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Catalytic synthesis of ethanol from methyl formate

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Abstract

Ethanol can be synthesized from aqueous methyl formate under ruthenium catalysis in the presence of tri-*n*-butylphosphine and an onium salt. Hydrogen chloride promotes the reaction which takes place above 180°C and does not need initial pressurization. It is highly selective with respect to ethanol (80–90%, methanol not being considered). Carbon monoxide and hydrogen are produced *in situ* with pressures high enough to induce homologation of the methyl group. The mechanism involves $HRu_3(CO)_{11}^-$ species. The role of the phosphine is to activate methyl formate assisted by the onium halide.

Key words: Ruthenium; Methyl formate; Hydrocarbonylation; Ethanol; Phosphine; Onium salt

1. Introduction

Enormous efforts, academic and industrial, have been made to convert methanol to ethanol [1–6]. It may be one of the most studied catalytic industrial reactions together with hydroformylation. Ethanol is a starting compound for the production of ethylene and is a gasoline extender.

Promotion by iodine [7] and phosphine [8] was the major improvement to the original cobalt catalyst [9]. However, the homologation process cannot be scaled up from the laboratory scale, despite high conversion and excellent selectivity with respect to ethanol [10]. The main reasons are the corrosive effect of iodine, the initial high CO and H_2 pressures, and the low selectivity with respect to ethanol. Notable progress to lower the pressure has been achieved using a complex rhodium–ruthenium catalyst and specific diphosphines, but iodine promotion is still essential [11].

Iodine-free catalyst systems based on cobalt–phosphine–Cl^- [12] or ruthenium–PPNCl–Cl^- [13] have been reported, but the turn-overs are significant only at a high synthesis gas pressure (300 bar) and temperature (230°C).

Some time ago, we studied the *in-situ* generation of carbon monoxide from alkyl formates [14] and the subsequent hydrogen production via the water gas shift reaction (WGSR) [15]. Both reactions are catalysed by $[Ru_3(CO)_{12}]$ and tricyclohexylphosphine. To generate the synthesis gas, the favoured starting material is aqueous methyl formate [15]. We expected that a number of hydrocarbonylation reactions could be achieved with adjusted methyl formate–water mixtures. For example, cycloalkenes and lower linear alkenes can undergo hydroformylation via *in-situ* generation of synthesis gas from methyl formate [16]. In some cases we also detected small amounts of ethanol; therefore we have been interested in the formation of ethanol either via a homologation reaction or via direct hydrogenation of carbon monoxide. If we could succeed in synthesizing ethanol from methyl formate, the major advantage would be that no initial pressure of CO and H_2 would be required.

Previous work on the hydrocarbonylation of methyl formate to yield ethanol (25%), using an Fe-trialkylamine catalyst should be mentioned. Thus the reaction requires 300 bar and 200°C [17]. It has been recently reported that acetaldehyde, the precursor of

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ethanol, can be synthesized via rhodium–LiI-catalysed carbonylation of methyl formate in *N*-methylpyrrolidone under CO pressure [18].

2. Results

Remembering the cited Japanese work [12,13] we added bis(triphenylphosphoranylidene) ammonium chloride (PPNCl) to our original catalytic system of $[Ru_3(CO)_{12}]$ + PCy_3 (tricyclohexylphosphine). This produced a considerable improvement in the ethanol yield. All runs were therefore carried out in the presence of an onium salt (quaternary ammonium or phosphonium salt).

The liquid products of a typical run were unreacted methyl formate, methanol, ethanol, methyl acetate and, in some runs, dimethyl ether, ethyl acetate and acetic acid. The gas phase contained CO, H_2, CO_2 and CH_4. Methane was generally present in small amounts (0–3%), whereas CO_2 was produced with up to 70% yield, well beyond what could be expected from the WGSR.

The pressure generated during the decarbonylation of methyl formate and the subsequent WGSR (or any other process generating dihydrogen) reached 100–150 bar in our autoclave. Such values are optimal because lower pressures cause a much slower reaction. Too high a pressure would prevent decomposition of the formate [14], and the reaction then reverses because methanol is the major product in the ruthenium-catalysed high pressure hydrogenation of carbon monoxide [19].

2.1. *Effect of onium halides*

Various quaternary salts were used (Table 1). Conversion of formate is high even in the absence of the onium halide, but then ethanol is formed only in a trace amount. The addition of the quaternary salt raises the yield to 18–23% (all yields are based on initial formate). Selectivity with respect to ethanol is high, at least in runs 1 and 2.

TABLE 1. Effect of the nature of the quaternary salt [a]

Run	Additive	Formate conversion (%)	Yield of ethanol (%)	Selectivity to ethanol [b] (%)
1	PPNCl	99.5	20.8	84.0
2	Bu_4PBr	99.6	22.6	85.5
3	Et_4NBr	99.6	18.4	66.4
4	None	93.3	0.1	–

[a] Formate (48.7 mmol), $[Ru_3(CO)_{12}]$ (0.04 mmol), additive (0.35 mmol), PBu_3 (0.76 mmol), H_2O (13.9 mmol), HCl (0.3 mmol), toluene (2 ml); 200°C; 5 h.

[b] See experimental part for the definition of selectivity.

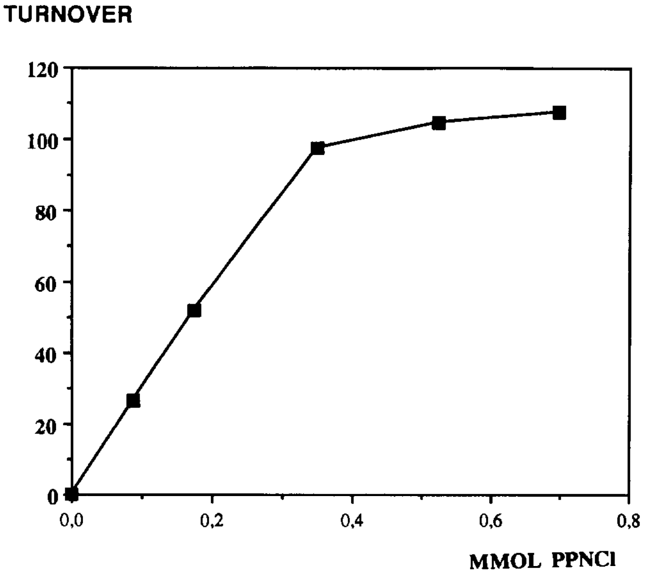

Fig. 1. Ethanol production as a function of PPNCl concentration (conditions in Table 1).

The effect of PPNCl concentration is shown in Fig. 1. The yield of ethanol is proportional to the PPNCl concentration up to an approximately 1 : 2 molar ratio of PPNCl : phosphine. Further additions of PPNCl have no effect on the maximum yield.

2.2. *Effect of the phosphine*

Phosphine is an essential component of the catalytic system in the decarbonylation of formates [14]. In the present reaction, the absence of phosphine precludes formation of ethanol (Table 2), despite high conversion of formate (compared with the facile formation of $[HRu_3(CO)_{11}]^-$ from H_2O and $[Ru_3(CO)_{12}]$, which is stabilized by the onium salt). Progressive addition of tri-*n*-butylphosphine increases the ethanol turn-over up

TABLE 2. Effect of phosphines [a]

Run	Phosphine	Concentration (mmol)	Formate conversion (%)	Yield of ethanol (%)
5	PCy_3 [b]	0.26	97.3	3.3
6	PBu_3	0.26	95.8	4.6
7	Diphosphine	0.26	95.2	2.7
8	PBu_3	0	93.6	0
9	PBu_3	0.52	95.3	5.2
10	PBu_3	0.80	98.2	7.0
11	PBu_3	1.20	97.4	5.6
12	PBu_3	1.60	96.5	3.6

[a] Formate (48.7 mmol), $[Ru_3(CO)_{12}]$ (0.04 mmol), PPNCl (0.35 mmol), H_2O (27.8 mmol), HCl (0.3 mmol); 180°C; 10 h.

[b] Tricyclohexylphosphine.

TABLE 3. Effect of the concentration of HCl

Run	Acid	Concentration (mmol)	Formate conversion (%)	Yield of ethanol (%)
13 [a]	None	–	98.0	2.1
5 [a]	HCl	0.30	97.3	3.3
14 [a]	HCl [b]	0.30	99.7	0.2
15 [c]	None	–	96.2	11.2
16 [c]	0.30	0.30	99.2	22.5
17 [c]	0.67	0.67	99.7	22.8
18 [c]	1.72	1.72	99.4	16.7

[a] Conditions as in Table 2 with PCy_3 (0.26 mmol).
[b] Other additive is H_3PO_4 (0.4 mmol).
[c] Conditions as in Table 1: PPNCl (0.35 mmol); no toluene added.

to a maximum value attained for a PBu_3: PPNCl molar ratio in the vicinity of 2. Higher phosphine concentrations have a detrimental effect on the formation of ethanol. Tri-*n*-butylphosphine is the most appropriate when comparing the results obtained with other phosphines (runs 5–7).

2.3. *Effect of HCl*

Ono *et al.* [13] found that the catalytic effect in the hydrogenation of carbon monoxide to methanol and ethanol was stimulated by hydrogen halide (HCl, HBr or HI). In our case, HCl induces a promoting effect, as shown in Table 3. The yield of ethanol is increased by a factor of 2, when 0.30 mmol of HCl are added. High concentrations of HCl lower this yield, consistent with the results in ref. 13. However, in sharp contrast, there is no synergistic effect of phosphoric acid [13] (run 14) which is, in fact, antagonistic.

Replacing HCl by HI with all other conditions constant is highly detrimental to the production of ethanol. Large amounts of methane and carbon dioxide are formed, indicating decarboxylation of methyl formate rather than decarbonylation. Iodine as LiI or HI in the reacting mixture leads invariably to partial or complete decomposition of formate into CH_4 and CO_2, limiting drastically or even suppressing the homologation reaction. Without iodine, this decomposition is very limited, despite the fact that the methanation reaction is thermodynamically very favourable [20].

2.4. *Effect of temperature*

The decarbonylation of methyl formate occurs at a high rate only at 180°C and above [14]. The addition of water permits lower temperatures [15]. Table 4 presents the results. An increase in temperature results in better yields of ethanol with quasi-conservation of the selectivity.

TABLE 4. Effect of temperature

Run	*T* (°C)	Formate conversion (%)	Yield of ethanol (%)	Selectivity to ethanol (%)
19	160	81.4	6.4	86.2
20	180	98.2	14.0	86.0
16	200	99.2	22.5	85.6
21	220	99.8	25.0	84.2
22	240	99.7	28.4	84.0

[a] As in Table 1: PPNCl (0.35 mmol); no toluene added.

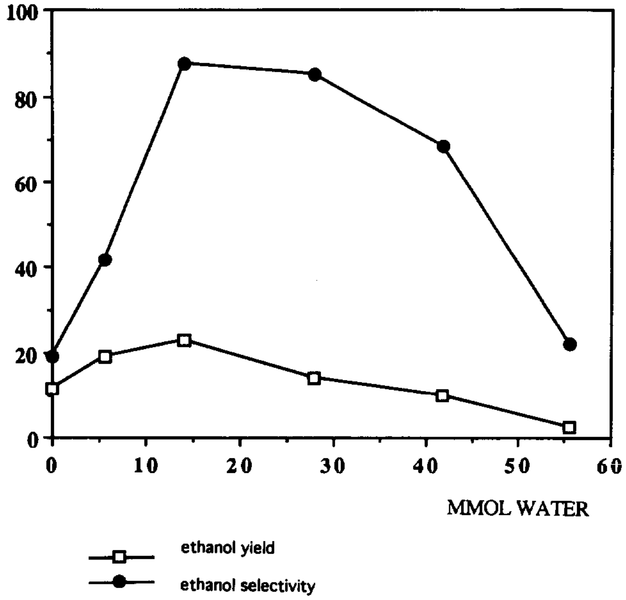

Fig. 2. Effect of reaction time on the synthesis of ethanol from methyl formate (conditions in Table 1).

2.5. *Effect of reaction time (Fig. 2)*

At 200°C, decarbonylation of methyl formate is fast (87.5% conversion within 1 h). This compares with the catalytic enhancement in the presence of water, as emphasized earlier [15]. The yield of ethanol and, more surprisingly, the selectivity parallel the decarbonylation curve.

2.6. *Effect of water*

According to Fig. 3, the reaction should be very sensitive to the concentration of water. High water concentrations lead to high H_2 : CO ratios (although CO_2 is still the most abundant gas in the mixture). However, the homologation reaction is not favoured, as shown by the low yield of ethanol in the run in pure water.

Water was originally supposed to be the exclusive source of hydrogen. However, even without initial addition of water, ethanol is formed together with a large

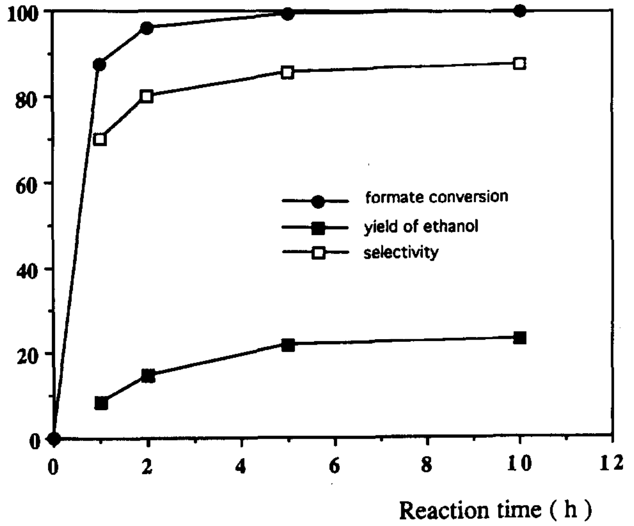

Fig. 3. Effect of initial water concentration in the synthesis of ethanol from methyl formate (conditions in Table 1).

amount of methyl acetate (carbonylation reaction), consistent with the results in the cobalt–iodine-catalysed hydrocarbonylation of methanol [21]. The fact that ethanol is formed without initial addition of water suggests the formation of dihydrogen, which was indeed found by analysis. This points to another source of H_2 than in the WGSR.

2.7. *Effect of a co-metal*

Because of their role as carbonylation catalysts, we added an Rh, Co, or Pd, compound to the original ruthenium compound (Table 5), but these was no effect on the conversion of methyl formate, which is almost total in every case. However, the yield and selectivity relative to ethanol are both reduced. Palladium gives the worst results with only half the yield (when compared with run 2), although selectivity is not altered. With the rhodium and the cobalt compounds, appreciable amounts of methane are formed, explaining the loss of selectivity. Even in the absence of ruthenium catalyst, ethanol is formed with $[Co_2(CO)_8]$ (run 26), but with poor selectivity.

TABLE 5. Effect of a co-metal [a]

Run	Co-metal	Formate conversion (%)	Yield of ethanol (%)	Selectivity to ethanol (%)
2	None	99.6	22.6	85.5
23	$[Co_2(CO)_8]$	99.3	17.9	64.4
24	$RhCl_3 \cdot 3H_2O$	99.9	12.1	68.6
25	$Pd(OAc)_2$	99.9	10.4	80.7
26 [b]	$Co_2(CO)_8$	92.6	7.7	21.5

[a] Conditions as in Table 1: Bu_4PBr (0.35 mmol); co-metal (0.06 mmol).

[b] In this run, no $[Ru_3(CO)_{12}]$ was present.

TABLE 6. Effect of the solvent [a]

Run	Solvent	Formate conversion (%)	Yield of ethanol (%)	Selectivity to ethanol (%)
27	None	99.7	22.8	88.0
2	Toluene	99.6	22.6	85.5
28	Chlorobenzene	98.0	19.4	89.0
29	Acetonitrile	98.0	5.1	43.7
30	Pyridine	99.9	1.7	21.5

[a] Conditions of Table 1: Bu_4PBr (0.35 mmol), solvent (2 ml).

2.8. *Effect of solvent*

We examined the effect of four solvents of different polarities (Table 6). Toluene and chlorobenzene did not affect the course of the reaction whereas, in acetonitrile and even more in pyridine, the yield of ethanol was low. Solvent has already been found to have an effect on the catalytic activity in the high pressure hydrogenation of carbon monoxide to yield methanol, ethanol and ethylene glycol catalysed by $[Ru_3(CO)_{12}]$ with onium halides as promoters [22]. It was suggested that the solvent exerts a stabilizing effect on the catalytically active ruthenium species [22].

3. Discussion

The decarbonylation of methyl formate catalysed by $[Ru_3(CO)_{12}]$ and a phosphine has been discussed previously [14]. In the presence of a hydrogen source, the catalytic species is $[HRu_3(CO)_{11}]^-$ [15]. The subsequent step, the WGSR, has been widely investigated [23]. The hydrocarbonylation reaction yielding ethanol could proceed either directly or via homologation of the methoxy group. Ethanol can be obtained at 220°C under high $CO + H_2$ pressure (850 bar) in the presence of a cobalt–ruthenium catalyst promoted by tetraalkyl-ammonium halides in oxygenated solvents [24]. Ethanol was also produced by hydrogenation of carbon monoxide with ruthenium catalysts in phosphine oxides used as the solvent [25].

TABLE 7. Peculiar experiments [a]

Run	Substrate	Additional parameter	Yield of ethanol (%)
2	Methyl formate	None	22.6
31	None	CO (120 bar)	0
32	Methanol	CO (120 bar)	2.1
33	Methyl formate	PBu_3 (0.35 mmol), + BuBr (0.35 mmol) [b]	11.3

[a] Conditions as in Table 1: Bu_4PBr (0.35 mmol).

[b] No initial Bu_4PBr.

However, under our standard conditions but omitting methyl formate, compressed carbon monoxide (120 bar) in the presence of water or hydrogen did not yield even a trace of ethanol (run 31 in Table 7). The addition of methanol under identical conditions (under CO pressure) gave only 2.1% ethanol (with poor selectivity), instead of 18.8% starting from methyl formate at atmospheric pressure (runs 32 and 2). The results emphasize the importance of the *in-situ* decarbonylation of methyl formate during the catalytic cycle, an observation also made by others, as in the hydroesterification of alkenes by methyl formate [26].

Since the origin of CO is clear, let us now examine the formation of dihydrogen. Some of the possibilities are as follows:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \text{ (WGSR)}$$

$$CH_3OH \rightleftharpoons HCHO + \tfrac{1}{2}H_2$$

$$2CH_3OH \rightleftharpoons HCOOCH_3 + 2H_2$$

$$HCOOH \longrightarrow CO_2 + H_2$$

We did not observe formation of dihydrogen in a separate experiment with methanol as substrate. Also, the WGSR does occur although it is less favoured when PBu_3 is used instead of PCy_3 which is known to activate the ruthenium catalyst in the WGSR (see Table 4 of ref. 15).

Dihydrogen could be produced from formic acid via hydrolysis of methyl formate, because formic acid plus a tertiary amine or phosphine is known to be a source [27]:

$$HCOOCH_3 \longrightarrow CH_3OH + CO \qquad (1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

$$HCOOCH_3 \longrightarrow CH_4 + CO_2 \qquad (3)$$

$$HCOOCH_3 + H_2O \rightleftharpoons CH_3OH + HCOOH \qquad (4)$$

$$HCOOH \longrightarrow CO + H_2O \qquad (5)$$

$$HCOOH \longrightarrow CO_2 + H_2 \qquad (6)$$

$$2CH_3OH \longrightarrow (CH_3)_2O + H_2O \qquad (7)$$

$$CH_3OH + CO + 2H_2 \longrightarrow CH_3CH_2OH + H_2O \qquad (8)$$

The water required to hydrolyse the formate is the initial water added or water formed in some other reaction such as reactions (5), (7) or (8).

Homologation may occur either in the usual way or by reduction of acetic acid starting from CH_3X formed by nucleophilic substitution between methyl formate and the onium salt Q^+X^-:

$$HCOOCH_3 + Q^+X^- \rightleftharpoons HCOO^-Q^+ + CH_3X \qquad (9)$$

$$CH_3X \xrightarrow{CO}$$

$$CH_3COX \begin{array}{l} \xrightarrow{H_2} CH_3CHO \xrightarrow{H_2} C_2H_5OH \qquad (10) \\ \xrightarrow{H_2O} CH_3COOH \xrightarrow{H_2} C_2H_5OH \qquad (11) \end{array}$$

Reaction (9) can be activated by HCl, X being either Cl or Br:

$$R_4PX \overset{H^+}{\rightleftharpoons} R_3X + RX \qquad (12)$$

$$HCOOCH_3 + HCl \longrightarrow HCOOH + CH_3Cl \qquad (13)$$

Equilibrium (12) has been suggested previously [13,22]. We have verified that replacing Bu_4PBr by a stoichiometric mixture of Bu_3P and BuBr led to ethanol formation (run 33 in Table 7). The retro-Mentshutkin reaction of phosphonium salts has been assumed to be accelerated in the presence of aqueous solutions of alcohols [28]. Reaction (13) occurs under catalytic conditions [29].

Sequence (11) is quite plausible. The synthesis of acetic acid from methyl formate with an iodine-promoted rhodium catalyst occurs at 180°C under a CO pressure of 30 bar [30]:

$$HCOOCH_3 + CO + H_2O \longrightarrow CH_3COOH + HCOOH \qquad (14)$$

However, in this case, it is very probable that methyl formate is first hydrolysed to formic acid and methanol which in turn is carbonylated in the usual way. In addition, the ruthenium-catalysed carbonylation of methanol to acetic acid has been observed [31]. An iodine-free ruthenium complex catalyst has even been found to convert methyl formate to acetic acid and methyl acetate [32]. Although we seldom observed the formation of acetic acid in our reaction, it is possible that acetic acid, once formed, is easily reduced to ethanol. We have checked that reaction (11) can take place with the easy formation of ethanol to give ethyl acetate as the ultimate product, consistent with earlier results [33]. However, the absence or the very low yield of ethyl acetate in the present method suggests that this route, if occurring, is marginal.

The present process offers good selectivity with respect to ethanol (methanol formation is not considered). The formation of ethyl formate (homologation reaction) is not observed, which is in contrast to the formation of this product in the iodine-promoted ruthenium-catalysed hydrocarbonylation of methyl formate [34]. In our case, as outlined above, addition of iodine promotes decomposition of HCOOH unless the pressure of CO or $CO + H_2$ is sufficient. Thus, the excellent selectivity of the present process is probably due to two factors: (i) CH_3COX is rapidly hydrogenated (reaction (10)) or subject to a hydration–hydrogenation sequence (reaction (11)); (ii) the non-occurrence of transesterification suggested by Keister and Gentile [35] between ethanol and methyl formate caused by the rapid decarbonylation of the initial methyl formate.

The anionic species detected by IR spectroscopy is $[HRu_3(CO)_{11}]^-$ (ν(CO) at 2020 and 1985 cm^{-1}). Neither $[Ru(CO)_3Cl_3]^-$ [13] nor $[Ru(CO)_3Br_3]^-$ [36] was detected. There are other IR bands (2050, 2035 and 1970 cm^{-1}) which could be attributed to complex anionic species containing the phosphine such as $[HRu_3(CO)_{10}(PR_3)]^-$ by analogy with similar species [37]. These species may be responsible for the transformation of the methoxy group, since, in the absence of phosphine, no ethanol is formed. On the contrary, a complex of type $[M(CO)_x \cdot PR_3 \cdot PR_2(O)]$ was claimed to be the active species in the homologation of methanol carried out with iodine-free metal catalysts [12,38].

The present ethanol synthesis from methyl formate has several requirements, in addition to necessary ruthenium catalysis.

(i) An onium salt is necessary. A possible explanation is provided by reaction (9). Onium salts are excellent counter-ions for anionic ruthenium carbonyl hydrides [12,24,39], making them appropriate additives in many hydrocarbonylation reactions [40].

(ii) An appropriate phosphine is required. The phosphine is probably involved in the production of dihydrogen and carbon monoxide ($HCOOH + PR_3$ is a source of dihydrogen). The phosphine may also act as agent for the transfer of the methyl group from formate to the catalyst (*vide infra*).

(iii) Promotion by HCl is essential. This is clearly shown in reactions (4), (7), (12), (13), and, possibly, (9).

We therefore propose the following scheme, by analogy with earlier proposals [41,42], in which the role of phosphine is to activate methyl formate assisted by the onium halide.

(1) Production of CO and H_2 occurs according to

$$HCOOCH_3 + PR_3 \rightleftharpoons CH_3PR_3^+ + HCOO^-$$

$$[Ru_3(CO)_{12}] + PR_3 + H_2 \rightleftharpoons [HRu_3(CO)_{11}]^- + HPR_3^+ + CO$$

$$HCOO^- + HPR_3^+ \longrightarrow H_2 + CO_2 + PR_3$$

$$HCOO^- + HRu_3(CO)_{11}^- + CO \longrightarrow H_2 + CO_2 + Ru_3(CO)_{12}$$

(2) Homologation takes place as follows:

$$[HRu_3(CO)_{11}^-]^- + CH_3PR_3^+ \longrightarrow [CH_3HRu_3(CO)_{11}] + PR_3$$

$$[CH_3HRu_3(CO)_{11}] + CO \longrightarrow [CH_3COHRu_3(CO)_{11}]$$

$$[CH_3COHRu_3(CO)_{11}] + CO \longrightarrow CH_3CHO + [Ru_3(CO)_{12}]$$

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

This scheme has some analogy with the hydrocarbonylation of methanol catalysed by $[Fe(CO)_5]$ [43] or by $[Mn_2(CO)_{10}]$ and promoted by amines [44]. However, there are two major differences: the iron- or manganese-catalysed reaction requires a high initial ($CO + H_2$) pressure (300 bar) and it uses methanol as the substrate. In our case, not only does the process not need initial application of pressure but, in addition, methanol is scarcely converted to ethanol at all (run 32 in Table 7), indicating that methanol is not the actual substrate.

4. Conclusion

The present novel catalytic process for synthesizing ethanol from methyl formate is encouraging, despite the modest ethanol yields. Turn-overs obtained in the present method, about 100 mol of ethanol per gram-atom of ruthenium, approach the turn-overs (60–80) reported for the synthesis of ethanol in the ruthenium-catalysed hydrogenation of carbon monoxide under 340 bar at 260°C [13].

The procedure does not need an initial synthesis gas pressure, thus avoiding handling, storage and compression of $CO–H_2$ mixtures. The gas required is generated *in situ*. Another advantage is that it uses iodine-free catalytic systems. The small amount of HCl used in the present method has no corrosive effect on the vessel whereas iodine is detrimental. All methanol homologation methods before this have required iodine promotion to give a convenient rate. This is particularly true in the homologation of higher alcohols. Without iodine, there is no formation of propanol from ethanol [45,46], whereas the present catalytic system is also active in the synthesis of higher alcohols RCH_2OH from alkyl formates HCOOR [47].

5. Experimental details

In a typical experiment, the onium salt (0.35 mmol) and $[Ru_3(CO)_{12}]$ (0.04 mmol) were placed in a stainless steel vessel under an inert atmosphere. Methyl formate (48.7 mmol), toluene (2 ml), tributyl phosphine (0.58 mmol) and diglyme (200 μl, internal chromatographic standard) were added successively. Finally, an aqueous HCl solution (250 μl) was introduced. The vessel was closed, positioned on a shaking device and heated. After reaction, the autoclave was cooled and slowly vented through a volumometer. A gas sample was taken for analysis. The vessel was opened and the liquid phase removed and analysed by vapour-phase chromatography under the following conditions.

(i) Gas analysis: IGC 120 ML; Hayesepp D(80-100 mesh); 8 m × $\frac{1}{8}$ in; methane and helium as successive carrier gases

(ii) Liquid analysis: Hewlett–Packard 5700A; Hayesepp S or Chromosorb 101 (80-100 mesh); 2.5 m × $\frac{1}{8}$ in; 50–240°C; 4°C min^{-1}.

IR analyses of catalyst solution were carried out on a Perkin–Elmer spectrometer (model 881).

The yield is defined as the ratio of multimoles of formate converted into ethanol to multimoles of formate charged. Since methyl formate is nearly fully converted, methanol is the major product (70–90% depending on the run). For that reason, selectivity data take into account methane and all liquid products, except methanol.

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