

# REDUCTIVE DECHLORINATION OF CHLORINATED BIPHENYLS BY PALLADIUM COATED ZINC

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**Abstract:** Zero valent metals (ZVMs) recently have received a lot of attention as media for permeable reactive barrier. A reductive degradation study for dichlorinated model compounds were conducted. It is known that halogenated aromatic compounds slowly degraded with plain ZVMs. To overcome the low reactivity of plain ZVMs, palladium was used as catalyst. Palladium coated zinc (Pd/Zn) was tested for the three dichlorobiphenyls. Pd/Zn degraded the target compounds rapidly and monochlorobiphenyls and biphenyl were detected as daughter compounds. The produced monochlorophenyl also gradually degraded and biphenyl was the final product. The reaction rate among the three compounds were in order of 3,4-DCBP > 2,4-DCBP > 2,3-DCBP. The degradation rate was proportional to the metal dose. The degradation pathway was mainly step-by-step dechlorination.

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**Key Words:** dechlorination, degradation, PCBs, reduction, ZVMs

## INTRODUCTION

Polychlorinated biphenyls (PCBs) were synthesized from 1930s for commercial use under the trade name Aroclor. They are complex mixture and their chemical and physical stabilities allow a variety of use as electric fluids, pesticide extenders, flame retardants, heat transfer fluids, and hydraulic lubricants all over the world.<sup>1)</sup> The production of PCBs ceased in 1970s due to the high toxicity but PCBs are still found from water and soil environments since heavy use of the compounds resulted in a direct or indirect release into environments and they are very stable under natural conditions. Since PCBs are stable under natural environ-

ment, they can accumulate through food chain and may cause health problems. It is very difficult to remove PCBs from subsurface and soil since they act as DNAPL (dense non-aqueous phase liquid) and have very low water solubilities. Therefore the released PCBs have adverse effect for a long term. Destruction technologies are incineration, chemical dechlorination, vitrification, and biodegradation. However, these methods are usually expensive. Incineration may produce undesirable products such as dioxins<sup>2)</sup> and it is hard to achieve low residual concentration through biodegradation.

Among several chemical dechlorination methods, zero valent metals (ZVMs) have drawn great attention as effective reductants in recent years.<sup>3~9)</sup> Some ZVMs are being applied as reductant for permeable reactive barrier (PRB).<sup>10~13)</sup> PRB employing ZVMs is a cost effective remediation technology for the long

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term and low concentration of recalcitrant contaminants, substituting high cost technologies such as pump and treatments. Zero valent iron was able to degrade several chlorinated C<sub>1</sub>-C<sub>2</sub> compounds including carbon tetrachloride, TCE, and PCE at very fast rates with half-life ranging from minutes to a few days.<sup>3,14-16)</sup>

However, there are some limitations to utilize ZVM to all kinds of contaminants. Halogenated aromatic compounds such as PCBs and PCP have not been as readily dechlorinated as trichloroethylene (TCE) and perchloroethylene (PCE).<sup>8,17,18)</sup> Among a few hundreds published ZVM related paper, only a few studies reported for the dechlorination of halogenated aromatic compounds by ZVMs. Dechlorination of PCBs by zero valent iron was showed at high temperatures of 400°C while no degradation was observed at room temperature.<sup>17)</sup> A few studies showed that rapid degradation of PCBs is possible with catalytically modified metals.<sup>19,20)</sup> Palladium coated iron was successfully tested for a few low chlorinated biphenyls.<sup>19)</sup> Zero valent zinc also has been used as reductant for PCE and PCP.<sup>18)</sup> Theoretically zinc has higher reduction potential ( $V^0 = -0.762V$  vs. SHE) than that of zero valent iron ( $V^0 = -0.447V$  vs. SHE). However, its toxicity prevent from its wide use for reduction of chlorinated contaminants.

In this study, we investigated the feasibility of Pd/Zn for dechlorination of chlorinated biphenyls. Since water solubility of PCBs decreases as the chlorine increases on the biphenyl rings, highly chlorinated PCBs have too low water solubilities to measure aqueous concentration for a kinetic study without concentrating pretreatments. Emphases were placed on the enhanced reactivity of Pd/Zn compared with plain ZVMs. Kinetic constants were also determined and discussed depending on the chlorinated position on the biphenyl ring.

## MATERIALS AND METHODS

### Chemicals and Methods

Hexane, 2-chlorobiphenyl (2-CP), 3-chlorobiphenyl (3-CP), 4-chlorobiphenyl (4-CP), 2,3-dichlorobiphenyl (2,3-DCP), 2,4-dichlorobiphenyl (2,4-DCP), 3,4-dichlorobiphenyl (3,4-DCP) (Chemical Service) were used as received. Pd/Zn was prepared through reductive coating of palladium on acid washed zinc surface. Acid washed zinc was added into the PdCl<sub>2</sub> solution. After 30 minutes mixing, the metal was rinsed with water and acetone and dried. More than 99% of added palladium was coated and resulted in palladium content of 0.05% (wt.) on zinc. EPA VOA amber vials (20 mL and 40 mL) were used as batch reactors. To each prewashed vial, 20.0 mL of water and 1.00~2.00 g of Pd/Zn were added. A schematic diagram of reaction vial and open-cap injection is shown in Figure 1. Chlorinated biphenyls were added as a spike of methanol stock solution. Three dichlorobiphenyls, 2,3-DCBP, 2,4-DCBP, and 3,4-DCBP were tested. Immediately after the chlorobiphenyls injection with micro-syringe, the vials were capped with Teflon lined silicone septa and open-top screw caps. Control vials were prepared identically except for the exclusion of

ZVMs. All vials were placed on an orbital shaker at room temperature (21°C) and shaken at 200 rpm. At each sampling time, three reaction vials and two control vials were removed for extraction and analysis of chlorinated biphenyls.

### Sample Extraction and Analysis

The sample was extracted using a typical liquid-liquid extraction with hexane and the volume ratio of sample to solvent was 20 to achieve concentrating effect. The extracted samples were analyzed with GC-FID (HP-6890, USA) equipped with an HP-5 (30 m × 0.25 mm I.D.) column. Split mode injection (20 : 1) of 1  $\mu$ L sample was injected. The oven temperature program was set as 1 minute at 80°C, 10°C/min to 180°C, 1 minute at 180°C, 20°C/min to 280 °C, 1 minute at 280°C. The carrier gas (helium) flow rate was 5.6 mL/min. The calibration curves were linear over the concentration range of interest.

## RESULTS AND DISCUSSIONS

Three DCBPs were tested with metal zinc and the results were shown in Figure 2. About 100% of all three target compounds were recovered implying zinc metal was not active for the DCBPs or the reaction was too slow to detect concentration difference over the experimental period. As discussed in previous section, zero valent zinc dechlorinated PCE and PCP with high reaction rates. Therefore, the current results imply that the reductive dechlorination of chlorinated compounds by ZVMs is compound specific and a metal with high reactivity to some contaminants is not always active to other targets. It is necessary to develop reactivity enhanced metals to shorten the reaction time and to apply relatively less reactive compounds such as PCBs.

Three DCBPs (2,3-DCBP, 2,4-DCBP, 3,4-DCBP) were dechlorinated by Pd/Zn and the results were in Figure 3~5. As 2,3-DCBP disappeared, 2-CBP and biphenyl were detected

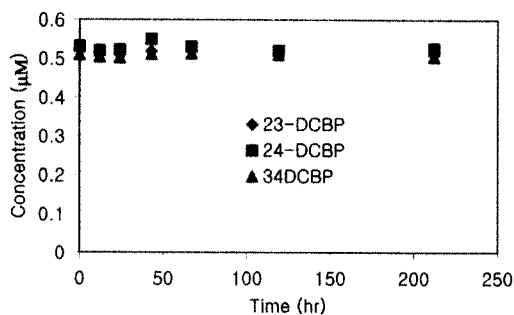


Figure 2. Degradation of DCBPs by zero valent zinc.

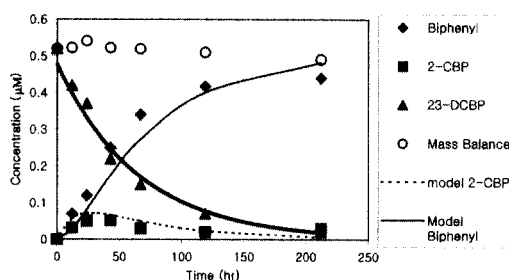


Figure 3. Reductive degradation of 2,3-DCBP by Pd/Zn.

as intermediate products (Figure 3). The produced 2-CBP began to be gradually dechlorinated through a typical step-by-step dechlorination pattern and the concentration of biphenyl increased continuously as the final product. The removal of 2,3-DCBP was exponential decrease indicating the kinetic follow a pseudo first order model as shown commonly in previous studies. The mass balance, sum of the target compounds and two intermediate products, was above 92% over the experimental periods, confirming that dechlorination was the predominant reaction.

Production of 2-CBP indicated that chlorine at position 3 ( $\beta$  chlorine) was more readily removed than that of position 2 ( $\alpha$  chlorine). In the Figure 4, the result of 2,4-DCBP was summarized. The degradation pattern was very similar with 2,3-DCBP and 2-CBP was detected as daughter compounds. In the competition of two chlorines at position 2 and 4 for dechlorination on the surface of zinc, position 4 was more easily dechlorinated than position

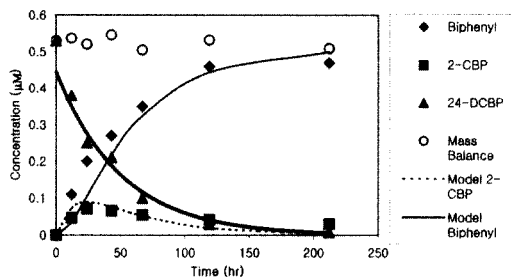


Figure 4. Reductive degradation of 2,4-DCBP by Pd/Zn.

2. In the case of 3,4-DCBP, chlorine at position 4 was removed and 3-CBP was detected as the intermediate product as shown in Figure 5. A regioselectivity, in which chlorine at closer to the phenyl connection bond remains and one located further from the connection bond is dechlorinated first, is observed. These regioselectivities were found in previous reports for reduction of chlorophenols, nitroaromatic compounds, and low chlorinated biphenyls.<sup>7,21)</sup> Dechlorination study of DCBPs using palladium coated iron showed very similar regioselectivity as palladium coated zinc used. However, when just zinc metal was used for polychlorinated phenol, a chlorine, which have two alpha carbon with chlorine or hydroxyl functional groups, was preferentially dechlorinated. It was rationalized that the stability of the radical formed after first one electron transfer from metal surface affect the regioselectivity. In another word, the degradation sequence where the formed radical is most stabilized is preferred in actual reaction. In current and a previous report,<sup>7)</sup> opposite results is obtained. Position 2 of 2,3-DCBP have two functional group of one chlorine and one phenyl but the chlorine at the position 2 is less reactive indicating the legioselectivity of current study is different from the previous one employed plain zinc.

The prediction of degradation product through a well elucidated regioselectivity is very important in applying ZVM in engineered system since reduction of toxicity is well predicted and it allows to manage the system toward making less toxic products. In the case of PCE

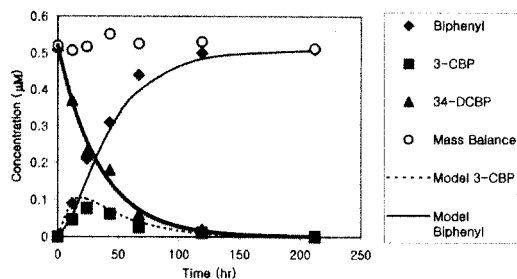


Figure 5. Reductive degradation of 3,4-DCBP by Pd/Zn.

degradation, it is preferred to avoid production of vinyl chloride due to it's high toxicity though less chlorinated compounds have lower toxicity in general.

Pseudo first order kinetic constants of the three DCBPs were in the order of 3,4-DCBP ( $0.029 \text{ hr}^{-1}$ ) > 2,4-DCBP ( $0.020 \text{ hr}^{-1}$ ) > 2,3-DCBP ( $0.015 \text{ hr}^{-1}$ ). In the studies using ZVM, the surface area normalized kinetic constants (normalized to unit surface in unit volume of solution) are frequently employed for comparing purpose with other results. The surface area normalized kinetic constants of the three DCBPs were summarized in Figure 6. Three dichlorobiphenyl were sequentially dechlorinated and the sequence was matched with the dechlorination preference of mono-chlorobiphenyl in a previous study.<sup>19)</sup> The preference of the three mono-chlorobiphenyls were in order of 4-CBP > 3-CBP > 2-CBP. In the current study, the preferred dechlorination position was 4 from 2,4-DCBP and 3,4-DCBP and 3 was removed first from 2,3-DCBP rather than position 2. It is worthwhile noting that reaction patterns of the chlorinated aromatic compounds are compound and reactant specific and the prediction of the daughter based on different compound is not feasible. In Figure 7, the reaction pathways are summarized.

Detection of monochlorobiphenyls (MCBPs) indicated the degradation is stepwise reaction. However, this does not exclude simultaneous dechlorination of the both chlorines on DCBPs. A sequential reaction model fitting is used to the experimental data. It is assumed that the reaction is a complete step-by-step reaction as

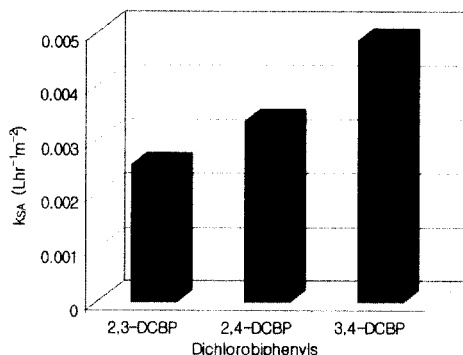


Figure 6. Surface area normalized kinetic constants of three DCBPs by Pd/Zn.

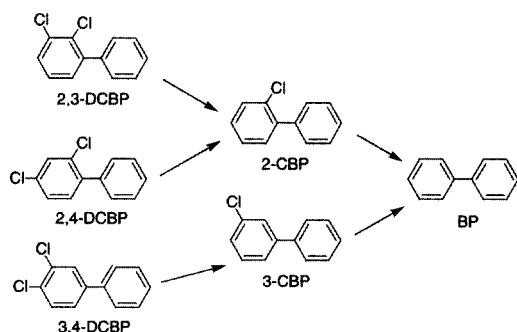
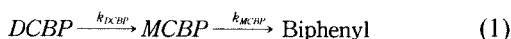


Figure 7. Summary of degradation pathways of DCBPs by Pd/Zn.

described in equation (1). Equations (2) and (3) was used to calculate the concentration of MCBP and DCBP during the reaction. Individual kinetic constant for MCBPs or DCBPs was obtained from experiments and a previous study.<sup>19)</sup>



$$[DCBP] = [DCBP]_0 e^{-k_{DCBP}t} \quad (2)$$

$$[MCBP] = \frac{k_{DCBP}[DCBP]_0}{k_{MCBP} - k_{DCBP}} (e^{-k_{DCBP}t} - e^{-k_{MCBP}t}) \quad (3)$$

where,  $k_i$  is dechlorination kinetic constant ( $\text{hr}^{-1}$ ),  $i = \text{MCBP}$  or  $\text{DCBP}$ .

The model results were plotted in the Figures 3~5. Dashed lines described the concentration of MCBPs and thin solid lines showed the concentration of biphenyl produced. Model fitting lines showed a similar

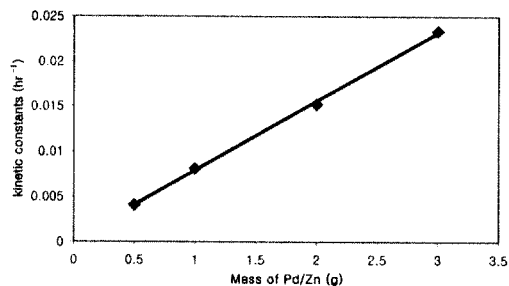


Figure 8. Kinetic constants of 2,3-DCBP with variable Pd/Zn dose.

trend with the observed data profile of each compound, although fitting was not perfectly matched with the data points. These results implied that dechlorination reaction was not completely achieved by stepwise reaction, and included simultaneous reactions in part. For example, major reaction pathway of 2,3-DCBP was stepwise dechlorination of position 3 and 2 sequentially, however, some portion of the reaction occurred on position 2 and 3 occurred simultaneously. This hypothesis rationalize that observed concentration of 2-CBP is slightly lower than that from model fitting with an assumption of complete stepwise reaction. It is also explained that observed biphenyl was slightly higher than the model prediction. It was concluded that the portion of stepwise dechlorination reaction was higher, even though concerted reaction also occurred simultaneously. In the previous studies for chloroethenes with Pd/Fe, no chlorinated intermediate products or relatively very small amounts of chlorinated products were detected indicating the major reaction pathway is a concerted dechlorination.<sup>7,22,23)</sup>

A trichlorobiphenyl, 2,3,4-TCBP was tested with Pd/Zn. About 2 mg/L (above water solubility) of 2,3,4-TCBP was removed by 4 g of Pd/Zn within 48 hours indicating the catalytic modified metal can be applied to highly chlorinated PCB congeners. Additional studies are under investigation.

In Figure 8, kinetic study with variable metal content was summarized. The kinetic constants linearly increased with metal contents. This

phenomenon was observed in several other studies with ZVMs.

## CONCLUSION

Reductive dechlorination study of three DCBMs as model compounds of PCBs was conducted with palladized zinc. Pd/Zn rapidly dechlorinate DCBMs while plain zinc was not active to the compounds. The degradation trends are agreed with previous studies. A regioselectivity was observed and the trend can be used to predict the daughter compounds distribution and toxicity from reduction using the ZVM. Based on the experimental result and model fitting the reaction was mainly stepwise dechlorination and a small portion of a concerted pathway is involved.

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