

HYDROGENATION MECHANISM OF BENZYL ALCOHOL IN POLAR SOLVENTS ESTIMATED BY MO CALCULATION

Hideyuki Takagi, Takaaki Isoda, Katsuki Kusakabe and Shigeharu Morooka

Department of Materials Physics and Chemistry, Graduate School of Engineering,
Kyushu University, Fukuoka 812-8581, Japan

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INTRODUCTION

The hydrogenation of aromatic structures is a key reaction in the hydrorefining of heavy oil, asphaltene and coal extracts. In previous studies,^{1,2} we examined the hydrogenation of benzyl alcohol, which was the model compound as the coal extracts from low rank coal, over a ruthenium catalyst at 120°C in a variety of solvents. Our findings showed that the hydrogenation reactivity of benzyl alcohol was related to the relative permittivity of the reaction medium, but the mechanism was not clarified in detail.

Recently, the computer chemistry have been developed, and the structures of intermediates during the chemical reaction can be estimated by molecular orbital (MO) calculation using the personal computer.³ In an earlier study,⁴ we calculated changes in the reaction coordinates during the hydrogenation of benzene and found that the calculated activation energy agreed with that obtained experimentally. A conductor-like screening model (COSMO) assumes that the solvent is a homogeneous medium with a relative permittivity. The reaction coordinate for the hydrogenation of an aromatic compound in a polar solvent can be then analyzed via the application of the COSMO method to the MO calculation.

In the present study, benzyl alcohol was hydrogenated using a ruthenium catalyst at 120°C at a hydrogen pressure of 6 MPa in polar solvents. The reaction coordinate for hydrogenation of benzyl alcohol was estimated by MO calculation, in conjunction with the COSMO method, and the hydrogenation mechanism in polar solvents was discussed.

EXPERIMENTAL SECTION

Benzyl alcohol and ethanol were used as the substrate and the solvent, respectively. An alumina-supported ruthenium catalyst (Ru/Al₂O₃, Wako Chemical) was used as a hydrogenation catalyst. A typical reaction involved the use of 3 g of benzyl alcohol, 0.5 g of catalyst, and 6 g of ethanol. In order to vary the permittivity of the medium, a 3 g portion of formic acid or acetic acid was added. The relative permittivity of a mixed solvent, P_{mix} , can be calculated from the following equation.

$$P_{\text{mix}} = (P_i X_i + P_j X_j) / (X_i + X_j) \quad (1)$$

where P_i and P_j are the relative permittivities of solvent i and solvent j , respectively. X_i and X_j are the mass fractions of solvent i and j , respectively, ($X_i + X_j = 1$). Table 1 shows the relative permittivity of solvents. All reactions were performed in a 50-mL batch autoclave at 120°C for 0-30 min under a hydrogen pressure of 6 MPa. After the reaction, the products were qualitatively and quantitatively analyzed by GC-FID (GC-14A, Shimadzu) and GC-MS (QP-5000, Shimadzu), equipped with a capillary column. Details of the reaction have been reported previously.² Reaction rate constants for the hydrogenation of benzyl alcohol in solvents were then determined from the yields of products.

SIMULATION

Figure 1 shows the pathways for reaction of benzyl alcohol over the Ru/Al₂O₃ catalyst.¹ Hydrogenation of the aromatic ring (route 1) and hydrogenolysis of hydroxy group (route 2) proceed competitively. Cyclohexanecarbaldehyde is produced via route 1, and toluene via route 2. Methylcyclohexane is produced via the hydrogenation of the produced toluene.

A molecular orbital (MO) calculation for hydrogenation of benzyl alcohol was carried out using WinMOPAC Vr.1 (Fujitsu) based on a PM3 Hamiltonian method, and the energy minimization

was defined by an EF method.³ A hydrogen atom was coordinated to an optional atom located on benzyl alcohol or an intermediate molecule. The reaction coordinate between the hydrogen atom and the substrate was then calculated from 3 Å to 1 Å at a step of 0.1-0.2 Å using the COSMO method. The heat of formation was plotted against the reaction coordinate, and the activation energy was calculated as follows:

$$E_c = E_t - E_p \quad (2)$$

where E_c is the activation energy. E_t and E_p are the heat of formation of the transition complex and that of the initial or intermediate compound, respectively.

RESULTS

Hydrogenation via route 1

Figure 2 shows the relationship between the reaction rate constant of route 1 for the hydrogenation of benzyl alcohol at 120°C and the relative permittivity of the medium. The rate constant for route 1 was $8.2 \times 10^{-4} \text{ s}^{-1}$ with no solvent, and $4.5 \times 10^{-4} \text{ s}^{-1}$ in ethanol as the solvent. The addition of acetic acid led to a decrease in the relative permittivity of the medium, and an increase in the rate constant to $8.2 \times 10^{-4} \text{ s}^{-1}$, which was equal to that for the reaction with no solvent. The hydrogenation was completely retarded by the addition of formic acid with a high relative permittivity. This indicates that the rate constant of route 1 can be related to the relative permittivity of the reaction medium.

Figure 3 shows the change in the reaction coordinate for the hydrogenation of benzyl alcohol via route 1. In step 1, the activation energy is 24.6 kcal/mol with no solvent (relative permittivity = 13.1), and 46.6 kcal/mol for the ethanol-formic acid solution (relative permittivity = 30.0). No activation energy is apparent for step 2. In step 3, the activation energy is 12.0 kcal/mol with no solvent, and 26.9 kcal/mol for the ethanol-formic acid solution. In addition, no activation energy is apparent for step 4. A hydrogen atom is not introduced into the double bond of 1-cyclohexanylmethanol, based on the MO calculation. This supports the experimental findings that 1-cyclohexanylmethanol was converted to cyclohexanecarbaldehyde.^{1,5}

Figure 4 shows the activation energy in route 1 for the hydrogenation of benzyl alcohol as a function of the relative permittivity. The activation energy is determined as the sum of the values of steps 1 and 3. The activation energy is 49.9 kcal/mol for the hydrogenation in ethanol and is decreased to 43.9 kcal/mol by the addition of acetic acid with a low relative permittivity. On the other hand, the activation energy is increased to 73.5 kcal/mol by the addition of formic acid with a high permittivity. In the route for hydrogenation of the aromatic ring in benzyl alcohol, the activation energy, which is estimated from the MO calculation, decreases with decreasing

Table 1. Relative Permittivity of Solvents

system	composition in weight [g] (substrate:solvent:additive)	relative permittivity of mixed solvent
in vacuum		0.0
benzyl alcohol (no solvent)		13.1
ethanol	3 : 6	20.6
ethanol/acetic acid	3 : 6 : 3	17.0
ethanol/formic acid	3 : 6 : 3	30.0

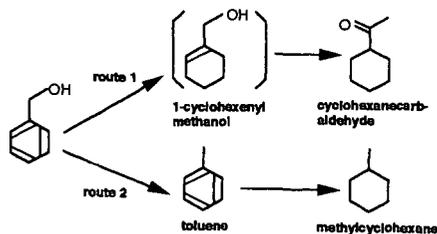


Figure 1. Pathways for reaction of benzyl alcohol over $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst.

relative permittivity of the solution.

Hydrogenolysis via route 2

Table 2 shows the reaction rate constant for hydrogenation of benzyl alcohol via route 2. The rate constant at 120°C was $0.59 \times 10^{-4} \text{ s}^{-1}$ with no solvent, and remained unchanged after the addition of ethanol. The addition of acetic acid in ethanol lead to an increase in the rate constant to $1.57 \times 10^{-4} \text{ s}^{-1}$. Figure 5 shows the hydrogenolysis reaction via route 2, as estimated by the MO calculation. A proton (H^+) is linked to the oxygen atom of the hydroxy group, and intermediate-1 is formed. However, hydrogen atom (H) cannot be attached to the hydroxy group nor the carbon atoms adjacent to the hydroxy group. Intermediate-2 is formed by the attack of a hydrogen atom and then is decomposed, producing toluene and water. This suggests that the hydrogenolysis of the hydroxy group

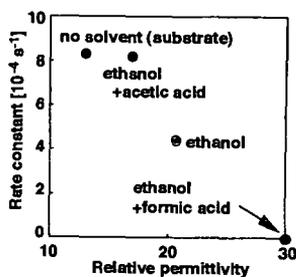


Figure 2. Relationship between reaction rate constant of route 1 for hydrogenation of benzyl alcohol 120°C and relative permittivity of medium.

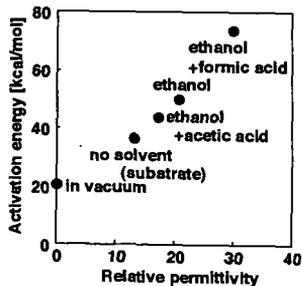
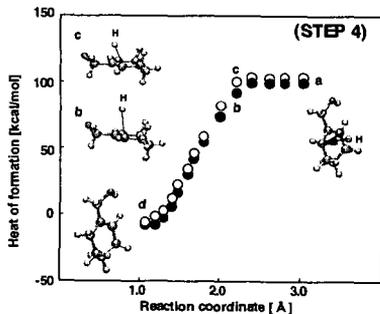
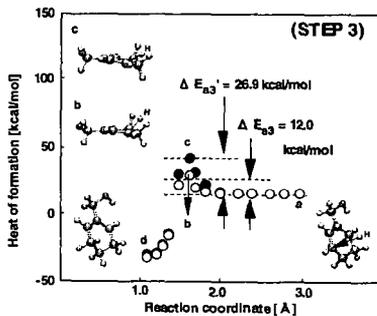
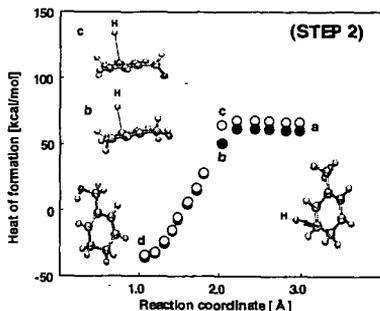
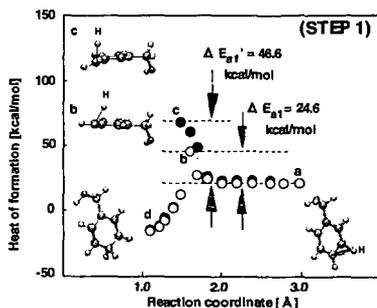


Figure 4. Activation energy in route 1 for hydrogenation of benzyl alcohol as a function of relative permittivity.



○ relative permittivity; 13.1
 ● relative permittivity; 30.0

Figure 3. Changes in reaction coordinate for hydrogenation of benzyl alcohol via route 1.

Table 2. Reaction Rate Constant for Hydrogenation of Benzyl Alcohol via Route 2

system	rate constant [10^{-4} s^{-1}]
benzyl alcohol (non-solvent)	0.59
ethanol	0.58
ethanol/acetic acid	1.57
ethanol/formic acid	0.0

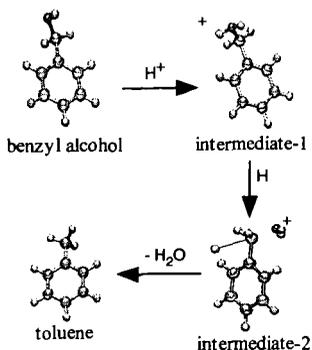


Figure 5. Hydrogenolysis reaction via route 2 estimated by MO calculation.

proceeds via an S_N2 mechanism.

DISCUSSION

The hydrogenation reaction of aromatic compounds with polar substituents, as well as benzyl alcohol, can be divided into two routes; hydrogenation of aromatic ring; and hydrogenolysis of oxygen-containing substituents and bridge bonds. As shown in Figure 2, the rate constant for hydrogenation of the aromatic ring, which was obtained by experimental results, increases with decreasing relative permittivity of the solution. The MO calculation indicates that the heat of formation for the transition state is dependent on the structure, which vary with the relative permittivity of the solution. The heat of formation for the transition state decreases with decreasing relative permittivity of the solution, and, as a result, the activation energy of route 1 decreases. This MO calculation suggests that the value of the heat of formation is related to the reaction rate of route 1. Present study also clarified that the hydrogenolysis of benzyl alcohol is an S_N2 reaction and is promoted by the donation of a proton from the solvent.

CONCLUSIONS

The reaction rate for route 1 increased with decreasing relative permittivity of the solution. The activation energy for hydrogenation of the aromatic ring in benzyl alcohol was estimated by an MO calculation, and decreased with decreasing relative permittivity of the reaction medium. Hydrogenolysis of the OH group in benzyl alcohol was promoted by donating a proton from the solvent, and was consistent with proceeding via an S_N2 reaction. The addition of acetic acid in ethanol enhanced the hydrogenation of the aromatic ring, as well as the hydrogenolysis of benzyl alcohol, but the addition of formic acid inhibited the catalyst activity. This concludes the role of the additives in hydrogenation of aromatic compounds with polar substituents.

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