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# Selective Formation of 2-Phenylethanol in the Homologation of Benzyl Alcohol

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High selectivity of 2-phenylethanol (87%) in the homologation of benzyl alcohol was obtained with cobalt-ruthenium mixed catalyst. The formation of toluene as the major by-product was suppressed by adding water at low reaction temperature. Bromide as promoter was more effective for the homologation than chloride or iodide. From in situ IR observation, $[Co(CO)_4]^-$, which was active species for the homologation, was found to be produced by the dissociation of $[CoH(CO)_4]$ but not by the disproportionation of $[Co_2(CO)_8]$ under the reaction temperature employed (120 °C). It was also revealed that ruthenium chloride as precatalyst was converted into a bromocarbonyl complex of ruthenium under the homologation conditions.

The homologation of benzyl alcohol to 2-phenylethanol is an important reaction because the latter can be dehydrated to styrene. This reaction was first reported by Wender and his co-workers.[1] Their results showed that the hydrocarbon, toluene, and the homologous alcohol, 2-phenylethanol, were formed in a ratio of about 2:1. Based on the effects of substituents on aromatic ring, they postulated[2] that the homologation (Eq. 1) and the reduction (Eq. 2)

$$C_6H_5CH_2OH + CO + 2H_2 \longrightarrow C_6H_5CH_2CH_2OH + H_2O, \quad (1)$$

$$C_6H_5CH_2OH + H_2 \longrightarrow C_6H_5CH_3 + H_2O, \quad (2)$$

proceeded via the same intermediate. In spite of their studies, the selectivity of the homologation products were insufficient and toluene derivatives were major products. Up to now, higher molar ratio of 2-phenylethanol to toluene in this homologation was only reported in a patent.[3] Thus the main aim of this work is to improve the selectivity of the homologation step.

It has been known[4] that cobalt-catalyzed methanol homologation is promoted by iodide such as methyl iodide and by the addition of ruthenium as co-catalyst. So, we explored optimum reaction conditions for the homologation of benzyl alcohol with this mixed catalyst and halides as promoters. We also discussed the reaction mechanism.

## Experimental

All materials other than solvent were commercially available and used without further purification. Solvent, 1,4-dioxane, was distilled over a Na–Pb alloy under nitrogen atmosphere. Hydrogen was commercial material (purity: above 99%) and carbon monoxide was prepared in our laboratory (purity: above 98%). Apparatus and procedure were similar to those used previously.[5,6]

## Result and Discussion

**Preliminary Experiments.** At first, we investigated the effect of various halides as promoters on the homologation of benzyl alcohol. By the use of hydriodic acid as promoter at high temperature (180 °C), toluene was obtained preferentially and 2-phenylethanol in much lower yield under the reaction conditions employed (Run 1 in Table 1). Wender and his co-workers suggested[2] that toluene was formed through the radical mechanism involving benzyl radical. Carbon-metal bond is generally weak, for instance, 105 kJ mol$^{-1}$ in $[C_6H_5CH_2Mn(CO)_6]$[7] and 92 kJ mol$^{-1}$ in $[C_6H_5CH_2Co(Saloph)(py)]$,[8] so that this bond in

Table 1. The Homologation of Benzyl Alcohol[a)]

| Run | Temp/°C | Promoter (M)[b)] | | Benzyl Alcohol Conversion/% | Yield/% | |
|---|---|---|---|---|---|---|
| | | | | | Homologous Comp.[c)] | Toluene |
| 1 | 180 | HI | (0.2) | 95 | 8.2 (8.6) | 78 |
| 2 | 120 | — | (—) | 10 | 5.0 (50) | 1.8 |
| 3 | 120 | HCl | (0.3) | 14 | 8.1 (57) | 0.8 |
| 4 | 120 | HI | (0.2) | 59 | 13 (22) | 44 |
| 5 | 120 | HBr | (0.2) | 30 | 21 (70) | 2.9 |
| 6 | 180 | HBr | (0.2) | 80 | 16 (20) | 57 |
| 7 | 150 | HBr | (0.2) | 47 | 30 (64) | 14 |
| 8 | 100 | HBr | (0.2) | 20 | 9.0 (45) | 1.2 |
| 9[d)] | 120 | $C_6H_5CH_2Br$ | (0.2) | 29 | 20 (69) | 3.8 |

a) Reaction conditions: Total pressure, 300 kg cm$^{-2}$ at room temp ($H_2$/CO=2/1); benzyl alcohol, 7 M; $Co(AcO)_2$, 0.23 M; $RuCl_3$, 0.023 M; 1,4-dioxane, 2 ml; reaction time, 4 h. b) Added as its aqueous solution, 1 M=1 mol dm$^{-3}$. c) Total yield of 2-phenylethanol and phenylacetaldehyde. The selectivity of homologous compounds is shown in the parentheses. d) $H_2O$ was added at the same concentration as that of hydrobromic acid used in Runs 5 to 8.

$[C_6H_5CH_2Co(CO)_4]$ is considered to be weak. Thus, the benzyl radical is supposed to be formed by homolysis of benzylcobalt complex and the reaction mechanism of toluene formation is considered as Eq. 3 to Eq. 7. On the other hand, if benzylcobalt complex (**1**)

$$C_6H_5CH_2OH + HX \rightleftharpoons C_6H_5CH_2X + H_2O \quad (3)$$

X : halogen atom

$$C_6H_5CH_2X + [Co(CO)_4]^- \rightleftharpoons \underset{\mathbf{1}}{[C_6H_5CH_2Co(CO)_4]} + X^- \quad (4)$$

$$\mathbf{1} \rightleftharpoons \underset{\mathbf{2}}{C_6H_5CH_2\cdot} + \underset{\mathbf{3}}{\cdot Co(CO)_4} \quad (5)$$

$$\mathbf{2} + [CoH(CO)_4] \rightleftharpoons C_6H_5CH_3 + \mathbf{3} \quad (6)$$

$$2\ \mathbf{3} \rightleftharpoons [Co_2(CO)_8] \quad (7)$$

undergoes CO insertion followed by hydrogenolysis (Eqs. 8 and 9), phenylacetaldehyde is produced which

$$\mathbf{1} + CO \rightleftharpoons \underset{\mathbf{4}}{[(C_6H_5CH_2CO)Co(CO)_4]} \quad (8)$$

$$\mathbf{4} + H_2 \rightleftharpoons C_6H_5CH_2CHO + [CoH(CO)_4] \quad (9)$$

is rapidly converted into 2-phenylethanol by ruthenium catalyst as shown later. 2-Phenylethanol and toluene are produced via the same intermediate, that is, benzylcobalt complex. Therefore, the suppression of homolytic cleavage (Eq. 5) or of the hydrogen abstraction reaction (Eq. 6) should improve the selectivity of 2-phenylethanol. Benzyl radical may also be formed by homolysis of benzyl iodide (Eq. 10).

$$C_6H_5CH_2I \rightleftharpoons C_6H_5CH_2\cdot + \cdot I \quad (10)$$

In order to suppress the radical cleavage such as Eq. 5 or Eq. 10, the reaction was carried out without iodide at low temperature (120 °C). Under these reaction conditions, 2-phenylethanol was a major product (Run 2 in Table 1) but its selectivity was not sufficient. By-products other than toluene were dibenzyl ether, ethylbenzene and benzyl acetate. The yield of dibenzyl ether was about 2% and that of ethylbenzene about 0.1% through the all runs. Benzyl acetate was formed by the reaction of benzyl alcohol with acetate anion originating in a precatalyst, cobalt(II) acetate, since benzyl acetate could not be detected by using octacarbonyldicobalt instead of cobalt(II) acetate. 1,2-Diphenylethane, the coupling product of benzyl radical, was also obtained in small amount through all runs. This result suggests the existance of benzyl radical.

Table 1 shows the effect of halides as promoters at low reaction temperature (Runs 3—5). Hydrobromic acid was more effective than hydrochloric acid for both the yield and selectivity of 2-phenylethanol. Hydriodic acid enhanced the conversion of benzyl alcohol but toluene was preferentially obtained. This implies that homolysis of benzyl iodide occurs to produce benzyl radical. From above results, we chose bromide as promoter and examined the effects of other reaction variables on the homologation.

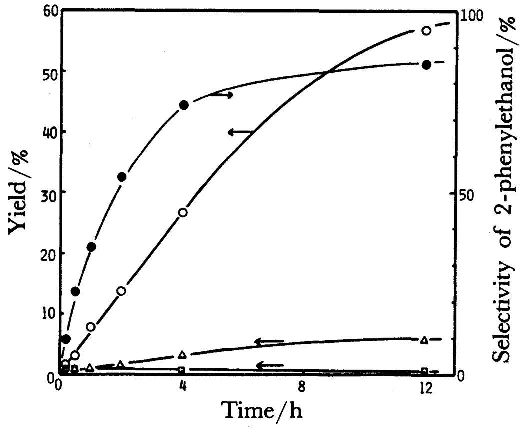

Fig. 1. Time dependent products yield in benzyl alcohol homologation. Reaction temp, 120 °C, total pressure, 320 kg cm$^{-2}$ at 120 °C, ($H_2/CO=2/1$); benzyl alcohol, 7 M; HBr, 0.2 M as aqueous solution; $Co(AcO)_2$, 0.23 M; $RuCl_3$, 0.023 M; 1,4-dioxane, 10 ml. Total pressure was kept constant during the reaction. ○: 2-Phenylethanol, △: toluene, □: phenylacetaldehyde and ●: selectivity of 2-phenylethanol.

**Effects of Temperature.** Table 1 also shows that the yield of toluene decreases and the selectivity of 2-phenylethanol increases as the reaction temperature decreases from 180 °C to 120 °C (Runs 5—7). At 100 °C, the activity of catalyst for the homologation fell down and dibenzyl ether was obtained as the major by-product (yield: 4%). Thus, the optimum temperature for the high selectivity of the homologation step was about 120 °C.

The time-yield curves of 2-phenylethanol, phenylacetaldehyde and toluene at 120 °C are shown in Fig. 1. From these curves, it is suggested that phenylacetaldehyde is the intermediate for the formation of 2-phenylethanol (Eqs. 11 and 12). Figure 1 also shows

$$C_6H_5CH_2OH + CO + H_2 \longrightarrow C_6H_5CH_2CHO + H_2O \quad (11)$$

$$C_6H_5CH_2CHO + H_2 \longrightarrow C_6H_5CH_2CH_2OH \quad (12)$$

that the selectivity of 2-phenylethanol increases with the reaction time. As discussed later, this phenomenon is explained by the increase in the concentration of water which is produced by the reaction of benzyl alcohol with hydrogen bromide (Eq. 3, X=Br).

**Effect of Ruthenium Concentration.** The addition of ruthenium is known[4] to improve the selectivity of ethanol in methanol homologation and we proved[5] that its effectiveness was ascribed to the high reactivity on the hydrogenation of acetaldehyde. Figure 2 shows that ruthenium is also effective for improving the selectivity of 2-phenylethanol on account of the fast hydrogenation of phenylacetaldehyde. This fast hydrogenation of phenylacetaldehyde implies that the decarbonylation of phenylacetaldehyde affording toluene

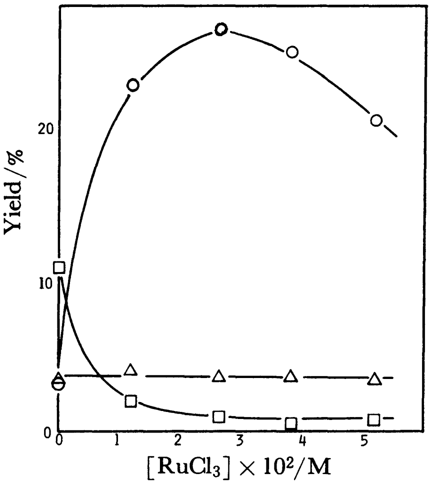

Fig. 2. Effect of ruthenium concentration on benzyl alcohol homologation. Reaction conditions were the same as those of Fig. 1, except ruthenium concentration and reaction time (4 h). ○: 2-Phenylethanol, △: toluene, □: phenylacetaldehyde.

is ruled out.

An optimum concentration of ruthenium existed and the yield of 2-phenylethanol decreased by the addition of ruthenium in large excess. This phenomenon was also observed in the case of methanol homologation.[6] As in the previous report,[5] this phenomenon is interpreted as resulting from the consumption of halogens which coordinate to ruthenium species (see later).

**Effect of $H_2O$.** As shown earlier, the concentration of water had an effect on the selectivity of 2-phenylethanol. In order to examine the effect of water in detail, we employed $C_6H_5CH_2Br$ as promoter instead of hydrobromic acid in this and the following experiments. The effect of $C_6H_5CH_2Br$ on the homologation was similar to that of HBr (Runs 5 and 9 in Table 1). $[Co_2(CO)_8]$ was employed as catalyst precursor to avoid the formation of benzyl acetate.

From the results of in situ IR observation as shown later, water enhances the dissociation of $[CoH(CO)_4]$ (Eq. 13). (An oxonium ion reacts rapidly with bromide anion which is produced by Eq. 4 affording water and hydrogen bromide as shown in Eq. 14).

$$[CoH(CO)_4] + H_2O \rightleftharpoons [H_3O]^+ + [Co(CO)_4]^- \quad (13)$$

$$[H_3O]^+ + Br^- \rightleftharpoons H_2O + HBr \quad (14)$$

When the initial concentration of water was lower than 2.0 M, both the yield and selectivity of 2-phenylethanol increased with the water concentration but the total yield of 2-phenylethanol and toluene was independent of it (Fig. 3 and Runs 1—3 in Table 2). Water inhibits the hydrogen abstraction reaction of benzyl radical from $[CoH(CO)_4]$ (Eq. 6) because the concentration of $[CoH(CO)_4]$ decreases with the initial concentration of water on account of the shift of equilibrium 13 to the right. On the other hand, addition of water in excess (higher than 2.0 M) diminished the total yield of 2-phenylethanol and toluene (Fig. 3) due to the shift of equilibrium 3 to the left. The selectivity of 2-phenylethanol, however, became not to be affected by the initial concentration of water (Runs 4, 6, and 7 in Table 2). Therefore, equilibrium 13 lies far to the right.

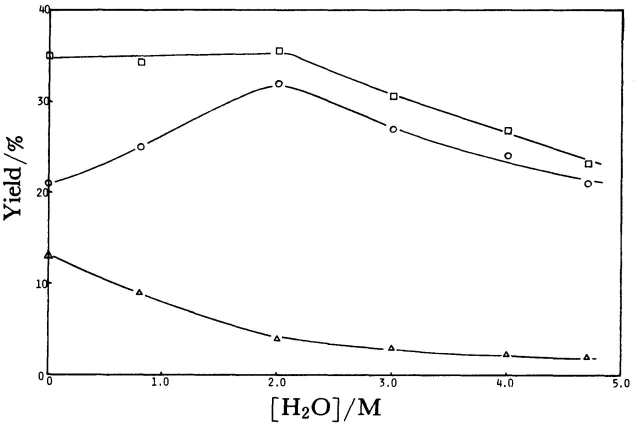

Fig. 3. Effect of $H_2O$ concentration on toluene formation. Reaction conditions were the same as those of Table 2. ○: 2-Phenylethanol, △: toluene, □: total yield of 2-phenylethanol and toluene.

Table 2. The Effect of $H_2O$

| Run | $[H_2O]$/M | Yield/% | |
|---|---|---|---|
| | | $C_6H_5CH_2CH_2OH$[a] | $C_6H_5CH_3$ |
| 1 | 0[b] | 22 (59) | 13 |
| 2 | 0.8 | 25 (67) | 9.2 |
| 3 | 2.0 | 32 (83) | 4.1 |
| 4 | 3.0 | 27 (85) | 3.1 |
| 5[c] | 3.0 | 41 (87) | 4.0 |
| 6 | 4.0 | 24 (84) | 2.6 |
| 7 | 4.7 | 21 (85) | 2.3 |

Reaction conditions: Reaction temp., 120 °C; total pressure, 320 kg cm$^{-2}$ at 120 °C ($H_2/CO=2/1$); benzyl alcohol, 7 M; $Co_2(CO)_8$, 0.11 M; $RuCl_3$, 0.029 M; benzyl bromide, 0.21 M; 1,4-dioxane, 10 ml; reaction time, 4 h; the consumed gas was supplied during the reaction. a) The selectivity of 2-phenylethanol is shown in the parentheses. b) $Ru_3(CO)_{12}$, $8.8\times10^{-3}$ M. c) Reaction time, 8 h.

As the reaction proceeded, the concentration of water increased by Eq. 3 and the selectivity of 2-phenylethanol increased as shown in Fig. 1. When the reaction was carried out for long period (12 h), one of the minor by-products, dibenzyl ether, was obtained in lower yield (0.5%) than that obtained for 4 h (1.4%). This result is due to the progress of the reverse reaction in equilibrium 15 since the concentration of water

$$2\,C_6H_5CH_2OH \rightleftharpoons C_6H_5CH_2OCH_2C_6H_5 + H_2O \quad (15)$$

increases and that of benzyl alcohol decreases with proceeding of the reaction. Thus the highest selectivity of 2-phenylethanol (87%, Run 5 in Table 2) was achieved, when the homologation was carried out for

Table 3. The Effect of $C_6H_5CH_2Br$

| Run | $[C_6H_5CH_2Br]$/M | Yield/% | | |
|---|---|---|---|---|
| | | $C_6H_5CH_2CH_2OH$[a] | $C_6H_5CH_2CHO$ | $C_6H_5CH_3$ |
| 1 | 0 | 14 (49) | 5.3 | 2.8 |
| 2 | 0.1 | 26 (78) | 1.2 | 3.1 |
| 3 | 0.2 | 32 (83) | 1.3 | 4.1 |
| 4 | 0.3 | 26 (63) | 1.0 | 4.6 |
| 5 | 0.4 | 17 (49) | 1.7 | 7.4 |

Reaction conditions: $H_2O$, 2.0 M; other reaction conditions were the same as those of Table 2. a) The selectivity of 2-phenylethanol is shown in the parentheses.

Table 4. Effect of Partial Pressure

| Run | $CO/H_2$[a] | Yield/% | | |
|---|---|---|---|---|
| | | $C_6H_5CH_2CH_2OH$[b] | $C_6H_5CH_2CHO$ | $C_6H_5CH_3$ |
| 1 | 1/3.5 | 25 (80) | 0.7 | 5.3 |
| 2 | 1/2 | 32 (82) | 1.3 | 4.1 |
| 3 | 1/1 | 28 (78) | 1.6 | 5.3 |
| 4 | 2/1 | 19 (55) | 3.0 | 7.0 |

Reaction conditions: Total pressure, 320 kg cm$^{-2}$ at 120 °C; $H_2O$, 2.0 M; other reaction conditions were the same as those of Table 2. a) Partial pressure ratio. b) The selectivity of 2-phenylethanol is shown in the parentheses.

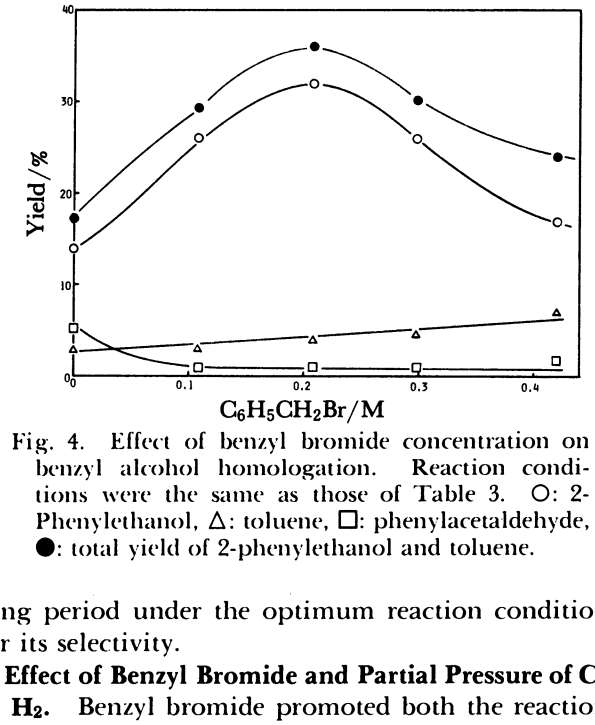

Fig. 4. Effect of benzyl bromide concentration on benzyl alcohol homologation. Reaction conditions were the same as those of Table 3. ○: 2-Phenylethanol, △: toluene, □: phenylacetaldehyde, ●: total yield of 2-phenylethanol and toluene.

long period under the optimum reaction conditions for its selectivity.

**Effect of Benzyl Bromide and Partial Pressure of CO to $H_2$.** Benzyl bromide promoted both the reactions of the homologation (Eq. 1) and the reduction (Eq. 2), when the initial concentration of benzyl bromide was lower than 0.2 M (Runs 1—3 in Table 3). The total yield of 2-phenylethanol and toluene, however, decreased with the initial concentration of benzyl bromide higher than 0.2 M (Fig. 4). These results indicate that the rate of benzylcobalt complex formation is retarded when the benzyl bromide is added in large excess. This is due to the suppression of the forward reaction of Eq. 4 by the high concentration of bromide anion. Although suppressing the forward reaction of Eq. 4 should lead to repression of the yield of toluene, that of toluene increased with the initial concentration of benzyl bromide. This implies that toluene is also produced via homolysis of benzyl bromide.

Figure 4 also shows that the hydrogenation of phenylacetaldehyde is slower in the absence of bromide than in the presence of it. As shown later, under the reaction conditions, ruthenium chloride as precatalyst was converted into chlorocarbonyl complex in the absence of bromide and into bromocarbonyl complex in the presence of it. Consequently, the former is supposed to be less reactive for the hydrogenation of phenylacetaldehyde than the latter.

Concerning the partial pressure ratio of CO to $H_2$, the highest yield and selectivity of 2-phenylethanol were found by using a CO to $H_2$ ratio of about 1:2 (Table 4). High partial pressure of $H_2$ increased the yield of toluene (Run 1 in Table 4) on account of high concentration of $[CoH(CO)_4]$ by equilibrium 16.

$$[Co_2(CO)_8] + H_2 \rightleftharpoons 2\,[CoH(CO)_4] \tag{16}$$

While low partial pressure of $H_2$ retarded the rate of hydrogenation of phenylacetaldehyde (Run 4 in Table 4) and also retards the formation of $[CoH(CO)_4]$ in equilibrium 16. In this case, homolysis of Co–Co bond in $[Co_2(CO)_8]$, the bond energy of which is very low (61 kJ mol$^{-1}$),[9] may occur to form cobalt carbonyl radical (Eq. 17). This radical abstracts $[Co(CO)_4]$ from

$$[Co_2(CO)_8] \rightleftharpoons 2\cdot Co(CO)_4 \tag{17}$$

benzylcobalt complex to afford benzyl radical (Eq. 18)

$$[C_6H_5CH_2Co(CO)_4] + \cdot Co(CO)_4 \rightleftharpoons C_6H_5CH_2\cdot + [Co_2(CO)_8] \tag{18}$$

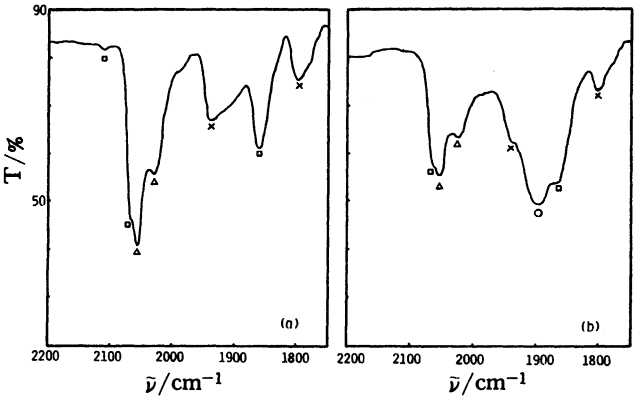

Fig. 5. IR spectra of $[CO_2(CO)_8]$, $[CoH(CO)_4]$ and $[Co(CO)_4]^-$ under high pressure of syngas. Conditions: total pressure, 125 kg cm$^{-2}$ at 120 °C ($H_2$/CO=2/1). Peaks ascribed to ○: $[Co(CO)_4]^-$, □: $[Co_2(CO)_8]$, △: $[CoH(CO)_4]$, ×: benzyl alcohol. (a) solvent: benzyl alcohol, (b) solvent: benzyl alcohol-$H_2O$-1,4-dioxane (50:1:0.5 volume ratio).

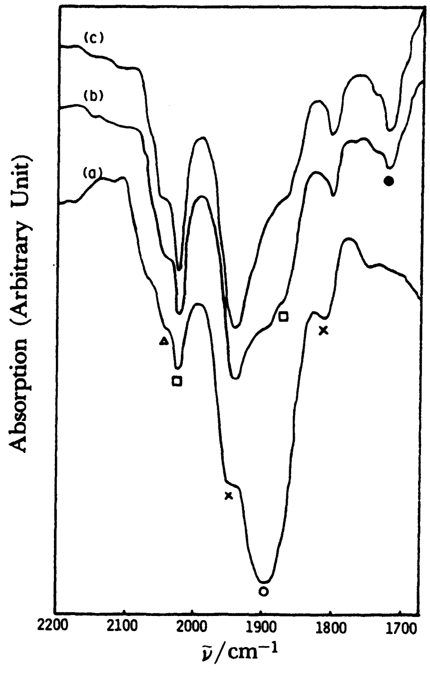

Fig. 6. IR spectra of $[CO_2(CO)_8]$ with benzyl bromide under high pressure of syngas in benzyl alcohol-$H_2O$-1,4-dioxane (50:1:0.5 volume ratio). Conditions: benzyl bromide, 0.04 M (bromide/Co=0.5). Peaks ascribed to ○: $[Co(CO)_4]^-$, □: $[Co_2(CO)_8]$, △: $[CoH(CO)_4]$, ●: phenylacetaldehyde, ×: benzyl alcohol. Spectra were observed under (a) 120 kg cm$^{-2}$ ($H_2$/CO=2/1) at 25 °C, (b) 125 kg cm$^{-2}$ at 100 °C and (c) 127 kg cm$^{-2}$ at 120 °C.

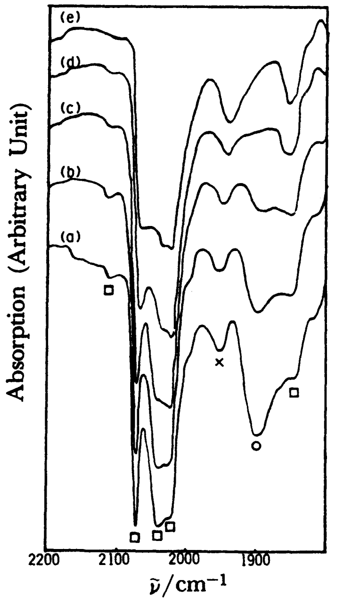

Fig. 7. IR spectra of $[CO_2(CO)_8]$ under high pressure of CO. Conditions: solvent: benzyl alcohol-$H_2O$-1,4-dioxane. Peaks ascribed to ○: $[Co(CO)_4]^-$, □: $[Co_2(CO)_8]$, ×: benzyl alcohol. Spectra were observed under (a) 30 kg cm$^{-2}$ of CO at 25 °C, (b) 32 kg cm$^{-2}$ at 50 °C, (c) 33 kg cm$^{-2}$ at 70 °C, (d) 34 kg cm$^{-2}$ at 100 °C and (e) 35 kg cm$^{-2}$ at 120 °C.

because the yield of toluene increases, although very little, with decreasing partial pressure of $H_2$ (Runs 3 and 4 in Table 4).

**In Situ IR Observation.** The respective infrared spectral changes of $[Co_2(CO)_8]$ and $RuCl_3$ as catalyst precursors were followed under high pressure of syngas ($H_2$/CO=2/1) from room temperature (25 °C) to optimum reaction temperature (120 °C). Typical spectra are shown in Figs. 5—7. Figure 5 illustrates that, at 120 °C, the characteristic absorption of $[Co(CO)_4]^-$, **5**, at 1890 cm$^{-1}$ 10) is not observed without adding water (Fig. 5-(a)) but observed with adding water (Fig. 5-(b)), with the characteristic bands of $[Co_2(CO)_8]$, **6**, (2105, 2068, 2024, and 1860 cm$^{-1}$)11) and those of $[CoH(CO)_4]$, **7**, (2053 and 2030 cm$^{-1}$).11) When benzyl bromide and water were added to this system, the absorption of **5** diminished as temperature was raised (Figs. 6-(a) and (b)) and ultimately disappeared at 120 °C (Fig. 6-(c)). On the other hand, the absorption of phenylacetaldehyde (at 1700 cm$^{-1}$) increased (Fig. 6-(a) to (c)). This result indicates that **5** is active species for the homologation as reported previously.5)

It is known that $[Co_2(CO)_8]$ reacts with water to afford **5** and Co(II) ion by disproportionation (Eq. 19).12) This disproportionation occurred at low temperature (25—75 °C, Figs. 7-(a) to (c)) but did not at high temperature (100—120 °C, Figs. 7-(d) and (e)). From above results, under the homologation conditions, **5** is deduced to be formed by the dissociation of **7** (Eq. 13), that is, the addition of water causes the large dissociation of **7** to produce **5**. Hence, the homologation is accelerated and formation of toluene is suppressed.

$$3[Co_2(CO)_8] + 12H_2O \rightleftharpoons 2\{[Co(H_2O)_6]^{2+}[Co(CO)_4]_2^-\} + 8CO \qquad (19)$$

It was found from in situ IR observation that

$RuCl_3$ was converted into dichlorodicarbonylruthenium (absorption bands: 2150, 2070, and 2030 $cm^{-1}$)[13] without adding hydrobromic acid and into dibromodicarbonylruthenium (absorption bands: 2135 and 2165 $cm^{-1}$)[13] with adding it (HBr/Ru=2) at 120 °C under syngas pressure. Although the number of bromide coordinating to ruthenium is obscure under the homologation conditions, bromoruthenium complex is more active for the hydrogenation of 2-phenylacetaldehyde than chlororuthenium complex (see Fig. 4). When ruthenium is added in excess to the homologation system, the concentration of bromide (HBr or $C_6H_5CH_2Br$) significantly decreases by the coordination to ruthenium and consequently the rate of phenylacetaldehyde formation promoted by bromide is retarded.

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