

UDC 547

Advanced Method for Catalytic Dechlorination of Polychlorinated Biphenyls

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(Received 28 March, 2011)

Abstract

Activated carbon was for the first time used as catalytic substrate in dechlorination process and a significant dechlorination (79 %) of most persistent 2,4,5- trichlorobiphenyl was achieved at 110 °C in water/ isopropanol solvent by applying reducing media. It was observed that carbon particles played a catalytic role to enhance the dechlorination process through substitution reactions and by suppressing further chlorination in reaction mixture. Dechlorination at the ortho position of biphenyl was clearly preceded through substitution reaction by hydroxyl and thiol ions. Moreover, in the absence of activated carbon, dechlorination was decreased and substituted products did not observed.

Key words: activated carbon, catalysis, water/organic solvent mixture, temperature

INTRODUCTION

Polychlorinated biphenyls (PCBs), classified as priority pollutants by EPA, have been widely used as insulator in transformer production, in flame retardation and dielectric fluids. In environment PCBs act as endocrine disruptors, human carcinogens and environment estrogens [1–3]. Few methods like incineration, photochemical dechlorination and catalytic dechlorination have been studied [4–7]. In continuation of our previous work at dechlorination of aromatic chlorides we developed a convenient and practicable method for dechlorination of PCBs. In our previous studies we used fly ash as a substrate to achieve hydrodechlorination. By using fly ash we observed a problem of further chlorination at high temperature. It was observed that carbon portion of fly ash acted as a substrate for dechlorination whereas the metal contents of fly ash played adverse roles to carry out further chlorination [8–11]. To overcome fur-

ther chlorination during dechlorination process, the present studies were conducted by using activated carbon. In this study reaction conditions were optimized and dechlorination of 2,4,5-trichlorobiphenyl was carried out on activated carbon.

EXPERIMENTAL

Activated carbon (particle size 125 µm, M.B value 25, Fe contents ≤ 0.05 %, ash ≤ 5 %, moisture ≤ 10 %) was used without any chemical treatment. Activated carbon was washed with dilute HCl and deionised water to leach out impurities. Calcium hydroxide, sodium hydroxide and sulphur were received as industrial chemical material (>99 %). Chlorinated aromatic compounds and organic solvents were received from Merck Co.

The experiments were carried out in a glass reactor equipped with an agitator (90–1000 rpm) and a digitally temperature controlled hot plate

(250 °C Max.). The experimental products were extracted twice with hexane, with a total final volume of 20–30 mL. Combined organic layers were washed, dried on MgSO_4 and then concentrated by evaporation to 5 mL volume. Reaction products were analyzed using a gas chromatograph (HP 5890 Series II) equipped with DB-5 m column (30 m \times 0.25 m \times 1 μm) and a quadruple mass spectrometer (JEOL). Ionization was performed under 70 eV electron impact conditions (300 μA , 400 V) where the initial temperature of the column was 35 °C, raised at 15 °C/min to 150 °C and then at 3 °C/min to 280 °C.

The solution of 2,4,5-trichlorobiphenyl (30 mmol) was treated with a mixture of carbon, calcium hydroxide/sodium hydroxide and sulphur in mixed water/organic solvents at 40–150 °C for different durations with agitation (250 rpm). Different concentrations of reactants

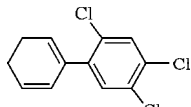
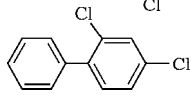
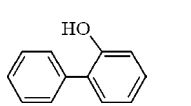
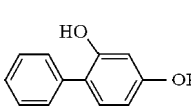
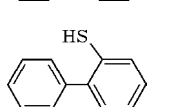
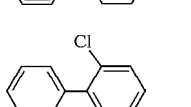
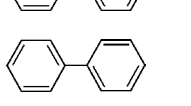
and different mixed water/organic solvents were used. It was found that the best results of dechlorination were obtained with 20 g activated carbon, 6 g calcium hydroxide, 3 g sodium hydroxide, 8 g sulphur in water/isopropanol solvent (3 : 1 v/v). In this paper, the results with optimized chemical conditions will be mentioned and discussed.

Experimental yields (amount of products obtained in experiments) are presented in Tables 1 and 2 in which the contents of chloro compounds substrates and dechlorinated products were expressed in mass %, and the extent of dechlorination was expressed as the percent of chlorine lost by dechlorination in comparison with the original chlorine content in the substrates by the following formula:

$$\text{Dechlorination (\%)} = [(C_s - C_p)/C_s] \cdot 100$$

TABLE 1

Dechlorination of 2,4,5-trichlorobiphenyl. Activated carbon 20 g, $\text{Ca}(\text{OH})_2$ 6 g, NaOH 3 g, sulphur 8 g, Cu 20 mmol, heating for 3 h; water/ isopropanol solvent 3 : 1 v/v

Organic species		Yield (%) at temperature (°C):						
		60	70	80	90	110	130	150
	$\text{C}_{12}\text{H}_7\text{Cl}_3$	43	36	32	22	8	14	13
	$\text{C}_{12}\text{H}_8\text{Cl}_2$	8	10	7	9	4	6	8
	$\text{C}_{12}\text{H}_9(\text{OH})$	6	8	9	4	6	7	8
	$\text{C}_{12}\text{H}_8(\text{OH})_2$	4	5	8	6	2	6	5
	$\text{C}_{12}\text{H}_7(\text{SH})$	8	8	6	5	2	7	7
	$\text{C}_{12}\text{H}_9\text{Cl}$	6	6	5	8	6	7	8
	$\text{C}_{12}\text{H}_{10}$	25	27	33	46	72	53	51
Net dechlorination		49 %	55 %	61 %	69 %	87 %	79 %	79 %

where C_s and C_p are the chlorine contents in the substrate and products, respectively, mass %.

RESULTS AND DISCUSSION

Higher dechlorination of 2,4,5-trichlorobiphenyl was obtained at 110 °C for 3 h (after 3 h dechlorination was constant). Dechlorination products were biphenyl, *o*-hydroxybiphenyls, 2,4-dihydroxybiphenyls and biphenyl-2-thiol, whereas dichlorobiphenyl and ortho chlorobiphenyls were also found as shown in Table 1. The resultant products revealed that dechlorination of 2,4,5-trichlorobiphenyl was proceeded through reduction and substitution reactions. The formation of biphenyl suggested a reduction process whereas the formation of *o*-hydroxybiphenyls and biphenyl-2-thiol advocated a substitution reaction where the chloride ion was substituted by the hydroxyl and thiol ions. The formation of the 2,4-dihydroxybiphenyl was an interesting phenomenon which can be explained that the *o*-hydroxybiphenyl undergoes further hydroxylation by the hydroxyl ions in the reaction mixture. The removal of chloride species from the ortho position was difficult because the C–Cl bond at the ortho position was more inactive and its removal was reported a real problem [19]. The removal of

chloride from the ortho position was supposed to happen by substitution reaction, whereas the formation of dihydroxybiphenyls advocated that hydrodechlorination process occurred in reaction mixture prior to that of substitution reactions.

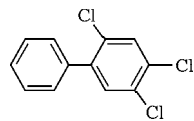
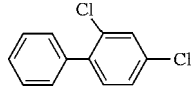
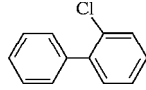
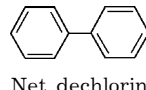
It was observed that dechlorination was achieved by providing organic media along with water, and dechlorination percentage was at maximum in isopropanol solvent as reported by Concibido [21]. This phenomenon proved that organic solvents act as a hydrogen donor as concluded by Ukisu [22], rather than dissolve the organic compounds in reaction media, contradicting observations by other researchers [6, 7, 18, 19].

The addition of water to organic solvents enhanced the dechlorination as was reported by other researchers [8–18]. The volume of water was optimized and maximum dechlorination was achieved when a relatively high ratio of water with isopropanol (3 : 1 v/v) was used. An increase in the dechlorination, in excess of water, was presumed to arise from controlling the solubility of substrate, the additives and the products other than the hydrogen source as reported by Ukisu [22]. This argument was supported by the work of other authors [16–18] who used metals in alcohols to reduce the chlorinated compounds in the absence of water.

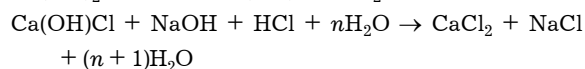
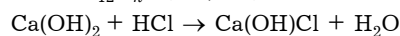
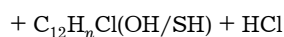
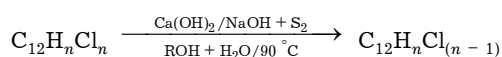
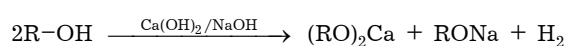
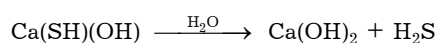
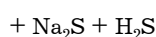
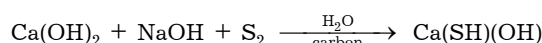
Furthermore, the formation of *o*-hydroxybiphenyls, 2,4-dihydroxybiphenyls and biphenyl-2-thiol suggested that free hydroxyl and hydrosulphide ions in reaction mixture substituted the chloride ions under specified conditions. Based on dechlorination results, a mechanism was postulated that calcium hydroxide and sulphur reacted to produce calcium polysulphide which decomposed in the presence of water to provide a mixture of $\text{Ca}(\text{SH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{SH})(\text{OH})$. In the presence of water $\text{Ca}(\text{SH})(\text{OH})$ further produced $\text{Ca}(\text{OH})_2$ and H_2S . On the other hand, sodium hydroxide reacted with sulphide to produce Na_2S . In the reaction mixture, H_2S and Na_2S acted as strong reducing agents to reduce chlorinated compounds. In addition, on the aromatic ring chlorine was substituted by the hydrogen from the hydroxyl group of the alcohols and the alkoxide ions were quenched by the Ca^{2+} and Na^+ cations. Furthermore, Ca^{2+} and Na^+ ions produced the respective salts with free chloride ions to stabilize them in the reaction mixture.

TABLE 2

Dechlorination of 2,4,5-trichlorobiphenyl without activated carbon at 110 °C. Activated carbon 20 g, $\text{Ca}(\text{OH})_2$ 6 g, NaOH 3 g, sulphur 8 g, Cu 20 mmol, heating for 3 h; water/isopropanol solvent 3 : 1 v/v

Organic species		Yield, %
	$\text{C}_{12}\text{H}_7\text{Cl}_3$	36
	$\text{C}_{12}\text{H}_9\text{Cl}_2$	10
	$\text{C}_{12}\text{H}_{10}$	16
	$\text{C}_{12}\text{H}_{10}$	36
Net dechlorination		52 %

Moreover, an increase in dechlorination (%) by the addition of sodium hydroxide along with calcium hydroxide was justified by the fact that the solubility of sodium chloride at a temperature $>90^{\circ}\text{C}$ is lower than that of calcium chloride. Thus the addition of sodium hydroxide in the solution of calcium hydroxide and sulphur decreased the free chloride ions in the reaction mixture and consequently favours the further chlorination. The resultant HCl in the reaction mixture favours the formation of H_2S and Na_2S :



The dechlorination yield (%) was substantially affected by the change in temperature as shown in Fig. 1. After achieving the highest dechlorination, temperature did not effect on dechlorination as it became almost constant. This temperature dependent phenomenon led us to assume need of reaction media to remain in reaction vessel in liquid phase. It is worthy to state that in contrast with our previous studies, this time we did not find any further chlorination in the reaction mixture. This phenom-

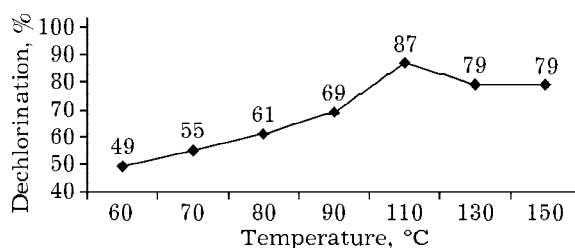
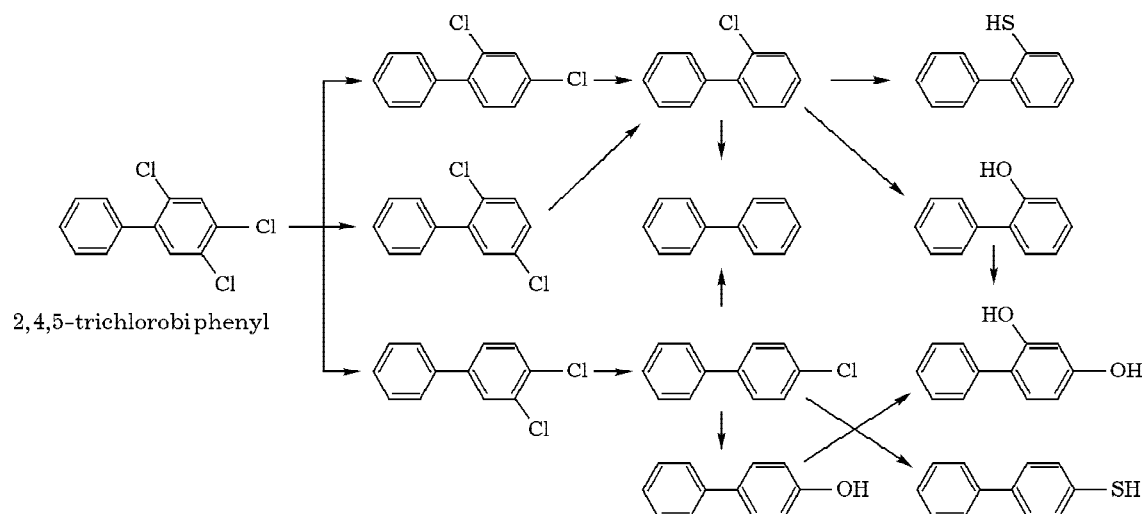


Fig. 1. Effect of temperature on dechlorination of PCB.

enon indicated that chloride ions in the reaction mixture remained adsorbed on the surface of activated carbon and were not available for further chlorination as was happened when we used fly ash under the same reaction conditions.

To assess the role of activated carbon, experiments were performed without activated carbon under the same optimized conditions. The results (see Table 2) suggested that dechlorination without activated carbon was significantly lower as compared to experiments with it. Furthermore, it was very revealing that we did not find *o*-hydroxybiphenyls, 2,4-dihydroxybiphenyls and biphenyl-2-thiol in resultant products. This clearly suggested that activated carbon played a vital role in substitution reactions. Consequently, it was concluded that activated carbon provided the required surface for hydroxyl and thiol ions given by base to facilitate the reduction/substitution of chlorinated compounds. The chlorinated compounds were adsorbed on the surface of carbon and were reductively dechlorinated and/or substituted by OH^-/HS^- ions.



Scheme 1.

CONCLUSION

The most common and persistent 2,4,5-trichlorobiphenyl was dechlorinated under very mild conditions. The reducing media of calcium hydroxide/sodium hydroxide and sulphur in water/isopropanol solution was utilized to achieve this goal. Activated carbon was for the first time reported as a catalytic substrate for dechlorination. Furthermore, reducing agents with the hydrogen donor (isopropanol) and water were necessary to carry out the dechlorination process more effectively. Activated carbon prohibited further chlorination by firmly adsorbing the chloride ions in the reaction media and facilitated the reduction and substitution reactions by adsorbing the chlorinated aromatic compound, hydrogen and hydroxyl/thiol ions.

REFERENCES

- 1 Hutzinger O., Safe S., Zitko V. *The Chemistry of PCB*. Boca Raton, FL: CRC Press, 1974.
- 2 Bumpus J. A., Tien M., Wright D., Aust S. D. // *Science*. 1985. Vol. 228. P. 1434.
- 3 Olea N., Pazos P. // *J. Cancer Prevent.* 1998. Vol. 7. P. 17.
- 4 Waid J. S. *PCB and the Environment*. Boca Raton, FL: CRC Press, 1986.
- 5 Hitchman M. L., Spackman N. C., Ross N. C., Agra C. // *Chem. Soc. Rev.* 1995. Vol. 24. P. 423.
- 6 Ishikawa M., Fukuzumi S. // *J. Am. Chem. Soc.* 1990. Vol. 112. P. 8864.
- 7 Ishikawa M., Fukuzumi S. // *Chem. Lett.* 1990. Vol. 6. P. 963.
- 8 Ghaffar A., Tabata M. // *Appl. Catal. B: Environ.* 2009. Vol. 86. P. 152.
- 9 Ghaffar A., Tabata M. // *Waste Management*. 2009. Vol. 29. P. 3004.
- 10 Ghaffar A., Tabata M. // *Reac. Kinet. & Catal. Lett.* 2009. Vol. 97, No. 2. P. 35.
- 11 Ghaffar A., Tabata M. // *Green Chem. Lett. Rev.* 2010. TGCL. P. 466522.
- 12 Alonso F., Beletskaya I. P., Yus M. // *Chem. Rev.* 2002. Vol. 102, No. 11. P. 4009.
- 13 Weber R., Yoshida S., Miwa K. // *Environ. Sci. Technol.* 2002. Vol. 36. P. 1839.
- 14 Zhijun Yang, Chuanhai Xia, Qing Zhang, Jiping Chen, Xinmiao Liang // *Waste Management*. 2007. Vol. 27. P. 588.
- 15 Hagenmaler H., Brunner H., Haag R., Kraft M. // *Environ. Sci. Technol.* 1987. Vol. 21. P. 1085.
- 16 Feng Zhang, Jiping Chen, Haijun Zhang, Yuwen Ni, Xinmiao Liang // *Chemosphere*. 2007. Vol. 68. P. 1716.
- 17 Guo-Bin Liu, Takehito Tsukinoki, Tadashige Kanda, Yoshiharu Mitoma, Masashi Tashiro // *Tetrahedron Lett.* 1998. Vol. 39. P. 5991.
- 18 Yoshiharu Mitoma, Taizo Uda, Naoyoshi Egashira // *Environ. Sci. Technol.* 2004. Vol. 38. P. 1216.
- 19 Yoshiharu Mitoma, Satoko Nagashima, Cristian Simion, Alina Marieta, Simion, Tomoko Yamada, Keisuke Mimura, Keiko Ishimoto, Masashi Tashiro // *Environ. Sci. Technol.* 2001. Vol. 35. P. 4145.
- 20 Rodríguez J. G., Lafuente A. // *Tetrahedron Lett.* 2002. Vol. 43. P. 964.
- 21 Concibido N. C., Okuda T., Nakano Y., Nishijima W., Okada M. // *Tetrahedron Lett.* 2005. Vol. 46, No. 21. P. 3613.
- 22 Yuji Ukisu, Tatsuo Miyadera // *React. Kinet. Catal. Lett.* 2006. Vol. 89, No. 2. P. 341.
- 23 Hoke J. B., Gramiccioni G. A., Balko E. N. // *Appl. Catal. B: Environ.* 1992. No. 1. P. 285.
- 24 Xia C., Xu J., Wu W., Liang X. // *Catal. Commun.* 2004. Vol. 5, No. 8. P. 383.
- 25 Ukisu Y., Miyadera T. // *Appl. Catal.* 1997. Vol. 125. P. 135.