

Further Study of Methanol Carbonylation Catalyzed by Cobalt, Rhodium, and Iridium Catalysts

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The effect of iodide ion was examined in methanol carbonylation with use of Co-, Rh-, and Ir-catalysts. Sodium iodide gives no noticeable effect on carbonylation catalyzed by Rh-catalyst to give acetic acid, and retards that catalyzed by Ir-catalyst. Methyl iodide is effective for methanol carbonylation with Co-catalyst in the presence of hydrogen to give mainly acetaldehyde, which is readily hydrogenated to ethanol during the course of carbonylation on addition of a catalytic amount of $\text{Ru}_3(\text{CO})_{12}$. Sodium iodide is also effective for acetaldehyde formation, although it strongly retards the hydrogenation of acetaldehyde with Ru-catalyst. The different effect of iodide ion on methanol carbonylation catalyzed by Co-, Rh-, or Ir-catalyst is discussed in terms of nucleophilicity of the active catalyst species.

Methyl iodide is known as an efficient promoter for methanol carbonylation with Co-, Rh-, or Ir-catalyst. A reaction scheme involving an oxidative addition of methyl iodide has been accepted in Rh- or Ir-catalyzed carbonylation.¹⁾ It has been pointed out that the presence of iodide ion promotes the oxidative addition of methyl iodide to rhodium(I) complexes.²⁾ The rate of methanol carbonylation with Co-catalyst increases with addition of iodide ion,³⁾ although no detailed discussion has been made on the role of iodide ion. It has not been clarified why Co-catalyst gives preferentially acetaldehyde when methanol carbonylation is performed in the presence of hydrogen,⁴⁾ while all attempts for acetaldehyde formation were unsuccessful with the use of Rh- or Ir-catalyst.

The present work was undertaken to elucidate the effect of iodide ion on methanol carbonylation as well as the significance of Co-catalyst in the acetaldehyde formation.

Experimental

Carbonylation was carried out according to the procedure described in a previous paper.⁵⁾ $\text{Co}_2(\text{CO})_8$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and $\text{IrCl}_4 \cdot \text{H}_2\text{O}$ were used as catalyst precursors. $\text{Co}_2(\text{CO})_8$ was prepared by reduction of cobalt carbonate suspended in toluene with a synthesis gas ($\text{CO}/\text{H}_2=1$, 150 kg/cm²) at 170 °C. Methyl iodide (extra pure grade, Tokyo Kasei), $\text{Ru}_3(\text{CO})_{12}$ (Strem Chemicals) and all the other materials were commercial products and used without purification. Acetophenone has been found to be useful solvent for preventing the formation of dimethyl ether during the course of Rh- or Ir-catalyzed methanol carbonylation.⁵⁾ However, it was readily hydrogenated to give 1-phenylethanol and ethylbenzene during the course of carbonylation when a mixture of carbon monoxide and hydrogen was used. Thus, methyl benzoate was used as the solvent in the present work. It was also partially transformed into benzoic acid during the carbonylation. The amount of benzoic acid formed was taken into account to evaluate the methyl-balance of product solutions.

The product solutions were analyzed by means of gas chromatography (carrier gas of He). A glass column of Diethylene Glycol Succinate Polyester (3 mm ϕ , 3 m) was used at 100—200 °C for carboxylic acids, and two copper columns of 3,3'-oxydipropionitrile (3 mm ϕ , 5 m) and PEG-400 (3 mm ϕ , 3 m) were separately used at 70 °C for acetaldehyde, methyl

iodide, acetaldehyde dimethyl acetal, methyl acetate, ethyl acetate, methanol, and ethanol. Methane in gaseous products was also analyzed by gas chromatography using a copper column of VZ-7 (3 mm ϕ , 3m) at room temperature.

Results and Discussion

Carbonylation with $\text{Co}_2(\text{CO})_8$. The carbonylation of methanol (125 mmol) with $\text{Co}_2(\text{CO})_8$ (1 mmol) in the presence of methyl iodide (10 mmol) was carried out in methyl benzoate (20 ml) at 173 °C under 30—75 kg/cm² of carbon monoxide (CO 98%) for 3 h, giving practically no acetic acid. Under the same reaction conditions, both Rh- and Ir-catalysts almost quantitatively converted methanol into acetic acid (115 mmol, 90% yield) within a shorter reaction period (0.5 h). When a mixture of carbon monoxide and hydrogen (100 kg/cm², $\text{CO}/\text{H}_2=1$) was used for the $\text{Co}_2(\text{CO})_8$ -catalyzed carbonylation of methanol under similar conditions, appreciable amounts of C_2 -oxygenated compounds such as methyl acetate, acetaldehyde and ethanol were obtained. The results are shown in Fig. 1. Analytical results of product solutions are represented by S_1 , S_2 , and M with the following definitions.

$$\text{total AcOH (mmol)} = [\text{AcOH}] + [\text{AcOMe}] + [\text{AcOEt}]$$

$$\text{total AcH (mmol)} = [\text{AcH}] + [\text{DMA}]$$

$$(\text{DMA} = \text{acetaldehyde dimethyl acetal})$$

$$\text{total EtOH (mmol)} = [\text{EtOH}] + [\text{AcOEt}]$$

$$\text{total } \text{C}_2 \text{ (mmol)} = [\text{total AcOH}] + [\text{total AcH}] \\ + [\text{total EtOH}]$$

$$S_1 (\%) = 100 \times \{([\text{total AcH}] + [\text{total EtOH}]) / [\text{total } \text{C}_2]\}$$

$$M (\%) = 100 \times \{([\text{AcOH}] + [\text{EtOH}] + 2[\text{AcOEt}] \\ + 2[\text{AcOMe}] + 3[\text{DMA}] + [\text{CH}_3\text{I}] + [\text{CH}_3\text{OH}]) / \\ ([\text{CH}_3\text{OH}]_0 + [\text{CH}_3\text{I}]_0 + [\text{PhCO}_2\text{H}])\}$$

$$S_2 (\%) = 100 \times [\text{total EtOH}] / [\text{total } \text{C}_2]$$

S_1 and S_2 are the selectivities to total C_2 -oxygenated products and ethanol respectively, and M is the percent methylbalance, where $[\text{CH}_3\text{OH}]_0$ and $[\text{CH}_3\text{I}]_0$ are molar amounts of methanol and methyl iodide initially charged. The amount of methyl group introduced from methyl benzoate during the course of carbonylation is evaluated from the amount of benzoic acid, $[\text{PhCO}_2\text{H}]$,

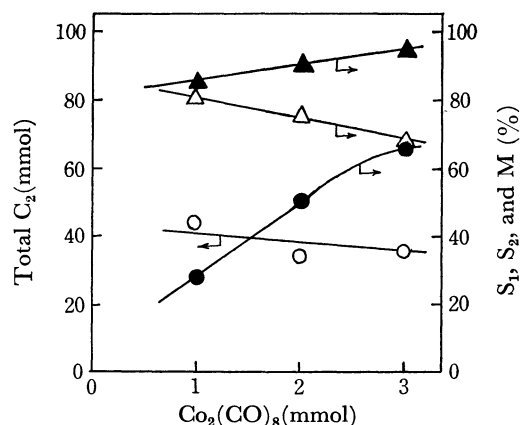


Fig. 1. Effect of the amount of $\text{Co}_2(\text{CO})_8$ on methanol homologation in methyl benzoate solvent.

Total C_2 (mmol)-○, S_2 (%)—●, M (%)—△, and S_1 (%)—▲.

remaining in the product solutions. A low methyl-balance indicates an increase in dimethyl ether and methane formed, since neither C_3 nor C_4 -compounds were detected in product solutions. Figure 1 shows that the selectivity to ethyl alcohol (S_2) increases with increase in the amount of $\text{Co}_2(\text{CO})_8$, despite no increase in total C_2 -compounds, suggesting that the Co-catalyst mostly works as a hydrogenation catalyst for the acetaldehyde formed. In fact, $\text{Co}_2(\text{CO})_8$ and its tertiaryphosphine derivatives are known to be active for the hydrogenation of aldehydes under oxo reaction conditions,⁶⁾ where the active species is the hydridocarbonyl.

A rapid hydrogenation of the acetaldehyde formed is desirable in order to examine the effects of methyl iodide and iodide ion on the methanol carbonylation to give acetaldehyde, otherwise the acetaldehyde is readily transformed into dimethyl acetal, resulting in consumption of 3 mol of methanol for a dimethylacetal formation ($2\text{CH}_3\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH}(\text{OCH}_3)_2 + \text{H}_2\text{O}$). Since the hydrogenation catalyst should work in the presence of carbon monoxide, some carbonyl compounds were examined. It was found that $\text{Ru}_3(\text{CO})_{12}$ is much more efficient for the hydrogenation of acetaldehyde than $\text{Co}_2(\text{CO})_8$ under the methanol carbonylation conditions⁷⁾ as shown in Table 1. It is apparent that the selectivity to ethanol is remarkably increased by the addition of a catalytic amount of $\text{Ru}_3(\text{CO})_{12}$. Although $\text{Ru}_3(\text{CO})_{12}$ shows a small

TABLE 1. EFFECT OF $\text{Ru}_3(\text{CO})_{12}$ ON THE HYDROGENATION OF ACETALDEHYDE FORMED CH_3OH 125 mmol, CH_3I 5 mmol, $\text{Co}_2(\text{CO})_8$ 1 mmol, PhCO_2CH_3 20 ml, press. 100 kg/cm² ($\text{CO}/\text{H}_2=1$) at room temp, temp 173 °C, and react. time 2 h.

	Run 1	Run 2	Run 3	Run 4 ^{a)}
$\text{Ru}_3(\text{CO})_{12}$ (mmol)	0	0.038	0.075	0.075
Total AcH (mmol)	30.4	17.0	4.5	0.5
(DMA mmol)	(8.8)	(2.5)	(0.9)	(tr.)
Total EtOH (mmol)	8.2	25.4	29.8	5.5
(Acetate mmol)	(tr.)	(1.0)	(0.9)	(tr.)
Total AcOH (mmol)	3.9	4.0	4.6	1.8
(Acetate mmol)	(tr.)	(tr.)	(tr.)	(tr.)
CH_3I (mmol)	2.5	3.2	3.6	4.4
Total C_2 mmol	42.5	46.4	38.9	7.8
S_1 (%)	19	55	75	71

a) Without $\text{Co}_2(\text{CO})_8$.

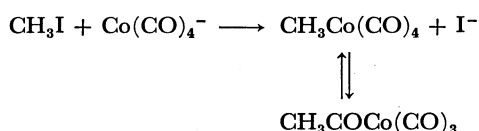
activity for methanol carbonylation (run 4), its contribution can be neglected in runs 2 and 3. The effects of methyl iodide and sodium iodide on the Co-catalyzed carbonylation were then examined in the presence of $\text{Ru}_3(\text{CO})_{12}$. The results are summarized in Table 2. The favorable effect of methyl iodide on methanol carbonylation levels off at higher concentration as shown by the change in total C_2 -compounds (runs 1—3). The increase in methyl iodide lowers the methyl-balance, presumably due to an increase in dimethyl ether formation. Sodium iodide is also effective for carbonylation without lowering the methyl-balance (runs 4—6), where small amounts of methyl iodide were detected in the product solutions. The amount of total C_2 -compounds is the largest when both methyl iodide and sodium iodide are added (runs 7 and 8). It should be noted, however, that the $\text{Ru}_3(\text{CO})_{12}$ -catalyzed hydrogenation of acetaldehyde is almost completely inhibited by the addition of sodium iodide. Since the $\text{Ru}_3(\text{CO})_{12}$ -catalyzed hydrogenation of acetaldehyde takes place in the absence of sodium iodide (runs 1—3), it can be concluded that methyl iodide supplies no appreciable amount of iodide ion during the course of Co-catalyzed methanol carbonylation, the rate of which is enhanced by both methyl iodide and iodide ion (runs 7 and 8).

In this respect, the chemical reaction of $\text{Co}_2(\text{CO})_8$, the catalyst precursor, with iodides should be referred

TABLE 2. EFFECT OF IODIDE ION ON THE $\text{Co}_2(\text{CO})_8$ - $\text{Ru}_3(\text{CO})_{12}$ CATALYZED METHANOL HOMOLOGATION CH_3OH 125 mmol, press. 100 kg/cm² ($\text{CO}/\text{H}_2=1$) at room temp, $\text{Co}_2(\text{CO})_8$ 1 mmol, $\text{Ru}_3(\text{CO})_{12}$ 0.075 mmol, PhCOOCH_3 20 ml, temp 173 °C, and time 2 h.

Run	CH_3I (mmol)	NaI (mmol)	Residual CH_3I (mmol)	Total AcH (mmol)	Total EtOH (mmol)	Total AcOH (mmol)	Total C_2 (mmol)	Methyl-balance (%)	CH_4 (mmol)
1	5	0	2.7	1.8	29.8	4.6	36	88	14.0
2	10	0	7.0	5.8	33.3	6.0	45	63	—
3	15	0	10.5	9.6	29.5	3.9	43	58	3.3
4	0	5	0.5	19.0	7.8	1.5	28	95	2.5
5	0	10	0.6	26.5	2.9	1.6	31	104	2.0
6	0	15	0.5	42.1	6.9	3.9	53	105	3.3
7	5	5	2.8	50.8	2.5	3.7	57	101	—
8	5	10	3.0	74.1	1.9	7.3	83	104	5.3

to. It is known that $\text{Co}_2(\text{CO})_8$ undergoes disproportion in polar solvents to give $\text{Co}(\text{CO})_4^-$ ($3\text{Co}_2(\text{CO})_8 + 2n\text{L} \rightarrow 2[\text{CoL}_n][\text{Co}(\text{CO})_4] + 8\text{CO}$, $\text{L}=\text{solvent}$).⁸⁾ In fact, $\text{Co}_2(\text{CO})_8$ dissolves in methyl benzoate with evolution of carbon monoxide. When sodium iodide is present in the solution, the carbon monoxide ligands of $\text{Co}(\text{CO})_4^-$ may be partly replaced by iodide ion giving rise to an increase in nucleophilicity of the complex. It is also known that methyl iodide undergoes an oxidative addition to $\text{Co}(\text{CO})_4^-$ to give $\text{CH}_3\text{Co}(\text{CO})_4$,⁹⁾ the oxidation state of which is lower than that of methyl rhodium(III) and iridium(III) complexes. The difference of oxidation state seems to constitute the main reason why cobalt catalyst behaves differently.



If the methanol carbonylation with Co-catalyst proceeds through a nucleophilic attack of the anion complex on the carbon of methyl iodide, the observed enhancement with iodide ion is reasonable. In view of the low oxidation state of the cobalt intermediate, an electrophilic oxidative addition of hydrogen would take place readily giving rise to the predominant formation of acetaldehyde.

Carbonylation with Rh- or Ir-catalysts. In the acetic acid synthesis catalyzed by Rh-complex, kinetic^{5,10)} and spectroscopic studies²⁾ have made it clear that the rate-determining step is the oxidative addition of methyl iodide to Rh(I) complex. The oxidative addition seems to take place through a nucleophilic attack of rhodium(I) species on the carbon of methyl iodide to give methyl rhodium(III) complex, which is readily transformed into the acetyl complex. Coordination of iodide ion evidently produces a highly nucleophilic rhodium(I) anion, resulting in an increase in the rate of oxidative addition of methyl iodide. The enhancement by iodide ion has been found by Forster upon addition of Bu_4NI in the oxidative addition of methyl iodide to $[\text{Rh}(\text{AsPh}_3)_2(\text{CO})\text{I}]$ or $[\text{Rh}(\text{SbPh}_3)_2(\text{CO})\text{I}]$ in dichloromethane solvent.¹¹⁾

The effect of iodide ion on the rate of Rh-catalyzed methanol carbonylation was examined by adding sodium iodide under the conditions given in Table 3 except that $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was used instead of $\text{IrCl}_4 \cdot \text{H}_2\text{O}$ as the catalyst precursor. No appreciable effect of iodide ion was found on the rate of carbonylation. The

inconsistency, however, can be understood by taking into account the fact that the predominant species during the course of the Rh-catalyzed carbonylation in the presence of an excess methyl iodide is anionic rhodium(I) complex, $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, spectroscopically verified by Forster.¹¹⁾ Thus, no appreciable enhancement was observed by the addition of sodium iodide.

On the other hand, in the acetic acid synthesis with Ir-catalyst in acetophenone solvent, the predominant species is an Ir(III) complex, acetyl iridium(III) being a plausible form with its methanolysis being rate-determining.¹²⁾ If the methanolysis proceeds *via* an electrophilic attack of the acetyl iridium(III) complex on the oxygen of methanol, replacement of the neutral ligands such as carbon monoxide and solvent molecule by iodide ion should lower the rate of methanolysis because of the decrease in the electrophilicity of iridium(III) species. Thus the effect of iodide ion on the Ir-catalyzed acetic acid synthesis was examined (Table 3). It is apparent that the addition of sodium iodide decreases the yield of acetic acid. The observed retardation of acetic acid synthesis by iodide ion is reasonably explained by the electrophilic attack of acetyl iridium(III) species on methanol being the rate-determining step as discussed in a previous paper.¹²⁾

As regards the lack of hydrogen activation by Rh- and Ir-catalysts in methanol carbonylation in spite of their high catalytic activities for olefin hydroformylation, the carbonylation of ethylene with Rh- or Ir-catalyst was carried out under methanol carbonylation conditions. The results are summarized in Table 4. Methanol carbonylation as well as ethylene hydroesterification which forms methyl propionate (propionic acid was not detected) take place (runs 1 and 2). Hydrogen, however, gives no appreciable effect on either carbonylation (runs 3 and 4), since the amounts of total acetic acid and methyl propionate are almost the same regardless of introduction of hydrogen. Hydroformylation of ethylene proceeds under the same conditions (runs 5 and 6), while it is completely suppressed by addition of methyl iodide (runs 7 and 8). The results are explained by the following simplified scheme on the assumption that the oxidative addition of methyl iodide takes place on rhodium(I) and iridium(I) complexes and that acetyl complexes of high oxidation state(III) thus formed are more rapidly attacked by methanol than hydrogen molecule. Preferential formation of methyl propionate can also be realized by an electrophilic attack of propionyl rhodium(III) and iridium(III) complexes,

TABLE 3. EFFECT OF IODIDE ION ON THE Ir-CATALYZED ACETIC ACID SYNTHESIS
 CH_3OH 125 mmol, $\text{IrCl}_4 \cdot \text{H}_2\text{O}$ 0.25 mmol, P_{CO} 30 kg/cm² at room temp, temp 173 °C, and time 2 h.

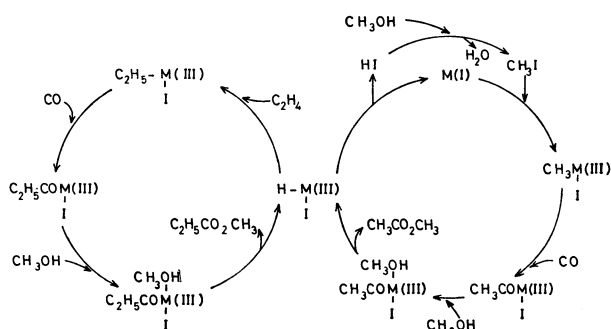
Run	CH_3I (mmol)	NaI (mmol)	Residual CH_3I (mmol)	Total AcOH (mmol)	Yield (%)
1	0.75	0	0.22	51	41
2	1.25	0	0.51	54	43
3	0	1.25	0.35	44	35
4	0	2.50	0.59	25	20
5	0.75	1.25	0.89	37	30
6	1.25	1.25	1.24	44	35

TABLE 4. CARBONYLATION OF ETHYLENE UNDER METHANOL CARBONYLATION CONDITIONS
 P_{C_2} 40 kg/cm²,^{a)} P_{CO} 20 kg/cm²,^{a)} $PhCOCH_3$ 20 ml,^{b)} temp 156 °C, and time 1 h.

Run	Catalyst (mmol)	CH ₃ I (mmol)	CH ₃ OH (mmol)	P_{H_2} ^{a)} (kg/cm ²)	Total AcOH (mmol)	EtCO ₂ CH ₃ ^{c)} (mmol)	EtCHO (mmol)
1	RhCl ₃ ·3H ₂ O (0.5)	10	125	20	23	63	12
2	IrCl ₄ ·H ₂ O (0.25)	10	125	20	27	29	5.1
3	RhCl ₃ ·3H ₂ O (0.5)	10	125	0	21	59	tr.
4	IrCl ₄ ·H ₂ O (0.25)	10	125	0	29	24	tr.
5	RhCl ₃ ·3H ₂ O (0.5)	0	0	20	0	0	14
6	IrCl ₄ ·H ₂ O (0.25)	0	0	20	0	0	7.4
7	RhCl ₃ ·3H ₂ O (0.5)	10	0	20	0	0	tr.
8	IrCl ₄ ·H ₂ O (0.25)	10	0	20	0	0	tr.

a) Partial pressure at room temperature. b) No hydrogenation of benzophenone observed at this temperature.
 c) No propionic acid observed.

formed from ethylene and the corresponding hydride complexes, on methanol, as shown in the scheme.



Scheme 1. Reaction scheme on the Rh- or Ir-catalyzed carbonylation in the presence of methyl iodide (M = Rh or Ir).

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