

## CHROMATOGRAPHIC AND THERMODYNAMIC DATA OF DECHLORINATION REACTIONS OF POLYCHLORINATED BIPHENYLS

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### Introduction

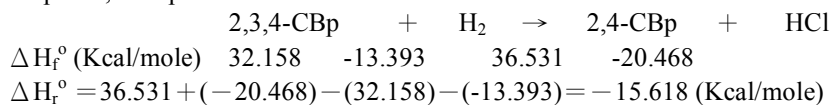
Reductive dechlorination is effective in the microbial degradation of polychlorinated biphenyls (PCBs) (1-3). Microbial specificity and properties of chemical molecules were the factors affect dechlorination. To acquaint the dechlorination in an aspect of the physical-chemical properties of the chlorinated aromatics was quite important. Holmes and Harrison calculated the Gibbs free energy for formation of halogenated aromatic compound (4) and used the data to evaluate the potential of the halogen atom as an electron acceptor in the dechlorination reaction. Beurskens and coworkers (5) found the dechlorination of chlorobenzenes (CBs) was accompanied with highly exergonic reaction which middle chlorine is easily removed. Relations between chromatographic data and molecular structure were referred to biological activity and thermodynamics properties (6,7). Chromatographic data, one of various expressions of extrathermodynamics, were reflects to the enthalpy and entropy changes of molecules passing through chromatographic column. The present research was designed to investigate the relationship between reaction heat and chromatographic data of reductive dechlorination of PCBs by indigenous microorganisms from Er-Jen River in southern Taiwan. The heats of reaction ( $\Delta H_r^\circ$ ) in the dechlorination reaction was computed, and the thermodynamic data ( $\Delta \ln RRT$ ) during dechlorination was calculated. The results were then compared to the values that estimated from the studies of Hudson River and Puget Sound sediments by Quensen et al. (8) and Øfjord et al. (9).

### Material and Methods

Microorganisms eluting from sediments of Er-Jen River located in southern Taiwan had been tested for their dechlorination ability in previous study (3). An isothermic gas chromatography was used to establish the value of retention time (RT) of PCB congeners. To minimize the effects of entropy change, the column temperatures were set on 220 °C, because the most of PCB congeners are liquid except 2,3,4,5,6,2',3',4',5',6'-decachlorobiphenyl (2,3,4,5,6,2',3',4',5',6'-CBp) is solid and several dichlorobiphenyl are gaseous on 220 °C. The gas chromatograph (Varian 3600, Walnut Creek, CA, USA) equipped with an electron capture detector (ECD) and a DB-5 fused silica capillary column (0.53 mm ID x 30 m, film thickness 1.5  $\mu$ m, J & W Scientific, Folsom, CA, USA) was used. The temperature for injection port and detector were 280 and 300 °C, respectively. Using nitrogen as carrier gas, the linear velocity was 27.3 cm/s and the split ratio was 15:1.

Formation heat ( $\Delta H_f^\circ$ ) of PCB congeners, hydrogen and hydrogen chloride molecules was computed by the PM3 (Parameterized Model revision 3) method provided by CS MOPAC Pro (Version MOPAC 93) in a desktop modeling software CS Chem3D Pro (Cambridge Soft Co., Cambridge, MA, USA). The formation heat of a selected molecules estimated by MOPAC is

under the gas phase at 298 °K for one mole in their standard state. Before the computation of  $\Delta H_f^\circ$ , the selected molecule was initially analyzed and converted to the structure with minimal energy. The formation heats were used to estimate the heat of reaction ( $\Delta H_r^\circ$ ) of the reductive dechlorination of PCBs with  $H_2$  as the electron donor. For example, the dechlorination reaction of 2,3,4-CBp to 2,4-CBp was



Retention times of PCB congeners were obtained by the isothermic gas chromatography and illustrated in the previous report (10). Relative retention time (RRT) of PCB congeners to 2-CBp, and their logarithmic values (ln RRT) were also calculated. In the same manner,  $\Delta H_r^\circ$  and  $\Delta \ln$  RRT values of dechlorination reactions that had occurred in Hudson River and Puget Sound sediments (8,9) were estimated.

## Results and Discussion

Because the retention condition of a compound in a chromatographic column is an expression of the dissolving and partitioning behaviors of the compound between the mobile and stationary phase, and the retention time is affected by their electronic and chemical properties. It is practicable to consider that the enthalpy change of PCBs molecules involving in the dechlorination

Table 1. Relationships between occurrences and values of  $\Delta H_r^\circ$  in the dechlorination reaction of PCB congeners.

reactant	product	$\Delta H_r^\circ$	reaction occurrence		
			EJ*	HR*	PS*
2342'4'-CBp	2342'-CBp	-0.68	---	×	×
	232'4'-CBp	-1.68	---	×	×
	242'4'-CBp	-2.64	---	○	○
2345-CBp	234-CBp	-1.77	×	---	---
	235-CBp	-2.64	○	---	---
	245-CBp	-2.65	×	---	---
234-CBp	23-CBp	-1.63	×	×	---
	24-CBp	-2.70	○	○	---
	34-CBp	-3.07	×	×	---
235-CBp	23-CBp	-0.76	×	×	---
	25-CBp	-1.85	×	○	---
	35-CBp	-3.08	×	×	---
245-CBp	24-CBp	-1.82	×	○	×
	25-CBp	-1.85	○	○	○
	34-CBp	-2.19	×	×	×
246-CBp	24-CBp	-1.82	×	×	×
	26-CBp	-0.20	×	○	×
345-CBp	34-CBp	-1.70	×	×	---
	35-CBp	-2.58	○	○	---
25-CBp	2-CBp	-0.43	×	○	---
35-CBp	3-CBp	-0.65	×	○	---

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\*:EJ:Er-Jen River, Tainan, Taiwan; HR:Hudson River, NY, USA; PS:Puget Sound, WA, USA, The  $\Delta H_r^\circ$  values of HR and PS were calculated from the results of references 8 and 9. \*\*:----:Not tested

processes is related to in the gas chromatographic process. Since  $\ln RRT$  can provide the information related to dechlorination, the difference of  $\ln RRT$  values ( $\Delta \ln RRT$ ) between the parent compound and its product in a dechlorination reaction could be valuable.

Observing the  $\Delta H_r^\circ$  values of the dechlorination reactions listed in Tables 1, PCB congeners were dechlorinated by selecting the step that release the largest energy in the reaction. In the dechlorination of PCBs by Er-Jen River microorganisms, those reactions gave  $\Delta H_r^\circ$  smaller than  $-1.70$  Kcal/mole (Table 1) were liable to occur. The same trend was also shown in the dechlorination by Hudson River and Puget Sound microorganisms, and the critical values of  $\Delta H_r^\circ$  were about  $-0.20$  and  $-1.78$  Kcal/mole, respectively (Table 1).

Comparing the  $\Delta \ln RRT$  of the reactions that from the same parent compound to different products (Table 2), it predicted a dechlorination reaction occurred or not. For example, three possible compounds, 2,3-, 2,4- and 3,4-CBp, are thought to be the product of the dechlorination of 2,3,4-CBp, and their  $\Delta \ln RRT$  of the reaction were 0.443, 0.514 and 0.276, respectively. 2,4-CBp was indeed produced during dechlorination and no other product was found in the system. Comparing the dechlorination of 2,3,4,5-CBp to 2,3,4-CBp ( $\Delta \ln RRT$  0.406) and 2,3,5-CBp ( $\Delta \ln RRT$  0.557), the latter reaction is easily occurred too. It indicated that the larger the  $\Delta \ln RRT$  obtained, the more willingly the dechlorinated reaction took place. For all the reactions of test PCBs, whose  $\Delta \ln RRT$  value larger than 0.50 were dechlorinated mostly. For the Hudson and Puget Sound sediments, the dechlorination reaction with the  $\Delta \ln RRT$  values larger than 0.29 and 0.40, respectively, were likely to occurred.

Table 2. Relationships between occurrences and values of  $\Delta \ln RRT$  in the dechlorination reaction of PCB congeners.

Er-Jen River				Hudson River*				Puget Sound*			
reactant	product	$\Delta \ln RRT$	reaction occurrence	reactant	product	$\Delta \ln RRT$	reaction occurrence	reactant	product	$\Delta \ln RRT$	reaction occurrence
2345-CBp	234-CBp	0.406	×	234-CBp	23-CBp	0.443	×	2343'4'-CBp	2343'-CBp	0.571	×
	235-CBp	0.557	○		24-CBp	0.514	○		2344'-CBp	0.518	×
	245-CBp	0.525	×		34-CBp	0.276	×		233'4'-CBp	0.518	×
234-CBp	23-CBp	0.443	×	236p-CBp	23-CBp	0.226	×	2453'4'-CBp	243'4'-CBp	0.600	○
	24-CBp	0.514	○		25-CBp	0.297	×		2453'-CBp	0.537	×
	34-CBp	0.276	×		26-CBp	0.386	○		2454'-CBp	0.482	×
235-CBp	23-CBp	0.288	×	245-CBp	24-CBp	0.471	×	253'4'-CBp	243'4'-CBp	0.448	○
	25-CBp	0.359	×		25-CBp	0.471	○		253'4'-CBp	0.463	×
	35-CBp	0.235	×		34-CBp	0.233	×		2352'3'6'-CBp	2352'6'-CBp	0.435
345-CBp	34-CBp	0.426	×	246-CBp	24-CBp	0.201	×	2362'3'-CBp	2362'3'-CBp	0.319	×
	35-CBp	0.540	○		26-CBp	0.290	○		2362'5'-CBp	0.401	○
246-CBp	24-CBp	0.201	×	25-CBp	2-CBp	0.320	○	2342'4'-CBp	2342'-CBp	0.459	×
	26-CBp	0.290	×		3-CBp	0.174	×		232'4'-CBp	0.503	×
24	2-CBp	0.320	×	26-CBp	2-CBp	0.231	×	-CBp	242'4'-CBp	0.586	○

-CBp	4-CBp	0.155	×	35-CBp	3-CBp	0.298	○
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\*: The  $\Delta \ln RRT$  values of Hudson River and Puget Sound were estimated from the results of references 8 and 9.

The critical values of  $\Delta \ln H_r^0$  and  $\Delta \ln RRT$  for microbial mediated dechlorination from the three different sediments showed that microorganisms from Hudson River were able to dechlorinate PCBs through the reaction with less energy released (larger  $H_r^0$  value) and with smaller  $\Delta \ln RRT$  value. That is to say, the microorganisms from Hudson River dechlorinated more PCB congeners than microorganisms from Er-Jen River and Puget Sound. Not as the slightly contaminated condition of Er-Jen River and Puget Sound sediments, Hudson River sediments were highly polluted by PCBs for several decades, and in some location the concentration of PCBs was even up to hundreds of ppm (11). The stress of PCB contaminant shall provide a suitable environment for PCB-utilizers and PCB-dechlorinators to grow and develop. This acclimation induced microorganisms to develop a diversified dechlorination system to dechlorinate a wide range of PCB congeners. Without such stress, microorganisms from Er-Jen River and Puget Sound still possessed dechlorination ability to PCBs, but only acted on fewer congeners that could release much enough energy.

### Acknowledgments

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