Tris (triphenylphosphine) rhodium(I) Chloride Catalyzed Synthesis of Methyl Formate from Methanol, Carbon Dioxide and Hydrogen in the Presence of a Tertiary Amine*

Heng Phala, Kiyoshi Kudo, Sadayuki Mori, and Nobuyuki Sugita**

The highest yields of methyl and ethyl formates ever reported have been obtained from methyl and ethyl alcohols, carbon dioxide and hydrogen in the presence of $RhCl(PPh_3)_3$ catalyst and a base triethylenediamine at the temperature around 100°C. A turnover number with respect to rhodium has been more than 120 for the reaction at 5 h. A two-step mechanism has been proved for the reaction: the first step is the fast metal-catalyzed formation of triethylenediammonium formate and the secand step is the rate-determinig esterification of the reeuting salt,

INTRODUCTION

Since the so-called Oil Crisis at 1973 many attempts for the effective use of carbon dioxide have been made. In the field of organometallic chemistry, direct coordination of carbon dioxide to the metal and CO_2 insertions into the metal-hydrogen, metal-oxygen, metal-nitrogen and metal-carbon bonds have been reported.[1] However, the application of these reactions to a catalytic organic synthesis is rather limited. The only successful reactions are a series of the reductions of carbon dioxide by hydrogen. These reactions have been investigated by several groups who often concentrated so much their attention on the final products such as formic acid,[2] alkyl formamide[3] and alkyl formate[4,5] that the reactions were thought to be independent each other.

Alkyl formates have been synthesized from carbon dioxide, hydrogen and alcohol in the presence of a tertiary amine with an organo-transition metal catalyst (Eq. 1).

$$CO_2+H_2+ROH \xrightarrow[NR_3']{MLn} HCOOR+H_2O \tag{1}$$

This reaction has been reported by Vol'pin et al.[4] and then by Inoue et al.[5] who used $Pd(diphos)_2$, $H_2Ru(PPh_3)_4$, $RhCl(PPh_3)_3$ and $H_3Ir(PPh_3)_3$ as catalysts. However, compared to the related formamide formation reaction,[3] the product yield of the reaction was still poor and no studies on the mechanism has been done. We, therefore,

---

have investigated the reaction in detail to find out the optimum reaction conditions for the product yield and also to clarify the reaction mechansim. In this paper, the result of the investigation will be reported.

RESULTS AND DISCUSSION

Formation of triethylenediammonium formate salt and its esterification in MeOH. The formate salt **1** was produced rapidly and remained almost constant during the reaction period (Fig. 1). Triethylenediamine (TED), which is the most effective (*vide infra*) was used as the base. Under the reaction conditions of Fig. 1, this salt can be regarded as the reaction intermediate of the two consecutive reactions (2) and (4), remaining at a stationary concentration. The diformate **2** should also be formed according to reaction (3). In fact, in the preparation of the formate salt from formic acid and
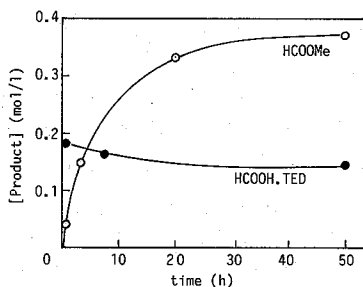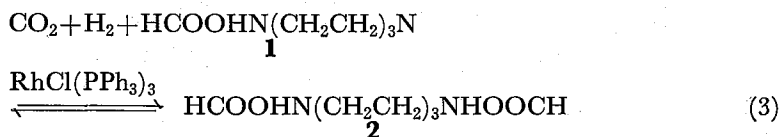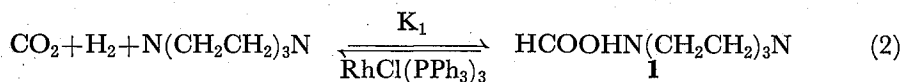
$$CO_2 + H_2 + N(CH_2CH_2)_3N \underset{RhCl(PPh_3)_3}{\overset{K_1}{\rightleftharpoons}} \underset{\textbf{1}}{HCOOHN(CH_2CH_2)_3N} \qquad (2)$$

$$CO_2 + H_2 + \underset{\textbf{1}}{HCOOHN(CH_2CH_2)_3N}$$

$$\overset{RhCl(PPh_3)_3}{\rightleftharpoons} \underset{\textbf{2}}{HCOOHN(CH_2CH_2)_3NHOOCH} \qquad (3)$$

Fig. 1. Formation of HCOOH. TED
Solvent=MeOH, temp=100°C, [TED]$_o$
=0.500 mol/l, [RhCl (PPh$_3$)$_3$]$_o$ =5.43
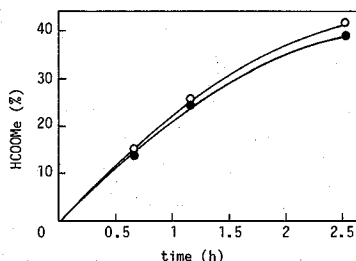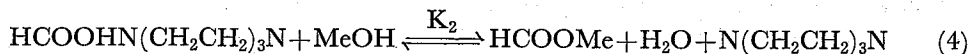mmol/l, P$_{CO_2}$=40 kg/cm², P$_{H_2}$=80
kg/cm².

Fig. 2. Effect of RhCl(PPh$_3$)$_3$ on the esterification of HCOOH. TED. Solvent=MeOH, temp = 100°C, [HCOOH]$_o$ = 0.530 mol/l, [TED]$_o$=0.530 mol/l, P$_{CO_2}$=40 kg/cm², P$_{H_2}$=80 kg/cm².
○ [RhCl(PPh$_3$)$_3$]$_o$=0
● [RhCl(PPh$_3$)$_3$]$_o$=3.33 mmol/l

TED (see experimental section), a mixture of monoformate **1** and diformate **2** was obtained at a mole ratio of 1 to 0.28. However, as the concentration of **1** is much smaller than TED* and also **1** is a very weak base compared to TED itself, we neglected **2**'s concentration in our reaction conditions. The esterification of **1** (prepared *in situ* from formic acid and TED) was carried out and the results are given in Fig. 2.

---

* TED: pK$_2$=8.7

The reaction was found to be independent of the catalyst and reversible (Fig. 2).

The formation of methyl formate from carbon dioxide, hydrogen and MeOH is thus a two-step reaction. The first step is the fast metal-catalyzed formation of the formate salt (Eq. 2) and the second step is the slow esterification of the salt (Eq. 4). From Fig. 3 where water was added to shift the reaction to the left side, K_2 (Eq. 4) is revealed to be 4.0×10^{-2} mol/l.

$$HCOOHN(CH_2CH_2)_3N + MeOH \underset{\longleftarrow}{\overset{K_2}{\longrightarrow}} HCOOMe + H_2O + N(CH_2CH_2)_3N \qquad (4)$$

The value of the overall equilibrium constant K_1K_2 (Eq. 5) could not be obtained

$$CO_2 + H_2 + MeOH \underset{\longleftarrow}{\overset{K_1K_2}{\longrightarrow}} HCOOMe + H_2O \qquad (5)$$
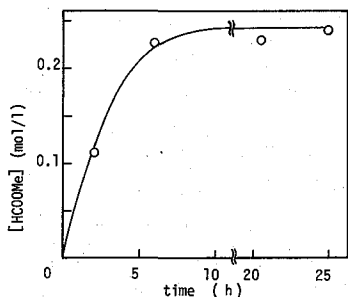

Fig. 3. Formation of HCOOMe from HCOOH. TED under the addition of water.
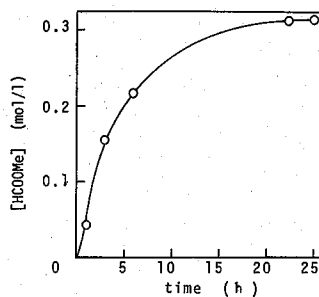Solvent=MeOH, temp=100°C, $[HCOOH]_o$ =0.395 mol/l, $[TED]_o$ =0.485 mol/l, P_{CO_2} =40 kg/cm², $[H_2O]_o$ =1.67 mol/l.

Fig. 4. Formation of HCOOMe from CO_2, H_2 and MeOH under the addition of water.
Solvent=MeOH, temp=100°C, $[TED]_o$ =0.485 mol/l, $[Cat]_o$ =5.41 mmol/l, $[H_2O]_o$ =1.67 mol/l, P_{CO_2} =40 kg/cm², P_{H_2} =80 kg/cm².

accurately because the reaction is too slow. The addition of water (Fig. 4) provoked complication caused by the deactivation of the catalyst.[2] However, a minimum value of K_1 can be found as 2.0×10^{-4} (kg/cm²)$^{-2}$.

Effects of various variables. Table 1 illustrates the effects of various variables on the formation of the formate esters. The results are given in the concentration of the ester and the turnover number at 5 h.

The Wilkinson complex was revealed to be the most effective among the catalysts examined (Runs 1 to 5). Contrary to the formation of *N, N*-dimethylformamide where $RhCl_3.3H_2O$ and $PdCl_2$ were also effective,[3] these catalysts are not effective here. Methanol and ethanol have been used here as solvents as well as substrates (Runs 12 and 13). The effectiveness of the alcohols is similar to the results by Inoue *et al.*[5]: MeOH>EtOH>PrOH. In the formation of formic acid at lower temperature, the order of the reactivity of alcohol as the solvent was the opposite.[2] However, as the formic acid formation is fast, the order observed here must reflect the reactivities of alcohols toward the esterification of carboxylic acid. When the reaction was carried out in other solvents containing a small amount of methanol (as substrate),

both the overall equilibrium and the rate were unfavorable for the product yield (Runs 16 to 20).

At 100°C, the reactivity of the base increases with pKb (Runs 5 to 8). A strong base like DBU may form a robust formate salt difficult to be esterified. γ-Picoline (Run 9) may be too weak to be effective for the formation of the formate salt. Here, the base TED produces the formate salt to be easily esterified and has a proper basicity making it an ideal one for the reaction. At higher temperature (Runs 11 to 13), the deactivation of the catalyst occurred (Fig. 5) and the results are rather complicated.

In Fig. 5, the effect of temperature on the yield is illustrated. The first step is very fast and irrespective of the temperature. Therefore, the raising of the temperature should enhance the second step. The yield increases up to about 100°C and then begins to fall due to the deactivation of the Wilkinson catalyst,[3b] and this is one of the obstacles for further improvement of the yield. However, since the concentration of the formate salt produced in the first step increases with the concentration of the base, higher yield may be obtained by increasing the base concentration. In fact, this is the case as shown in Fig. 6. A turnover number larger than 100 (5 h) obtained here is the highest value ever reported. It should be added that the increase of the base concentration will not affect the maximum yield at a given pressure. The yield increases also by increasing the partial pressure of either carbon dioxide or hydrogen (Fig. 7).
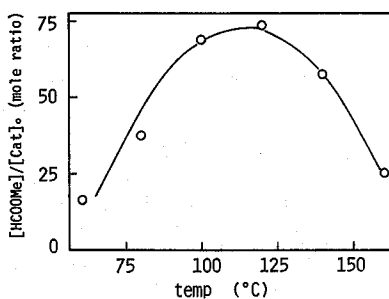

Fig. 5. Effect of temperature.
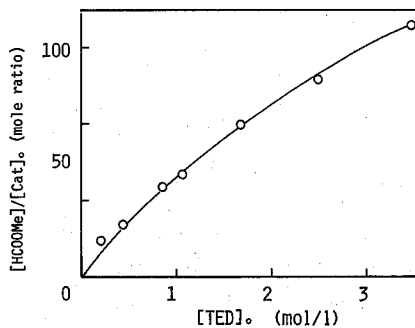MeOH=7 ml, $[RhCl(PPh_3)_3]_o$=7.86 mmol/l, $[TED]_o$=1.71 mol/l, P_{CO_2} =48 kg/cm² (at room temp), P_{H_2}=64 kg/cm² (at room temp), time=5 h.

Fig. 6. Effect of the initial concentration of TED.
MeOH=7 ml, $[RhCl (PPh_3)_3]_o$ = 7.86 mmol/l, P_{CO_2}=48 kg/cm² (at room temp), P_{H_2}=64 kg/cm² (at room temp), time=5 h, temp=100°C.

The effect of the initial concentration of $RhCl(PPh_3)_3$ on the yield was also examined (Fig. 8). The yield reaches a constant value when $[Cat]_o$ exceeds 5 mmol/l. This feature of the reaction observed here is the same as in the formation of the for-mamide,[3] i.e. the formate salt reaches its equilibrium concentration at high catalyst concentration. At low catalyst concentration, the same phenomenon as in the for-mation of formic acid[2] is observed, proving the participation of the released PPh_3 in the catalytic cycle.
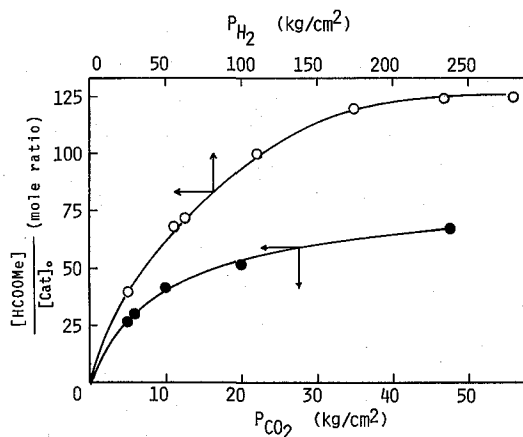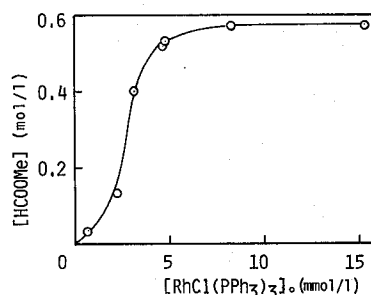
Fig. 7. Effect of the partial pressures.
MeOH $=7$ ml, [TED]$_o$ $= 1.71$ mol/l,
[RhCl (PPh$_3$)$_3$]$_o$=7.86 mmol/l, temp=
100°C, time=5 h. The values of pres-
sures are those at room temparature.
○ P_{CO_2}=48 kg/cm^2 (at room temp)
● P_{H_2}=64 kg/cm^2 (at room temp)

Fig. 8. Effect of the initial concentration of
RhCl(PPh$_3$)$_3$.
MeOH=7 ml, [TED]$_o$=1.71 mol/l,
P_{CO_2}=48 kg/cm^2 (at room temp),
P_{H_2}=64 kg/cm^2 (at room temp),
temp=100°C, time=5 h.

Table 1. Effects of various variables on the formation of methyl and ethyl formates[a]

Run	Catalyst	Base	pK$_b$	Solvent	temp (°C)	HCOOMe (M)	(t. n)[b]	HCOOEt (M)	(t. n)[b]
1	Rh (CO)$_2$ (acac)$_2$	TED[e]	5.8	MeOH	100	0.31	5.6		
2	RhCl$_3$·3H$_2$O	//	//	//	//	0.13	2.1		
3	PdCl$_2$	//	//	//	//	0.10	1.1		
4	PdCl$_2$ (PPh$_3$)$_2$	//	//	//	//	0.06	1.1		
5	RhCl (PPh$_3$)$_3$	//	//	//	//	4.0	69		
6	//	DBU[d]	2.5	//	//	0.91	19		
7	//	NPr$_3^n$	3.3	//	//	1.83	34		
8	//	N-Me-Pyrrolidine	3.8	//	//	2.7	52		
9	//	Picoline	8.0	//	//	1.1	21		
10	//	DBU[d]	2.5	EtOH	140			2.3	30
11	//	Et$_3$N	3.3	//	//			1.0	16
12	//	TED[d]	5.8	//	//			2.1	37
13	//	//	//	MeOH	//	3.2	58		
14	//	K$_2$CO$_3$[e]	//	//	100	1.6	35		
15	//	—	—	//	//	trace —			
16	//	TED[e]	5.8	Benzene[f]	//	0.55	9.7		
17	//	//	//	MC[f]	//	2.3	40		
18	//	//	//	TEGDE[f]	//	2.0	38		
19	//	//	//	DMF[f]	//	1.2	21		
20	//	//	//	HMPA[f]	//	0.36	7.1		

a) P_{CO_2}=48 kg/cm^2 (at room temp), P_{H_2}=65 kg/cm^2 (at room temp), [Base]$_o$=1.6~1.7 mol/l,
[Cat]$_o$=7~10 mmol/l, solvent=7 ml, reaction time=5 h, b) a turnover number expressed in
mole ratio of the ester produced and the catalyst, c) triethylendediamine, d) 1, 8-diazabi-
cyclo[4. 5. 0]undec −7−ene, e) heterogenous solution, f) [MeOH]=5.51 mol/l, MC:
methyl cellosolve, TEGDE: tetraethylene glycol dimethylether, DMF: N, N-dimethyl-
formamide, HMPA: hexamethylphosphoric triamide.

Some kinetic examination. The effect of the initial concentration of the catalyst and the addition of PPh_3 upon the rate have been examined to make sure that the first step of the present reaction proceeds with the same mechanism as in the formation of formic acid. From Fig. 9, the initial rates of the reaction were obtained and they were plotted against $[Cat]_o$ as shown in Fig. 10. As expected, similar results to Fig. 8 were obtained. The rate will reach a constant at high $[Cat]_o$, but this fact could not be verified because the reaction solution became heterogeneous after $[Cat]_o$ surpassed 10 mmol/l.
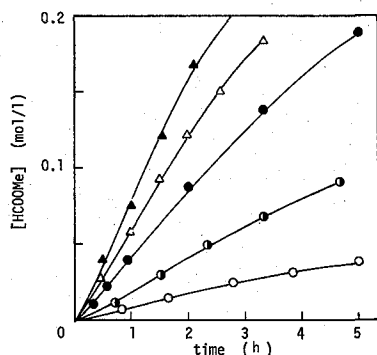

Fig. 9. Time-yield curves under various initial concentration of $RhCl(PPh_3)_3$.

MeOH=solvent, $[TED]_o$=0.500 mol/l,
P_{CO_2}=40 kg/cm², P_{H_2}=80 kg/cm², temp
=100°C.

$[RhCl(PPh_3)_3]_o$= ○ 1.08 mmol/l,
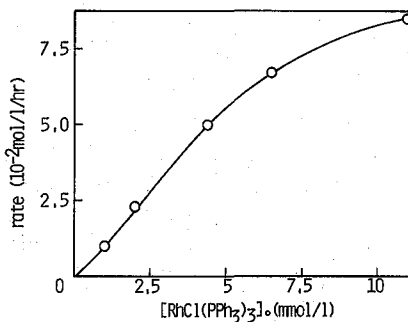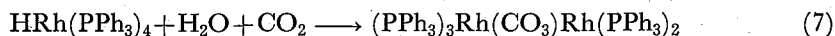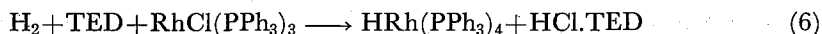◑ 2.19 mmol/l,
● 4.32 mmol/l,
△ 6.48 mmol/l,
▲ 10.9 mmol/l.

Fig. 10. Relation between the initial rate and $[RhCl(PPh_3)_3]_o$. The conditions are the same as in Fig. 9.

The feature of released PPh_3 has been verified by experiments of the addition of this ligand (Fig. 11). The rate was accelerated dramatically and a turnover number higher than 200 was obtained. But when PPh_3 was present in excess, the rate became constant and the sum of the concentration of the formate salt and that of the ester remained constant during the reaction period (Fig. 12). The catalyst was deactivated completely within about 15 min. The deactivation of the catalyst was enhanced by an amine as the yield of the formate salt (based on the charged amine) became low at high amine concentration. This fact can be correlated to the occurrence of the following reactions:[6]

$$H_2+TED+RhCl(PPh_3)_3 \longrightarrow HRh(PPh_3)_4+HCl.TED \qquad (6)$$

$$HRh(PPh_3)_4+H_2O+CO_2 \longrightarrow (PPh_3)_3Rh(CO_3)Rh(PPh_3)_2 \qquad (7)$$

Reaction mechanism. The mechanism of the formation of formate salt from CO_2, H_2 and a tertiary amine in methyl cellosolve has been established in our laboratory from kinetic studies. The results of alkyl formate formation described above proved
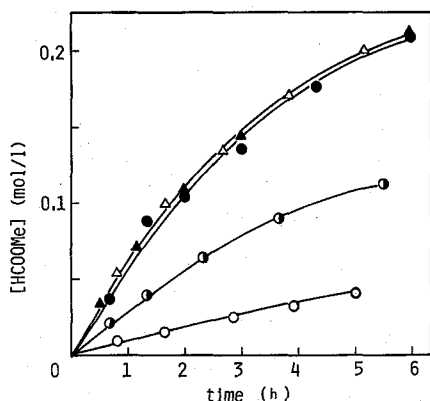
Fig. 11. Effect of added PPh₃.

Solvent = MeOH, temp = 100°C, $[TED]_o = 0.500$ mol/l, $[RhCl(PPh_3)_3]_o = 1.08$ mmol/l, $P_{CO_2} = 40$ kg/cm², $P_{H_2} = 80$ kg/cm², $[PPh_3]_o/[Cat]_o$ (mole ratio) = ○ 0, ◐ 4.97, ● 10.3, △ 20.3, ▲ 84.2
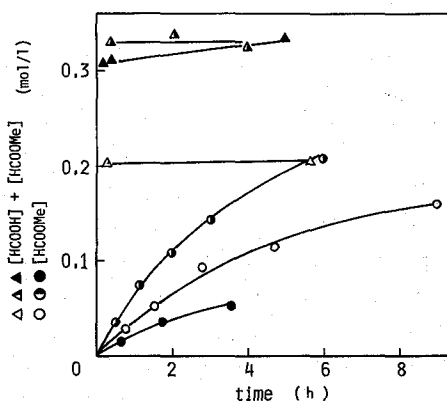
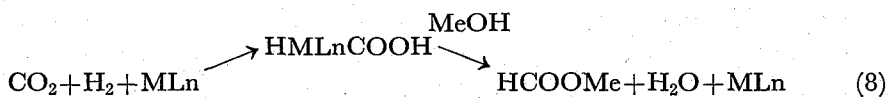**Fig. 12.** Formation of HCOOH and HCOOMe under the addition of PPh₃.

Solvent = MeOH, temp = 100°C, $[PPh_3]_o/[Cat]_o = 20.0$ mole ratio, $P_{CO_2} = 40$ kg/cm², $P_{H_2} = 80$ kg/cm².
$[TED]_o = $ ●▲ 0.988 mol/l, ◐▲ 0.500 mol/l, ○△ 0.248 mol/l.

that in MeOH, the first step of the present reaction proceeds with the same mechanism (Scheme 1). Contrary to many speculations (Eq. 8),[1] where various forms of metal formates have been postulated as the intermediates, the formation of the formate salt is the core of the series of the reduction reactions of carbon dioxide by hydrogen.
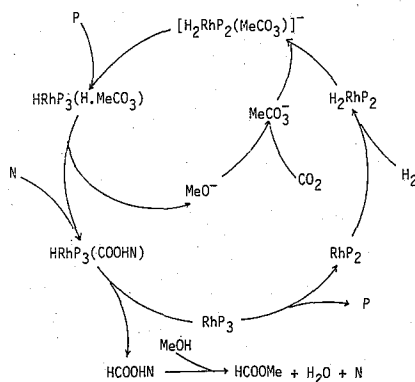
$RhP_3 = RhCl(PPh_3)_3$, $P = PPh_3$, $N = N(CH_2CH_2)_3N$

Scheme 1. Mechanism of the formation reaction of methyl formate from CO_2, H_2 and MeOH in the presence of $N(CH_2 CH_2)_3N$, catalyzed by $RhCl(PPh_3)_3$

$$CO_2 + H_2 + MLn \underset{\searrow HMLnOOCH}{\overset{\nearrow HMLnCOOH}{}} \overset{MeOH}{\underset{\nearrow}{\searrow}} HCOOMe + H_2O + MLn \qquad (8)$$

EXPERIMENTAL

Materials.   Tris(triphenylphosphine)rhodium(I) chloride was obtained from Strem Chemicals and used without further purification.   All solvents were distilled and dried by the usual methods.   Tertiary amines were used without further purification. Hydrogen and carbon dioxide were of purity higher than 99%.

Procedure[I]: the synthesis surveys.   Reactions were carried out in a stainless-steel autoclave (20 ml) coated with Teflon to avoid direct contact with the autoclave wall.   The solution of $RhCl(PPh_3)_3$ (1 to 15 mmol/l) and triethylenediamine (TED) (2 to 5 mol/l) in 7 ml of MeOH was put into the autoclave.   The air inside the autoclave was purged several times with carbon dioxide.   Carbon dioxide was charged to the desired pressure while the autoclave was shaken to enhance the dissolution of the gas.   Hydrogen was then added (the total pressure was from 70 to 350 kg/cm²).   The autoclave was heated for about 20 min to the desired reaction temperature (20°C to 160°C) and then the rocking was started.   This time was taken as the beginning of the reaction.   After the rocking was stopped, the solution was cooled to be analyzed.

Procedure[II]: the rate measurements.   Reactions were carried out in a stainless-steel autoclave (234 ml) equipped with a magnet stirrer and a sampling line.   A glass tube was put inside to avoid direct contact of the reaction solution with the autoclave wall.   The catalyst $RhCl(PPh_3)_3$ (0.05 to 7 mmol) and a solution of TED (0.5 mol/l) in methanol were put into the autoclave.   The air inside was purged several times with carbon dioxide and the autoclave was heated up to 100°C.   Then carbon dioxide was charged up to 40 kg/cm² and after this was completely dissolved hydrogen was added to the total pressure of 120 kg/cm².   An aliquot of the solution (1 to 2 ml) was taken out from time to time through the sampling line for the analysis.   The pressure was kept constant by introducing a mixture of the gases (mole ratio 1/1) from a reservoir. The esterifications of triethylenediammonium formate were also carried out in the autoclave in the same way.

Analysis.   For the analysis of the formate salts, 5 ml of the reaction solution was removed from the autoclave, diluted with water, passed through a column of ion-exchange resin and the eluted formic acid was titrated with 0.1 N NaOH.   Formic acid was identified by the gas chromatography [Shimadzu GC–5A, Porapak Q column (2 m, 3 mm ϕ) with helium carrier at 150°C].   Methyl and ethyl formates were determined by the gas chromatography with benzene as an internal standard [Yanagimoto GCF–510F, polyethylene glycol column (2 m, 3 mm ϕ) with nitrogen carrier at 90°C].

Preparation of triethylenediammonium formates.   To a solution of 10 ml of HCOOH in 30 ml of diethyl ether, was dropped a solution of 37 g of TED in 100 ml of the ether. White crystals were formed rapidly which were separated, washed 4 times with dimethyl ether and then dried in vacuo.   Yield=32 g.   They were dissolved in water, passed through a column of ion-exchange resin and titrated with 0.1 N NaOH to be revealed as a mixture of $HCOOHN(CH_2CH_2)_3N$ and $HCOOHN(CH_2CH_2)_3NHOOCH$ (mole ratio=1/0.28).

Tris (triphenylphosphine) rhodium (I) Chloride

REFERENCES

(1) a) *"Organic and Bioorganic Chemistry of Carbon Dioxide"*, ed. by S. Inoue and N. Yamazaki, Kodansha, Tokyo, 1981. b) M. E. Vol'pin, *Pure Appl. Chem.*, **30**, 607 (1972). c) M. E. Vol'pin and I. S. Kolomnikov, *Pure Appl. Chem.*, **33**, 567 (1973). d) M. E. Vol'pin and I. S. Kolomnikof, *Organometallic Reactions*, **5**, 313 (1975). e) D. J. Darensbourg and R. A. Kudaroski, *"Advances in Organometallic Chemistry"*, **22**, 129 (1983). f) R. P. A. Sneeden *"Comprehensive Organometallic Chemistry"*, ed. by G. Wilkinson, F. A. G. Stone, and A. W. Abel, Pergamon Press, New York, 1982, Ch. 50.4.

(2) H. Phala et al., to be published

(3) a) K. Kudo, H. Phala, N. Sugita and Y. Takezaki, *Chem. Lett.*, 1495 (1977). b) H. Phala, K. Kudo, N. Sugita and Y. Takezaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **29**, 88 (1981).

(4) I. S. Kolomnikov, T. S. Lobeeva, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2329 (1972).

(5) Y. Inoue, Y. Sasaki, and H. Hashimoto, *J. Chem. Soc., Chem. Comm.*, 718 (1975).

(6) a) S. H. Strauss, S. E. Diamand, F. Mares, and D. F. Shriver, *Inorg. Chem.*, **17**, 3064 (1978). b) S. Krogsrud, S. Komiya, T. Ito, I. A. Ibers and A. Yamamoto, *Inorg. Chem.*, **15**, 2798 (1976).