Dechlorination of *o*-Dichlorobenzene with Various Hydrogen Donors

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o-Dichlorobenzene (*o*-DCB) was perfectly converted into benzene and hydrogen chloride by dechlorination with cyclohexane at 300 °C over activated carbon-supported palladium(II) chloride and cerium(III) chloride. The long term stability of catalyst was assessed.

Chlorinated aromatic compounds are the hazardous matters which taint the global environment. Detoxification and disposal of chlorinated aromatics is one of the most serious problems in environmental chemistry. Many disposal treatments were proposed and investigated for the detoxification of these harmful compounds.[1–8] We have previously reported upon the transchlorination of *o*-DCB with benzene into chlorobenzene.[9–12] However, since the transchlorination is reversible, *o*-DCB is not completely converted into chlorobenzene.

We have found that the reaction of *o*-DCB with hydrogen donors such as cyclohaxane and cyclohexene is irreversible and *o*-DCB is completely converted into benzene and hydrogen chloride. Herein these experimental results are reported.

After a mixture of 1.0 g of palladium(II) chloride and 2.1 g of cerium(III) chloride heptahydrate was dissolved in hydrochloric acid, 30 g of granular activated carbon (Wako Pure Chemical Industries, Ltd.) was impregnated with the solution and was dried on a hot plate. The reaction was carried out with a conventional flow-type reaction system under the atmospheric pressure.[11] A mixture of *o*-DCB and hydrogen donor was fed into the reactor at the rate of $10\,\mathrm{mL\,h^{-1}}$ with a microfeeder. Nitrogen was used as carrier gas in the reactor at the rate of $10\,\mathrm{mL\,min^{-1}}$. The reaction temperature was controlled by the regulator with a Chromel-Alumel thermocouple in the thermowell placed in the catalyst bed. 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 a packed column and 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.

Table 1 shows the effect of various hydrogen donors on the dechlorination of *o*-DCB at 300 °C. These values indicate the analytical data obtained between three and four hours after the start of reaction. Among the hydrogen donors, decaline and tetraline donated hydrogen smoothly and converted into naphthalene, which deposited in the effluent line. Consequently, the reaction could not help stopping. The dechlorination of *o*-DCB was incomplete with propene, *n*-hexane and 1-hexene. Moreover, the bond fissions of carbon–carbon partially took place and many unidentified compounds were formed. The formation of various unidentified compounds was assumed that the free radical reactions took place. The reaction of *o*-DCB and benzene was carried out in order to compare with other saturated hydrocarbons. *o*-DCB and benzene were mainly transchlorinated into chlorobenzene, owing to the lack of movable hydrogen. Therefore, hydrogen chloride was formed in a small quantity. On the other hand, *o*-DCB was perfectly converted into benzene and hydrogen chloride by the donation of hydrogen in the case of cyclohexane and cyclohexene.

Table 2 and 3 indicate the effect of reaction temperature on dechlorination of *o*-DCB with cyclohexane and cyclohexene, respectively. Although both reactions proceeded at lower temperature, the satisfactory results were obtained at 300 °C. Table 4 shows the effect of the elapse of time on the recovery of hydrogen chloride and the conversion of *o*-DCB with cyclohexane into benzene at 300 °C. It is remarkable that hydrogen chloride is recovered perfectly and the conversion of *o*-DCB is maintained at high level for long time.

Table 2. The effect of reaction temperature on dechlorination of *o*-DCB with cyclohexane[a]

Temp. /K	Conversion/%[b]		Yield/%[b]		Recovered HCl/%
	o-DCB	C_6H_{12}	C_6H_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]Molar ratio of cyclohexane/*o*-DCB = 4/3, Feed rate = $10\,\mathrm{mL\,h^{-1}}$.
[b]Sample was taken from the condensate of effluent during three and four hours after the start of the reaction.

Table 1. The effect of hydrogen donors on the dechlorination of *o*-DCB at 300 °C[a]

Hydrogen donor	Molar ratio (Donor: *o*-DCB)	Conv. of *o*-DCB/%	Yield/%[b]			Recovered HCl/%
			Benzene	Chlorobenzene	Others	
Propene	5 : 2	59	1.7	12.1	45.7	35
n-Hexane	4 : 1	98	86.1	5.0	7.5	88
1-Hexene	4 : 1	82	37.1	15.8	64.3	79
Cyclohexane	4 : 3	100	99.9	0.0	0.0	108
Cyclohexene	2 : 1	100	97.9	0.0	2.0	107

[a]Reaction conditions: $PdCl_2/CeCl_3{\cdot}7H_2O$/Activated carbon = 1.0/2.1/30 (g), Feed rate = $10\,\mathrm{mL\,h^{-1}}$.
[b]Sample was taken from the condensate of effluent during three and four hours after the start of the reaction.

Table 3. The effect of reaction temperature on dechlorination of *o*-DCB with cyclohexene[a]

Temp. /K	Conversion/%[b]		Yield/%[b]			Recovered HCl/%
	o-DCB	C_6H_{10}	C_6H_6	C_6H_{12}	Others	
473	100	100	85.5	14.5	0.0	109
523	100	100	98.2	1.8	0.0	107
573	100	100	97.9	2.0	0.0	107
623	100	100	94.6	5.2	0.2	109

[a]Molar ratio of cyclohexene/*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.

Table 4. The effect of elapse of time on HCl recovery and product composition at 300 °C[a]

Elapse of time/h	Conversion/%		Yield/%		Recovered HCl/%
	o-DCB	C_6H_{12}	C_6H_6	C_6H_5Cl	
1	100	99.8	99.7	0.5	120
2	100	99.6	99.8	0.0	103
3	100	99.5	99.7	0.0	104
4	100	99.3	99.6	0.0	93
5	100	99.3	99.6	0.0	107
6	100	99.3	99.6	0.0	102
7	100	99.3	99.6	0.0	95
8	100	99.1	99.5	0.0	99
9	100	98.8	99.3	0.0	108
10	100	98.1	98.9	0.0	96

[a]Molar ratio of cyclohexane/*o*-DCB = 4/3.

The dechlorination of *o*-DCB with cyclohexane over Pd/activated carbon catalyst yields benzene and hydrogen chloride via dehydrogenation of cyclohexane as follows:

$$C_6H_{12} = C_6H_6 + 3H_2$$
$$C_6H_4Cl_2 + 2H_2 = C_6H_6 + 2HCl$$

The dehydrogenation of cyclic alkanes and alkenes to aromatics is one of the key reactions and is considerably investigated, including the study on mechanism.[13–15] On the other hand, the mechanisms of heterogeneously catalyzed dechlorinations have not been irrefutably established and the reaction has been viewed in terms of both nucleophilic[16–18] and electrophilic[19] attack.

From these results, it was assumed that the dechlorination of *o*-DCB proceeds by using hydrogen gas. Certainly, as it was confirmed that the dechlorination of *o*-DCB with hydrogen gas took place, we will report in our next paper.

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