 (2,2',6,6'-tetrachlorobiphenyl), BZ #207 (2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl), and BZ #209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl) were purchased from ChemService (West Chester, PA) and used without further purification. Aroclor 1260 standards were made by appropriate dilution with HPLC grade n-hexanes in volumetric glasswares. An Isco 260D Syringe Pump was used to pressurize the water and a GC oven was used for maintaining the temperature to  $\pm 2$  °C. A HPLC solvent pump was teed into the system to deliver the n-hexanes. High temperature and pressure extraction cells were purchased from Keystone Scientific, Inc. (Bellefonte, PA). A Hewlett-Packard 5890A GC-ECD/FID was used for analyses of the PCB standard and samples. The 30- m EC-1 capillary column purchased from Alltech (Deerfield, IL) had a 0.45 mm i.d. and 1.0  $\mu\text{m}$  film thickness. The carrier gas was chromatographic grade He (Oxarc, Spokane, WA). Sample injection volume was 1  $\mu\text{L}$  splitless with the injector temperature set at 200 °C and the detector set at 300°C. Separation was conducted with a temperature program that held column temperature at 150 °C for 2 minutes, then ramped at 4°C/min until it reached 300°C, where it was held for 10 minutes.

### Procedures

100 g of iron powder was washed once with 100 mL HPLC grade n-hexanes followed by 100 mL acetone to rid any organic substances. The washed iron was then dried by nitrogen purge and stored. A 3.0-g sample of this iron powder was transferred to a

plastic weighing boat and the desired amount of Arochlor 1260 in methanol solution was spiked directly onto the iron powder and the methanol was allowed to air-dry. The PCB-spiked iron powder was transferred into a 2.2-mL stainless-steel extraction cell. The extraction cell was tightened and filled with HPLC grade water by using a syringe before it was placed in the oven, connected to the extraction system, and brought to pressure for leak check. The column was then brought to temperature. Timing began after the temperature readout corresponded with the set temperature. Figure 1 depicts the apparatus. Reduction and extraction were carried out *in situ* statically (without flow of solvent) for the desired amount of time. The system was then flushed with ca. 10 mL of HPLC grade water, followed by ca. 5 mL of n-hexanes by using a HPLC solvent pump, and finally with another ca. 5 mL of HPLC grade water, all collected in a 40-mL glass vial. The hexane phase was separated from the aqueous phase with a 60-mL separatory funnel. The aqueous phase was washed twice, each with ca. 3 mL of n-hexanes, and all three portions were pooled together before nitrogen-purged to a volume of ca. 6 mL. BZ #207 was added as internal standard before each sample was brought to a final volume of 10 mL. 1.0 mL of each sample was transferred to a 1.5-mL autosampler vial with Teflon-coated stopper for GC analyses. For the studies of temperature effect on dechlorination efficiency using BZ #54 and BZ #207, the procedure was the same. BZ #209 was added as the internal standard for studies using BZ #207. Dechlorination efficiency was calculated by normalizing peak areas of both the sample and the standard with respect to an internal standard solution spiked into the solutions.

## Results and Discussions

The congener BZ #54 was used for quantitation of mass recovery owing to the complex nature of the Arochlor 1260 chromatogram. By performing recovery experiments at room pressure and temperature and at 250 °C and 10 MPa for 0 minutes, mass recovery of BZ #54 was found to be close to 95% in both cases. This degree of recovery indicates that PCBs can be fully recovered from this system and the 5% loss may be due to loss of analyte during the spiking and transferring processes. Because the vapor pressure of water at 300 °C is 8.58 MPa<sup>17</sup>, operating pressure of 10 MPa was selected to ensure that the water remain in the liquid state throughout the temperature range used in this study. In the various initial experiments performed by using BZ #54 and BZ #207 and by varying the reaction temperature it was found that 250 °C was the optimal temperature. The presence of zero-valent iron was also found to be imperative for the dechlorination of these congeners to occur at any appreciable rate. The BZ #54 congener (2,2',6,6'-tetrachlorobiphenyl) was found to be especially tenacious with respect to dechlorination under the studied conditions and is an ideal candidate for studies such as recovery and temperature effect. However, it is important to note that this particular congener does not appear in any Arochlor mixture<sup>18</sup>.

Nine major and well-resolved peaks were chosen from the chromatogram of Arochlor 1260 for quantification purpose since they represent the majority and also provide accurate quantitation results. Direct comparison of the individual peak area before and after reduction was made by normalizing the peak areas with respect to the peak area

of the internal standard (BZ #207). For Aroclor 1260, the detection limit was close to 0.2 mg Aroclor 1260/mL hexanes on this particular instrument. Table 1 summarizes the approximate reduction efficiencies of the selected peaks. These preliminary results indicate that the higher chlorinated PCBs are much more easily reduced than the lower homologues. The resistance of the lower homologues towards reductive dechlorination can be explained by the increase in LUMO energy which decreases the probability of the reductive electron to occupy the LUMO, thus decreasing the probability of the formation of the reactive excimer of the PCB molecule<sup>19</sup>.

Homologue composition of various Aroclor mixtures are well studied and the weight percent of Aroclor 1260 is given as 12% pentachlorobiphenyl, 42% hexachlorobiphenyl, 38 % heptachlorobiphenyl, 7% octachlorobiphenyl, and 1% nonachlorobiphenyl<sup>18</sup>. Although dechlorination did not proceed toward completion after the eight-hour reaction, it is apparent that the majority of the original PCBs in the mixture--the higher-substituted congeners which are predominant in Aroclor 1260 and typically more toxic--were completely reduced. These results suggest that reductive dechlorination using SWE and zero-valent iron may be a promising remediation alternative for PCB-contaminated soils and sediments. Further research such as designing an on-line approach and optimization of the dechlorination efficiency, particularly those of the lower-substituted homologues, is being pursued at this writing and the results will be published in a separate report.

### Literature Cited

1. Jones, G.R.N. *The Lancet*, Sep 30, 1989, 791.
2. Panel on Hazardous Trace Substances. *Environmental Research*, 1972, 5, 249-362.
3. Hitchman, M.L.; Spackman, N.C.; Ross, N.C. Agra, C; *Chem. Soc. Rev.* 1995, 24, 423-430.
4. Arbon, R.E.; Mincher, B.J.; Knighton, W.B. *Environ. Sci. Technol.* 1996, 30, 1866-1871.
5. Renner, R. *Environ. Sci. Technol.* 1998, 32, 360A-363A.
6. Marques, C.A.; Selva, M.; Tundo, P. *J. Org. Chem.*, 1994, 59, 3830-3837.
7. Matheson, L.; Tratnyek, P.G. *Environ. Sci. Technol.* 1994, 28, 2045-2053.
8. Chuang, F.W.; Larson, R.A. Wessman, M.S. *Environ. Sci. Technol.* 1995, 29, 2460-2463.
9. Muftikian, R.; Fernando, Q.; Korte, N. *Water Res.* 1995, 29, 2434-2439.
10. Johnson, T.L.; Scherer, M.M.; Tratnyek, P.G. *Environ. Sci. Technol.* 1996, 30, 2634-2640.
11. Grittini, C.; Malcomson, M.; Fernando, Q.; Korte, N. *Environ. Sci. Technol.* 1995, 29, 2898-2900.
12. Langenfeld, J; Hawthorne, S.B.; Miller, D.J.; Pawliszyn, J. *Anal. Chem.* 1993, 65, 338-344.
13. Van der Velde, E.G.; de Haan, W.; Liem, A.K.D. *J. Chromatogr.* 1992, 626, 135-143.
14. Lee, H.B.; Peart, T.E. *J. Chromatogr. A*, 1994, 663, 87-95.

15. Hawthorne, S.B.; Yang, Y.; Miller, D.J. *Anal.Chem.* 1994, 66, 2912-2920.
16. Yang, Y.; Bowadt, S.; Hawthorne, S.B.; Miller, D.J. *Anal.Chem.* 1995, 67, 4571-4576.
17. Handbook of Chemistry and Physics, 71<sup>st</sup> ed., CRC Press, Boca Raton, Fla., 1991.
18. Erickson, M.D. *Analytical Chemistry of PCBs*, 2<sup>nd</sup> ed.; CRC/Lewis Publ., Boca Raton, Fla. 1997.
19. Mincher, B.J. Ph.D. Dissertation, University of Idaho, Moscow, Idaho, 1997.

**Table 1.** Percent reduction efficiency of nine selected peaks of Aroclor 1260 after one, four, and eight hour reaction times (T=250 °C and P=10 MPa). Peak area was individually normalized to area of internal standard (BZ#207).

	Peaks*								
Time (Hr)	1	2	3	4	5	6	7	8	9
1	100	100	95.6	88.8	82.0	76.7	73.7	72.4	58.9
4	100	100	100	96.0	93.0	87.4	83.2	48.5	30.1
8	100	100	100	100	100	97.5	93.2	84.8	54.5

\* Peak 1 = nonachlorobiphenyl  
 Peak 3= octachlorobiphenyl  
 Peak 5= heptachlorobiphenyl  
 Peak 7=hexachlorobiphenyl  
 Peak 9=pentachlorobiphenyl

Peak 2=octachlorobiphenyl  
 Peak 4=heptachlorobiphenyl  
 Peak 6=hexachlorobiphenyl  
 Peak 8=hexachlorobiphenyl