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Transchlorination between Polychlorobiphenyl and Benzene

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Polychlorobiphenyl (PCB) was transchlorinated with benzene into biphenyl and chlorobenzene in the presence of palladium(II) chloride/cerium(III) chloride supported on activated charcoal. The transchlorination proceeded smoothly for a long time at 375 °C.

There have been many attempts to convert PCB into harmless matter by means of chemical treatments, but with less satisfactory results.[1-7] Transchlorination of o-dichlorobenzene and benzene in the presence of palladium(II) chloride supported on activated charcoal was reported.[8] However, the activity of this catalyst was gradually decreased with the elapse of time and was not sufficient to continue the reaction for a long time. Since the catalytic activity of transchlorination was remarkably promoted by the addition of cerium(III) chloride to palladium(II) chloride on activated charcoal, the transchlorination was applied to the reaction of PCB with benzene.

After a mixture of 1.0 g of palladium(II) chloride and 2.09 g of cerium(III) chloride heptahydrate were dissolved in hydrochloric acid, 30 g of activated charcoal was impregnated with the solution and was dried at 110 °C. PCB was purchased from Tokyo Kasei Kogyo and was a mixture of isomers, which mainly composed of tetrachlorobiphenyls. PCB was mixed with benzene at a weight ratio of 12 : 88.

Table 1. Effect of Reaction Temperature on Product Composition

Reaction temperature/°C	Product composition/wt%					
	C_6H_6	C_6H_5Cl	$C_6H_4Cl_2$	$C_{12}H_{10}$	$C_{12}H_9Cl$	PCB
275	98.08	1.84	0.011	0.064	0.004	<0.001
300	98.80	1.14	0.007	0.047	0.003	<0.001
325	98.37	1.56	0.005	0.064	0.002	<0.001
350	95.05	4.50	0.040	0.397	0.015	<0.001
375	92.56	7.03	0.065	0.303	0.039	<0.001
400	92.65	6.84	0.125	0.357	0.024	<0.001
425	94.80	4.86	0.034	0.293	0.007	0.009
450	99.45	0.17	0.014	0.352	0.002	0.009

The experiments were conducted in a continuous-flow type reactor, the details of which were reported in the previous paper.[8] A mixture of PCB and benzene was fed into the reactor with a microfeeder at a rate of 10 ml/h. Gas chromatographic analyses were performed using a GC-14A (FID) type apparatus from Shimadzu Seisakusho. The column was Silicone OV-17 on Chromosorb. The effect of the reaction temperature on the product composition for the transchlorination between PCB and benzene into biphenyl and chlorobenzene is shown in Table 1. The sample was taken from the condensate of effluent between two and three hours after start of the reaction. Table 2 shows the product composition with the elapse of time at 375 ° C.

Table 2. Product Composition for Transchlorination between PCB and Benzene at 375 °C

Elapse of time/h	Product composition/wt%[a]				
	C_6H_6	C_6H_5Cl	$C_6H_4Cl_2$	$C_{12}H_{10}$	$C_{12}H_9Cl$
1	92.48	7.01	0.12	0.36	0.03
2	92.69	6.86	0.08	0.35	0.02
3	92.56	7.03	0.07	0.30	0.04
4	90.38	8.68	0.29	0.61	0.04
5	86.99	11.75	0.23	0.96	0.07
6	81.16	16.64	0.08	2.04	0.08
7	81.28	15.87	0.35	2.39	0.11

a)Gas chromatography showed that there was no detectable amount of PCB.

The conversion of PCB was maintained at high level throughout the reaction. However, it was observed that the evolution of hydrogen chloride took partly place on the catalyst. The formation of biphenyl was gradually increased with the elapse of time. It could be assumed that the desorption of biphenyl from the catalyst was slower than the other products.

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