Studies on the Hydroalkylation of Benzene and Methylbenzenes in the Presence of a Combination Catalyst of Pd–Al₂O₃ and NaCl–AlCl₃

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The mechanism of the hydroalkylation of benzene and methylbenzenes to cyclohexylbenzenes was studied in the presence of a palladium-fused salt (NaCl–AlCl₃) catalyst under hydrogen pressure. The activities of the hydrogenation catalyst and the alkylation catalyst were each estimated kinetically. The activity of the fused salt was compared with that of anhydrous aluminum chloride for the alkylation of aromatic compounds. The rate constants and Arrhenius parameters of the hydrogenation on palladium and the alkylation on the fused salt supported the presence of the cyclohexyl cation as an intermediate species in the hydroalkylation.

Keywords—hydroalkylation; mechanism; palladium catalyst; fused salt; benzene; cyclohexene; cyclohexylbenzene

The hydroalkylation reaction, giving cyclohexylbenzene (4) from benzene (1) in one step, was found by Truffault, using Ni–P₂O₅ catalyst. Several reports2–4) and patents5–9) have been published on the hydroalkylation of 1. Most of them refer to a bifunctional catalyst system of a Group VIII metal such as Ni, Pt, Pd, Ru, and Rh supported on solid acids. Several authors have studied the reaction of 1 and suggested cyclohexene (2) to be the key intermediate,2–4) though the details of the mechanism are not known.

We previously prepared the combination catalyst of palladium and the fused salt (NaCl–AlCl₃).10) The catalyst was applied for the hydroalkylation of 1 to 4,11) aniline to p-cyclohexylaniline12) and phenol to p-cyclohexylphenol.13) We have now successfully separated the intermediate olefins from the reaction products and confirmed the reaction pathway for the hydroalkylation of 1 and methylbenzenes. In this paper, the characterization of the combination catalyst, the palladium catalyst and the fused salt, is described. A reaction mechanism is proposed on the basis of the kinetics of hydrogenation and alkylation of 1 and methylbenzenes.

Results and Discussion

1) Isolation of the Reaction Intermediates from the Hydroalkylation Products

For the hydroalkylation of 1 to 4, several possible reaction intermediates were considered (Chart 1). One is a partial hydrogenation product of biphenyl (7), formed by the condensation of two molecules of 1 on the fused salt. However, with our catalyst, 7 was not detected by gas-liquid chromatography (GLC) on heating 1 (30 g) with the fused salt (4 g) and 0.25% Pd–Al₂O₃ (1 g) at 120 °C for 5 h in the absence of hydrogen. Another one is the cyclohexyl cation, formed by the abstraction of a hydride ion from cyclohexane (3) on palladium. When 3 was heated at 120 °C for 10 h in the presence of 0.24% Pd–Al₂O₃ (1 g) and the fused salt (4 g) in the absence of hydrogen, no 2 or high-boiling-point products such as bicyclohexyl were detected.
Therefore, among the reaction intermediates, 2 was the most probable key intermediate in the hydroalkylation of benzene, as already suggested by Slaugh and Leonard. We tried to separate 2 from the hydroalkylation products of 1, and found that the hydrogenation was retarded by the addition of AlCl₃·6H₂O, and corresponding olefins were obtained from methylbenzenes, although the yields were poor (Table I). However, under these conditions, 2 was not obtained. If the hydrogenation of 1 proceeds in a stepwise manner, it is plausible that 3 is produced by way of 2. Therefore, it was suggested that the reduction of 2 was so rapid that the intermediate could not be isolated.

Among methylbenzenes examined, the yields of dimethylcyclohexenes were higher than that of 1-methylcyclohexene (6). The highest yield (0.7%) was obtained for 1,2-dimethylcyclohexene; presumably the two adjacent methyl groups stabilized the olefin. These results showed that easily reducible olefins are formed as intermediate compounds during the hydrogenation of methylbenzenes to cyclohexanes.
2) The Catalytic Behavior of the Fused Salt of NaCl–AlCl₃

To study the role of NaCl–AlCl₃ in the hydroalkylation, the kinetics of alkylation of 1 or methylbenzenes with 2 were examined. The results obtained were compared with the activity of AlCl₃ alone. The initial rate of alkylation of benzenes with 2 increased with increase in the relative basicity of the aromatic compounds. A linear relationship between the logarithm of

![Graph](image1)

**Fig. 1. Relationship between Relative Basicity and Relative Rate of Alkylation with Cyclohexene**

○, catalyzed by AlCl₃; ●, catalyzed by NaCl-AlCl₃.

![Graph](image2)

**Fig. 2. Arrhenius Plots for the Alkylation of Benzene with Cyclohexene in the Presence of the Fused Salt or AlCl₃**

Benzene (11.25 M), cyclohexene (0.19 M), and NaCl–AlCl₃ (1:1) (0.40 M) were used for the fused salt-catalyzed reaction. $E_a = 24.8$ kcal·mol⁻¹. Benzene (11.25 M), cyclohexene (0.19 M), and AlCl₃ (0.007 M) were used for the AlCl₃-catalyzed reaction. $E_a = 24.5$ kcal·mol⁻¹.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Initial rate constant</th>
<th>Rel. reactivity&lt;sup&gt;d)&lt;/sup&gt;</th>
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<tr>
<td></td>
<td>NaCl–AlCl₃&lt;sup&gt;b)&lt;/sup&gt; (× 10⁻⁵ mol/l·min)</td>
<td>AlCl₃&lt;sup&gt;c)&lt;/sup&gt; (× 10⁻⁵ mol/l·min)</td>
</tr>
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<sup>a</sup> See ref. 15. <sup>b</sup> Hydrocarbon (2.33 M), cyclohexene (2.33 M), NaCl–AlCl₃ (1:1) (0.54 M), and cyclohexane were used. The reaction was carried out at 60°C. <sup>c</sup> Hydrocarbon (0.89 M), cyclohexene (0.89 M), AlCl₃ (0.41 M), and cyclohexane were used. The reaction was carried out at 0°C. <sup>d</sup> Relative reactivities were recalculated on the basis of p-xylene = 1.00.
the relative rate of the alkylation and the logarithm of the relative basicity was obtained (Fig. 1).

The alkylation of o-xylene proceeded approximately 4.5 times faster than that of 1 (Table II). These results are typical of Friedel-Crafts catalysts. The activation energies obtained from the Arrhenius plots of the initial rate in the presence of NaCl–AlCl₃ and AlCl₃ were 24.8 and 24.5 kcal·mol⁻¹, respectively (Fig. 2). These results also indicated that NaCl–AlCl₃ catalyzed the alkylation through a similar mechanism to AlCl₃.

Therefore, a plausible reaction path is as follows: 1 is hydrogenated to 2 on Pd–Al₂O₃, and then 2 migrates from palladium to the fused salt to form the cyclohexyl cation. In the case of toluene (5), both the 1-methylcyclohexyl cation (6–1) and the 2-methylcyclohexyl cation (6–2) can be considered as candidates for the intermediate species. The former seems more probable than the latter since a tertiary carbonium ion is more stable than a secondary one. Therefore, 6–1 attacked the electron-rich carbon of the phenyl ring (p-position) to give 4,1'-dimethylcyclohexylbenzene as the major product. However, substitution at the ortho position did not take place owing to the steric effect of the methyl group on 5.

3) Kinetics of Hydrogenation and Alkylation of Benzene

In the hydroalkylation, the relative rates of hydrogenation and alkylation affected the yield of 4. We measured the rate of the hydrogenation of 2 using 0.25% Pd–Al₂O₃ (1 g) in the presence of the fused salt (NaCl–AlCl₃, 4 g). The rate constants (kₘₚ₉₀) were calculated according to the following equation.¹⁶)

\[
\log \frac{P_0}{P} = \frac{k_{\text{hydro}}}{2.303}
\]

\(P_0\): initial H₂ pressure; \(P\): H₂ pressure at time \(t\)

The Arrhenius plots for the hydrogenation of 2 in the presence of NaCl–AlCl₃ are shown in Fig. 3.

The values of the activation energy and the rate constant for the hydrogenation at 120 °C were 5.95 kcal·mol⁻¹ and 0.24 min⁻¹. The rate constant for the alkylation at 120 °C (kₐₗ₉₀ = 1.56 min⁻¹) was obtained by extrapolation of the Arrhenius plots (Fig. 2). In the hydroalkylation of 1 at 120 °C, the yields of 3 and 4 were 8.4 and 16.4%, respectively. From kinetic data, kₐₗ was 6.5 times faster than kₘₚ₉₀. If the hydrogenation and the alkylation of 2 are competitive, the yield of 4 may also reach 6.5 times that of 3. This discrepancy was explained by considering the delayed desorption of 2 from the palladium surface. Thus, the successive hydrogenation of 2 on the palladium catalyst took place to give 3. On the other hand, a part of 2 migrated from the surface of Pd–Al₂O₃ onto the surface of NaCl–AlCl₃ and

![Fig. 3. Arrhenius Plots for the Hydrogenation of Cyclohexene in the Presence of the Fused Salt](image)
was swiftly alkylated with 1 to give 4.

**Experimental**

Gas-liquid chromatography (GLC) for the analyses of benzene, methylbenzenes, olefins, and hydrogenated products was carried out on a Shimadzu GC-3BF gas chromatograph by using a column packed with 25% Apiezon grease M on C-22 (30—60 mesh, 1 m)—20% polyethylene glycol (PEG) on Chromosorb W (60—80 mesh, 2 m).17) Hydroalkylated products were also analyzed by GLC (Hitachi 063; column packing, 2% silicone OV-17 on Chromosorb W, 60—80 mesh, 2 m). Proton nuclear magnetic resonance (1H-NMR) spectra were recorded on a Hitachi R-600 (60 MHz) or JEOL GX-270 (270 MHz) instrument in CDCl3. Carbon-13 nuclear magnetic resonance (13C-NMR) spectra were obtained on a Varian XL-200 spectrometer. Chemical shifts are given in δ-values referred to internal tetramethylsilane.

**Preparation of Catalysts**—Palladium on alumina and the fused salt were prepared according to the previously reported method.11) The palladium catalyst was activated before use (200 °C, 1 h in an H2 stream).

**General Procedures**—Hydrogenations and hydroalkylations were carried out in a stainless steel autoclave (SR-10, 100 ml). The substrate, Pd—Al2O3, and the fused salt were put in the autoclave. The air in the autoclave was displaced with hydrogen, the autoclave was heated to the desired temperature, and then hydrogen was introduced to 130 kg/cm². The reaction was started by magnetic stirring. The partially hydrogenated olefins were isolated by preparative GLC on a column packed with a 20% PEG 20 m (2 m)—25% Apiezon grease M (2 m).

**Physical Properties of Hydroalkylation Products and Olefins**—The physical data for hydroalkylation products were previously reported.11) NMR data for olefins are as follows. For 1-methylcyclohexane: 1H-NMR δ: 1.25—2.35 (m, 7H), 1.89 (s, 3H). For 1,2-dimethylcyclohexene; 1H-NMR δ: 1.24—2.30 (m, 8H), 1.72 (s, 6H). For 1,3-dimethylcyclohexene; 1H-NMR δ: 0.89 (d, 3H, J=7.2 Hz), 1.03—2.34 (m, 7H), 1.76 (s, 3H), 5.23 (s, 1H). 13C-NMR δ: 21.90, 22.03, 30.02, 30.34, 31.19, 127.80, 133.34.18) For 1,4-dimethylcyclohexene; 1H-NMR δ: 0.93 (d, 3H, J=6.2 Hz), 1.21—2.03 (m, 7H), 1.70 (s, 3H), 5.34 (s, 1H).

**References and Notes**