# Homologation of Methyl Esters Catalyzed by Ruthenium-Cobalt Bimetallic Systems[1)]

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(Received July 8, 1982)

**Synopsis.** Reactions of methyl esters such as methyl acetate with synthesis gas have been investigated by use of the mixed clusters such as $[Et_4N][RuCo_3(CO)_{12}]$ and $[Et_4N][Ru_3Co(CO)_{13}]$ or a combination of $Ru(acac)_3$ and $Co_2(CO)_8$ as catalyst and methyl iodide as promoter. In the homologation of methyl acetate, the catalytic activity for formation of ethyl acetate was much improved when both ruthenium and cobalt existed in the reaction system.

Mixed transition metal clusters have recently attracted much attention since the compounds might be used as unique homogeneous catalysts or precursors to well defined bimetallic or multimetallic heterogeneous catalysts.[2)] In a previous paper[3)] we reported that both a combination system of $RuCl_3 \cdot 3H_2O$ and $Co_2(CO)_8$ with the Ru/Co ratio of about 1/3 and the mixed clusters containing the $[RuCo_3(CO)_{12}]^-$ moiety show a more remarkable catalytic activity for methanol homologation. We wish here to describe that the similar bimetallic catalysts are also effective for the homologation of methyl esters, especially methyl acetate.

Recently Braca *et al.*,[4)] repoted that methyl esters such as methyl acetate and propionate were homologated to the corresponding ethyl esters with $Ru(acac)_3$ as catalyst and methyl iodide as promoter (Eq. 1). For example, the reaction of methyl acetate with synthesis

$$CH_3COOCH_3 + CO + 2H_2 \longrightarrow CH_3COOC_2H_5 + H_2O \tag{1}$$

gas ($CO/H_2=4.5$; initial pressure at room temperature, 165 kg/cm$^2$) at 200 °C gave 73% conversion of methyl acetate into ethyl acetate with the selectivity of 28% after 76 h.[4b)] More recently, Jenner *et al.*,[5)] reported the homologation of methyl acetate catalyzed by group VIII metals and their various binary combinations. We have here independently investigated the similar type of reaction with ruthenium–cobalt bimetallic catalysts.[6)]

## Results and Discussion

The results are shown in Table 1. When $Ru(acac)_3$ was used as catalyst, ethyl acetate was formed in 16% yield based upon methyl acetate initially added, together with acetic acid in 11% yield (Run 1). On the other hand, $Co_2(CO)_8$ gave ethyl acetate in 11% yield as well as acetaldehyde and acetic acid in moderate yields (Run 8). The combination of these two kinds of compounds or ruthenium–cobalt mixed clusters such as $[Et_4N][RuCo_3(CO)_{12}]$ and $[Et_4N][Ru_3Co(CO)_{13}]$ where the total amount of metals was kept constant (0.4 mg atom) increased the catalytic activity for formation of ethyl acetate; the yield of ethyl acetate was about twice as much as that with $Ru(acac)_3$ alone and three times as much as that with $Co_2(CO)_8$ alone, although acetic acid was formed in *ca.* 20—30% yield. Both the yield and selectivity of ethyl acetate were not so much affected by the ratio of cobalt to ruthenium as in the case of the homologation of methanol.[3)] However it is of interest to note that the cluster $[Et_4N][Ru_3Co(CO)_{13}]$ gave the best yield of ethyl acetate among the catalysts shown in Table 1. As the ratio of carbon monoxide to hydrogen was increased, formation of ethyl acetate and acetic acid was promoted (Runs 9, 10, and 11). Methyl propionate was also transformed into ethyl propionate (8.7% yield) and propionic acid (15.5% yield) under the same reaction conditions with the cluster $[Et_4N][RuCo_3(CO)_{12}]$ as catalyst.

The reaction mechanism is at present not clear. It is known that catalysts based on Ni, Co,[7—8)] or Rh[9)] compounds can convert methyl acetate into acetic

Table 1. Homologation of methyl acetate with Ru–Co bimetallic catalysts[a)]

| Run | Catalyst[b)] | Co/Ru | $CO/H_2$[c)] (kg/cm$^2$) | Conversion/% | Yields[d)] of products[e)]/% | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | AcH | AcOEt | EtOH | AcOH | Ethers[f)] |
| 1 | $Ru(acac)_3$ | — | 60/60 | 33.2 | tr. | 15.5 | 3.8 | 11.0 | 12.0 |
| 2 | $Ru(acac)_3+Co_2(CO)_8$ | 0.21 | 60/60 | 48.8 | tr. | 20.4 | 5.5 | 11.9 | 12.0 |
| 3 | $Ru(acac)_3+Co_2(CO)_8$ | 0.35 | 60/60 | 51.6 | 0.5 | 24.4 | 7.4 | 19.7 | 15.8 |
| 4 | $Ru(acac)_3+Co_2(CO)_8$ | 1.09 | 60/60 | 68.3 | 1.2 | 27.8 | 8.6 | 29.2 | 13.3 |
| 5 | $Ru(acac)_3+Co_2(CO)_8$ | 2.08 | 60/60 | 63.3 | 2.4 | 27.6 | 6.8 | 22.9 | 12.1 |
| 6 | $Ru(acac)_3+Co_2(CO)_8$ | 3.14 | 60/60 | 49.0 | 1.2 | 24.1 | 9.2 | 22.1 | 8.1 |
| 7 | $Ru(acac)_3+Co_2(CO)_8$ | 5.01 | 60/60 | 50.3 | 4.3 | 28.1 | 10.8 | 22.4 | 15.1 |
| 8 | $Co_2(CO)_8$ | — | 60/60 | 33.1 | 18.4 | 10.9 | 1.6 | 25.3 | 1.3 |
| 9 | $[Et_4N][RuCo_3(CO)_{12}]$ | 3.00 | 40/75 | 60.2 | tr. | 20.3 | 7.6 | 19.3 | 8.0 |
| 10 | $[Et_4N][RuCo_3(CO)_{12}]$ | 3.00 | 60/60 | 52.0 | tr. | 21.2 | 8.5 | 22.1 | 7.1 |
| 11 | $[Et_4N][RuCo_3(CO)_{12}]$ | 3.00 | 73/49 | 65.2 | tr. | 30.1 | 9.0 | 29.6 | 9.1 |
| 12 | $[Et_4N][Ru_3Co(CO)_{13}]$ | 0.33 | 60/60 | 68.9 | 0.9 | 33.1 | 9.6 | 26.0 | 15.9 |

a) Methyl acetate 125 mmol, methyl iodide as promoter 3—5 mmol, benzene as internal standard 5 mmol, 180 °C, 18 h. b) The total amount of metals was 0.4 mg atom. c) Initial pressure at room temperature. d) Yield of the product was calculated as follows; [product (mmol)/AcOMe charged (mmol)] × 100. e) $CH_4$ was formed in *ca.* 5—10% yield in every reactions. f) Yield of ethers was calculated by [$Me_2O$ (mmol)+MeOEt (mmol)+E t$_2$O(mmol)/AcOMe charged (mmol)] ×2×100.

anhydride under a high pressure of carbon monoxide and the anhydride is transformed into ethyl acetate and acetic acid under a pressure of hydrogen with $H_4Ru_4(CO)_8(PBu_3)_4$ as catalyst.[10] Thus, one possible mechanism for the homologation of methyl acetate is a combination of the above two types of reactions. Investigation of the product distribution showed that the total amount of acetyl groups (AcOMe%+AcOEt%+AcOH%) was in the range of 90—110% while that of methyl groups (AcOMe%+AcOEt%+EtOH%+$CH_4$%+ethers%) lay between 90% and 110%. This fact may exclude the above mechanism. A possible reaction mechanism compatible with the above finding is proposed below. In the first step, methyl acetate is hydrolyzed to give methanol and acetic acid (Eq. 2). A trace amount of water involved in methyl acetate may initiate the first reaction. The methanol is then converted into ethanol *via* the homologation reaction (Eq. 3) followed by condensation of ethanol with acetic acid to give ethyl acetate (Eq. 4).

$$CH_3COOCH_3 + H_2O \longrightarrow CH_3COOH + CH_3OH \quad (2)$$

$$CH_3OH + CO + 2H_2 \longrightarrow C_2H_5OH + H_2O \quad (3)$$

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O \quad (4)$$

## Experimental

*Materials.* Methyl acetate and benzene were purified by the conventional methods and distilled under nitrogen atmosphere. The compounds $RuCl_3 \cdot 3H_2O$, $[Et_4N]Cl$, and $Co_2(CO)_8$ were commercially obtained and used without further purification. The compounds $Ru(acac)_3$,[11] $NaCo(CO)_4$,[12] and $[Et_4N][Ru_3Co(CO)_{13}]$[13] were prepared by the published methods. The mixed metal cluster $[Et_4N][RuCo_3(CO)_{12}]$[3] was prepared with $RuCl_3 \cdot 3H_2O$ and $NaCo(CO)_4$ followed by the cation exchange with $[Et_4N]Cl$ in a aqueous solution.

*General Procedures.* A 100 ml stainless-steel autoclave was used as a reactor. In a typical run, $[Et_4N][RuCo_3(CO)_{12}]$ (0.10 mmol), methyl acetate (125 mmol), methyl iodide (3—5 mmol) as a promoter, and benzene (5 mmol) as initial standard were placed into the reactor under nitrogen atmosphere. The reactor was then pressurized to 120 kg/cm$^2$ with $CO/H_2$ in a typical run, 1/1) at room temperature, and heated up to 180 °C within 30 min. The reaction was allowed to proceed at that temperature for 17.5 h and then the autoclave was cooled to room temperature within 1 h. The gas phase and the reaction solution were immediately analyzed by gas chromatography.

*Analysis.* Analysis of the off-gas was carried out by using gas chromatography with a 2 m column of Porapak Q (100 °C, 20 ml/min He). Liquid products were quantitatively analyzed by gas chromatography equipped with a flame ionization detector using a 3 m column of PEG20M (the oven temperature was elevated at the ratio of 5 °C/min from 70 °C; $N_2$ 30 ml/min).

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