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# Transchlorination of o-Dichlorobenzene and Benzene into Chlorobenzene

Kiyonori SHINODA
Toyama National College of Technology, Hongo, Toyama 939

The transchlorination of o-dichlorobenzene (o-DCB) and benzene into chlorobenzene (CB) was carried out in the presence of catalyst at 400 °C. $o\text{-}C_6H_4Cl_2 + C_6H_6 = 2\ C_6H_5Cl$ Noble metal chloride supported on activated charcoal promoted remarkably the transchlorination.

The isomerization of chlorobenzenes in the presence of Lewis acid catalyst has been extensively investigated by Erykalov and his co-workers.$^{1-5)}$ If undesirable aromatic polychlorides are converted into useful monochloride or dichlorides by the transchlorination with benzene, it is suggested that polychlorides are available as a chlorinating reagent of benzene. However, there has been no report on transchlorination and disporportionation of chlorinated aromatic compounds. In the present study, the transchlorination of o-DCB and benzene into CB was carried out in order to find the catalyst suitable for the vapor phase reaction. On use of carrier alone, the weight of carrier was 30 g in all experiments. 1.0 g of metal chloride was supported on 10 g of activated charcoal, while 10 g of activated charcoal was impregnated with 2.0 g of palladium sodium chloride trihydrate. Taking into account the volatility of metal chloride, the reaction temperature was maintained at 400 °C throughout the experiment. o-DCB was mixed with benzene at the molar ratio 1 : 1.5. A stream of nitrogen was passed through the apparatus to displace the air. A mixture of o-DCB and benzene was fed into an evaporator with a microfeeder at the rate of 10 ml/h and preheated to 200 °C. Therefore, the vapor was passed to a tubular reactor with carbon pellets impregnated with metal chloride. As the activity of catalyst was gradually decreased with the elapse of time, the sample was taken from the condensate of effluent between one and two hour after start of the

Table 1. Effect of carrier on product composition at 400 °C

| Carrier | Product composition/mol% | | | | |
|---|---|---|---|---|---|
| | $C_6H_6$ | CB | m-DCB | p-DCB | o-DCB |
| Alumina | 60.3 | 0.3 | | 0.1 | 39.3 |
| Silica gel | 59.0 | 0.1 | 0.1 | 0.1 | 40.7 |
| Activated charcoal | 61.4 | 1.3 | | 0.1 | 37.2 |

reaction and analyzed by gas chromatography. The product distribution in the transchlorination of o-DCB and benzene with the various catalysts is shown in Tables 1 and 2. Noble metal chlorides supported on activated charcoal promoted remarkably the reaction, compared with the carrier alone. o-DCB was converted into CB by the transchlorination with benzene, accompanied with isomerization into m- and p-DCB.

Table 2. Effect of metal chloride supported on activated charcoal upon product composition at 400 °C

| Metal chloride | Product composition/mol% | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C_6H_6$ | CB | m-DCB | p-DCB | o-DCB | 1,2,4-$C_6H_3Cl_3$ | 1,2,3-$C_6H_3Cl_3$ |
| $MgCl_2$ | 61.7 | 0.6 | | 0.1 | 37.6 | | |
| $IrCl_3$ | 59.4 | 2.3 | 0.1 | 0.1 | 37.9 | 0.2 | |
| $RhCl_3\cdot 3H_2O$ | 60.1 | 4.2 | 0.2 | 0.2 | 35.0 | 0.3 | |
| $OsCl_3$ | 60.6 | 2.7 | 0.1 | 0.2 | 35.8 | 0.6 | |
| $PdCl_2$ | 50.1 | 13.5 | 2.7 | 2.1 | 28.7 | 2.4 | 0.5 |
| $PdCl_2\cdot 2NaCl\cdot 3H_2O$ | 56.7 | 11.3 | 2.1 | 2.1 | 25.5 | 1.9 | 0.4 |

The nucleophilic behavior of bromine produced in the thermal decomposition of bromobenzenes was confirmed by MO method.6) It can be assumed that noble metal chloride functions as a Lewis acid and accepts a chlorine from o-DCB to form a coordinate complex.7) The coordinate complex may play an important role in the postulated step. Therefore, the following mechanism is suggested to account for the transchlorination of o-DCB and benzene.

$$o\text{-}C_6H_4Cl_2 + PdCl_2 \rightleftharpoons [C_6H_4Cl]^+[PdCl_3]^- \qquad (1)$$

$$[C_6H_4Cl]^+[PdCl_3]^- + C_6H_6 \rightleftharpoons 2\ C_6H_5Cl + PdCl_2 \qquad (2)$$

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