JOURNAL OF CATALYSIS 51, 96–100 (1978)

Mechanistic Study of Methanol Carbonylation Catalyzed by an Iridium Complex in the Presence of Methyl Iodide

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Received April 15, 1977; revised September 16, 1977

Kinetics of methanol carbonylation in acetophenone solvent catalyzed by an iridium complex in the presence of methyl iodide was found to be first order with respect to methanol, under reaction conditions of apparent zero order with respect to both carbon monoxide and methyl iodide, where carbon monoxide pressures higher than 15 kg/cm^2 and a CH_3I/Ir ratio higher than 20 were adopted at 125–175°C. Acetyl iridium(III) complexes were isolated from product solutions by stabilizing with triphenylphosphine. Both the observed kinetics and the formation of acetyl iridium(III) complexes are consistent with the rate-determining methanolysis of an acetyl iridium(III) species in the catalytic cycle.

INTRODUCTION

Rhodium compounds have been reported to be highly active and selective, in the presence of methyl iodide, for the catalytic carbonylation of methanol to acetic acid (*1*, *2*). On the basis of reaction kinetics, it has been claimed that the rate-determining step is the oxidative addition of methyl iodide to a rhodium(I) complex (*3*, *4*). Recently Forster elaborately showed that the active species is an anionic rhodium(I) complex, $[Rh(CO)_2I_2]^-$ (*5*). Iridium compounds are reportedly active for the catalytic carbonylation of methanol (*1*), while no mechanistic study has been reported. We examined the kinetics of methanol carbonylation by iridium catalyst to compare with that by rhodium catalyst under similar conditions, and found that the kinetics are significantly different from each other in nature, suggesting different rate-determining steps. Thus the isolation of an intermediate complex was attempted to elucidate the mechanism of carbonylation with iridium catalyst.

EXPERIMENTAL

Reaction procedure. All runs were carried out using $IrCl_4 \cdot H_2O$ as the catalyst precursor in acetophenone solvent. Acetophenone has been found to be effective in preventing the formation of dimethyl ether in rhodium-catalyzed methanol carbonylation (*6*). Kinetic measurements were performed in a Ti-Mn alloy autoclave (100 ml) equipped with a magnetic stirrer by following consumption of carbon monoxide as a function of time. A given amount of $IrCl_4 \cdot H_2O$ (0.06–0.25 mmol) and a mixture of methyl iodide (0.75–20 mmol), methanol (50–250 mmol), and acetophenone (20 ml) were placed in the autoclave, and the mixture was heated up to a reaction temperature (125–175°C). Carbonylation was initiated by introducing carbon monoxide to a desired pressure (7–50 kg/cm^2), which

0021-9517/78/0511-0096$02.00/0

TABLE 1

Analytical Results for Carbonylation Products[a]

Reaction conditions			Carbonylation products (mmol)				Calculated results (%)		
Temp. (°C)	$IrCl_4 \cdot H_2O$ (mmol)	CH_3OH (mmol)	AcOH	$AcOCH_3$	CH_3OH	CH_3I	Conv.[b]	Mass balance[c]	CO balance[d]
125	0.06	250	2.9	28	190	8.1	12	99	107
140	0.06	250	4.0	42	148	7.7	18	94	106
156	0.06	250	6.5	60	104	7.4	26	92	115
173	0.06	250	7.0	83	50	7.3	36	90	112
173	0.25	250	126	39	2.5	7.5	66	87	93
173	0.25	125	55	28	Trace	8.2	66	90	94
173	0.25	85	37	22	1.0	8.5	69	96	95
173	0.25	50	19	12	1.5	7.5	63	96	105

[a] Conditions: CH_3I, 10 mmol; $C_6H_5COCH_3$, 20 ml; pCO, 30 kg/cm^2 (at reaction temp.); time, 2 hr.

[b] $\{[AcOH] + [AcOCH_3]\}/[CH_3OH]_{init.} \times 100$ (Ac = CH_3CO).

[c] $\{[AcOH] + 2[AcOCH_3] + [CH_3OH]\}/[CH_3OH]_{init.} \times 100$.

[d] $\{[AcOH] + [AcOCH_3]\}/[CO]_{abs.} \times 100$.

was kept constant during the run by supplying carbon monoxide from a high-pressure gas reservoir (100 ml). The product solutions were analyzed by gas chromatography for acetic acid, methyl acetate, methanol, and methyl iodide.

Isolation of acetyl iridium(III) complex. $IrCl_4 \cdot H_2O$ (0.5 mmol) and a mixture of methyl iodide (5 mmol), methanol (125 mmol), and acetophenone (10 ml) were placed in the autoclave, and it was heated up to 140°C. Carbon monoxide was introduced up to 30 kg/cm^2, and both the temperature and pressure were kept constant for 20 min, during which period about 20 mmol of carbon monoxide was consumed. The autoclave was rapidly (in a few minutes) cooled to 0°C and carbon monoxide was purged out. The orange–yellow product solution was transferred into a flask (100 ml) containing a mixture of triphenylphosphine (5 mmol), methanol (20 ml), and acetophenone (5 ml) under a nitrogen atmosphere. The solution was stirred at 25°C for 1 hr, and then cooled to 0°C, a yellow crystal being precipitated. The precipitate was washed with methanol, and recrystallized from dichloromethane and methanol.

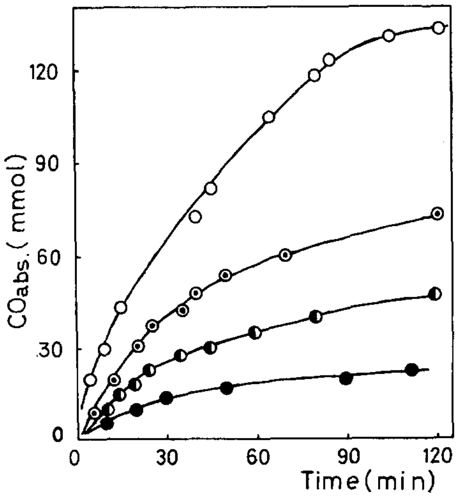

FIG. 1. Time courses of CO absorption at various amounts of CH_3OH. CH_3OH (mmol): ●, 50; ◐, 85; ⊙, 125; ○, 250. CH_3I, 10 mmol; $IrCl_4 \cdot H_2O$, 0.25 mmol; $PhCOCH_3$, 20 ml; pCO, 30 kg/cm^2; 173°C.

RESULTS AND DISCUSSION

Kinetics

Dependence of the carbonylation rate on the amount of methanol was examined in acetophenone at 173°C under 30 kg/cm^2 pressure. Carbonylation proceeded without induction time, suggesting a rapid formation of active species. Analytical results for products are given in Table 1. As is the case with rhodium catalysts, the initial product in the presence of large amounts of methanol is methyl acetate, while production of acetic acid increases with the extent of conversion as the product water accumulates in the reaction mixture. The selectivity of carbonylation to form acetic acid or methyl acetate is close to 100% so that the rate of carbonylation can be obtained from consumption of carbon monoxide, as shown in Fig. 1, as a function of reaction time.

It is obvious that the initial rate is proportional to the initial amount of methanol. In order to confirm the proportionality to methanol during runs, the amount of methanol remaining at time t, $[\mathrm{MeOH}]_t$, is estimated by the relation, $[\mathrm{MeOH}]_t = [\mathrm{MeOH}]_0 - 2[\mathrm{CO}]_t$, where $[\mathrm{MeOH}]_0$ and $[\mathrm{CO}]_t$ are the amounts of methanol at time zero and the carbon monoxide consumed up to time t, respectively. This relation is valid for the initial period where methyl acetate is the predominant product, in conformity with the equation

$$2\mathrm{MeOH} + \mathrm{CO} \rightarrow \mathrm{MeCOOMe} + \mathrm{H_2O}.$$

The first-order plot with respect to the estimated amount of methanol gives a straight line, at least for the initial 0.5-hr period, as shown in Fig. 2. Thus a first-order rate constant, 2.8 $\mathrm{hr^{-1}}$, is obtained from the slope.

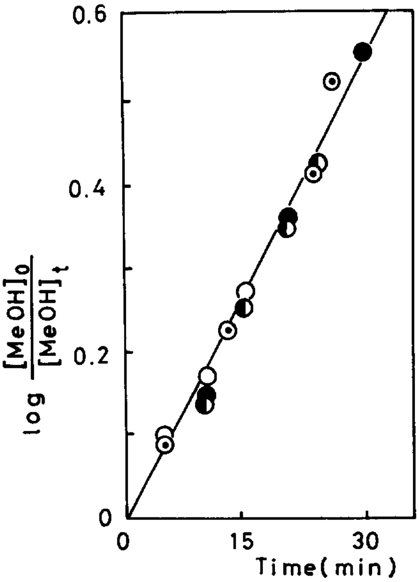

FIG. 2. First-order plot of the rate. CH_3OH (mmol): ●, 50; ◐, 85; ⊙, 125; ○, 250.

In this way, the first-order rate constants were obtained under different reaction conditions, and are summarized in Table 2. It is obvious that the rate constant is proportional to the amount of iridium catalyst, as expected, while independent of carbon monoxide pressure above 15 $\mathrm{kg/cm^2}$ and also independent of the amount of methyl iodide above 5 mmol ($CH_3I/Ir > 20$), in marked contrast to the result with rhodium catalysts (*6*) that the rate of carbonylation linearly increases with a CH_3I/Ir ratio of 20 to 160. It is noteworthy that first-order dependence on methanol is invariably found for runs with lower methyl iodide concentration or carbon monoxide pressure, again in marked contrast with the result with rhodium catalysts (*6*) that the rate of carbonylation is independent of methanol concentration. The activation energy of the carbonylation is obtained from the rate constants given in Table 2 to be 8.9 kcal/mol, which is considerably lower than that obtained previously with a rhodium catalyst in the same solvent, 19 kcal/mol (*6*). Thus the rate-determining step of carbonylation with the iridium catalyst is likely different from that with the rhodium catalysts. The first-order kinetics in methanol as well as the zero-order kinetics in both carbon monoxide and methyl iodide strongly suggested that methanol is involved as a reactant in the rate-determining step of carbonylation with the iridium catalyst.

Relevance to the Mechanism and Characterization of the Iridium Complex Isolated

In the accepted scheme of methanol carbonylation with rhodium catalysts (*3*, *5*), methyl iodide is oxidatively added to rhodium(I) complex to give methyl rhodium(III) complex, which is believed to be rapidly transformed into acetyl rhodium(III) complex. Two competitive reaction

TABLE 2

Apparent First-Order Rate Constants, $d[\mathrm{CO}]/dt = d[\mathrm{AcOCH_3}]/dt = k_1[\mathrm{CH_3OH}]$, in Acetophenone (20 ml)

Temp. (°C)	CH_3OH (mmol)	CH_3I (mmol)	$IrCl_4 \cdot H_2O$ (mmol)	pCO at reaction temperature[a] (kg/cm^2)	k_1 (hr^{-1})
173	125	10	0.08	30	0.62
173	125	10	0.13	30	1.3
173	125	10	0.25	30	2.8
173	125	20	0.25	30	2.8
173	125	10	0.25	30	2.8
173	125	5	0.25	30	2.8
173	125	2.5	0.25	30	1.9
173	125	1.3	0.25	30	1.4
173	125	0.75	0.25	30	0.75
173	125	10	0.25	50	2.8
173	125	10	0.25	30	2.8
173	125	10	0.25	15	2.6
173	125	10	0.25	11	1.5
173	125	10	0.25	7	0.54
173	250	10	0.06	30	0.42
156	250	10	0.06	30	0.27
140	250	10	0.06	30	0.19
125	250	10	0.06	30	0.12

[a] Pressures of carbon monoxide at the reaction temperature.

paths have been suggested for the fate of acetyl rhodium(III) complex, i.e., (1) reductive elimination of acetyl iodide followed by methanolysis and (2) direct methanolysis of acetyl rhodium(III) complex. If we apply the above reaction scheme to carbonylation with the iridium catalyst, the most probable rate-determining step would be the methanolysis of acetyl iridium complex to give methyl acetate and a hydrid complex. In this case, the large part of iridium, during catalysis in the presence of an excess amount of methyl iodide, should be in the oxidation state of Ir(III), with the oxidative addition of methyl iodide being very fast in conformity with the zero-order kinetics in methyl iodide. The positive order observed with lower CH_3I/Ir ratios may be understood as a thermodynamic control of the amount of Ir(III) complexes. In view of the above consideration, it was attempted to isolate the iridium complex from the reaction mixture.

The yellow iridium complex (Calcd for $C_{39}H_{33}O_2P_2I_2Ir$: C, 45.0; H, 3.19; I, 24.4. Found: C, 45.4; H, 3.33; I, 24.1%), which was isolated from the carbonylation product by stabilizing with triphenylphosphine as described in Experimental, was identified to be a mixture of stereoisomers of acetyl iridium(III) complex, $CH_3COIrI_2(CO)(PPh_3)_2$. The IR spectrum of the complexes with KBr showed two strong and broad bands, 2020 and 1620 cm^{-1}, in the carbonyl stretching region, both of which consisted of several neighboring bands. The bands at 2020 and 1620 cm^{-1} can be reasonably assigned to terminal carbonyls and acetyl frequencies, respectively, because an analogous acetyl iridium(III) complex prepared from the oxidative addition of acetyl iridium(III) complex prepared from the oxidative addition of acetyl bromide to iridium(I) complex, $CH_3COIrBr_2(CO)(PEt_2Ph)_2$, was reported to have two strong bands at 2036 and 1633 cm^{-1} (*7*). ^1H NMR of the iridium complexes in CD_2Cl_2 solution showed several peaks (8.8–9.4τ) due to methyl protons, indicating a mixture of stereoisomers. The mass spectrum of the iridium complex taken by the field desorption method[1] showed three strong fragment peaks at 869–872(±1), 779–782(±1), and 262, whose mass numbers corresponded to $CH_3COIrI_2(CO)(PPh_3)$ (870, 872), $IrI(CO)(PPh_3)_2$ (778, 780) (^{191}Ir, 38.5%; ^{193}Ir, 61.5%), and PPh_3(262), respectively, although no parent peak (1040, 1042) was observed. All these spectroscopic data are reasonably explained as a mixture of stereoisomers of acetyl iridium complexes, $CH_3COIrI_2(CO)(PPh_3)_2$.

The isolation of acetyl iridium(III) complex from the reaction mixture is reasonable if the methanolysis of this complex is rate-determining in the catalytic cycle, as discussed above. However, there is a possibility that the intermediate complex has undergone a transformation under the isolation conditions, rendering the isolated complex to be one of the possible forms of the intermediate. For example, $CH_3IrI_2(CO)_3$ also is a possible form, since it can be readily transformed into the acetyl complex during isolation and is consistent with the observed kinetics. But if an iridium(I) complex is the predominant species, with the oxidative addition of methyl iodide being rate-determining, the kinetics should be first order in methyl iodide, as is the case with the rhodium catalyst (*6*). Thus it may be concluded that the oxidation state of the iridium catalyst is Ir(III) during carbonylation, with the acethyl iridium(III) complex being a plausible form (*8*).[2]

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[1] Taken at the Japan Electron Optics Laboratory with JMS-01SG-2.

[2] After the completion of this report, D. Brodzki *et al.* reported the isolation of anionic Ir(III) complexes such as $[PPh_4]^+[Ir(CO)_2I_4]^-$ and $[CH_3PPh_3]^+[Ir(CO)_2I_4]^-$ from the carbonylation products of methanol catalyzed by iridium(I) complexes using acetic acid or propionic acid as the solvent ($CH_3I/Ir(I)$ ~200, pCO ~60 kg/cm^2, 190°C) (*8*).