JOURNAL OF CATALYSIS **157**, 334–343 (1995)

Selectivity Behavior in Hydrocarbonylation of Methyl Acetate Using Homogeneous Rh Complex Catalyst[1]

A. A. Kelkar and R. V. Chaudhari[2]

Chemical Engineering Division, National Chemical Laboratory, Pune, 411 008, India

Received May 26, 1994; revised May 31, 1995; accepted July 18, 1995

Hydrocarbonylation of methyl acetate using various homogeneous transition metal complex catalysts has been studied. It was observed that $Rh(CO)Cl(PPh_3)_2$ was the most active and selective catalyst for ethylidene diacetate synthesis. The effect of the catalyst, methyl acetate, and methyl iodide concentrations; temperature; and partial pressures of CO, H_2, and various transition metal complexes as co-catalysts on the selectivity behavior has been studied. Palladium complexes were found to enhance the selectivity of ethylidene diacetate substantially. Catalyst concentration, partial pressures of CO and H_2, and temperature also influence the selectivity pattern substantially. On the basis of these results, a possible reaction mechanism is discussed. © 1995 Academic Press, Inc.

INTRODUCTION

Hydrocarbonylation of methyl acetate to ethylidene diacetate (EDA) is an industrially important reaction, since it provides an alternative route for the synthesis of vinyl acetate monomer, based on C_1 raw materials such as CO and H_2 instead of ethylene (1). The formation of ethylidene diacetate is believed to occur in the following steps (2):

$$CH_3COOCH_3 + CO \rightarrow (CH_3CO)_2O \quad [i]$$

$$CH_3COOCH_3 + CO + H_2 \rightarrow CH_3CHO + CH_3COOH \quad [ii]$$

$$CH_3CHO + (CH_3CO)_2O \rightarrow CH_3CH(OCOCH_3)_2. \quad [iii]$$

The overall reaction stoichiometry is

$$2CH_3COOCH_3 + 2CO + H_2 \xrightarrow{\text{Catalyst}} CH_3CH(OCOCH_3)_2 + CH_3COOH. \quad [iv]$$

The formation of acetaldehyde is also likely to occur as (3)

$$(CH_3CO)_2O + H_2 \rightarrow CH_3CHO + CH_3COOH. \quad [v]$$

Thus, during hydrocarbonylation of methyl acetate, acetic anhydride and acetaldehyde can be formed as co-products, in addition to ethylidene diacetate. The selectivity of these products would depend on the type of catalysts, promoters, and reaction conditions.

Various catalyst systems consisting of Rh, Co, Pd, and Ni complexes with iodide promoters and N- or P-containing ligands have been suggested for this reaction (4–13). Kudo *et al.* (6) have studied hydrocarbonylation of methyl acetate using a Rh catalyst with n-Bu_3P as a ligand. They have reported that $Pd(OAc)_2$ as a co-catalyst enhances the selectivity of EDA but other Pd compounds such as Pd metal and $PdCl_2$ were found to be ineffective. Rizkalla and Goliaszewski (3) have also studied hydrocarbonylation of methyl acetate using Rh and Pd catalysts and discussed the possible pathways and mechanistic features of both the catalyst systems. However, the variation of selectivity of EDA with reaction conditions (e.g., P_{CO}, P_{H_2}, catalyst concentration and temperature) for Rh complex catalyst is not well studied and needs further investigation. We wish to present in this paper specific results on the activity and selectivity of $Rh(CO)Cl(PPh_3)_2$ catalyst in hydrocarbonylation of methyl acetate. The effect of ligands, solvents, and reaction conditions on selectivity of EDA has been discussed.

EXPERIMENTAL

Materials

Catalyst precursors, $RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot 3H_2O$ were obtained from Aldrich, USA, while $PdCl_2$ and $RuCl_3 \cdot 3H_2O$ were obtained from Arrora Mathey, India. Reactants, methyl acetate, methyl iodide, and solvents were freshly distilled before use. Ligands of AR quality were obtained from Fluka AG, Switzerland. Carbon monoxide and hydrogen were used directly from the cylinders.

Catalyst precursors, $Rh(CO)Cl(PPh_3)_2$ (14), $RhPy_3Cl_3$ (Py, pyridine) (15), $HRh(CO)(PPh_3)_3$ (16), $Ir(CO)Cl(PPh_3)_2$ (17), *trans*-$Ru(CO)_2Cl_2(PPh_3)_2$ (18), and $Pd(PPh_3)_2Cl_2$ (19) were prepared by the procedures de-

---

[1] NCL Communication No. 6021.

[2] To whom all correspondence should be addressed.

0021-9517/95 $12.00

scribed in the literature. The elemental analysis for these complexes was found to be consistent within 2% of the theoretical value.

Apparatus

Carbonylation experiments were carried out in a 600-cm^3 autoclave (made of hastelloy C-276, supplied by Parr Instruments Co., USA). This autoclave was provided with arrangements for sampling of liquid and gas phase, automatic temperature controller, and variable stirrer speed.

Experimental Procedure

In a typical experiment, known quantities of catalyst, ligand, methyl iodide, methyl acetate, and solvent (total volume = 100 cm^3) were charged into the reactor and the contents were flushed with nitrogen and then with CO and H_2. The contents were then heated to a desired temperature and CO/H_2 was introduced. A sample of liquid was withdrawn, and the reaction was initiated by switching the stirrer on. To ensure that the activity data are obtained under kinetic regime, the agitation speed of 1000 rpm was used. The reaction was then continued at a constant pressure, by supply of CO/H_2 (2:1) from the reservoir. In most cases, the reactions were carried out till almost complete conversion was achieved. At the end of the reaction, the samples were analyzed for reactants and products by gas chromatography. In all the experiments, the gas phase was also analyzed for CO using an Orsat apparatus and CH_4 by gas chromatography. Liquid reactants and products were analyzed with a Hewlett–Packard gas chromatograph (model No. 5840) using $\frac{1}{8}$-in. × 8-ft column packed with 5% OV-17 on chromosorb W-AW, 80-100 mesh, and FID detector. Methane was analyzed using a porapak Q column and TCD detector.

RESULTS

Preliminary Experiments

Initial experiments on hydrocarbonylation of methyl acetate were carried out using $Rh(CO)Cl(PPh_3)_2$ as a catalyst and acetic acid as a solvent. In a few experiments, pure methyl acetate was also used as a reactant. The material balance of methyl acetate consumed and products acetic anhydride (Ac_2O) and ethylidene diacetate (EDA) formed were found to agree to the extent of 95% and above. The experiments with variable agitation speed indicated that the activity was constant beyond 600 rpm. Hence, in all the experiments, an agitation speed of 1000 rpm was used to ensure kinetic control. Acetaldehyde was not detected in most of the experiments, indicating that the condensation of acetaldehyde and acetic anhydride (reaction [iii]) was a fast reaction. In the experiments with pure methyl acetate, it was difficult to maintain a desired ratio of CO:H_2 at a constant value due to the differences in the stoichiometric coefficients in the formation of acetic anhydride and ethylidene diacetate. Therefore, in order to study the effect of various process parameters at a constant desired CO:H_2 ratio, a lower methyl acetate concentration (<20%) was used so that the amount of CO and H_2 consumed in a single run was small enough to affect the CO/H_2 ratio during an experiment. Several experiments were carried out to study the role of ligands, solvents, and reaction conditions on the activity and selectivity. Activity and selectivity are defined as

$$\text{Activity} = \frac{\text{Methyl acetate consumed}}{\text{Catalyst} \times \text{time}}, \frac{\text{mol}}{\text{mol} \times \text{hr}}$$

Selectivity:

$$Ac_2O = \frac{Ac_2O \text{ formed, mol}}{\text{MeOAc consumed, mol}} \times 100$$

$$\text{EDA} = \frac{2 \times \text{EDA formed, mol}}{\text{MeOAc consumed, mol}} \times 100.$$

The results are discussed below.

Effect of Catalyst Precursors

The results on the activity and selectivity of different transition metal complex catalysts are presented in Table 1. Rhodium-containing catalyst systems, $Rh(Cl_3(Py)_3/Py$, $Rh(CO)Cl(PPh_3)_2/PPh_3$, $HRh(CO)(PPh_3)_3/PPh_3$, and $RhCl_3 \cdot 3H_2O/PPh_3$, were found to give higher activity and selectivity to EDA compared to $Ir(CO)Cl(PPh_3)_2$, *trans*-$Ru(CO)_2C_2(PPh_3)_2$, and $Pd(PPh_3)_2Cl_2$. Among the Rh complexes studied, $Rh(CO)Cl(PPh_3)_2$ was found to be the most active and selective catalyst. A typical concentration profile for this reaction is shown in Fig. 1, which indicates that the selectivity of EDA is dependent on the conversion level of methyl acetate and increases with the increase in conversion. For this case, 87.1% conversion of methyl acetate with EDA selectivity of 50% has been observed. Further studies were carried out using $Rh(CO)Cl(PPh_3)_2$ as a catalyst precursor.

Effect of Ligands

The effect of various N- and P-containing ligands on the conversion and selectivity in hydrocarbonylation of methyl acetate was studied at 443 K. The results are presented in Table 2. When $RhCl_3 \cdot 3H_2O$ alone was used as a catalyst precursor, precipitation of Rh metal was observed at the end of the reaction indicating poor stability of the catalyst. However, in the presence of PPh_3 or a suitable ligand, the activity of the catalyst as well as the selectivity to ethylidene

TABLE 1

Screening of Catalysts for Hydrocarbonylation of Methyl Acetate[a]

Sr. No.	Catalyst system	Temperature (K)	Time (min)	Turnover No. (mol/mol/h)[b]	Conversion (%)	Selectivity (%) EDA	Selectivity (%) Ac_2O
1	$RhCl_3 \cdot 3H_2O/PPh_3$	443	240	117	91.2	42.10	56.14
2	$Rh(CO)Cl(PPh_3)_2/PPh_3$	443	240	110	86.00	44.10	54.38
3	$HRh(CO)(PPh_3)_3/PPh_3$	443	225	109	79.81	43.40	54.72
4	$Ir(CO)Cl(PPh_3)_2/PPh_3$	473	270	83	73.00	05.30	89.00
5	$RhCl_3Py_3/Py$	443	240	93	72.45	36.00	62.00
6	trans-$Ru(CO)_2Cl_2(PPh_3)_2/PPh_3$	498	360	32	37.10	03.00	94.20
7	$Pd(PPh_3)_2Cl_2/PPh_3$	473	325	20	21.28	16.20	83.52

[a] Reaction conditions: catalyst, 2.44×10^{-4} mol; ligand, 19.52×10^{-4} mol; methyl acetate, 0.125 mol; methyl iodide, 6.43×10^{-2} mol; partial pressure of H_2, 18.36 atm; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm^3.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

diacetate was found to increase substantially. Also, the stability of the catalyst was improved in the presence of these ligands. Even after keeping the reaction mixture overnight no metal precipitation was observed. Therefore, ligands like triphenyl phosphine, quinoline, and isoquinoline may be playing an important role in stabilizing the active catalytic species, $[Rh(CO)_2I_2]^-$, as a counterion after quaternization (20). In an independent study, Fulford *et al.* (20) have shown that the rate of oxidative addition of methyl iodide to $[Rh(CO)_2I_2]^-$ was improved when $[Rh(CO)_2I_2]^-$ was stabilized by forming a salt of the form $A[Rh(CO)_2I_2]$, where, A = n-Bu_4, Ph_4P, Li. It was observed that the conversion as well as the selectivity pattern was not significantly affected by a change in the type of ligand. Thus methyl acetate conversion in a range 75–90% with 31–45% selectivity to EDA was obtained. However, for tributyl phosphite, triphenyl phosphite, triphenyl arsine, and 2,2′-bipyridyl, a significantly lower activity was observed. The selectivity to EDA was also lower in the latter case, but this is not likely to be the ligand effect since EDA selectivity is known to increase with conversion (see Fig. 1).

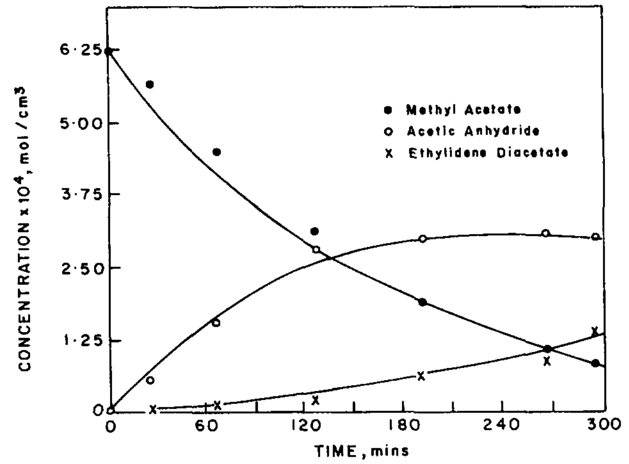

FIG. 1. Concentration–time plot for hydrocarbonylation of methyl acetate.

Effect of Co-catalysts

The effect of various transition metal co-catalysts on the activity and selectivity of $RhCl_3 \cdot 3H_2O$ and $Rh(CO)Cl(PPh_3)_2$ as catalyst precursors was also studied and the results are presented in Table 3. In these experiments the co-catalyst : catalyst ratio of 1 was kept constant. Palladium complexes such as $Pd(OAc)_2$ and $Pd(PPh_3)_2Cl_2$ were found to increase the selectivity of EDA when used along with $Rh(CO)Cl(PPh_3)_2$ without affecting the conversion (see Table 3). For other transition metal complexes such a behavior was not observed. Kudo *et al.* (6) have also reported the synergistic effect of $Pd(OAc)_2$ on the selectivity of EDA. The synergistic effect of palladium can be explained on the basis of hydrogenation activity. The hydrogenation of acetic anhydride to EDA is known to be catalyzed in the presence of Pd catalysts (21) and hence, an improved selectivity to EDA is observed.

Effect of Solvents

The effect of solvents on the activity and selectivity was studied at 443 K using polar as well as nonpolar solvents and the results are presented in Table 4 for a constant time duration. Acetic acid was found to be the best solvent in the presence of which 88.8% conversion of methyl acetate and 46.84% selectivity to EDA was observed. With nonpolar solvents such as benzene and n-hexane, lower conversion (<24%) was observed with only acetic anhydride as the product. In these experiments the catalyst was also found to be settled at the bottom forming a separate layer. This can lead to a poor activity due to solubility limitations

TABLE 2

Effect of Ligands on Activity and Selectivity[a]

Sr. No.	Ligand	Turnover No. (mol/mol/h)[b]	Conversion of methyl acetate (%)	Selectivity (%)	
				EDA	Ac$_2$O
1	Nil	74	57.60	25.00	73.60
2	Triphenyl phosphine	117	91.20	42.10	56.14
3	Quinoline	112	87.20	38.53	57.79
4	Isoquinoline	110	86.01	37.50	61.60
5	2,6-Lutidine	109	85.25	41.44	56.75
6	Tributyl phosphine	107	83.20	34.61	64.42
7	Pyrrolidine	106	82.40	31.06	66.99
8	N,N,N',N'-Tetra-methylethylenediamine	105	81.60	41.29	56.86
9	2,6-Diphenyl pyridine	103	80.62	41.20	56.70
10	Triphenyl arsine	92	72.20	38.29	59.57
11	2-Phenyl pyridine	92	71.82	37.62	61.38
12	3-Picoline	90	70.51	39.60	57.42
13	Triphenyl phosphite	82	63.76	38.63	59.10
14	Tributyl phosphite	75	58.40	21.92	75.34
15	2,2'-Bipyridyl	45	35.20	27.27	68.18

[a] Reaction conditions: $RhCl_3 \cdot 3H_2O$, 2.44×10^{-4} mol; ligand, 19.52×10^{-4} mol; methyl acetate, 0.125 mol; methyl iodide, 6.43×10^{-2} mol; partial pressure of H_2, 18.36 atm; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm^3; reaction time, 240 min; temperature, 433 K.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

of the catalytic species. For rhodium-catalyzed carbonylation of methyl acetate in the presence of CO and I^-, $[Rh(CO)_2I_2]^-$ is known to be the active species (22). In the present reaction CO/H_2 is used as a feed gas instead of CO and, therefore, anionic Rh complex is expected to be a catalytically active species. Such anionic species may not be stabilized in nonpolar solvents, resulting in a poor activity. With polar solvents like dichloromethane and methyl ethyl ketone, higher conversion (48%) compared to the nonpolar solvents was obtained, but the selectivity to EDA was very low. The higher selectivity to EDA in acetic acid as a solvent is also expected, since the condensation of aldehyde and carboxylic acid anhydride is known to be catalyzed in the presence of protic acids (23, 24).

Effect of P:Rh Ratio

The effect of P:Rh ratio on the activity and selectivity was studied at 443 K and the results are presented in Table 5. The conversion of methyl acetate was found to increase

TABLE 3

Effect of Co-catalysts on Activity and Selectivity[a]

Sr. No.	Catalyst system	Co-catalyst No.	Turnover (mol/mol/h)[b]	Conversion (%)	Selectivity (%)	
					EDA	Ac$_2$O
1	$Rh(CO)Cl(PPh_3)_2/PPh_3$	$Pd(PPh_3)_2Cl_2$	119	92.80	53.45	44.83
2	$RhCl_3 \cdot 3H_2O/PPh_3$	$Pd(OAc)_2$	118	92.00	50.43	47.82
3	$RhCl_3 \cdot 3H_2O/PPh_3$	$NiCl_2 \cdot 6H_2O$	116	90.40	40.71	57.52
4	$Rh(CO)(Cl(PPh_3)_2/PPh_3$	Trans-$Ru(CO)_2Cl_2(PPh_3)_2$	114	88.80	39.64	58.56
5	$RhCl_3 \cdot 3H_2O/PPh_3$	$IrCl_3 \cdot 3H_2O$	111	86.40	35.18	62.96
6	$Rh(CO)Cl(PPh_3)_2/PPh_3$	$Ir(CO)Cl(PPh_3)_2$	110	85.60	37.38	62.62
7	$RhCl_3 \cdot 3H_2O/PPh_3$	$CoCl_2 \cdot 6H_2O$	106	82.70	42.10	54.38
8	$RhCl_3 \cdot 3H_2O/PPh_3$	$RuCl_3 \cdot 3H_2O$	104	81.23	41.20	56.36

[a] Reaction conditions: Catalyst, 2.44×10^{-4} mol; co-catalyst, 2.44×10^{-4} mol; PPh_3, 19.52×10^{-4} mol; methyl acetate, 0.125 mol; methyl iodide, 6.43×10^{-2} mol; partial pressure of H_2, 18.36 atm; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm^3; reaction time, 240 min; temperature, 443 K.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

TABLE 4

Effect of Solvents on Activity and Selectivity[a]

Sr. No.	Solvent	Turnover No. (mol/mol/h)[b]	Conversion of methyl acetate (%)	Selectivity (%)	
				EDA	Ac_2O
1	Acetic acid	114	88.8	44.04	54.15
2	Dichloromethane	61	48.0	6.66	91.66
3	Methyl ethyl ketone	61	48.0	6.40	92.55
4	*n*-Hexane	31	24.0	0	97.94
5	Benzene	27	21.2	0	98.84

[a] Reaction conditions: $Rh(CO)Cl(PPh_3)_2$, 2.44 × 10^{-4} mol; PPh_3, 19.52 × 10^{-4} mol; methyl acetate, 0.125 mol; methyl iodide, 6.43 × 10^{-2} mol; partial pressure of H_2, 18.36 atm; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm^3; reaction time, 240 min; temperature, 443 K.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

with an increase in the ratio of P : Rh up to 4, beyond which it was found to be constant. The selectivity pattern, however, was not affected by a change in the P : Rh ratio. At a lower P : Rh ratio (up to 2) an induction period of 15 to 20 min was observed. With increase in triphenyl phosphine concentration, the induction period was reduced to less than 5 min. Therefore, for further work P : Rh ratio was kept constant at 8.

Effect of Temperature

The effect of temperature on the activity and selectivity was studied in a range 433–463 K and in these experiments concentration–time profiles were observed. The results are presented in Table 6 for different conversion levels and temperatures. It was observed that for the same conversion level, the turnover number increased significantly with increase in temperature. The results on selectivity of products vs conversion are shown in Fig. 2 for different temperatures. The selectivity to acetic anhydride increased with temperature but that of ethylidene diacetate was reduced. The change in selectivity pattern can be due to a change in the relative rates of the two reactions, namely carbonylation of methyl acetate (reaction [i]) and hydrogenation of acetic anhydride (reaction [v]). From the general trends in Fig. 1, it was noted that up to 10–20% conversion of methyl acetate, acetic anhydride was the major product. The formation of EDA increases only after appreciable quantity of acetic anhydride is formed. Thus, with increase in temperature, the rate of carbonylation increases compared to the rate of hydrogenation of acetic anhydride leading to a reduction in the EDA selectivity.

Effect of Methyl Acetate Concentration

The effect of methyl acetate concentration was also studied at different temperatures (433–463 K) and the results are presented in Table 7. The turnover number was found to increase with increase in methyl acetate concentration, but the selectivity pattern was not significantly affected.

TABLE 5

Effect of the PPh_3 : Rh Ratio on Activity and Selectivity[a]

Sr. No.	PPh_3 : Rh ratio	Turnover No. (mol/mol/h)[b]	Conversion of methyl acetate (%)	Selectivity (%)	
				EDA	Ac_2O
1	No ligand	71	55.24	43.90	54.88
2	2	87	68.04	46.50	51.45
3	4	112	87.60	44.99	54.07
4	8	114	88.80	46.84	53.15
5	16	115	89.60	46.40	53.57

[a] Reaction conditions: $Rh(CO)Cl(PPh_3)_2$, 2.44 × 10^{-4} mol; methyl acetate, 0.125 mol; methyl iodide, 6.43 × 10^{-2} mol; partial pressure of H_2, 18.36 atm; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm^3; reaction time, 240 min; temperature, 443 K.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

TABLE 6

Effect of Temperature on Activity and Selectivity[a]

Sr. No.	Temperature (K)	Turnover No. (mol/mol/h)[b] 50% Conv.	Turnover No. (mol/mol/h)[b] (85% Conv.)	Selectivity (%) EDA 50% Conv.	Selectivity (%) EDA (85% Conv.)	Selectivity (%) Ac_2O 50% Conv.	Selectivity (%) Ac_2O (85% Conv.)
1	433	131	(89)	9.6	(28.2)	88.0	(69.77)
2	443	213	(158)	14.4	(26.35)	84.8	(67.76)
3	453	317	(220)	10.4	(22.5)	88.8	(77.30)
4	463	454	(268)	6.0	(22.5)	93.5	(76.50)

[a] Reaction conditions: $Rh(CO)Cl(PPh_3)_2$, 2.44×10^{-4} mol; PPh_3, 19.52×10^{-4} mol; methyl acetate, 0.125 mol; methyl iodide, 6.43×10^{-2} mol; partial pressure of H_2, 18.36 atm; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm^3.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

Effect of Methyl Iodide Concentration

The results on the activity of the catalyst at different conversion levels and methyl iodide concentrations are presented in Table 8 for 433–463 K. The activity of the catalyst was found to increase with increase in the methyl iodide concentration, but the selectivity pattern was not affected.

Effect of CO Partial Pressure

The effect of CO partial pressure on the activity and selectivity was studied in a temperature range of 433 to 463 K. In these experiments H_2 partial pressure of 18.36 atm was kept constant. The results are presented in Table 9. The turnover number increases with increase in CO partial pressure up to 36.78 atm and beyond which it is independent of CO. Also, with increase in CO partial pressure the selectivity to acetic anhydride increased, reducing selectivity to EDA. The results on selectivity vs conversion at different CO partial pressures at 433 K are presented in Fig. 3.

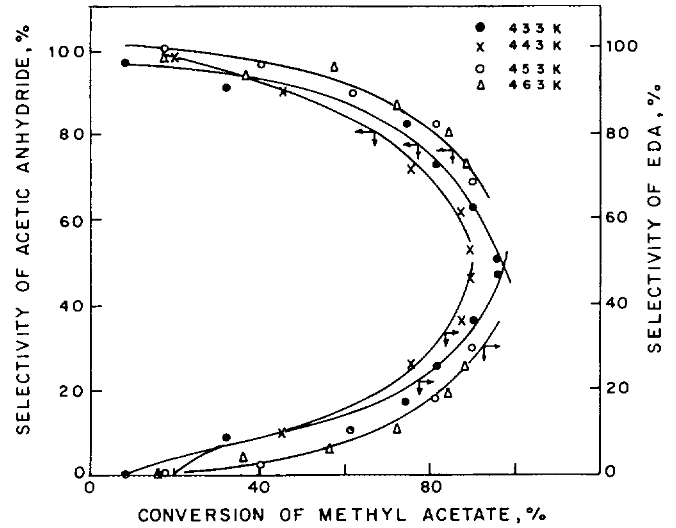

FIG. 2. Effect of temperature on conversion and selectivity. Concentrations: PPh_3, 19.52×10^{-6} mol/cm^3; $Rh(CO)Cl(PPh_3)_2$, 2.44×10^{-6} mol/cm^3; methyl iodide, 6.42×10^{-4} mol/cm^3; methyl acetate, 1.25×10^{-3} mol/cm^3. Partial pressure of CO, 36.73 atm; partial pressure of H_2, 9.52 atm; agitation speed, 1000 rpm.

Effect of H_2 Partial Pressure

The effect of H_2 partial pressure on the activity and selectivity was studied in a temperature range 433–463 K (see Table 10). With an increase in H_2 partial pressure, a marginal increase in the turnover number was observed, but the selectivity to acetic anhydride was found to decrease. The selectivity of ethylidene diacetate increased substantially with increase in H_2 pressure. Thus the highest selectivity to EDA (58.0%) was obtained at a H_2 partial pressure of 36.73 atm (Fig. 4).

Effect of $Rh(CO)Cl(PPh_3)_2$ Concentration

The effect of $Rh(CO)Cl(PPh_3)_2$ concentration on the activity and selectivity was studied in a temperature range 433–463 K. The results are presented in Table 11. With the increase in catalyst concentration, the turnover number was found to increase substantially, but the selectivity to EDA was marginally improved (up to 85% conversion). At lower conversion, the selectivity of acetic anhydride was very high, while as the reaction progressed, the hydrogenation of acetic anhydride dominated improving the selectivity of ethylidene diacetate. Thus, at a catalyst concentration of 9.76×10^{-6} mol/cm^3, 69.35% selectivity to ethylidene diacetate was achieved. The results on selectivity vs conversion at 433 K are presented in Fig. 5.

From the above study, palladium complexes used as co-catalysts were found to enhance the selectivity to

TABLE 7

Effect of Methyl Acetate Concentration on Activity[a] and Selectivity

Sr. No.	MeOAc ×10² (mol)	Temperature (K)	Turnover No. (mol/mol/h)[b]		Selectivity (%) EDA		Selectivity (%) Ac_2O	
			50% Conv.	(85% Conv.)	50% Conv.	(85% Conv.)	50% Conv.	(85% Conv.)
1	6.29	433	55	(48)	15.9	(32.0)	83.1	(66.8)
2	12.58	433	131	(96)	9.6	(28.2)	88.0	(69.17)
3	25.10	433	179	(89)	16.0	(40.0)	81.6	(59.22)
4	6.29	443	83	(76)	7.98	(24.5)	89.45	(75.3)
5	12.58	443	213	(158)	14.4	(26.35)	84.8	(67.76)
6	18.87	443	275	(172)	12.8	(26.35)	78.93	(70.9)
7	25.10	443	289	(151)	11.2	(37.2)	86.4	(60.23)
8	6.29	453	124	(110)	15.8	(22.6)	83.6	(76.60)
9	12.58	453	317	(220)	10.4	(22.5)	88.8	(77.3)
10	25.10	453	392	(234)	16.0	(27.5)	83.2	(72.10)
11	6.29	463	200	(144)	16.0	(20.6)	79.8	(78.10)
12	12.58	463	447	(268)	6.0	(22.5)	93.5	(76.50)
13	25.10	463	668	(282)	4.8	(22.6)	95.0	(77.10)

[a] Reaction conditions: $Rh(CO)Cl(PPh_3)_2$, 2.44×10^{-4} mol; PPh_3, 19.52×10^{-4} mol; methyl iodide, 6.43×10^{-2} mol; partial pressure of H_2, 18.36 atm; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm³.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

EDA, indicating that reduction of acetic anhydride is a dominant pathway for the formation of acetaldehyde. Of all the reaction conditions, temperature, catalyst concentration, and partial pressure of CO and of H_2 were found to influence the selectivity pattern considerably. Thus, relative rate of carbonylation and hydrogenation steps are affected by a change in partial pressure of CO and H_2. Higher selectivity to EDA at higher catalyst concentration may be due to the increase in the rate of hydrogenation of Ac_2O.

TABLE 8

Effect of Methyl Iodide Concentration on Activity and Selectivity[a]

Sr. No.	MeI ×10² (mol)	Temperature (K)	Turnover No. (mol/mol/h)[b]		Selectivity (%) EDA		Selectivity (%) Ac_2O	
			50% Conv.	(85% Conv.)	50% Conv.	(85% Conv.)	50% Conv.	(85% Conv.)
1	1.61	433	55	(34)	9.4	(27.5)	88.4	(71.3)
2	6.43	433	131	(89)	9.6	(28.2)	88.0	(69.77)
3	12.85	433	241	(158)	9.6	(24.0)	89.6	(75.80)
4	1.61	443	76	(62)	14.4	(25.53)	84.8	(67.76)
5	3.21	443	131	(96)	17.6	(30.90)	81.6	(68.70)
6	6.43	443	213	(158)	14.4	(26.35)	84.8	(67.76)
7	9.64	443	365	(227)	9.6	(24.5)	86.4	(73.40)
8	12.85	443	454	(282)	9.6	(25.4)	89.6	(69.17)
9	1.61	453	103	(83)	10.0	(20.40)	89.2	(78.55)
10	6.43	453	316	(220)	10.4	(22.5)	88.8	(77.30)
11	12.58	453	592	(392)	6.2	(14.2)	96.0	(85.10)
12	1.61	463	131	(96)	10.4	(20.5)	89.4	(79.00)
13	6.43	463	454	(268)	6.0	(16.0)	93.4	(78.10)
14	12.58	463	929	(626)	6.2	(16.0)	93.4	(78.10)

[a] Reaction conditions: $Rh(CO)Cl(PPh_3)_2$, 2.44×10^{-4} mol; PPh_3, 19.52×10^{-4} mol; methyl acetate, 0.125 mol; partial pressure of H_2, 18.36 atm; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm³.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

TABLE 9

Effect of CO Partial Pressure on Activity and Selectivity[a]

Sr. No.	P_{CO} (psig)	Temperature (K)	Turnover No. (mol/mol/h)[b] 50% Conv.	Turnover No. (mol/mol/h)[b] (85% Conv.)	Selectivity (%) EDA 50% Conv.	Selectivity (%) EDA (85% Conv.)	Selectivity (%) Ac_2O 50% Conv.	Selectivity (%) Ac_2O (85% Conv.)
1	70	433	55	(43)	32.5	(52.5)	66.5	(46.8)
2	540	433	131	(98)	11.6	(28.2)	86.0	(69.17)
3	810	433	124	(98)	12.8	(16.9)	87.2	(79.06)
4	70	443	103	(76)	25.4	(48.8)	73.8	(45.3)
5	140	443	124	(83)	20.8	(47.05)	75.2	(49.01)
6	210	443	172	(103)	16.0	(36.7)	86.4	(53.6)
7	540	443	213	(158)	14.4	(26.35)	84.8	(67.76)
8	810	443	261	(144)	11.2	(29.17)	80.0	(65.9)
9	70	453	158	(103)	25.6	(52.4)	72.0	(44.23)
10	540	453	317	(220)	10.4	(22.5)	88.8	(77.30)
11	810	453	317	(268)	8.0	(10.3)	91.3	(88.9)
12	70	463	213	(138)	12.8	(28.2)	86.3	(71.52)
13	540	463	447	(268)	6.0	(22.5)	93.5	(76.50)
14	810	463	413	(289)	4.8	(12.2)	94.0	(84.7)

[a] Reaction conditions: $Rh(CO)Cl(PPh_3)_2$, 2.44×10^{-4} mol; PPh_3, 19.52×10^{-4} mol; methyl acetate, 0.125 mol; methyl iodide, 6.43×10^{-2} mol; partial pressure of H_2, 18.36 atm; volume of liquid, 100 cm^3.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

DISCUSSION

The mechanism of hydrocarbonylation of methyl acetate has not been studied in detail earlier and it is important to discuss a possible reaction mechanism. During this reaction, it was possible to isolate a catalytic intermediate species when $RhCl_3 \cdot 3H_2O$ with 2,6-diphenylpyridine and methyl iodide was used as a catalyst. The details of characterization are discussed by Kumbhar *et al.* (25), wherein it is shown that the isolated complex consists of $[Rh(CO)_2I_4]^-$ stabilized by 2,6-diphenylpyridinium cation. Polichnowski (26) has characterized the active catalytic species in the carbonylation of methyl acetate, by *in situ* IR spectroscopy. He has shown that $[Rh(CO)_2I_2]^-$ and $[Rh(CO)_2I_4]^-$ are present under reaction conditions and $[Rh(CO)_2I_2]^-$ is the catalytically active species. When hydrogen (5%) is introduced in the gas phase, $[Rh(CO)_2I_4]^-$ is completely converted to $[Rh(CO)_2I_2]^-$ as follows:

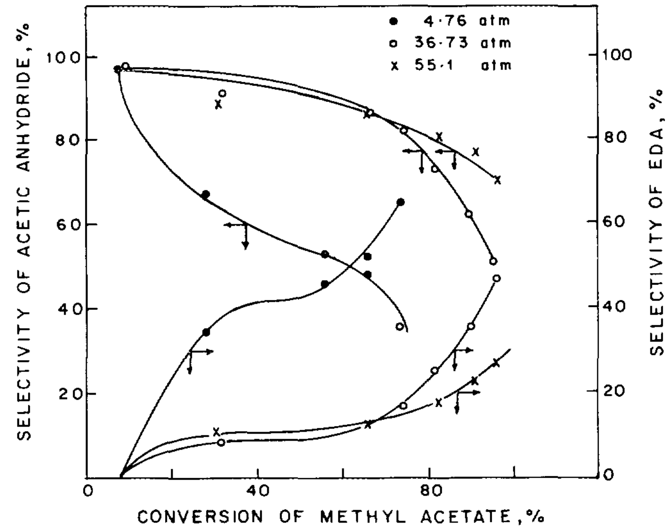

FIG. 3. Effect of CO partial pressure on conversion and selectivity. Concentrations; $Rh(CO)Cl(PPh_3)_2$, 2.44×10^{-6} mol/cm^3; PPh_3, 19.52×10^{-6} mol/cm^3 (temperature, 433 K); methyl acetate, 1.25×10^{-3} mol/cm^3; methyl iodide, 6.42×10^{-4} mol. Partial pressure of H_2, 9.52 atm; agitation speed, 1000 rpm.

$$[Rh(CO)_2I_4]^- + H_2 \rightarrow [Rh(CO)_2I_2]^- + 2HI. \qquad [vi]$$

Drawing analogy from the above results, in the present work $[Rh(CO)_2I_2]^-$ may be the catalytically active species, which can be converted to $[Rh(CO)_2I_4]^-$, when H_2 is removed from the gas phase (at the end of the reaction).

It is also important to consider the pathway for formation of acetaldehyde, which is formed as an intermediate. The possible routes are shown in reactions [ii] and [v]. However, reductive carbonylation of methyl acetate is not likely to be significant as it generally requires severe pressures in the range of 340 atm (27 and 28).

TABLE 10

Effect of H_2 Partial Pressure on Activity and Selectivity[a]

Sr. No.	P_H (psig)	Temperature (K)	Turnover No. (mol/mol/h)[b] 50% Conv.	Turnover No. (mol/mol/h)[b] (85% Conv.)	Selectivity (%) EDA 50% Conv.	Selectivity (%) EDA (85% Conv.)	Selectivity (%) Ac_2O 50% Conv.	Selectivity (%) Ac_2O (85% Conv.)
1	70	433	124	(83)	6.4	(13.2)	92.0	(83.76)
2	270	433	131	(96)	9.6	(28.2)	88.0	(69.17)
3	540	433	131	(96)	22.4	(37.64)	76.6	(59.3)
4	70	443	213	(151)	4.8	(8.47)	91.2	(88.4)
5	140	443	200	(158)	3.2	(13.7)	92.8	(86.6)
6	270	443	213	(158)	14.4	(26.35)	84.8	(67.76)
7	540	443	254	(151)	12.8	(39.53)	86.4	(56.0)
8	70	453	275	(248)	1.6	(5.6)	97.6	(94.0)
9	270	453	317	(220)	10.4	(22.5)	88.8	(77.30)
10	540	453	317	(234)	12.8	(22.6)	89.6	(76.8)
11	70	463	413	(268)	3.2	(7.6)	96.0	(91.3)
12	270	463	447	(268)	6.0	(22.5)	93.5	(76.50)
13	540	463	427	(282)	10.2	(20.6)	88.0	(77.1)

[a] Reaction conditions: $Rh(CO)Cl(PPh_3)_2$, 2.44×10^{-4} mol; PPh_3, 19.52×10^{-4} mol; methyl acetate, 0.125 mol; methyl iodide, 6.43×10^{-2} mol; partial pressure of CO, 36.73 atm; volume of liquid, 100 cm^3.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

When we consider hydrogenation of acetic anhydride as a possible route, the co-catalytic effect of palladium observed in the present work can be explained very easily. From the literature both Pd and Rh are good catalysts for the reduction of acetic anhydride to EDA (29–31). To confirm this, hydrogenation of acetic anhydride was carried out in the presence of CO, H_2, and $R(CO)Cl(PPh_3)_2$ as a catalyst. In this reaction, 84% conversion of Ac_2O was achieved with 90% selectivity to EDA, with traces of methyl acetate. The results obtained in the present work and the literature references indicate that the most likely pathway for the formation of acetaldehyde is the hydrogenation of Ac_2O.

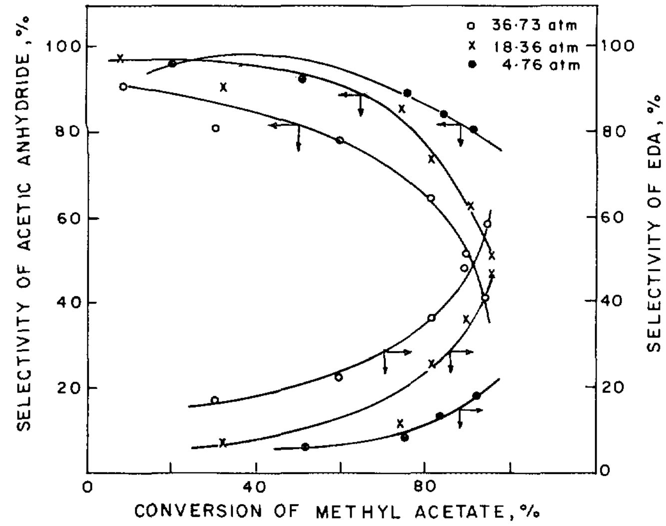

FIG. 4. Effect of H_2 partial pressure on conversion and selectivity. PPh_3: concentration, 19.52×10^{-6} mol/cm^3; temperature, 433 K. MeI: concentration, 6.42×10^{-4} mol/cm^3; agitation speed, 1000 rpm. Concentration of $Rh(CO)Cl(PPh_3)_2$, 2.44×10^{-6} mol/cm^3. Concentration of methyl acetate, 1.25×10^{-3} mol. Partial pressure of CO, 36.73 atm.

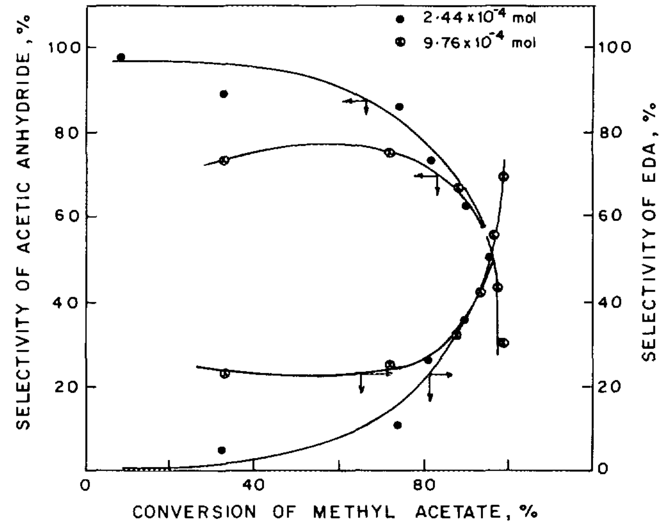

FIG. 5. Effect of catalyst concentration on conversion and selectivity. PPh_3 : $Rh(CO)Cl(PPh_3)_2$ ratio, 8. Concentration of methyl acetate, 1.25×10^{-3} mol/cm^3. Concentration, of methyl iodide, 6.42×10^{-4} mol/cm^3. Partial pressure of CO, 36.73 atm. Partial pressure of H_2, 9.52 atm. Temperature, 433 K. Agitation speed, 1000 rpm.

TABLE 11

Effect of Catalyst Concentration on Activity and Selectivity[a]

			Turnover No. (mol/mol/h)[b]		Selectivity (%)			
					EDA		Ac_2O	
Sr. No.	Catalyst $\times 10^5$ (mol)	Temperature (K)	50% Conv.	(85% Conv.)	50% Conv.	(85% Conv.)	50% Conv.	(85% Conv.)
1	6.1	433	206	(192)	6.4	(24.5)	92.8	(74.8)
2	24.4	433	131	(96)	9.6	(28.2)	88.0	(69.17)
3	97.6	433	89	(69)	20.8	(26.35)	78.4	(71.53)
4	6.1	443	303	(261)	6.4	(18.8)	86.4	(70.6)
5	12.2	443	248	(206)	16.0	(26.35)	83.2	(73.4)
6	24.4	443	213	(158)	14.4	(26.35)	84.8	(67.76)
7	48.8	443	165	(89)	12.8	(35.76)	78.9	(64.0)
8	97.6	443	144	(103)	19.2	(32.9)	75.2	(64.94)
9	6.1	453	365	(330)	6.2	(16.15)	93.3	(82.6)
10	24.4	453	317	(220)	10.4	(22.5)	88.8	(77.30)
11	97.6	453	213	(110)	12.4	(26.2)	86.8	(72.5)
12	6.1	463	502	(461)	10.2	(17.0)	89.2	(78.6)
13	24.4	463	447	(268)	6.0	(22.5)	93.5	(76.50)
14	97.6	463	254	(158)	6.4	(15.0)	93.1	(78.7)

[a] Reaction conditions: $Rh(CO)Cl(PPh_3)_2 : PPh_3$ ratio, 8; methyl acetate, 0.125 mol; methyl iodide, 6.43×10^{-2} mol; partial pressure of CO, 36.73 atm; partial pressure of H_2, 18.36 atm; volume of liquid, 100 cm^3.

[b] Turnover of methyl acetate consumed, mol/mol (complex)/h.

CONCLUSIONS

Hydrocarbonylation of methyl acetate using Rh catalyst was studied in a temperature range 433–463 K, and the selectivity to EDA was found to be sensitive to a change in the reaction condition. The following important observations were made:

(a) Palladium complexes used as co-catalysts were found to enhance the selectivity to EDA.

(b) Selectivity to EDA was enhanced by increase in catalyst concentration, H_2 partial pressure, and reducing temperature as well as CO partial pressure.

(c) The highest selectivity (69.35%) to EDA was obtained at 433 K and catalyst concentration of 9.76×10^{-6} mol/cm^3.

(d) Hydrogenation of acetic anhydride (reaction [v]) is the most likely pathway for the formation of acetaldehyde.

(e) A possible reaction pathway and nature of active catalytic species have been discussed.

REFERENCES

1. Ehler, J., and Juran, B., *Hydrocarbon Process.* **61**(2), 109 (1982).
2. Falbe, J., "New Syntheses with Carbon Monoxide." Verlag Chemie, Berlin, 1980.
3. Rizkalla, N., and Goliaszewski, A., "Industrial Chemicals Via C_1 Processes," ACS Symposium Series 136. Am. Chem. Soc., Washington, DC, 1987.
4. Isshiki, T., Kijima, Y., and Kondoh, T., EP 28, 515 (1981).
5. Drent, E., EP 48, 046 (1982).
6. Kudo, K., Mori, S., and Sugita, J., *Chem. Lett.*, 265 (1985).
7. Paulik, F. E., and Schulz, R. G., U.S. Patent No. 5, 117, 046 (1992).
8. Rizkalla, N., and Winnik, C. N. U.S. Patent No. 5, 138, 093 (1992).
9. Isshiki, T., Kijima, Y., Miyauchi, Y., and Yasunaga, T., EP 25, 515 (1981).
10. Rizkalla, N., U.S. Patent No. 4, 323, 697 (1982).
11. Lindner, E., Reber, J. P., and Wegner, P., DE 3, 934, 860.
12. Drent, E., U.S. Patent No. 4, 319, 038 (1982).
13. Kuebbler, H. K., Erpenbach, H., Gehrmann, K., and Kohl, G., U.S. Patent No. 4, 429, 150 (1984).
14. Evans, D., Osborn, J. A., and Wilkinson, G., *Inorg. Syntheses* **11**, 99 (1968).
15. Gupte, S. P., and Chaudhari, R. V., *J. Mol. Catal.* **24**, 197 (1984).
16. Evans, D., Yagupsky, G., and Wilkinson, G., *J. Chem. Soc. A*, 2260 (1983).
17. Collman, J. P., Sears, Jr., C. T., and Kubota, M., *Inorg. Syntheses* **11**, 101 (1968).
18. Stephenson, T. A., and Wilkinson, G., *J. Inorg. Nucl. Chem.* **28**, 945 (1965).
19. Itatani, H., and Bailar, Jr., J. C., *J. Am. Oil. Chem. Soc.* **44**, 147 (1967).
20. Fulford, A., Hickey, C. E., and Maitlis, P. M., *J. Organomet. Chem.* **398**, 311 (1990).
21. Moy, D., U.S. Patent No. 4356328 (1982).
22. Schrod, M., Luft, G., and Grobe, J., *J. Mol. Catal.* **22**, 169 (1983).
23. Freeman, F., and Karchewski E., *J. Chem. Eng. Data* **22**, 355 (1977).
24. Olah, G., and Mehrotra, A., *Synthesis*, 962 (1982).
25. Kumbhar, A. S., Padhye, S. B., Puranik, V. G., Dhaneshwar, N. N., Tavale, S. S., Kelkar, A. A., and Chaudhari, R. V., *J. Mol. Catal.* **75**, 187 (1992).
26. Polichnowski, S. W., *J. Chem. Educ.* **63**, 206 (1986).
27. Wegman, R. W., and Busby, D. C., *J. Chem. Soc. Chem. Commun.*, 332 (1986).
28. Pretzer, W., and Kobylinski, T., U.S. Patent No. 4, 133, 966 (1979).
29. Daicel Chemical Industries Ltd., JP 81, 25, 132 (1981).
30. Isshiki, T., Ito, A., Kijima, Y., and Watanabe, T., EP 34, 062 (1981).
31. Polichnowski, S. W., and Larkins, Jr., T. H., WO 82, 02, 172 (1982).