Vapor Phase Hydrodechlorination of Polychlorobenzenes

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The vapor phase hydrodechlorination of polychlorobenzenes was carried out with palladium (II) chloride and cerium (III) chloride supported on active charcoal or activated alumina under various reaction conditions. Polychlorobenzenes were converted into benzene and hydrogen chloride with cyclohexane or hydrogen gas. The hydrodechlorination of polychlorobenzenes proceeded smoothly under the mild reaction conditions.

KEY WORDS : Catalytic hydrodechlorination/ Vapor phase/ Polychlorobenzenes/ Cyclohexane/ Active charcoal/ Activated alumina/ Pd

1. Introduction

Aromatic polychlorides are the hazardous compounds bringing about the pollution of the environment.[1-3] There have been many attempts to convert aromatic polychlorides into harmless matters by means of chemical treatments, but with less satisfactory results.[4-15] Above all, as the higher homologs have higher melting point and lower solubility, the treatment of them is difficult to do anything.

In generally, the catalytic hydrodechlorinations of aromatic polychlorides are carried out in the liquid phase.[16, 17] It is thought that the separation of catalyst from the reaction solution and the regeneration of catalyst are important problems to develop this reaction process. Regardless of the vapor or liquid phase, the catalysts are nickel, palladium, their alloys, and so on.[9-11, 13, 16-21] There has been few report in which the hydrodechlorinations of chlorobenzene derivatives were performed by using palladium (II) chloride as the catalyst.

We have reported that o-dichlorobenzene (o-DCB) reacted with various hydrogen donors into benzene and hydrogen chloride over palladium (II) chloride and cerium (III) chloride on active charcoal.[22] Especially, in the case of cyclohexane and cyclohexene, the vapor phase dechlorination of o-DCB proceeded easily and steadily at 573 K. From the reaction mechanism, it was assumed that the hydrodechlorination of o-DCB proceeds on this catalyst with hydrogen instead of cyclohexane and cyclohexene. According to this assumption, hydrogen gas was used as one of hydrogen donors. Consequently, the vapor phase hydrodechlorination of o-DCB took place smoothly with hydrogen gas. Since activated alumina is more useable than active charcoal on the reactivation of catalytic activity, activated alumina was attempted to use as the catalytic carrier in place of active charcoal. Furthermore, the substrates were extended from o-DCB to not only liquid but also solid polychlorobenzenes.

2. Experimental

2.1. Materials

o-DCB was a industrial reagent (Kureha Chemical Industries). Cyclohexane, 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2,4,5-tetrachlorobenzene, and hexachlorobenzene were purchased from Tokyo Kasei Kogyo Co., Ltd. and were used without further purification. Active charcoal, palladium (II) chloride, and cerium (III) chloride heptahydrate were purchased from Wako Pure Chemical Industries, Ltd.. The active charcoal was cylindrical in form, 7 mm in length, and 4 mm in diameter. On the other hand, activated alumina was obtained from Mizusawa Industrial Chemicals, Ltd. and was spherical in form, 4 mm in diameter. Hydrogen and nitrogen were in bomb on the market.

2.2. Preparation of Catalyst

Metal chlorides used as catalyst were palladium (II)

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chloride and cerium (III) chloride. Carriers were active charcoal and activated alumina, and 30g of carriers was used, unless it stated. The solution was prepared by dissolving 1.0 g of palladium (II) chloride and 2.1 g of cerium (III) chloride heptahydrate (1:1 in molar ratio) in 60 mL of hydrochloric acid. After 30 g of the carrier was impregnated with this solution, the solution was evaporated to dry on the hot plate in the air.

2.3. Apparatus

The reactor was made of Pyrex glass, consisting of double cylindrical pipes as shown in Fig. 1. The inside cylinder was 10 mm in diameter and was empty which played the role of the evaporator and the preheater. The outside cylinder was 30 mm in diameter and was packed with the catalyst. The reactor was inserted into the crucible type furnace which was 30 cm in depth.
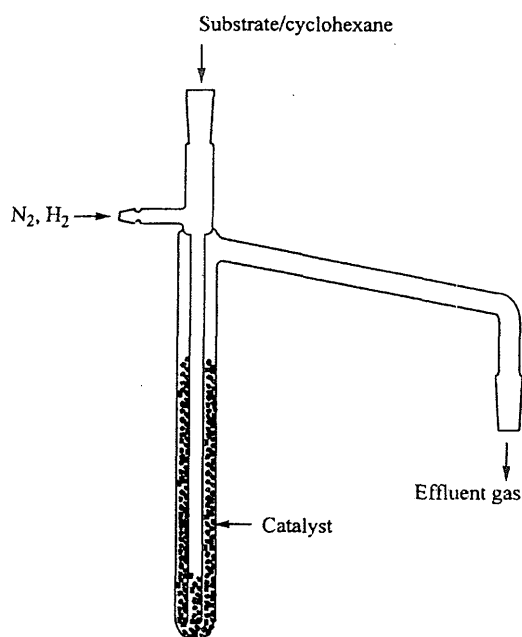

Fig. 1. Double cylindrical type reactor

2.4. Dechlorination of o-DCB and 1,2,4-TCB with Cyclohexane over Active Charcoal Carrier

A mixture of o-DCB and cyclohexane (3 : 2 in molar ratio) was fed into the reactor at the rate of 10 mL h^{-1} with a microfeeder. Nitrogen was used as carrier gas in the reactor at the rate of 10 mL min^{-1}. The reaction temperature was maintained at 573 K. The product

gas stream was led to a cooler and was condensed in a water-ice trap. Furthermore, hydrogen chloride in the effluent gas was absorbed in standard sodium hydroxide solution by using wetted-wall tower and was then determined by the back-titration. The organic condensates were analyzed by gas chromatograph (Shimadzu GC-8A) equipped with a flame ionization detector using a PEG 6000 column. Similarly, the dechlorination of 1,2,4-TCB was carried out under the same reaction condition. The molar ratio of 1,2,4-TCB and cyclohexane was 1 : 2.

2.5. Hydrodechlorination of Polychlorobenzenes with Hydrogen Gas

Liquid substrates, o-DCB and 1,2,4-TCB were fed into the reactor with the microfeeder at the rate of 5 mL h^{-1}. On the other hand, solid substrates, 1,2,4,5-tetrachlorobenzene and hexachlorobenzene were dissolved into the liquid substrate and were fed into reactor as the mixed solution with the microfeeder at the rate of 5 mL h^{-1}. Hydrogen gas was fed into the reactor at the rate of 54 - 98 mL min^{-1}.

3. Results and Discussion

3.1. Dechlorination of o-DCB and 1,2,4-TCB with Cyclohexane over Active Charcoal Carrier

In the previous paper,[22] it was reported that the various hydrogen donors upon the dechlorination of o-DCB was studied. Cyclohexane was the most useful reagent among the various hydrogen donors. Hence, the dechlorination over active charcoal-supported pal-

Table 1. Effect of Reaction Temperature on the Dechlorination of o-DCB with Cyclohexane[a]

Temp. /K	Conversion/%[b]		Yield/%[b]		Recovered HCl/%
	o-DCB	C$_6$H$_{12}$	C$_6$H$_6$	Others	
473	100	46.2	69.2	0.0	71
523	100	99.8	99.8	0.0	108
573	100	99.8	99.9	0.0	108
623	100	86.2	91.9	0.2	106

a) Carrier is active charcoal. Molar ratio of cyclohexane/o-DCB= 2/1,Feed rate=10 mL h^{-1}.

b) Sample was taken from the condensate of effluent during three and four hours after the start of the reaction.

ladium (II) chloride and cerium (III) chloride was in vestigated with cyclohexane under various reaction conditions.

The effect of reaction temperature on the dechlorina-tion of o-DCB with cyclohexane is shown in Table 1. Although the dechlorination of o-DCB with cyclohexane proceeded at 473 K, o-DCB was completely converted into benzene and hydrogen chloride at 573 K.
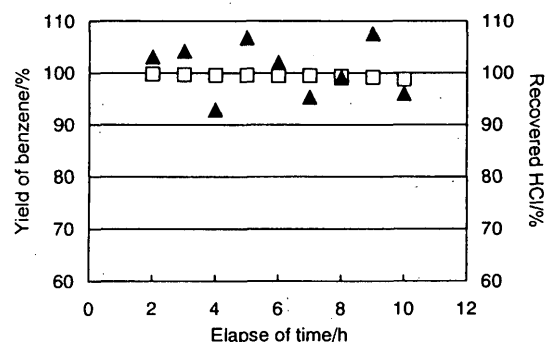

Fig. 2. Effect of elapse of time on the dechlorination of o-DCB with cyclohexane; (□) yield of benzene, (▲) recovered HCl.

Figure 2 shows the effect of the elapse of time on the dechlorination of o-DCB with cyclohexane at 573 K. Table 2 indicates that the dechlorination of 1,2,4-TCB with cyclohexane proceeded perfectly and 1,2,4-TCB was converted into benzene and hydrogen chloride. The by-product were scarcely found in the dechlori-nated products. Of course, benzene was formed from both cyclohexane and chlorobenzene derivatives. It is understandable that the dechlorinations of o-DCB and 1,2,4-TCB with cyclohexane took place smartly and perfectly.

Table 2. Dechlorination of 1,2,4-TCB with Cyclohexane at 573 K[a]

Elapse of time/h	Conversion/%		Yield/%		Recovered HCl/%
	1,2,4-TCB	C_6H_{12}	C_6H_6	$C_6H_5CH_3$	
1	100	100	99.8	0.1	107
2	100	99.9	99.9	0.1	112
3	100	99.9	99.9	0.1	105
4	100	99.9	99.9	0.1	102
5	100	99.9	99.9	0.1	97

a) Carrier is active charcoal. Molar ratio of cyclohexane/1,2,4-TCB =2/1, Feed rate=10 mL h⁻¹.

3.2. Hydrodechlorination of o-DCB with Hydrogen over Active Charcoal Carrier

In the dechlorination with cyclohexane, cyclohexane was converted into benzene. In other words, cyclo-hexane produced benzene and hydrogen. It was thought that the attacking reagent to o-DCB was hy-drogen. We tried to use the hydrogen instead of cyclohexane. Table 3 indicates that the hydrodechlo-rination of o-DCB with hydrogen took place and pro-ceeded similarly to cyclohexane.

Table 3. Hydrodechlorination of o-DCB with Hydrogen at 573 K[a]

Elapse of time/h	Conversion of o-DCB/%	Yield of product/%			Recovered HCl/%
		C_6H_6	C_6H_{12}	$C_6H_5CH_3$	
1	100	99.9	0.1	0.0	107
2	100	99.9	0.1	0.1	112
3	100	99.9	0.1	0.1	105
4	100	99.9	0.1	0.1	102
5	100	99.9	0.1	0.1	97

a) Carrier is active charcoal. Molar ratio of H_2/o-DCB=4/1, Feed rate of o-DCB=5 mL h⁻¹.

3.3. Hydrodechlorination of 1,2,4-TCB with Hydrogen over Activated Alumina

Figures 3 and 4 show the effect of reaction condi-tions on the formation of cyclohexane. While the weights of palladium (II) chloride and cerium (III) chloride were kept constant, the amount of activated alumina was varied from 30 g to 60 g. The increase of carrier weight increased the ratio of cyclohexane to benzene. However, it was assumed that the active site of hydrogenolysis was deteriorated in the progress of time in case of 60 g of alumina carrier. On the contra-
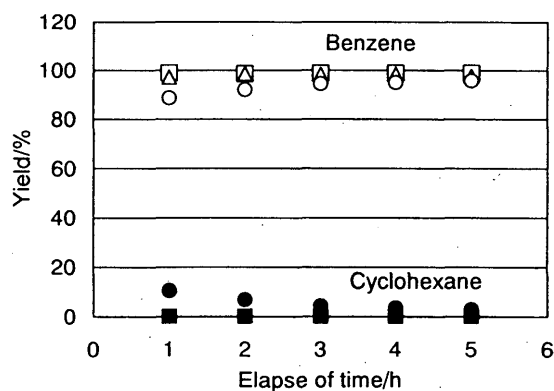

Fig. 3. Effect of amount of activated alumina of the formation of benzene and cyclohexane on the hydro-dechlorination of 1,2,4-TCB with hydrogen; (□, ■) Al_2O_3 30 g, (△, ▲) Al_2O_3 47 g, (○, ●) Al_2O_3 60 g.
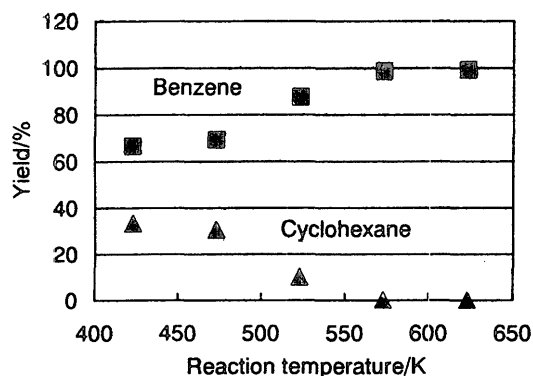
Fig. 4. Effect of reaction temperature of the formation of benzene and cyclohexane on the hydrodechlorination of 1,2,4-TCB with hydrogen. Sample was taken from the condensate of effluent during three and four hours after the start of the reaction.

ry, the higher the reaction temperature was, the less the formation of cyclohexane was. It was a proof that the formation of cyclohexane from benzene proceeded slowly at the lower temperature.

The effect of elapse of reaction time on the hydrodechlorination of 1,2,4-TCB is shown in Table 4. 1,2,4-TCB was converted into benzene and hydrogen chloride, accompanied with the formation of a few amount of toluene and biphenyl derivatives. As the acidic site on activated alumina is more than on active charcoal, it was assumed that the dimerization of benzene was the type of Friedel-Crafts reaction and took place on the surface of activated alumina. However, the hydrodechlorination of 1,2,4-TCB with hydrogen gas continued at the perfect conversion for long time.

3.4. Hydrodechlorination of Polychlorobenzenes with Hydrogen over Activated Alumina Carrier

A mixture of 1,2,4,5-tetrachlorobenzene and o-DCB was prepared to dissolve 1,2,4,5-tetrachlorobenzene into o-DCB. A mixed solution of hexachlorobenzene and 1,2,4-TCB was prepared in the same method. The hydrodechlorination was carried out by feeding the

Table 4. Hydrodechlorination of 1,2,4-TCB with Hydrogen at 573 K[a]

Elapse of time/h	Conversion of 1,2,4-TCB/%	Yield/%					Recovered HCl/%
		C_6H_6	C_6H_{12}	$C_6H_5CH_3$	Biphenyl	Others	
1	100	98.2	0.1	0.7	0.2	0.8	108
3	100	99.4	0.1	0.1	0.2	0.2	97
5	100	99.6	0.1	0.1	0.1	0.1	94
7	100	99.6	0.1	0.1	0.1	0.1	99
9	100	99.5	0.1	0.1	0.1	0.2	97
11	100	99.4	0.1	0.1	0.1	0.3	99
13	100	99.6	0.1	0.1	0.1	0.1	98
15	100	99.6	0.1	0.1	0.1	0.1	95

a) Carrier is activated alumina. Molar ratio of hydrogen/1,2,4-TCB=6/1, Feed rate of 1,2,4-TCB =10 mL h^{-1}.

Table 5. Hydrodechlorination of 1,2,4,5-Tetrachlorobenzene and o-DCB with Hydrogen at 573 K[a]

Elapse of time/h	Conversion/%		Yield/%				Recovered HCl/%
	1,2,4,5-$C_6H_2Cl_4$	o-DCB	C_6H_6	C_6H_{12}	Biphenyl	Others	
1	100	100	98.0	0.6	0.5	0.9	90
2	100	100	97.9	0.7	0.4	1.0	100
3	100	100	98.2	0.6	0.4	0.8	97
4	100	100	98.2	0.7	0.4	0.7	103
5	100	100	98.0	0.7	0.6	0.7	107

a) Carrier is activated alumina. Reactant is a mixture of 1,2,4,5-tetrachlorobenzene and o-DCB (molar ratio =1:20). Molar ratio of H$_2$/Cl=2/1, Feed rate=3.75 mL h^{-1}.

Table 6. Hydrodechlorination of Hexachlorobenzene and 1,2,4-TCB with Hydrogen at 573 K[a]

Elapse of time/h	Conversion/%		Yield/%					Recovered HCl/%
	C_6Cl_6	1,2,4-TCB	C_6H_6	C_6H_{12}	$C_6H_5CH_3$	Biphenyl	Others	
1	100	100	98.9	0.1	0.6	0.3	0.1	92
2	100	100	99.1	0.2	0.5	0.3	0.0	96
3	100	100	99.2	0.2	0.3	0.2	0.1	100
4	100	100	99.4	0.2	0.2	0.1	0.1	97
5	100	100	99.1	0.3	0.2	0.3	0.1	97

a) Carrier is activated alumina. Reactant is a mixture of hexachlorobenzene and 1,2,4-TCB (molar ratio =1:70). Molar ratio of $H_2/Cl=2/1$, Feed rate=5.0 mL h^{-1}.

mixed solution into the reactor. Table 5 shows the hydrodechlorination of 1,2,4,5-tetrachlorobenzene and o-DCB. Table 6 shows the hydrodechlorination of hexachlorobenzene and 1,2,4-TCB. In spite of poly-chlorides, the hydrodechlorination proceeded smmothly without difficulty at 573 K.

The mechanism of heterogeneously catalyzed hydrodechlorination have not been definitely established. There have been two contrary mechanisms which are nucleophilic and electrophilic.[13, 16, 20, 23-28]

However, the electrophilic reaction was confirmed by the transchlorination between o-DCB and benzene derivatives.[29-32] The mechanism of transchlorination might be shown in Scheme 1. First reaction is the dissociation of benzene into phenyl cation and hydride ion. As hydrogen chloride was merely formed in a small amount, hydride ion is not the subtracting reagent but phenyl cation may subtract chlorine of o-DCB. Third reaction is the combination of chlorophenyl cation with hydride ion. In consequence, the transchlorination of o-DCB and benzene is able to describe by Eq. 4.
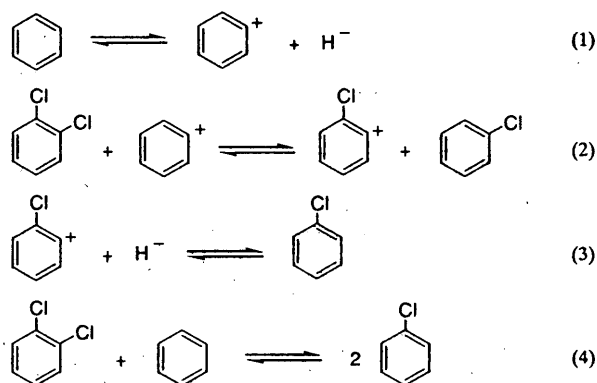
Scheme 1.

On the other hand, the hydrodechlorination might

start with the dissociation of hydrogen which abounds in the reaction field (Scheme 2). It is assumed that the hydrodechlorination is proceeded by the electrophilic subtraction of proton to chlorine of polychlorobenzenes as same as the subtraction of phenyl cation to chlorine of o-DCB. Finally, polychlorobenzenes react with hydrogen to convert into benzene and hydrogen chloride.
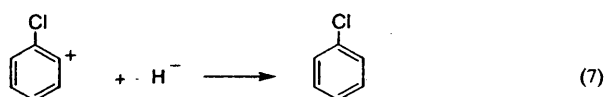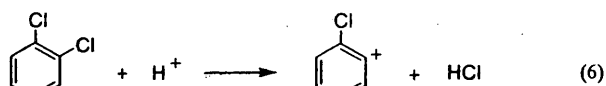
Scheme 2.

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