# Reaction Kinetics of PCB Destruction
# by the Base Catalyzed Decomposition Process

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## 1. Introduction

The base catalyzed decomposition (BCD) process employs hydrogen free radicals to replace halogens contained in hazardous halogenated compounds.[1] Hydrocarbons with high boiling points from 310 to 387°C can be used as hydrogen donors to produce free radicals of hydrogen in the presence of sodium hydroxide (NaOH) at temperatures from 250 to 350°C. Under these conditions, high-boiling point hydrocarbons undergo a chemical transformation that releases their hydrogen atoms as free radicals, which in turn, replace the halogen atoms in the halogenated compounds to be degraded. This hydrogen-transfer reaction results in virtually complete dechlorination of many chlorinated organics.[2] In fact, recent laboratory experiments have confirmed that the BCD process can completely dehalogenate a variety of halogenated compounds including polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), 2,4,5-T, 2,4-D, and pentachlorophenol (PCP).[3] When applied to liquid waste PCBs from electrical transformers and capacitors, non-toxic hydrocarbons such as biphenyl, sodium chloride, and water are produced. Taniguchi et al.[4] attained a 99.999% PCB destruction rate without gaseous emission of PCBs or dioxins, i.e., the BCD process is a liquid-phase reaction. However, no information is available concerning the reaction kinetics of the BCD process. This led to the present study which uses the BCD process to carry out PCB decomposition experiments in order to obtain information on transformation of PCBs, as well to determine the effects of reaction temperature and NaOH on PCB destruction.

## 2. Materials and Methods

### 2.1 Reagents

We used fuel oil C as the hydrocarbon source because it is an inexpensive, readily available, high-boiling point hydrocarbon. A low-active carbonaceous material was used as a proprietary hydrogen donor-catalyst, while reagent-grade sodium hydroxide (NaOH) and n-hexane were respectively used to maintain the alkaline condition and to dilute to the residues and distillates produced from a BCD-treated PCB mixture. Kanechlor KC-300 and para-chlorobiphenyl were used as the target halogenated compounds for decomposition.

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## 2.2 Methods

The experimental methods applied here to investigate reaction kinetics are similar to those used by Tiernan et al.[3] Briefly, we employed a glass, three neck-batch reactor (vol.: 300 ml) equipped with a motor-driven stirrer, thermometer, and water-cooled condenser. The reactor was immersed in a heating mantle and a thermocouple was used to monitor the reactor temperature.

PCBs (1.0–3.0 g), NaOH (0.5–15 g), and the carbonaceous catalyst (1.5 g) were added to 150 ml of fuel oil. While being mixed at 400 rpm under a $N_2$ atmosphere, the mixture was heated from 255 to 350°C for 1 to 12 h. After sampling the resultant BCD-treated PCB residues and distillates and then diluting them with n-hexane, the concentration of each of the PCB isomers was determined using gaschromatograph mass spectrometry (GC/MS) (5890 Series 2/5971, Hewlett Packard) on a column of HP-5MS (cross-linked 5% Ph Me Silicone, 30 m x 0.25 mm, 0.25-μm filmthickness). Minimum detectable PCB concentration was 1 μg/g.

## 3. Results and Discussion

### 3.1 PCB transformation

To determine the fate of PCBs in the BCD process, we selected a milder destruction condition (330°C) than used by Taniguchi et al.[4] KC-300 mainly contains tri-chlorobiphenyls (3-Cl), followed by tetra-chlorobiphenyls (4-Cl), di-chlorobiphenyls (2-Cl), penta-chlorobiphenyls (5-Cl), hexa-chlorobiphenyls (6-Cl), and hepta-chlorobiphenyls (7-Cl). Figure 1 shows concentrations of its main PCB isomers (1- to 6-Cl) over reaction time, where the higher chlorides disappear as the lower chlorides are simultaneously generated. Note that the elimination of chlorine continuouly occurs in a stepwise manner. Figure 2 shows the corresponding fate of mono-chlorobiphenyls (ortho-, meta-, and para-chlorobiphenyls), which increase for 2 h and then decrease to zero at 6 h. The standard formation enthalpies of ortho-, meta-, and para-chlorobiphenyls are respectively 159, 154, and 152 kJ/mol, and are consistent with the results in Fig. 2. Consequently, this suggests that a difference exists in the C-Cl bond and/or dissociation energy associated with each substitution position, with this difference reflecting the generation and disappearance rate of these three isomers.

### 3.2 Temperature effects

Because the dehydrogenation reaction from the hydrogen donor is generally endothermic, the reaction is accelerated by high temperature. Figure 3 shows the residual ratio of PCBs at various temperatures (255–335°C) over reaction time, where the decomposition of KC-300 is obviously a first-order reaction. Using each slope, we calculated the apparent rate constant k at each temperature, with Fig. 4 showing the relationship between k and the reaction temperature. KC-300's activation energy was susequently determined from the slope to be 130 kJ/mol.

Next, we correspondingly reacted para-chlorobiphenyl, which is a not mixture like KC-300 but instead a pure compound, where Fig. 5 shows that its decomposition reaction is also first-order. The resultant activation energy for para-chlorobiphenyl (Fig. 6) was found to be 53.6 kJ/mol.

KC-300 consists of on the average trichloride of PCBs. In this PCB decomposition experiment, it should be noted that the apparent activation energy for para-chlorobiphenyl decomposition was approximately one-third of that for KC-300. The difference of standard formation enthalpies between mono-chlorobiphenyl and its reduced biphenyl form is about 30 kJ/mol, being close to the apparent activation energy (53.6 kJ/mol) for para-chlorobiphenyl decomposition. The general value of the C-Cl bond and dissociation energy is about 300 kJ/mol. In the BCD process, the dechlorination reaction took place with one-sixth of the C-Cl bond and dissociation energy by using the

catalyst. Because a low active carbonaceous catalyst was used here to analyze the reaction kinetics, a lower activation energy and reaction temperature is expected if a more active catalyst is selected.

## 3.3 Effect of NaOH

Figure 7 shows the relationship between the amount of NaOH added and k for KC-300, where the reaction rate increases and peaks at about five times the stoichiometric ratio, and then decreases in a similar fashion to seven times the ratio. The amount of water generated as a by-product was also a maximum at five times the stoichiometric ratio; hence suggesting that NaOH participates in dechlorination reaction occurring at the surface of catalyst. In other words, a hydrogen acceptor may be necessary to stabilize the hydrogen radical during the dechlorination reaction, and the subsequent dehydrogen reaction will not occur if the concentration of the hydrogen acceptor is either too high or low for the free hydrogen radicals to be generated at the activation site on the catalyst surface. It is also hypothesized that eliminating the reactants from the catalyst surface and/or decreasing the concentration of the hydrogen radical in the reactor will decrease the reaction rate due to the spill over-phenomenon created by sodium atoms.[6] We also found that PCB decomposition occurred below NaOH's melting point. Taken together, these results clearly indicate that the effect of adding NaOH on the decomposition of PCBs in the BCD process is significant, though the mechanism remains to be elucidated.

## 4. Conclusions

We found that the overall reaction for the decomposition of PCBs in the BCD process was a first-order reaction since the rate constant for the dechlorination of mono-chlorobiphenyl was dependent on the position of the chloride substituent. In addtion, the dechlorination reaction continuously occurred without the presence of a rate limiting step, with the chloride groups on the aromatic nucleus being completely eliminated. The apparent activation energies for KC-300 and para-chlorobiphenyl were respectively 130 kJ/mol and 53.6 kJ/mol, and NaOH addition increased the reaction rate of the BCD process. The optimum amount of NaOH for PCB decomposition was determined to be five times the stoichiometric ratio.

## 5. References

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3) Tiernan T.O., D.J. Wagel, G.F. VanNess, J.H. Garrett, J.G. Solch, M.S. Hanes, C.J. Rogers, and A. Kornel (1993): Treatment of Complex Chemical Wastes with the Base Catalyzed Decomposition (BCD) Process. DIOXIN' 93, 289–292.
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6) Nakamura I, K. Aimoto, and K. Fujimoto (1989): AIChE Symposium Series No.273, 85, 15.

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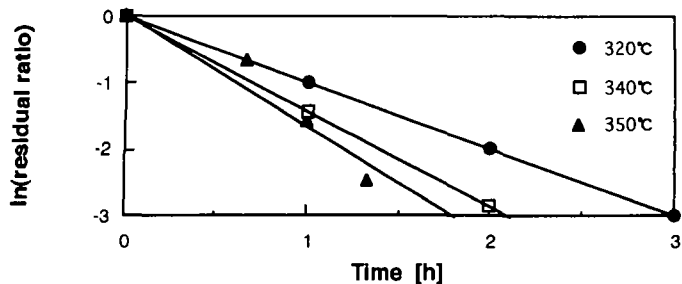


Figure 5    Residual ratio of para-chlorobiphenyl versus reaction
time (donor oil: Fuel oil C, 150 ml; para-chlorobiphenyl,
0.75 g).



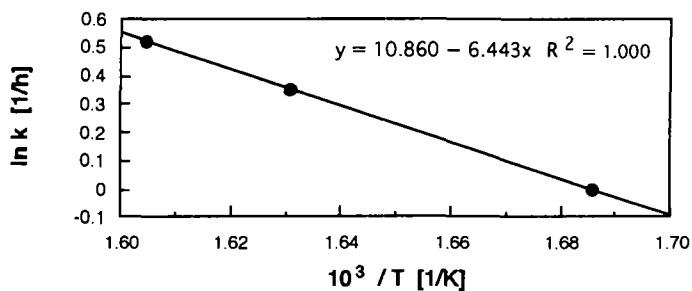$y = 10.860 - 6.443x$   $R^2 = 1.000$

Figure 6    Relationship between rate constant k of para-chlorobiphenyl
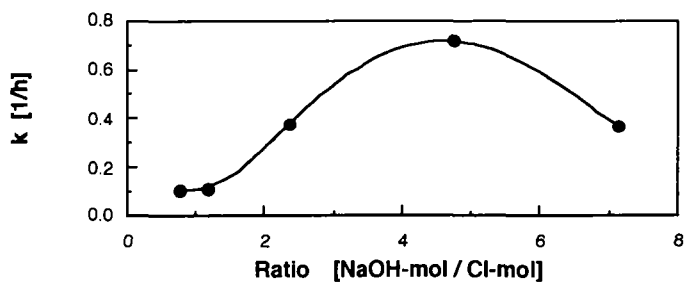and reaction temperature.



Figure 7    Relationship between amount of sodium hydoroxide added
and k of KC-300 (donor oil: Fuel oil C, 150 ml; KC-300, 3 ml;
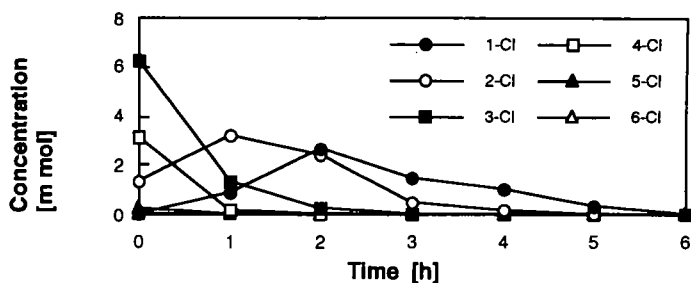reaction Temp.: 330℃).

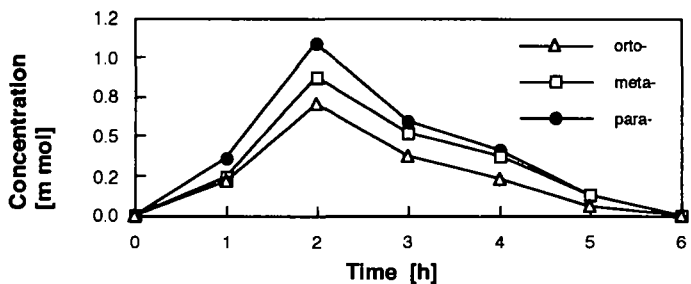Figure 1    Concentration of PCB isomers in KC-300 versus reaction time.



Figure 2    Concentration of mono-chlorinated biphenyls in KC-300 versus reaction time.
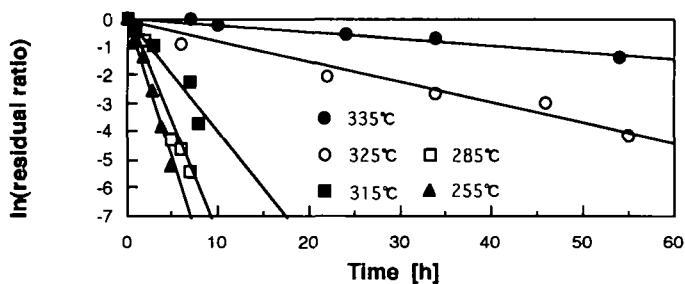


Figure 3    Residual ratio of PCBs at various temperatures versus reaction time (donor oil: Fuel oil C, 150 ml; PCB: KC-300, 3 g).
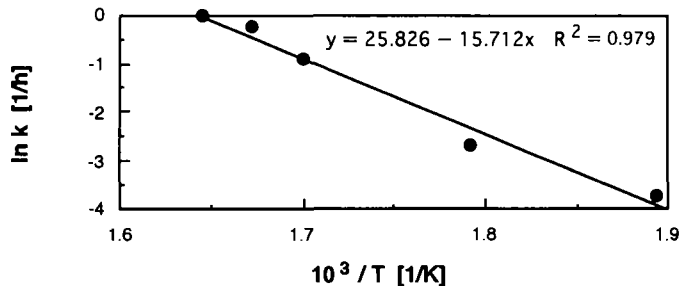


$y = 25.826 - 15.712x$    $R^2 = 0.979$

Figure 4    Relationship between rate constant k of KC-300 and reaction temperature.