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The Effect of a Solvent on the Carbonylation of Methanol Catalyzed by Rhodium Complexes in the Presence of Methyl Iodide

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In the synthesis of acetic acid by the carbonylation of methanol catalyzed by $RhCl_3 \cdot 3H_2O$ or $Rh_2Cl_2(CO)_4$ in the presence of methyl iodide, it was found that ketone solvents, such as acetophenone and benzophenone, keep both the catalytic activity and selectivity high, even at an elevated temperature. The kinetic results in acetophenone are in agreement with the mechanism proposed by Paulik and Roth.[11] The effect of the ketone solvent was discussed by taking account of the competitive oxidative addition of hydrogen iodide with methyl iodide.

The oxidative addition of aryl iodide to nickel(0),[1,2] palladium(0),[3–8] and rhodium(I)[9,10] has been shown to play an important role in the catalytic carbonylation and arylation of olefin. It has been reported that, in the carbonylation of iodobenzene catalyzed by palladium-black in a basic medium to give methyl benzoate, the oxidative addition of iodobenzene to a palladium(0) complex is the rate-determining step, a step which is considerably influenced by ligands weakly bonded to the palladium complex.[4] Recently the oxidative addition of methyl iodide was demonstrated to be the rate determining step in the carbonylation of methanol catalyzed by rhodium compounds in liquid[11,12,16] and gas-phase reactions.[13–15] In this methanol carbonylation, the effect of ligands (including solvents) should also be reflected in its rate, as may be seen in the palladium-catalyzed carbonylation of iodobenzene. It was observed, however, that, when methanol was used as the solvent, the selectivity was very low (<20%) because of the formation of dimethyl ether in considerable amounts. The formation of dimethyl ether made it very difficult to elucidate the kinetic results. Thus, we examined the effects of the solvents in increasing the selectivity, and found that both the rate and the selectivity are highest in a ketone solvent, such as acetophenone or benzophenone.

During the preparation of this paper, a kinetic study of the carbonylation of methanol in an acetic acid solvent was reported,[16] and it was also noticed that much dimethyl ether was formed on initiating the carbonylation in a pure methanol solvent. The effect of solvents, however, was not described.

The purpose of this work is to investigate the effect of the solvent on the rate and selectivity of the rhodium complex-catalyzed carbonylation of methanol in the presence of methyl iodide and to discuss the role of solvents.

Experimental

Materials. Dichlorotetracarbonyldirhodium(I), $Rh_2Cl_2(CO)_4$, was prepared from $RhCl_3 \cdot 3H_2O$ and carbon monoxide according to the literature[17] (Found: C, 11.2; Cl, 18.8%. Calcd: C, 12.4; Cl, 18.2%.). $RhCl_3 \cdot 3H_2O$ (Koso Chemical Co., Ltd,), carbon monoxide (>98%), methanol (>99%), methyl iodide (Tokyo Kasei's extra pure grade), and all the solvents used in this work were obtained from commercial sources. The solvents listed in Table 1 were checked by gas chromatography before use, and were used without purification.

Procedure. All the carbonylations were carried out using a Ti–Mn alloy autoclave (100 ml) equipped with a magnetic stirrer. A given amount of $RhCl_3 \cdot 3H_2O$ or $Rh_2Cl_2(CO)_4$ (0.125—1.00 mmol) and a mixture of methyl iodide (5—20 mmol), methanol (50—250 mmol) and a solvent (20 ml) were placed in the autoclave. Carbon monoxide was then introduced up to the desired pressure (7—90 kg/cm^2). Subsequently the autoclave was heated up to a reaction temperature within 15—20 min, the temperature and the pressure being kept constant for 1—4 h. The autoclave was then cooled rapidly to room temperature with water, and the carbon monoxide was purged out. The product solution was analyzed by gas chromatography. The reaction rate was measured as follows. A rhodium catalyst and a solution were placed in the autoclave, and it was heated up to a reaction temperature before introducing carbon monoxide. The carbonylation was initiated by introducing carbon monoxide. The pressure was kept constant during the reaction by supplying carbon monoxide from a high-pressure gas reservoir (100 ml). The amount of carbon monoxide consumed was measured by means of the pressure decrease in the gas reservoir.

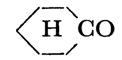
Analysis. The product solutions were quantitatively analyzed by means of gas chromatography. A glass column (3 mmϕ, 3 m, carrier gas of H_2) of diethylene glycol succinate polyester on Celite was used at 100—200 °C for carboxylic acids with an internal standard substance (C_6H_5Br or 1-$C_{10}H_7Br$). For the determination of the methyl acetate, methanol, and methyl iodide, a copper column (3 mmϕ, 3 m, carrier gas of H_2) of 3,3′-oxy-dipropionitrile on an insulating brick was used at 70 °C with dibutyl ether as the internal standard substance.

Results and Discussion

Effect of Solvents. The carbonylation of methanol catalyzed by $RhCl_3 \cdot 3H_2O$ and methyl iodide was examined in various solvents under the same reaction conditions. The results are summarized in Table 1. The use of the solvents with a carbonyl group improved the yield and selectivity of the carbonylation of methanol. The yield and selectivity of more than 100% in the methyl benzoate solvent seemed to be caused by the hydrolysis of methyl benzoate or by its ester exchange with acetic acid. This idea was supported by the detection of benzoic acid in the reaction product.[25] The methyl iodide was restored almost completely after the carbonylation except in the case of the *N,N*-dimethylacetamide solvent. Acetophenone was employed to show the effectiveness of the ketone solvents in Table 2. The addition of acetophenone significantly increases

Table 1. Effect of solvent

CH_3OH 50 mmol, CH_3I 20 mmol, Solvent 20 ml, $RhCl_3 \cdot 3H_2O$ 0.5 mmol, P_{CO} 20 kg/cm² (at room temp), temp 140 °C, and time 90 min.

Solvent	Yield[a) (%)]	Select.[b) (%)]	Resid. CH_3I (mmol)
$C_6H_5COOCH_3$	109	177	19
	82	90	19
$CH_3COC_2H_5$	81	94	17
$C_6H_5COCH_3$	80	96	19
$C_2H_5COC_2H_5$	71	93	16
$C_6H_5OCH_3$	58	98	18
C_6H_5CN	50	99	18
C_6H_5Cl	49	99	19
DMA	32	51	8.9
$C_6H_5CH_3$	31	81	20
n-C_6H_{14}	16	26	16
$C_6H_5NO_2$	2.0	9.5	17

a) $\text{Yield}(\%) = \dfrac{[AcOH]+[AcOCH_3]}{[CH_3OH]_{init.}} \times 100,$

b) $\text{Selet.}(\%) = \dfrac{([AcOH]+[AcOCH_3]) \times 100}{[CH_3OH]_{init.} - [CH_3OH]_{resid.} - [AcOCH_3]}$

(AcO = CH_3COO, DMA = N,N-dimethylacetamide).

Table 2. Effects of acetophenone

CH_3I 10 mmol, $RhCl_3 \cdot 3H_2O$ 0.25 mmol, P_{CO} 30 kg/cm² (at room temp), temp 173 °C, and time 60 min.

CH_3OH (ml)	$C_6H_5COCH_3$ (ml)	Total AcOH[a)] (mmol)	Select.[b)] (%)	$(CH_3)_2O$[c)] (mmol)
25	0	42	13	140
20	5	68	37	60
15	10	69	43	48
10	15	76	65	23
5	20	71	83	6.6

a) Total AcOH = AcOH + $AcOCH_3$. b) Defined in Table 1. c) The amount of $(CH_3)_2O$ formed was calculated as follow: $(CH_3)_2O = 1/2 \times ([CH_3OH]_{init.} - [AcOH] - 2[AcOCH_3] - [CH_3OH]_{resid.})$.

the amount of total acetic acid, retarding the formation of dimethyl ether, at a smaller volume ratio of methanol to acetophenone. The effect of acetophenone on the rate of carbonylation at 156 °C is shown in Fig. 1; anisole or toluene was added to keep the concentrations of the methyl iodide, the rhodium catalyst, and the methanol constant. In both cases, the rates effectively increase with an increase in the volume ratio of acetophenone added and reach a constant rate (138 mmol/h) above the ratio of 1. In no runs was any metallic substance detected in the product solutions.

A kinetic study of the carbonylation was undertaken in the acetophenone solvent. The amounts of carbon monoxide absorbed during the reaction are plotted against the time at various amounts of the rhodium catalyst and methyl iodide under 30 kg/cm² of carbon monoxide at 112 °C in Figs. 2 and 3. The total consumption of carbon monoxide almost corresponded to the amount of total acetic acid produced in each run. Accordingly, the rates of carbonylation are independent of the feed of methanol. The rate is first order with respect to the amount of methyl iodide, and also with respect to that of the rhodium catalyst. The rate was also independent of the pressure of carbon monoxide (10—90 kg/cm²). These kinetic relations were independently confirmed in the higher-temperature range.

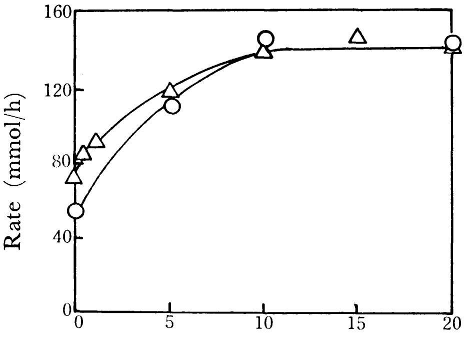


Fig. 1. Effect of acetophenone.

CH_3OH 125 mmol, CH_3I 20 mmol, $RhCl_3 \cdot 3H_2O$ 0.5 mmol, Total volume of solvent 20 ml, P_{CO} 30 kg/cm² (at 156 °C), and temp 156 °C.

△ In anisole-acetophenone and ○ in toluene-acetophenone.

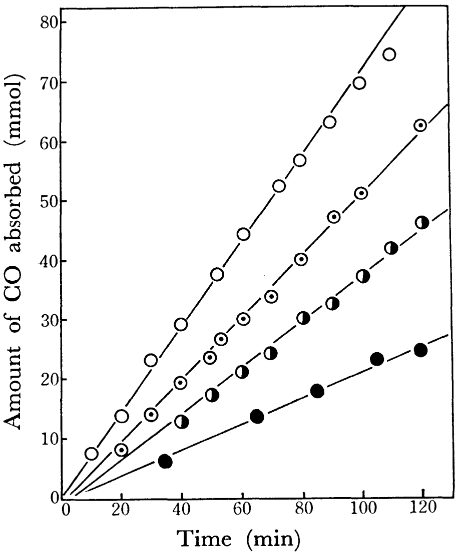


Fig. 2. Effect of the amount of $RhCl_3 \cdot 3H_2O$ on the rate.

CH_3OH 125 mmol, CH_3I 40 mmol, acetophenone 20 ml, P_{CO} 30 kg/cm² (at 112 °C), and temp 112 °C. $RhCl_3 \cdot 3H_2O$: ● 0.25 mmol, ◑ 0.50 mmol, ⊙ 0.75 mmol, and ○ 1.00 mmol.

Effect of Temperature. The effect of the temperature was examined in stable solvents, such as acetophenone, benzophenone, anisole, and toluene (Figs. 4 and 5). Benzonitrile and chlorobenzene, which gave a high selectivity at 140 °C, as is shown in Table 1, were not investigated in detail, since the hydrogenolysis of benzonitrile and the oxidative addition of chlorobenzene seemed to interfere with the carbonylation of methanol at higher temperatures. In the toluene sol-

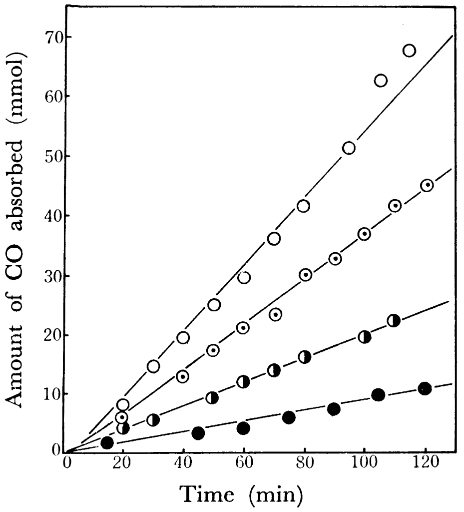


Fig. 3. Effect of the amount of CH_3I on the rate.
CH_3OH 125 mmol, $RhCl_3\cdot3H_2O$ 0.5 mmol, acetophenone 20 ml, P_{CO} 30 kg/cm^2 (at 112 °C), and temp 112 °C. CH_3I: ● 10 mmol, ◑ 20 mmol, ⊙ 40 mmol, and ○ 60 mmol.

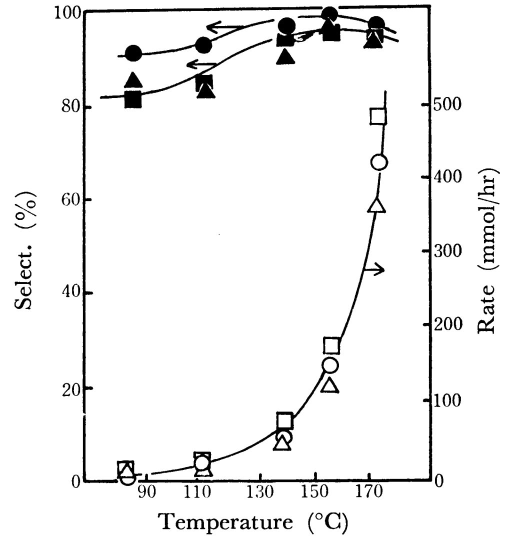


Fig. 4. Effect of temperature in acetophenone or benzophenone.
CH_3OH 125 mmol, CH_3I 20 mmol, $RhCl_3\cdot3H_2O$ 0.5 mmol or $Rh_2Cl_2(CO)_4$ 0.25 mmol, solvent 20 ml, P_{CO} 30 kg/cm^2 (at react temp), and time 120 min.
□ and ■: in benzophenone with $RhCl_3\cdot3H_2O$,
○ and ●: in acetophenone with $RhCl_3\cdot3H_2O$,
△ and ▲: In acetophenone with $Rh_2Cl_2(CO)_4$.

vent, the selectivity is very low because of the formation of dimethyl ether in considerable amounts. At 173 °C, the rates in the ketone solvents were 6 to 8 times larger than in anisole and 13 to 18 times larger than in toluene. There was no essential difference between $RhCl_3\cdot3H_2O$ and $Rh_2Cl_2(CO)_4$ with respect to the rate and selectivity of carbonylation, as is shown in Fig. 4. Arrhenius plots of the rates in ketone solvents gave good linearities, from which the apparent activation energy was estimated to be 19 kcal/mol (Fig. 6).

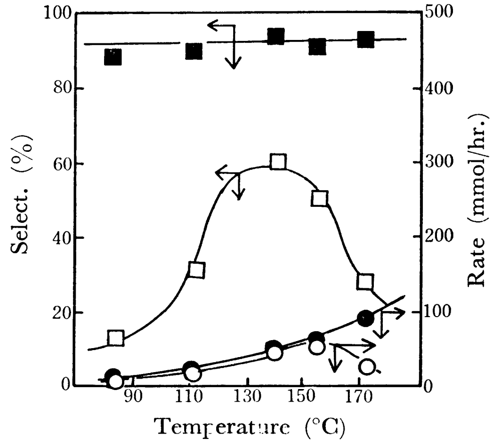


Fig. 5. Effect of temperature in toluene or anisole.
CH_3OH 125 mmol, CH_3I 20 mmol, $RhCl_3\cdot3H_2O$ 0.5 mmol, solvent 20 ml, P_{CO} 30 kg/cm^2 (at react temp), and time 120 min.
○ and □: in toluene, ● and ■: in anisole.

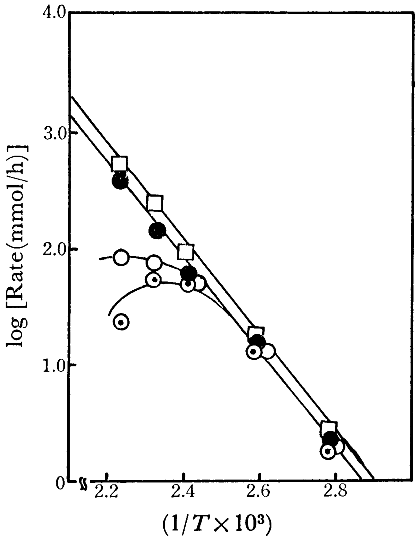


Fig. 6. Arrhenius plot of the rates with $RhCl_3\cdot3H_2O$.
□ In benzophenone, ● in acetophenone, ○ in anisole, and ⊙ in toluene.

To examine whether or not low rates in anisole or toluene at elevated temperatures were caused by an irreversible deactivation of the catalyst, the dependence of the rates on temperature was reinvestigated. The rate in anisole initially measured at 173 °C for 30 min under the conditions specified in Fig. 5 was 75±10 mmol/h. After the temperature had been lowered to 156 °C within 5 min, the rate was measured again for 45 min to give the value of 65±5 mmol/h. The temperature was, then, further lowered to 140 °C within 5 min; the rate measured for 40 min was 32±5 mmol/h. These rates were almost entirely consistent with those obtained by the separate experimental runs shown in Fig. 6, namely, 80, 67, and 40 mmol/h at 173, 156, and 140 °C respectively. The rates obtained in toluene by the same manner were 52(50), 40(38), and 15(16) mmol/h at 156, 140, and 112 °C respectively; the rates given in Fig. 6 are shown in parentheses. These results indicate that the catalytic activity is reproducible with respect to the reaction temperature. It seems most likely that there is no essential change in the mechanism, since the kinetic behavior in anisole or toluene is almost the same as in acetophenone, even at higher temperatures.

The effect of hydrogen on the methanol carbonylation was examined in the acetophenone solvent using $RhCl_3 \cdot 3H_2O$. Under a lower pressure of carbon monoxide (P_{H_2} 40 kg/cm^2, P_{CO} 10 kg/cm^2, 140 °C), acetophenone was hydrogenated to give ethylbenzene and a trace amount of styrene, while practically no hydrogenation of acetophenone was observed under a higher pressure of carbon monoxide ($P_{CO} > 20$ kg/cm^2). Neither acetaldehyde nor ethanol was detected in the product solutions in any case. The treatment of methyl iodide without methanol under 60 kg/cm^2 of a H_2–CO ($H_2/CO = 1$) mixture gave only a trace amount of acetic acid, but no acetaldehyde, and more than 80% of the methyl iodide was recovered in the product solution.

Role of the Solvent. The kinetic results suggest that the carbonylation of methanol in ketone solvents proceeds *via* a scheme similar to that proposed by Roth *et al.*12) Recently a more elaborate scheme has been reported by Forster.18) The most reasonable rate-determining step is the oxidative addition of methyl iodide to the rhodium(I) complex, assuming that the equilibrium between methyl iodide and hydrogen iodide ($CH_3OH + HI \rightarrow CH_3I + H_2O$) is much shifted to the formation of methyl iodide during the carbonylation. Figure 6 shows that the rates at lower temperatures (<140 °C) are almost the same in any solvent examined, indicating no essential role of solvent molecules as ligands.19) Accordingly, the active species in ketone solvents is probably the same as that observed by Forster during a catalytic carbonylation of methanol in a heptanoic acid solvent, using $RhCl_3 \cdot 3H_2O$ as the catalyst precursor.18) The reaction scheme with this species is illustrated.20) It was reported that the oxidative addition of alkyl halide to a rhodium(I) complex such as $RhCl(CO)(PPh_3)_2$ and $RhCl(CO)_2(PPh_3)$ proceeds *via* electrophilic attack of alkyl halide.22–24) Since hydrogen iodide is less crowded and more electrophilic, a small amount of hydrogen iodide in the solution should be competitive with the methyl iodide for the oxidative addition. The equilibrium concentration of hydrogen iodide should increase with elevating the temperature, because the formation of methyl iodide is exothermic. In ketone solvents, hydrogen iodide may be effectively solvated so as to prevent its oxidative addition to the rhodium(I) complex.

$$[Rh(CO)_2I_2]^- \xrightarrow{CH_3I} [CH_3Rh(CO)_2I_3]^- \xrightarrow{CO}$$

$$[CH_3CORh(CO)_2I_3]^{-\,21)} \xrightarrow[-AcOCH_3 \text{ or } AcOH]{+CH_3OH \text{ or } H_2O}$$

$$[HRh(CO)_2I_3]^- \xrightarrow[+\text{Solvent-HI}]{+\text{Solvent}} [Rh(CO)_2I_2]^-$$

$$\text{Solvent-HI} + CH_3OH \rightleftharpoons CH_3I + \text{Solvent} + H_2O$$

References

1) M. Nakayama and T. Mizoroki, *Bull. Chem. Soc. Jpn.*, **42**, 1124 (1969).

2) L. Casser and M. Foa, *J. Organomet. Chem.*, **51**, 381 (1973).

3) K. Mori, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **46**, 1505 (1973).

4) T. Ito, K. Mori, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **48**, 2091 (1975).

5) R. F. Heck and J. P. Nolley, Jr., *J. Org. Chem.*, **37**, 2320 (1972).

6) A. Schoenberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).

7) A. Schoenberg, and R F. Heck, *J. Org. Chem.*, **39**, 3327 (1974).

8) H. A. Dieck and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 1133 (1974).

9) J. Tsuji and K. Ono, *J. Am. Chem. Soc.*, **90**, 99 (1968); *Tetrahedron Lett.*, **1966**, 4713.

10) K. Mori, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **49**, 758 (1976).

11) F. E. Paulik and J. F. Roth, *Chem. Commun.*, **1968**, 1578.

12) J. F. Roth, J. H. Craddock, A. Hershman, and F. E. Paulik, *Chemtech*, **1971**, 600.

13) K. K. Robinson, A. Hershman, J. H. Craddock, and J. F. Roth, *J. Catal.*, **27**, 389 (1972).

14) R. G. Schultz and P. D. Montgomery, *J. Catal.*, **13**, 105 (1969).

15) A. Krzywicki and G. Pannetier, *Bull. Soc. Chem. Fr.* **1975**, 1093.

16) J. Hjortkjaer and V. W. Jensen, *Ind. Eng. Chem., Prod. Res. Dev.*, **15**, 46 (1976).

17) *Inorg. Synth.*, Vol. 8, McGraw-Hill (1966), p. 211.

18) D. Forster, *J. Am. Chem. Soc.*, **98**, 846 (1976).

19) The activation energy in acetic acid has been reported to be 14.7 kcal/mol,16) suggesting that an activated complex is in a highly polar state.

20) The counter cation may be a solvated proton.

21) Forster *et al.* prepared a dimeric anion of the rhodium acetyl complex $[CH_3CORh(CO)I_3]_2^{2-}$, which is held together by Rh–I–Rh bridges.18)

22) I. C. Douck and G. Wilkinson, *J. Chem. Soc., A*, **1969**, 2604.

23) P. Uguagliati, A. Palazzi, G. Deganello, and U. Belluco, *Inorg. Chem.*, **9**, 724 (1970).

24) A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **9**, 2685 (1970); **10**, 1653 (1970).

25) The product solution contained AcOH (35.5 mmol), $AcOCH_3$ (19.2 mmol), C_6H_5COOH (19.5 mmol), and no methanol, indicating that 20—24 mmol of methyl benzoate were consumed during the carbonylation to give benzoic acid.