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Rhodium–Iodide Catalyzed Carbonylation of Methyl Formate into Acetaldehyde or Methyl Acetate: Mechanistic Aspects

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Under CO pressure, the rhodium/ionic-iodide system catalyzes either the reductive carbonylation of methyl formate into acetaldehyde or its homologation into methyl acetate. The influence of the reaction conditions on the selectivity of these two reactions was investigated and it was found that the former occurs selectively only in *N*-methylpyrrolidone (NMP) (or related solvents), for low I^-/Rh ratio, low substrate concentration, and high CO pressure, whereas methyl acetate is preferentially formed, in the same solvent, at higher I^- and substrate concentrations and under lower CO pressure. By using labeled methyl formate ($H^{13}CO_2CH_3$) it was also shown that the carbonyl group of acetaldehyde or methyl acetate does not result from that of methyl formate. *In situ* **IR studies conducted under catalytic conditions (high-pressure, high-temperature) have not enabled the identification of any other catalytic species than $RhI_2(CO)_2^-$ (which is also the active species in methanol or methyl acetate carbonylations), whatever the reaction conditions ([I^-], P_{CO} . . .). Plausible mechanisms are proposed for these reactions in which the essential role played by NMP in controlling the CH_3I content in the reaction medium is clarified and taking into account these experimental data.**

1. INTRODUCTION

During the past decade methyl formate (MF) has been the subject of great attention as a convenient C_1 building block (1). Indeed, it can be readily synthesized from methanol and carbon monoxide and as the reaction is equilibrated, it can be regarded as a convenient liquid source of its precursors:

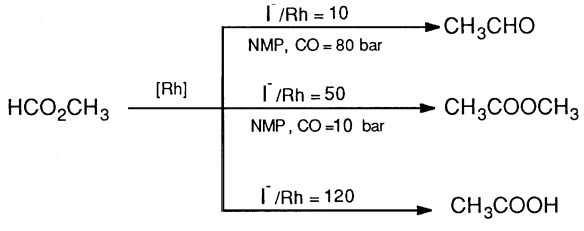
$$HCO_2CH_3 \overset{CH_3O^-}{\rightleftharpoons} CH_3OH + CO. \qquad [1]$$

In this context, we have previously reported that rhodium iodide systems can catalyze, in *N*-methylpyrrolidone (NMP) as solvent, the reductive carbonylation of methyl formate into acetaldehyde (2) or its homologation into methyl acetate (3) (Scheme 1). In these two unprecedented reactions, we have shown that among the parameters which influence the selectivity, the nature and content of the iodide promoter are the most important ones. On the other hand, it is well known that in the absence of solvent and at high promoter concentrations, acetic acid is preferentially obtained (4). For this last reaction two mechanisms have been proposed: decarbonylation of MF and subsequent carbonylation of methanol (5) (analogous to the Monsanto process) or more recently direct carbonylation of the ester to the mixed formic acetic anhydride with subsequent decomposition to acetic acid and CO (4).

In the same way, the hydrocarbonylation of methanol catalyzed by cobalt–iodide systems and giving acetaldehyde is also a well-known process (6).

$$CH_3OH + CO + H_2 \xrightarrow{[Co]-CH_3I} CH_3CHO + H_2O. \qquad [2]$$

The fact that reductive carbonylation of MF into acetaldehyde presents a stoichiometry totally different from this last reaction and the great differences in selectivity resulting from slight changes in the catalytic system and/or conditions have led us to look at the mechanistic aspects of these reactions. We report here the results of our investigations.



SCHEME 1. Methyl formate carbonylation.

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2. EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were recorded on Bruker AM400 or AC300 spectrometers. High-pressure, high-temperature infrared spectra were obtained on a Nicolet 510 spectrometer equipped with a MCT-A detector and integration, subtraction capabilities (NIC/IR Macintosh station). Typically 250 scans were taken per spectrum with a 4 cm^{-1} resolution. The optical bench attachment used the design developed by Barnes Analytical-Spectra Tech. The CIR autoclave (Parr modified reactor, 15 ml) equipped with a mechanical stirring and with an internal silicon or germanium reflection crystal was previously described by Moser *et al.* [7] and was purchased from Spectra Tech. GC analyses were performed on Chrompack 9000 or 9001 chromatographs equipped with a FID or a micro TCD (He as carrier gas) as detector. Different fused silica capillary columns were used: a 25 m × 0.53 mm Poraplot Q column (Chrompack) for gas analyses ($T = 25^\circ$C, μTCD). Liquids were analyzed on a 50 m × 0.53 mm CP-Sil 5CB column (Chrompack) or a 25 m × 0.32 mm FFAP-CB (Chrompack) ($T = 60$–180°C, μTCD). The above Poraplot Q column or a 30 × 0.25 m DB1 column (JW) were used for GC-mass coupled analyses.

Materials

All compounds except deuterated methyl formate were commercial products and were generally used without purification except methyl formate and solvents which were dried over molecular sieves (4A) and distilled under nitrogen. It should be noted that commercial methyl formate contains about 3–4% of methanol and that classical distillation does not improve its purity.

HCO_2CD_3 was synthesized by esterification of formic acid (25 g, 0.54 mol) by CD_3OD (11.5 g, 0.32 mol). The distillation of deuterated methyl formate formed during the reaction shifts the equilibrium and allows one to achieve the esterification with a high yield. A further distillation of the crude HCO_2CD_3 on an efficient column (spinning band) leads to a purity of about 99%.

DCO_2CH_3 was obtained by carbonylation of CH_3OD catalyzed by $NaOCH_3$. The reaction was performed in a 100 ml stirred autoclave at 80°C under 80 bar CO pressure with 25 g (0.75 mol) of CH_3OD and 0.5 g of $NaOCH_3$. At the end of the reaction, 1 ml of water was added to the reaction mixture in order to destroy the catalyst and avoid the decarbonylation of MF. A distillation as above then gave deuterated methyl formate with the same purity.

Typical Procedure for Reductive Carbonylation of Methyl Formate

All reactions were carried out in a 100-ml stainless-steel autoclave equipped with a mechanical stirrer. The batch reactor was enclosed in an electric furnace whose temperature was monitored and controlled by a thermocouple and a PID temperature controller. In a standard experiment $RhCl_3 \cdot 3H_2O$ (0.125 mmol), LiI (1.9 mmol), methyl formate (80 mmol), and NMP (50 ml) were charged into the reactor under nitrogen. The autoclave was purged and pressurized with CO (10 bar) prior to stirring and heating. When the reaction temperature was reached (180°C), the pressure was adjusted by addition of CO (80 bar) and the reaction performed under vigorous agitation. The reaction medium was sampled during the reaction for GC analyses. For kinetic measurements the time corresponding to the last addition of CO was considered as the beginning of the reaction. After reaction, the autoclave was cooled to room temperature and degassed. The exact volume of the off-gas was determined and the gas and liquid phases were analyzed by GC.

Procedure for Homologation of Methyl Formate

The same procedure as above was used for homologation of methyl formate after adjustment of the reaction conditions (amount of products, P_{CO} and temperature).

Procedure for Studies with Labeled Methyl Formate

Due to the low reaction volume, the experiments conducted from $H^{13}CO_2Me$ were carried out in a 50-ml autoclave in order to obtain a better stirring. The autoclave was equipped with a Teflon liner and a magnetic stirrer and was heated in an oil bath. On the other hand, the reactions using deuterated methyl formate were achieved in the standard 100-ml reactor.

3. RESULTS

3.1. Reaction Stoichiometry and By-products

Acetaldehyde

As previously reported (2), carbon dioxide is coproduced during acetaldehyde synthesis from methyl formate. The determination of its quantity in the gas phase has shown that 1 mol of CO_2 is formed per mole of acetaldehyde according to Eq. [3]. In addition, the gas-phase analysis has also proved that a small amount of methane ($CH_4/CO_2 = 0.1$) is produced during the reaction.

$$HCO_2CH_3 + CO \xrightarrow[NMP]{[Rh]-I^-} CH_3CHO + CO_2 \qquad [3]$$

In the liquid phase, under optimized experimental conditions for acetaldehyde synthesis, methanol and butanal are the main by-products (see Table 1). Methanol is produced by decarbonylation of methyl formate according to Eq. [1]. Butanal is only observed at high conversion. This observation suggests that it arises from aldolization of acetaldehyde followed by dehydration to butenal which is further

hydrogenated at the C=C double bond.

$$2\,CH_3CHO \rightarrow CH_3CH{=}CHCHO + H_2O \quad [4]$$

$$H_2O + CO \rightarrow CO_2 + H_2 \quad [5]$$

$$CH_3CH{=}CHCHO + H_2 \rightarrow CH_3CH_2CH_2CHO \quad [6]$$

The hydrogen required for this latter reaction (Eq. [6]), is probably formed via Eq. [5], by a water gas shift reaction (WGSR), which is known to be catalyzed by rhodium complexes (8).

Methyl Acetate

According to the stoichiometry of the reaction 2 mol of methyl formate are necessary to obtain 1 mol of methyl acetate (Eq. [7]).

However, formic acid which is formally expected to be coproduced (Eq. [7a]), has never been detected by gas chromatography (using a microcatharometer as detector). Moreover, when it was introduced into the autoclave during the reaction course (with a high-pressure metering pump) its decomposition was very slow. Therefore, it could be deduced that methyl acetate does not arise from simple transesterification between acetic acid (which may be the primary product of the reaction) and unreacted methyl formate. Hence, the overall homologation reaction of methyl formate into methyl acetate should be expressed by Eq. [7b] rather than Eq. [7a], consistent with the determination of CO_2 in the gas phase.

$$2\,HCO_2CH_3 \xrightarrow[NMP-CO]{Rh/I^-} CH_3COOCH_3 + HCO_2H \quad [7a]$$

$$2\,HCO_2CH_3 \rightarrow CH_3COOCH_3 + CO_2 + H_2 \quad [7b]$$

TABLE 1

Reductive Carbonylation of Methyl Formate into Acetaldehyde: Influence of the Nature of Catalytic Precursors

No.	Catalytic precursor	t (h)	Conversion (%)	Selectivity[a] (mol%) AcH	AcOMe	AcOH	MeOH
1	CoI_2	1	40	0	2	98	0
2	$PdCl_2(PPh_3)_2$	6	19	20	55	0	25
3	$Fe_2(CO)_9$	6	15	18	31	0	51
4	NiI_2	14	82	0	20	78	2
5	$IrCl(CO)(PPh_3)_2$	1	34	70	0	0	30
6	$RuCl_3 \cdot 3H_2O$	1	46	85	0	0	15
7	$RhCl_3 \cdot 3H_2O$	1	35	73	0	0	20[b]
8	$[RhCl(CO)_2]_2$	1	34	83	0	0	14[b]
9	$RhCl(CO)(PPh_3)_2$	2	46	85	0	0	2[b]
10	$Rh_6(CO)_{16}$	1	32	86	0	0	13

Note. Conditions: Catalytic precursor, 0.125 mmol; LiI, 1.9 mmol; HCO_2Me, 81 mmol; NMP, 50 ml; T, 180°C; P_{CO}, 80 bar.

[a] Selectivity in the liquid phase.

[b] Butanal is also formed.

TABLE 2

Homologation of Methyl Formate into Methyl Acetate: Influence of the Nature of Catalytic Precursors

No.	Catalytic precursor	t (h)	Conversion (%)	Selectivity[a] (mol%) AcH	AcOMe	AcOH	MeOH
1	CoI_2	4	16	11	83	0	5
2	CoI_2	5	90	0	98	0	0
3	$PdCl_2(PPh_3)_2$	2	89	6	48	45	0
4	$IrCl(CO)(PPh_3)_2$	1.5	91	15	6	43	21
5	$RuCl_3 \cdot 3H_2O$	1.5	81	14	48	0	28
6	$RhCl_3 \cdot 3H_2O$	5	95	3	90	3	0
7	$RhCl(CO)(PPh_3)_2$	5	62	7	88	0	0

Note. Conditions: Catalytic precursor, 0.125 mmol, except No. 2; CoI_2, 8 mmol; LiI, 7.5 mmol; HCO_2Me, 250 mmol; NMP, 15 ml; T, 195°C; P_{CO}, 10 bar.

[a] Selectivity in the liquid phase.

As shown in Table 2, the selectivities into methyl acetate are high (~90%) even at high conversion (Nos. 6 and 7), the main side products under optimized conditions being acetaldehyde, ethyl formate, ethyl acetate, and acetic acid. It should be noted that a specific search for dimethyl ether was also carried out, as suggested by a referee. Chromatographic analysis on different columns showed the presence, in the gas phase, of a compound that presented the same retention time as an authentic sample of CH_3OCH_3 with a ratio CH_3OCH_3/CO_2 of about 0.05. On the other hand, under acetaldehyde formation conditions, dimethyl ether was detected only as a very small trace.

3.2. Influence of Reaction Conditions on Activity and Selectivity

(a) Catalytic Precursor

We have been studying the reactivity of various catalytic systems classically used in carbonylation reactions (Tables 1 and 2). Among them, rhodium has given the best results, although ruthenium and iridium can also catalyze acetaldehyde synthesis with a high liquid phase selectivity (see Table 1, Nos. 5 and 6); however, in both of these cases the amount of methane in the gas phase is higher ($CH_4/CO_2 = 1/4$ to $1/2$) than that observed with rhodium. In addition, they are not selective toward methyl acetate synthesis (Table 2, Nos. 4 and 5). On the other hand, the exact nature of the rhodium precursor generally has only little influence on the reaction course (see Table 1, Nos. 7–10 and Table 2, Nos. 6 and 7).

(b) Role of the Solvent

Table 3 shows that in the absence of solvent the yields of acetaldehyde and methyl acetate are very low (Nos. 1 and 11). In both cases MeOH resulting from decarbonylation of MF (Eq. [1]) or acetic acid are the main by-products

TABLE 3

Solvent Effect on the Selectivity in Methyl Formate Carbonylation

No.	Conditions	Solvent	*t* (h)	Conversion (%)	Selectivity[a] (mol%)			
					AcH	AcOMe	AcOH	MeOH
1	A	None	1.5	9	0	20	0	80
2	A	Toluene	3	5	0	100	0	0
3	A	Octane	3	10	0	80	20	0
4	A	DMF	1	49	15	5	0	80
5	A	Pyrrolidone	6	53	0	4	0	96
6	A	DMA	2	24	52	6	0	42
7	A	γ-Butyrolactone	6	57	40	56	0	4
8	A	NMP	2	38	85	0	0	10
9	A	DMI	4	70	75	4	0	20
10	A	NMP + H_2O[b]	2	50	50	0	0	49
11	B	None	5	38	0	75	20	0
12	B	Toluene	4	50	0	23	77	0
13	B	Octane	5	90	0	40	60	0
14	B	γ-Butyrolactone	5	60	1	85	10	3
15	B	DMF	4	48	4	50	23	13
16	B	DMA	4	50	2	80	0	12
17	B	DMI	4	87	10	28	0	60
18	B	NMP	5	95	2	92	3	0

Note. Conditions: $RhCl_3 \cdot 3H_2O$, 0.125 mmol. A: solvent, 50 ml; LiI, 1.9 mmol; HCO_2Me, 81 mmol; *T*, 180°C; P_{CO}, 80 bar. B: solvent, 15 ml; $RhCl_3 \cdot 3H_2O$, 0.125 mmol; LiI, 9.5 mmol; HCO_2Me, 250 mmol; *T*, 195°C; P_{CO}, 10 bar.

[a] Selectivity in the liquid phase.

[b] H_2O, 80 mmol.

whatever the amount of lithium iodide. To obtain high acetaldehyde yield and selectivity it is necessary that the reaction takes place in *N*-methylpyrrolidone as solvent, or in similar solvents such as *N*,*N*-dimethylimidazole (DMI) and *N*-ethylpyrrolidone. In other amides such as pyrrolidone, dimethylformamide (DMF), and dimethylacetamide (DMA), the main reaction is again decarbonylation of MF, which is favored by the solvent basicity or more probably catalyzed by amines resulting from decomposition of amides at high temperature. The same behavior is also observed in tertiary amines: triethylamine, *N*-ethylpiperidine, etc. (9).

Finally, in less polar or nonpolar solvents, activity and/or selectivity are low and the reaction gives a mixture of methyl acetate and acetic acid (Table 3, Nos. 2, 3, 12, and 13).

NMP is also needed to obtain methyl acetate in high yields; nevertheless, good results are still observed with γ-butyrolactone or DMA (Table 3, Nos. 14 and 16) and it should also be noted that selective synthesis of methyl acetate requires a lower solvent/substrate ratio than acetaldehyde (typically 1/1 (vol/vol) and 10/1, respectively).

(c) Influence of Halide Promoters

We refer first to the qualitative aspects. Numerous rhodium-based catalyzed carbonylations such as that of methanol into acetic acid (Monsanto process) are carried out in the presence of methyl iodide as promoter (10). It has been reported that ionic iodides (LiI, etc.) are much more active promoters than covalent iodides (CH_3I, I_2, etc.) for isomerization of methyl formate into acetic acid (4). Table 4 shows, in the same way, that in NMP, acetaldehyde, and methyl acetate are selectively obtained only in the presence of ionic iodides. Other ionic halides (bromide or more markedly chloride) are practically inactive, whereas with covalent iodides, the activities are not only poor, particularly at high dilution (Table 4, Nos. 5 and 6) but also the selectivities drastically decrease (compare Table 4, Nos. 3 and 5 or 13 and 16). In that case, the addition of triaryl phosphines or tertiary amines (one equivalent of phosphine or amine per iodide) which are able to generate phosphonium or ammonium iodide salts according to Eqs. [8] and [9], respectively, restores the initial activities and selectivities.

$$CH_3I + PR_3 \rightarrow CH_3PR_3^+I^- \qquad [8]$$

$$CH_3I + NR_3 \rightarrow CH_3NR_3^+I^- \qquad [9]$$

The nature of the phosphonium or ammonium group as well as that of the alkaline cation in the case of ionic promoter have only little influence on the results (see Table 4, Nos. 3, 4, 13, and 14).

Turning to quantitative aspects, classically the activity is enhanced by increasing the promoter concentration; however, this parameter has a greater effect on the selectivity. Figure 1 shows the influence of the I^-/Rh ratio on the

TABLE 4

Influence of the Halogen Source as Promoter on the Carbonylation of Methyl Formate

No.	Conditions	Promoter	*t* (h)	Conversion (%)	Selectivity (mol%)			
					AcH	AcOMe	AcOH	MeOH
1	A	LiCl	3	6	40	0	0	60
2	A	LiBr	2	12	64	0	0	36
3	A	LiI	2	22	86	1	0	11
4	A	NaI	2	20	82	2	0	15
5	B	CH_3I	15	20	18	12	0	64
6	B	I_2	15	26	15	0	0	77
7	B	$I_2 + PPh_3$ (1/1)	2	38	84	0	0	2
8	B	$CH_3I + PPh_3$ (1/1)	3	38	82	0	0	10
9	B	$PhI + PPh_3$ (1/1)	1	34	78	6	0	13
10	B	$CH_3I + NEt_3$ (1/1)	1	30	84	0	0	12
11	C	HI (aq.)	6	30	60	14	0	26
12	C	$HI + PPh_3$ (1/1)	6	64	81	0	0	19
13	D	LiI	5	95	3	88	3	0
14	D	NaI	5	84	3	82	0	3
15	D	LiBr	5	26	7	57	0	0
16	D	CH_3I	5	90	0	20	72	0
17	D	I_2	5	88	0	41	57	0
18	D	$CH_3I + NEt_3$ (1/1)	5	94	0	43	44	0
19	D	$LiI + CH_3I$ (1/1)	5	95	2	70	26	0

Note. Conditions: A: $RhCl_3 \cdot 3H_2O$, 0.125 mmol; promoter, 1.86 mmol; HCO_2Me, 81 mmol; NMP, 50 ml; P_{CO}, 80 bar; *T*, 180°C. B: same conditions as A except $Rh(CO)Cl(PPh_3)_2$, 0.125 mmol; promoter, 0.3 mmol (Nos. 5 and 6) or 0.6 mmol. C: same conditions as A except HCO_2Me, 52 mmol; P_{CO}, 100 bar; *T*, 170°C. D: $RhCl_3 \cdot 3H_2O$, 0.15 mmol; promoter, 7.5 mmol; HCO_2Me, 250 mmol; NMP, 15 ml; P_{CO}, 10 bar; *T*, 195°C.

acetaldehyde selectivity under other optimized conditions. The selectivity drastically decreases by formation of methyl acetate upon increasing the I^- amount. However, a I^-/Rh ratio of about 10–15 seems to be the best compromise in order to obtain a high activity and to preserve a high selectivity.

As illustrated in Fig. 2, the same observations can be made in the case of the synthesis of methyl acetate, i.e., an increase of I^- concentration leads to the formation of acetic acid. The substitution of ionic iodide by covalent iodide at the same concentration has the effect of shifting

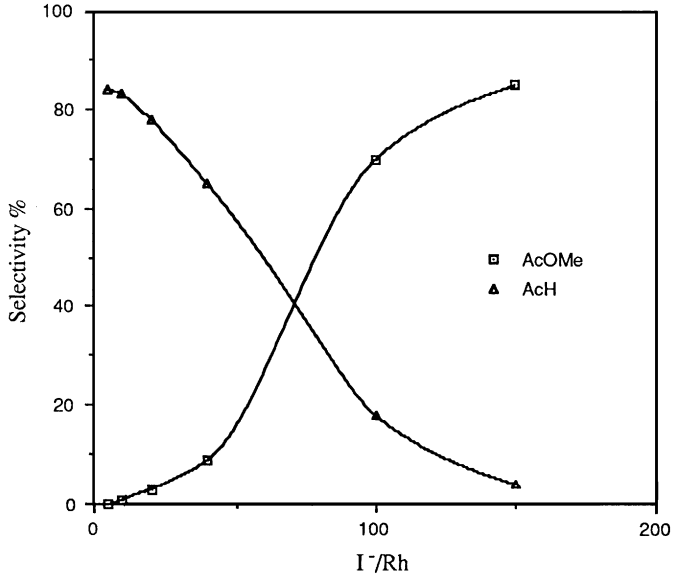


FIG. 1. Selectivity versus I^-/Rh at high CO pressure and high solvent/substrate ratio. Conditions: $RhCl_3 \cdot 3H_2O$, 0.125 mmol; HCO_2Me, 80 mmol (5 ml); NMP, 50 ml; P_{CO}, 50 bar; *T*, 180°C.

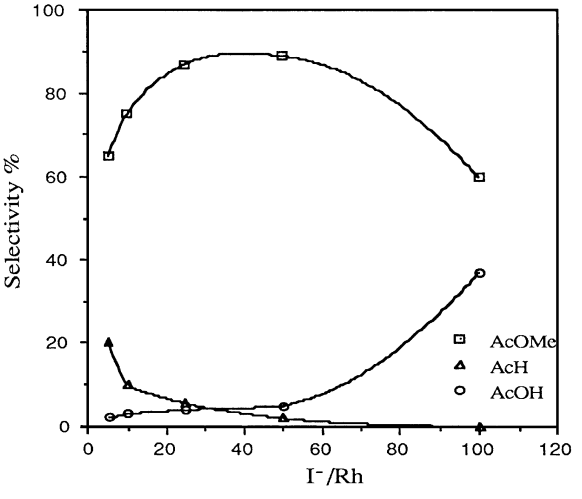


FIG. 2. Selectivity vs I^-/Rh ratio at low CO pressure and moderate solvent/substrat ratio. Conditions: $RhCl_3 \cdot 3H_2O$, 0.125; HCO_2Me, 250 mmol (15 ml); NMP, 15 ml; P_{CO}, 10 bar; *T*, 190°C.

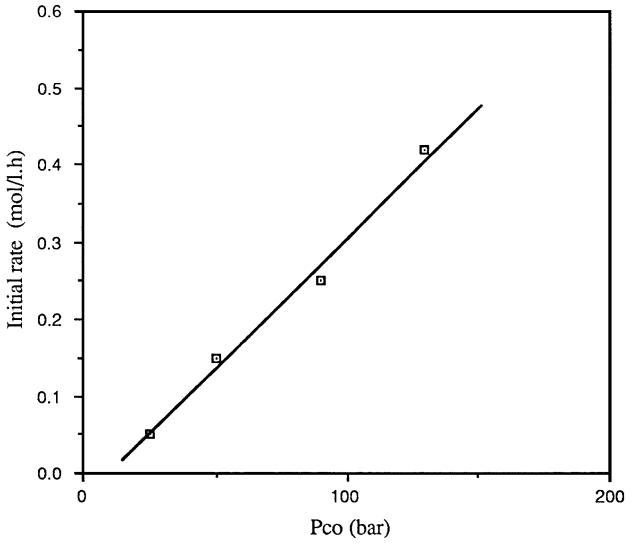


FIG. 3. CO pressure effect on initial rate of reductive carbonylation of methyl formate into acetaldehyde. Conditions: $RhCl_3 \cdot 3H_2O$, 0.125 mmol; LiI, 1.86 mmol; HCO_2Me, 160 mmol; NMP, 30 ml; *T*, 180°C.

the observed curves in Figs. 1 and 2 to the left and therefore in those conditions acetaldehyde can never be obtained selectively.

(d) Influence of CO Pressure

According to the stoichiometry of Eq. [3], 1 mol of CO is consumed per mole of acetaldehyde, so a CO pressure is necessary to achieve the reaction with a high yield. Figure 3 shows that the activity is directly related with the CO pressure. In contrast, CO is not theoretically involved in the formation of methyl acetate. However, a CO pressure near to 10 bar gives the best yields (see Table 5). Below this value, an improvement in activity was observed, but the selectivity drastically decreases essentially by formation of acetic acid. On the other hand, increasing the CO pressure has not only a considerable inhibition effect on the rate but the selectivity decreases again by formation of ethanol and ethyl formate (Table 5, No. 5). These by-products probably arise via the hydrogenation of acetaldehyde which is the primary by-product of the reaction followed by subsequent transesterification:

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH \quad [10]$$

$$CH_3CH_2OH + HCO_2CH_3 \rightarrow HCO_2Et + CH_3OH \quad [11]$$

TABLE 5

Effect of CO Pressure on the Synthesis of Methyl Acetate

No.	CO pressure (bar)	*t* (h)	Conversion %	Selectivity (mol%) AcH	AcOMe	AcOH	Others
1	0	1	95	0	16	84	0
2	5	3	98	0	21	79	0
3	10	5	95	3	88	3	6
4	20	5	74	6	83	0	10[a]
5	60	5	70	19	37	0	43[b]

Note. Conditions: NMP, 15 ml; HCO_2Me, 250 mmol; $RhCl_3 \cdot 3H_2O$, 0.125 mmol; LiI, 7.5 mmol; *T*, 195°C.

[a] MeOH, HCO_2Et, EtOH, and AcOEt, 2, 6, 1, and 1%, respectively.

[b] MeOH, HCO_2Et, EtOH, and AcOEt, 9, 24, 6, and 4%, respectively.

(e) Influence of Temperature

A high activity of the Rh/I^- catalytic system is achieved at 180 and 195°C for acetaldehyde and methyl acetate syntheses, respectively. As usual, the activity is enhanced when the temperature increases; above 210–220°C, however, the formation of side-products significantly increases, whereas the efficiency of the system is very low below 150°C.

Under other standard conditions as described above for acetaldehyde or methyl acetate syntheses, liquid samples taken at periodic times and analyzed by GC allow us to draw the curves depicting the product distribution as a function of time at various temperature. From these curves, the initial rate of formation of acetaldehyde or methyl acetate vs temperature can be determined over the range 170–210°C and the apparent activation energy (E_a) can be calculated from a simple Arrhenius plot (Fig. 4). The E_a for acetaldehyde (21.4 kcal mol^{-1}) is much higher than that for methyl acetate (11.5 kcal mol^{-1}).

3.3. Mechanistic Considerations

3.3.1. Use of Labeled Substrates

In order to increase knowledge on the mechanism of these reactions, the origin of the atoms of acetaldehyde,

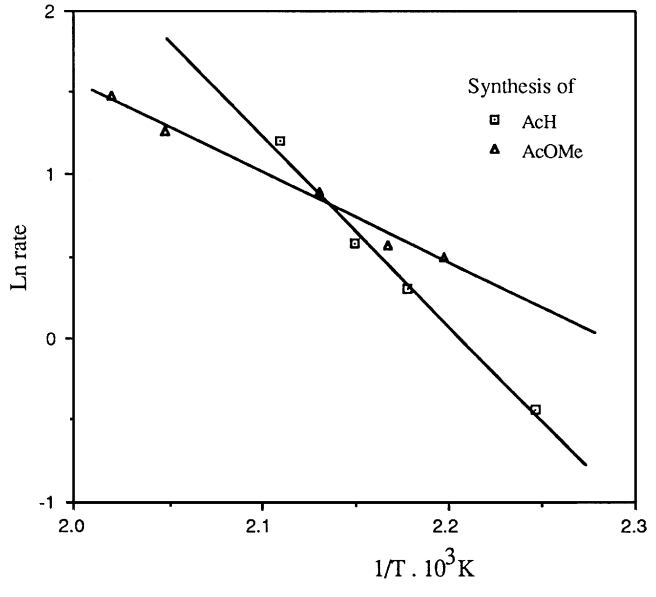


FIG. 4. Arrhenius plot for acetaldehyde and methyl formate synthesis.

TABLE 6

Reductive Carbonylation of Labeled Methyl Formate into Acetaldehyde

No.	Substrate (isotopic purity %)	Isotopic distribution[a] (%) Acetaldehyde 43	44	45	46	47	CO_2 44	45
1	HCO_2CH_3	35	64	2	0	0	99	1
2	$H^{13}CO_2CH_3$ (92)	35	63	3	0	0	26	74
3	HCO_2CD_3 (99)	0	0	0	34	62	—	—
4	DCO_2CH_3 (99)	0	28	39	25	9	—	—

Note. Conditions: $RhCl_3 \cdot 3H_2O$, 0.125 mmol; LiI, 1.86 mmol; substrate, 81 mmol; NMP, 50 ml; P_{CO}, 80 bar; T, 180°C except No. 2: $Rh_6(CO)_{16}$, 0.6 mmol; LiI, 5 mmol; substrate, 8 mmol; NMP, 15 ml.

[a] The isotopic distribution was determined from the molecular peak of mass spectra and verified by NMR.

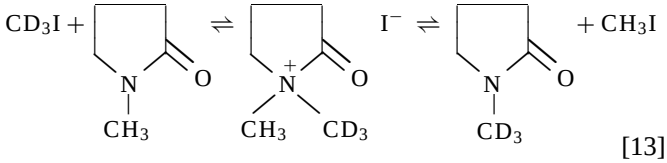
methyl acetate, and coproducts has been determined by using isotopically enriched reactants.

Acetaldehyde synthesis. When the synthesis of acetaldehyde was carried out from methyl formate with a totally ^{13}C-labeled carbonyl group, the acetaldehyde formed contained a $^{13}C/^{12}C$ ratio corresponding strictly to the ratio observed in the natural product. Moreover, the carbon dioxide coproduced exhibited more than 75% of ^{13}C (Table 6, No. 2).

These results indicate that the carbonyl group of MF is not retained in acetaldehyde. The finding that CO_2 is not totally labeled can be explained by the existence of a WGSR between CO and water present in the solvent and substrate. As the amount of labeled MF used in this experiment compared with that in the solvent is much smaller than in a standard reaction, the part of CO_2 resulting from WGS, and consequentlly unlabeled, is more important.

Deuterated methyl formates were also tested. Thus, when the reaction was conducted with HCO_2CD_3 as substrate, the methyl group of acetaldehyde was practically totally labeled and no transfer of CD_3 to NMP was observed (Table 6, No. 3). From this result, we can deduce that the solvent does not intervene in a reaction where it could have participated via ammonium cation exchange reactions (Eq. [13]) after cleavage of HCO_2CD_3 by ionic iodide (vide infra).

$$HCO_2CD_3 + I^- \rightleftharpoons CD_3I + HCO_2^- \qquad [12]$$



[13]

On the other hand, acetaldehyde obtained from DCO_2CH_3 showed a wider isotopic distribution (Table 6, No. 4). This observation is probably connected with the enolization of acetaldehyde and proton exchange with methanol resulting from decarbonylation of methyl formate according to the following reactions:

$$DCO_2CH_3 \rightarrow CH_3OD + CO \qquad [14]$$

$$CH_3CDO \rightleftharpoons CH_2{=}C(OH)(D) \underset{-CH_3OH}{\overset{+CH_3OD}{\rightleftharpoons}} CH_2{=}C(OD)(D) \rightleftharpoons CH_2D{-}C(=O)(D) \qquad [15]$$

The fact that this process does not occur with CD_3CHO (resulting from the carbonylation of HCO_2CD_3) is consistent with the large isotope effect generally observed in enolization reactions (11).

Methyl acetate synthesis. Table 7 shows the results observed in the homologation of labeled methyl formate ($H^{13}CO_2CH_3$, HCO_2CD_3, and DCO_2CH_3) into methyl acetate.

With regard to the initial amount of $H^{13}CO_2CH_3$, about one-third of ^{13}C is found in methyl acetate, and the main part is distributed among its coproducts CO and CO_2 (Table 7, No. 2).

$$2\,H^{13}CO_2CH_3 + CO \xrightarrow[NMP]{Rh-I} \underset{1/3\,\text{initial}\ ^{13}C}{CH_3{}^{13}CO_2CH_3} + \underbrace{{}^{13}CO + {}^{13}CO_2}_{2/3\,\text{initial}\ ^{13}C} + H_2 \qquad [16]$$

Although it is difficult to conclude with certainty, this result seems again rather in favor of the nonretention of the methoxycarbonyl group of MF. The fact that an important part of the methyl acetate was labeled may be due to the reincorporation of a part of ^{13}CO released in

TABLE 7

Homologation of Labeled Methyl Formate into Methyl Acetate

No.	Substrate (isotopic purity%)	Methyl acetate isotopic distribution[a] (%) 74	75	76	77	80
1	HCO_2CH_3	96	3	—	—	—
2	$H^{13}CO_2CH_3$ (46)	80	20	—	—	—
3	HCO_2CD_3 (99)	—	—	—	1.5	98
4	DCO_2CH_3 (99)	95	4	—	—	—

Note. Conditions: $RhCl_3 \cdot 3H_2O$, 0.125 mmol; LiI, 7.5 mmol; substrate, 250 mmol; NMP, 15 ml; P_{CO}, 10 bar; T, 190°C except No. 2: substrate, 17 mmol; NMP, 5 ml.

[a] The isotopic distribution was determined from the molecular peak of mass spectra and verified by NMR.

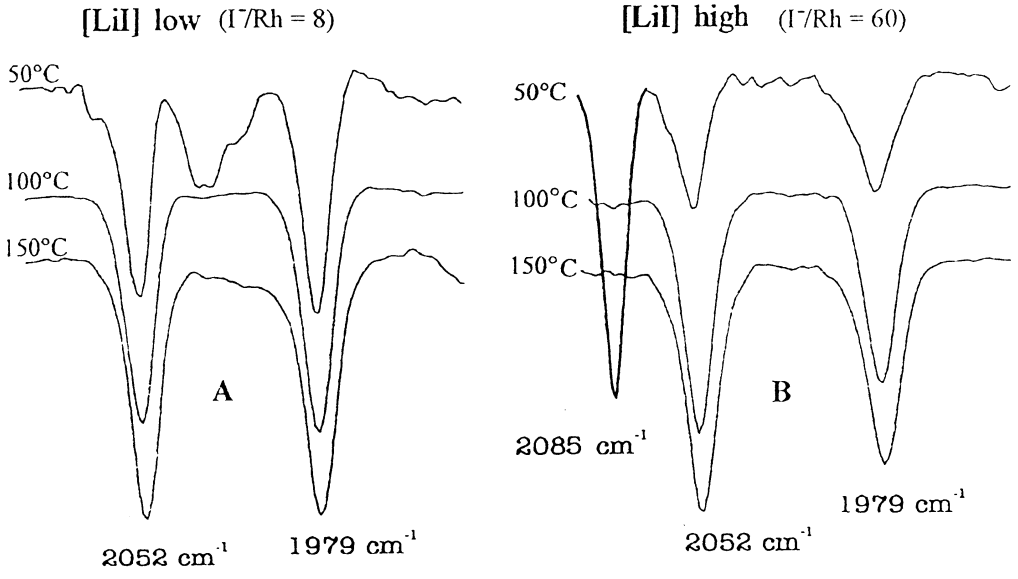


FIG. 5. High-pressure FTIR spectra (νCO region) presented as transmission vs wavenumber (cm^{-1}) for Rh catalyst under different reaction conditions. Spectra A: $RhCl_3 \cdot 3H_2O$, 0.25 mmol; LiI, 2 mmol; HCO_2Me, 25 mmol; NMP, 10 ml; P_{CO}, 50 bar. Spectra B: Same conditions as spectra A except LiI, 15 mmol; HCO_2Me, 100 mmol; NMP, 6 ml.

the liquid phase during the last step of the reaction (see Scheme 4).[4]

Finally, methyl acetate resulting from HCO_2CD_3 was completely deuterated, whereas when DCO_2CH_3 was used as substrate, methyl acetate exhibited no label at all.

3.3.2. High-Pressure in Situ Infrared Spectroscopic Study

It is interesting to compare our systems with that described for the well-known methanol carbonylation reaction for which a great deal of work has been done from a mechanistic point of view. The $[RhI_2(CO)_2]^-$ ion **1** was early identified as the active species (12). Later, acyl and alkyl rhodium complexes, $[Rh(CO)(COMe)I_3]^-$ and $[MeRh(CO)_2I_3]^-$, were spectroscopically detected and characterized as reactive intermediates but not under catalytic conditions (13). Recently rhodium (III) hydrides, $[HRh(CO)I_3]^-$ and $[HRh(CO)_2I_2]$, were detected by ^1H and ^{13}C NMR spectroscopy and also proposed as intermediates (14). Using rhodium/iodide-based catalytic precursor, it has to be pointed out that the presence of *N*-methylpyrrolidone as solvent and the Rh/I^- ratio are crucial to obtain selective carbonylations of methyl formate. In order to gain insight into the nature of the species involved in the catalytic cycles, an *in situ* HP-FTIR spectral study was conducted utilizing a high-pressure CIR reactor (see Experimental).

Both catalytic reactions were followed *in situ* by FTIR and the results are presented in Fig. 5. Spectra A show the evolution of the system with temperature leading to the formation of acetaldehyde. For this system, a weak amount of lithium iodide is required. At 50°C the infrared spectrum showed two main absorption bands in the carbonyl region at 2052 and 1979 cm^{-1}. By comparison with literature data and an authentic sample prepared separately, these absorptions can be assigned to the square planar Rh^I anion $[RhI_2(CO)_2]^-$ **1**. Upon heating to 150°C, no other absorption band appears or disappears.

Now, if we compare the series of infrared spectra A with those of spectra B (Fig. 5) for which the amount of lithium salt is present in large excess and thus favours the synthesis of methyl acetate, we can observe at 50°C, besides the peaks in spectra A, a supplementary absorption band at 2085 cm^{-1}. When the temperature increases, this last peak disappears (around 80°C). Furthermore, coming back to the initial temperature restores this absorption.

We have tried to attribute this absorption band at 2085 cm^{-1}. For that we ran some experiments for which the rhodium precursor, solvent or substrate were changed. Thus the reactions which were realized with RhI_3 alone have the same behavior as those using $RhCl_3 \cdot 3H_2O$. Indeed in the absence of lithium iodide (that is to say when the unique source of iodide is the complex itself), only the typical signal due to $[RhI_2(CO_2)]^-$ is observed. When the lithium salt is added in excess to the starting solution, we observed the peak at 2085 cm^{-1} and the influence of the temperature is similar to the $RhCl_3$ based system. Thus we can eliminate

[4] Calculations of ^{12}CO consumed and ^{13}CO released during the reaction according to the mechanism outlined in Scheme 4 and considering the gas as perfect, indicates that with a 50-ml reactor used in this experiment and for 10 bar initial CO pressure, about 50 to 60% of CO in the gas phase should be labeled at the end of the reaction for 80% methyl formate conversion.

the formation of a mixed halogenorhodium complex such as $[RhCl(I)(CO)_2]^-$. In the same way the use of hexadecacarbonylhexarhodium, $Rh_6(CO)_{16}$, with or without LiI in excess, led in both cases only to $[RhI_2(CO)_2]^-$. Only its formation rate is different (slowest under these conditions).

It was also noticed that in the absence of NMP (i.e. in pure methyl formate or in a nonpolar solvent such as toluene) the peak at 2085 cm^{-1} is the only one observed in the νCO region and remains present until 120°C. Moreover, when methyl formate was replaced in the absence of solvent by another ester such as methyl or ethyl acetate under the same conditions, the IR spectrum exhibits the same absorption band at 2085 cm^{-1}, which seems to indicate that this signal is not characteristic of a catalytic intermediate. This assertion was confirmed by an experiment conducted in pure toluene (without methyl formate) in which the peak at 2085 cm^{-1} was also observed. However, under these conditions, due to the very weak solubility of LiI in toluene, its appearance was very slow (3 h vs 10 min in the other cases) and occurred only at a temperature up to 80°C.

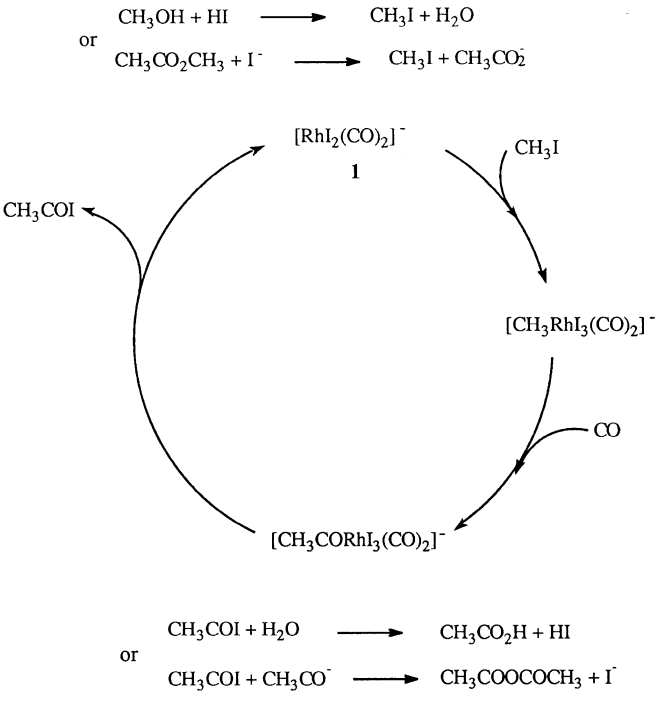
From these results, as the signal at 2085 cm^{-1} is not related to an intermediate in the catalytic cycle and as it is only observed at high iodide content, we can assume that it corresponds to a Rh(III) species, probably to the *trans*-$[RhI_4(CO)_2]^-$ anion which is known to absorb in CH_2Cl_2 solution in the νCO region as a single stretch at 2091 cm^{-1} (15, 16). The monocarbonyl anion $[RhI_4(CO)]^-$ cannot be totally excluded as this compound exhibits in the carbonyl vibration region a single band at 2076–2078 cm^{-1} in solution (8a, 15) and as its synthesis was previously reported, although with moderate yield, by Vallarino (17) working under nearly identical conditions ($Rh(III)/I^-$/Pco). However, as these two Rh(III) species are easily interconvertible under CO atmosphere (15), under our conditions the presence of $[RhI_4(CO)_2]^-$ seems more probable.

Finally, as $[RhI_2(CO)_2]^-$ was the sole species observed under catalytic conditions at low or high I^- contents, in order to obtain more spectroscopic information on the mechanism and on the basis of the known reaction cleavage of esters by ionic iodides (see Eq. [15]), different experiments were carried out in which methyl formate was replaced by sodium formate. Thus the peaks at 2052 and 1979 cm^{-1} initially formed when $RhCl_3$ and LiI were stirred in NMP under CO pressure, quickly disappeared after addition of $NaHCO_2$ and a strong absorption band at 1898 cm^{-1} was the sole one observed in the νCO region when the reaction medium was heated. This signal can be assigned to the presence of $[Rh(CO)_4]^-$ (18).

4. DISCUSSION

Preliminary Remarks

The *in situ* IR studies have shown that in our reaction conditions ($T > 150$°C, $P_{CO} > 5$ bar) the only observable carbonyl rhodium species is the complex $[RhI_2(CO)_2]^-$, whatever the iodide content or the nature of solvent.



SCHEME 2. Catalytic cycle for methanol or methyl acetate carbonylation.

As previously mentioned, this complex **1** is also the active species in the carbonylation of methanol into acetic acid (12) (Monsanto process) or of methyl acetate into acetic anhydride (19) (Eastman Kodak process), catalyzed by rhodium/iodide systems. In both cases, the currently accepted mechanisms involve oxidative addition of CH_3I to **1**, followed by CO insertion into the alkyl–rhodium bond. The subsequent reductive elimination gives acetyl iodide. The main differences between these two mechanisms consist in the formation of CH_3I (which is the real substrate of these carbonylations) and in the last step of the catalytic cycle, namely hydrolysis of CH_3COI into acetic acid (methanol carbonylation) or its reaction with AcO^- giving acetic anhydride (Eastman Kodak process) (see Scheme 2). In the same way, the changes in selectivity observed in the reactions leading to the acetaldehyde or methyl acetate synthesis, could rather be due to a change in reaction conditions than as a result of an evolution of the catalytic species.[5]

In this context, the concentration value of methyl iodide in the reaction medium is probably a key parameter of the selectivity. Indeed, the cleavage of esters by ionic iodides

[5] Although infrared spectra of reaction medium exhibit no other bands in the CO absorption region than those corresponding to the complex **1**, the existence of a very active catalytic species, in too low concentration to be detected, cannot be totally excluded.

TABLE 8

Solvent Effect on the Cleavage of Methyl Formate by LiI

No.	Solvent	Concentration (mol%) HCO_2Me	Concentration (mol%) CH_3I	$K \times 10^{3a}$
1	NMP	96.2	0.32	4.3
2	nC_8H_{18}	92.6	2.9	356
3	HCO_2Me	96.1	1	42

Note. Conditions: HCO_2Me, 250 mmol (15 ml); LiI, 7.5 mmol; solvent, 15 ml; *T*, 195°C; *t*, 1 h; *P*, 35 bar N_2.

[a] $K = [CH_3I] \cdot [HCO_2^-]/[HCO_2CH_3] \cdot [I^-]$.

is a well-known reaction (20) which leads in this case to methyl iodide and formate anion by reaction of an ionic iodide on methyl formate.

$$HCO_2CH_3 + MI \rightleftharpoons CH_3I + HCO_2M, \qquad [17]$$

where *M* is alkali metal. This reaction is an equilibrium and as shown in Table 8 the equilibrium constant *K* is greatly solvent-dependent. Although the values listed above are essentially indicative, it clearly appears that for a given initial amount of ionic iodide, the cocentration of CH_3I at equilibrium is much smaller in NMP than in pure methyl formate or in a nonpolar solvent. Hence the role played by NMP on the selectivity could be to regulate the CH_3I content in the reaction medium and to allow the presence of a sufficient quantity of ionic iodide to easily generate anion **1**.

On the basis of these mechanistic considerations and from the results obtained with labeled methyl formate, plausible mechanisms can be drawn up for the synthesis of these compounds, as presented below.

Mechanism for Acetaldehyde Production

Although anion **1** was found as the main rhodium species, the hypothesis of a direct reaction of CH_3I with this complex as an effective way of synthesis of acetaldehyde can be ruled out if we consider that this reaction should lead to acetyl iodide as in methanol or methyl acetate carbonylation (see Scheme 2). From the fact that the presence of water does not affect the synthesis of acetaldehyde and does not give any acetic acid (see Table 3, No. 10), we can exclude CH_3COI as intermediate.

Moreover, CH_3COI should also react with formate ions to give the mixed formic–acetic anhydride which is relatively stable in the cold but very unstable at high temperature (21). Actually, when this anhydride is introduced into the autoclave during the reaction course with a high-pressure pump, it decomposes quickly into acetic acid.

Therefore, the key point of acetaldehyde synthesis is probably the formation of a hydride rhodium complex, **3** from **1** (see Eqs. [18] and [19]). This species could result from the substitution of an iodide of **1** by the formate anion giving complex **2** which at high temperature decomposes into **3** (Scheme 3).

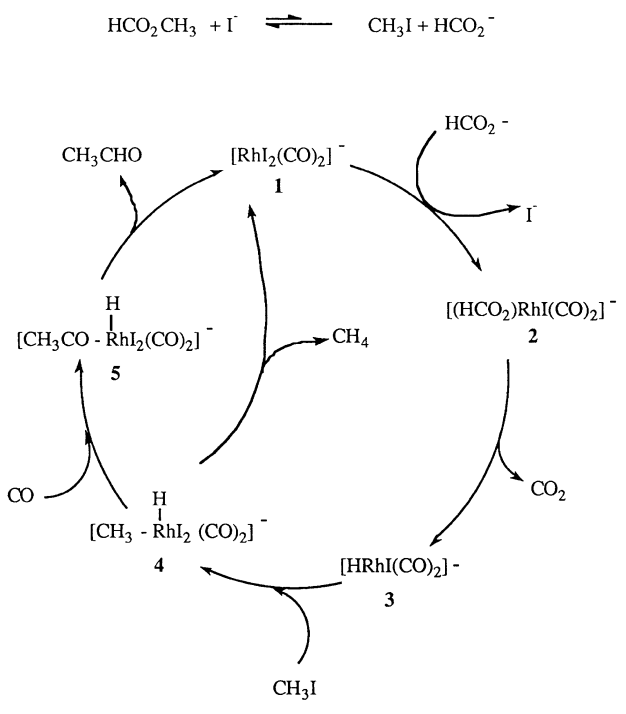
$$\underset{\mathbf{1}}{RhI_2(CO)_2^-} + HCO_2^- \rightleftharpoons \underset{\mathbf{2}}{(HCO_2)RhI(CO)_2^-} + I^- \qquad [18]$$

$(HCO_2)RhI(CO)_2^-$ ≡ H–C(O)(O)–$RhI(CO)_2^-$

$$\longrightarrow \underset{\mathbf{3}}{H{-}RhI(CO)_2^-} + CO_2 \qquad [19]$$

This assumption is in accordance with the fact that alkali formates have been reported as efficient precursors of transition metal hydrides (22) and moreover with the fact that the decarboxylation of formate complexes has also been reported several times (23). From complex **3**, the steps leading to acetaldehyde are classical (Scheme 3). Thus oxidative addition of CH_3I to **3** followed by CO insertion to the metal–alkyl bond gives the acylrhodium **5**. Reductive elimination produces acetaldehyde and regenerates the initial active species **1**.

In the absence of CH_3I and under high CO pressure (FTIR experiments carried out with $NaHCO_2$ instead methyl formate), reductive elimination of HI from **3** can occur leading to $[Rh(CO)_4]^-$ according to the following



SCHEME 3. Proposed catalytic cycle for reductive carbonylation of methyl formate into acetaldehyde.

reaction:

$$[RhI_2(CO)_2]^- + HCO_2^- \rightarrow\rightarrow [HRhI(CO)_2]^- \xrightarrow{CO} Rh(CO)_4^- + HI \quad [20]$$

3

In the same way, methane identified in the gas phase may result from reductive elimination of methyl and hydride ligands from the complex intermediate **4** before CO insertion.[6] Its important formation observed with Ir-based catalyst (see Section 3.2) can be attributed to a more difficult insertion of CO into the metal–alkyl bond with Ir than with Rh (25).

The mechanism depicted above can be related to that given for the synthesis of aromatic aldehydes by carbonylation of aryl halides, under CO pressure, in the presence of palladium and stoichiometric amount of alkali formate. (26)

$$ArX + NaHCO_2 \xrightarrow[CO]{[Pd]} ArCHO + NaX + CO_2. \quad [21]$$

This is also in agreement with the isotopic distribution observed in experiments conducted with labeled substrates.

Mechanism for Methyl Acetate Formation

Considering that the ligand exchange reaction (Eq. [16]) involved in the first step of this catalytic cycle is equilibrated, an increase of the I^- concentration must result in a shift of the equilibrium to the left and to reduce the formation of complex **2**. Thus, although we are not able to detect complexes **2** or **3** by infrared studies, the influence of I^- on the stoichiometric decarboxylation of formate salts by rhodium complex, in the absence of methyl formate is proved by the results given in Table 9.

Consequently at higher I^- contents than those needed for acetaldehyde synthesis complex **3** does not form and a new mechanism must be taken into account to explain the formation of methyl acetate.

As the direct carbonylation of CH_3I into CH_3COI must still be dismissed (for the same reasons as those aforementioned), methyl acetate synthesis could proceed as previously reported (3) according to the mechanism outlined in Scheme 4, by oxidative addition of methyl formate to **1**, reductive elimination of HCOI followed by oxidative addition of CH_3I to complex **7**, CO insertion and reductive elimination of AcOMe. In a parallel reaction, HCOI reacts with a formate anion to give the unstable formic anhydride which at the reaction temperature immediately decomposes into CO, CO_2, and H_2, without formation of formic acid.

[6] Methane might also be formed by direct decarboxylation of methyl formate according to $HCO_2CH_3 \rightarrow CH_4 + CO_2$ as reported by Pruett and Kacmarick (24). However, when a blank experiment was performed in the absence of catalyst the methane content in the gas phase was much lower.

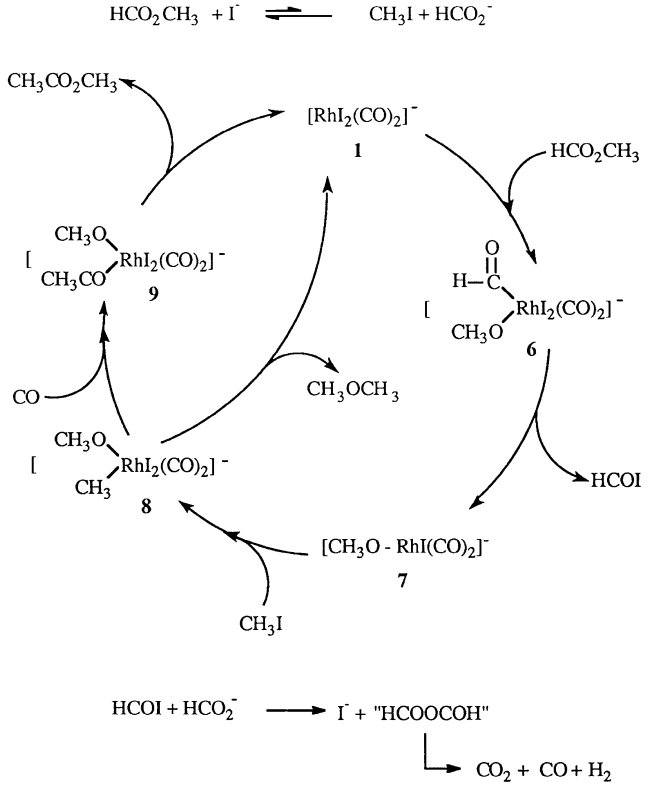
TABLE 9

Influence of [I^-] on the Decarboxylation of Formate Salts

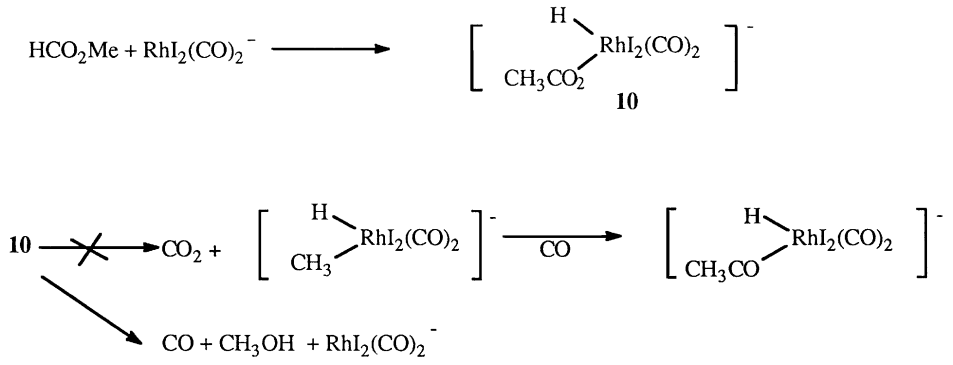
No.	LiI (mmol)	I^-/Rh	Gas phase composition (%) CO	CO_2
1	12	80	99.4	0.6
2	0.45	3	97.6	2.4

Note. Conditions: HCO_2Na, 0.4 mmol; $RhCl_3 \cdot 3H_2O$, 0.15 mmol; NMP, 4 ml; P_{CO}, 10 bar; *T*, 180°C; *t*, 2h.

The last part of this catalytic cycle (i.e., the steps following the addition of CH_3I to complex **7**) is supported by the work of Bernard and Atwood (27) in which the reaction of acyl chloride with alkoxyiridium complex giving selectively the corresponding ester is described. On the other hand, the first step (i.e., the oxidative addition of methyl formate to **1** by cleavage of the C–O bond) is much less documented, but a similar reaction has been invoked with nickel complex (28). Moreover, activation of the C–O bond of several esters by various transition metal complexes including Rh has been reported (29). In addition, the formation of dimethyl ether, identified in the gas phase, gives further evidence in favor of this mechanism as complex **8** can undergo reductive elimination before CO insertion, giving CH_3OCH_3.



SCHEME 4. Proposed catalytic cycle for homologation of methyl formate into methyl acetate.



SCHEME 5. Reductive carbonylation of methyl formate into acetaldehyde. Alternative reaction mechanism via oxidative addition of methyl formate to Rh.

At very high iodide contents acetic acid is probably formed, as recently reported (4), by carbonylation of CH_3I via its oxidative addition to $RhI_2(CO)_2^-$ (see Scheme 2) and subsequent reaction of CH_3COI with HCO_2^-.

$$CH_3I \xrightarrow[CO]{RhI_2(CO)_2^-} CH_3COI \xrightarrow{+HCO_2^-} HCO_2COCH_3$$

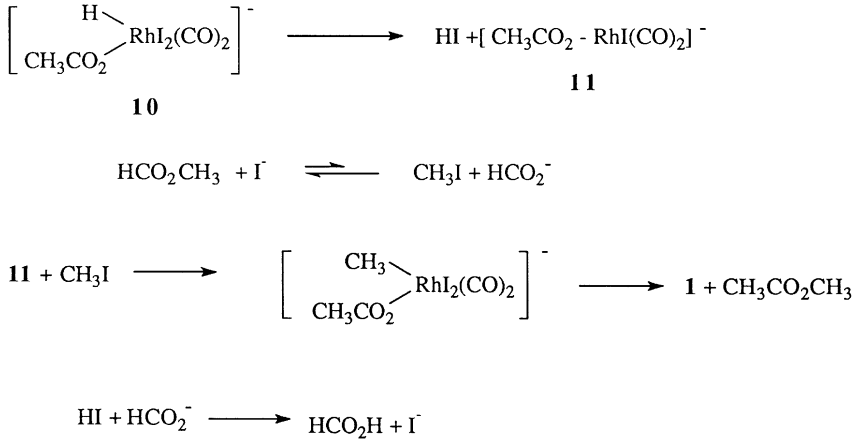
$$HCO_2COCH_3 \xrightarrow{\Delta} CH_3COOH + CO.$$

As CH_3I adds to **1** probably much more easily than HCO_2Me, the methyl acetate vs acetic acid selectivity is certainly connected with the relative amounts of CH_3I and HCO_2Me in the medium. From this point of view, the use of NMP as the solvent is crucial as it allows one to limit the CH_3I concentration when an ionic iodide is used as promoter. On the other hand, with covalent iodides, NMP cannot play this role and acetic acid is always obtained as the major product.

A mechanism involving the activation of the H–C bond of methyl formate giving complex **10**, could also have been considered (30). However, acetaldehyde synthesis from complex **10** requires its decarboxylation (see Scheme 5). The fact that the latter is unlikely with Rh complexes (28) has induced us to discard this possibility. In the case of methyl acetate synthesis, such a mechanism could be plausible (see Scheme 6). It would nevertheless lead to the formation of HCO_2H which has been found stable under our reaction conditions; moreover, when the reaction was conducted with $H^{13}CO_2CH_3$ the methyl acetate obtained according to Scheme 6 should be totally labeled. The fact that HCO_2H has never been observed in catalytic reactions giving AcOMe (see Section 3.1) and that the methyl acetate resulting from $H^{13}CO_2CH_3$ was largely nonlabeled, lead us to the conclusion that the mechanism outlined in Scheme 4 is more credible.

5. CONCLUSION

These results illustrate the great versatility of methyl formate. Thus, starting from this compound, with the same Rh-based catalyst precursor and the same ionic iodide promoter, LiI, it is possible to have access selectively to very different products such as acetaldehyde, methyl acetate and



SCHEME 6. Alternative mechanism for homologation of methyl formate into methyl acetate via its oxidative addition to Rh.

acetic acid by a judicious control of the reaction conditions. Mechanistic studies seem to indicate that a single species, $RhI_2(CO)_2^-$, **1** is involved in all these reactions. According to our experimental data different catalytic cycles in which the anion **1** reacts with HCO_2^-, HCO−OMe, or CH_3I in the initial steps of the catalytic reaction are proposed to explain the formation of the final products.

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