Palladium-catalyzed hydroesterification of propene into methyl 2-methylpropanoate at room temperature and atmospheric pressure. Influence of various parameters on the activity and selectivity of the reaction

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The hydroesterification of propene into methyl 2-methylpropanoate by homogeneous catalytic systems consisting of palladium, copper, oxygen and acid is investigated under very mild conditions (room temperature, atmospheric pressure). From experimental results it appears that: (i) very high selectivities (up to 95%) into the branched ester can be obtained; (ii) the presence of $CuCl_2$ and O_2 as final reoxidant of palladium is required; (iii) the activity increases with partial pressure of O_2 in the gas phase.

Keywords: hydroesterification, palladium, copper, propene, methyl 2-methylpropanoate

1. Introduction

In contrast with hydroformylation (scheme 1, Z = H), hydrocarboxylation (scheme 1, Z = OH) or hydroesterification (scheme 1, Z = OR′) reactions have not been the subject of important industrial development in spite of their potential synthetic interest and although they are known for a long time [1].

Among the different metals known to catalyze these reactions, palladium is generally considered as the most active under mildest conditions [2]. However, from simple terminal alkenes, even if high selectivities into the linear product have been reported with the $Pd/SnCl_2$ system [3], usually palladium-based catalytic systems lead to a mixture of the two isomers (linear n and branched i).

From an industrial point of view, obtaining selectively the branched carbonylated product from linear alkenes, inaccessible with a high purity by hydroformylation [4], could present a great interest. For example, methyl methacrylate (an important industrial monomer) could be obtained via dehydrogenation of isobutyric ester or acid resulting from the carbonylation of propene (scheme 2).

In this context, we have focused our attention on previous reports of Alper et al. [5] who described a $Pd^{II}–CuCl_2–O_2$ system, particularly selective towards the synthesis of the branched isomer in hydroesterification or hydrocarboxylation of higher olefins. We wish to report here the results of our investigations on the hydroesterification of propene with this system. Experiments were carried out with the aim to analyze the role played by the different elements of the catalytic combination.

2. Experimental

2.1. Materials

Methanol, the different reoxidants except the heteropolyacids and the acids except anhydrous HCl were purchased in their highest available purity from Aldrich Chemical and were used as received without further purification. Palladium chloride was obtained from Acros Chemical (99% pure). The heteropolyacids were prepared according to a literature method [6]. Anhydrous HCl (>99.9%; Aldrich Chemical) and the other gases (>99.9% each; Air Liquide) were used directly from cylinders.

2.2. Apparatus and instrumentation

All experiments conducted under atmospheric pressure were performed in the apparatus depicted in figure 1.

In a well-ventilated hood, a four-necked 100 ml flask was attached to a vacuum line (F) and equipped with a gas/liquid inlet (C), a magnetic stirrer (D), a Suba Seal septum pierced with a teflon tube (E) and a reflux condenser (H) overtopped with a gas tank (B) (1 or 3 l). The gas tank was connected to a Hg bubbler (G) to avoid overpressure in the glass reactor and to control the vacuum or the gas consumption. In order to prevent corrosion by HCl, glass tubes (I) (internal diameter: 8 mm) were used

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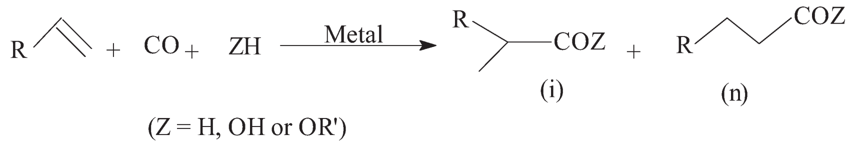
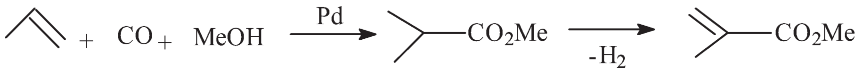


Scheme 1.



Scheme 2.

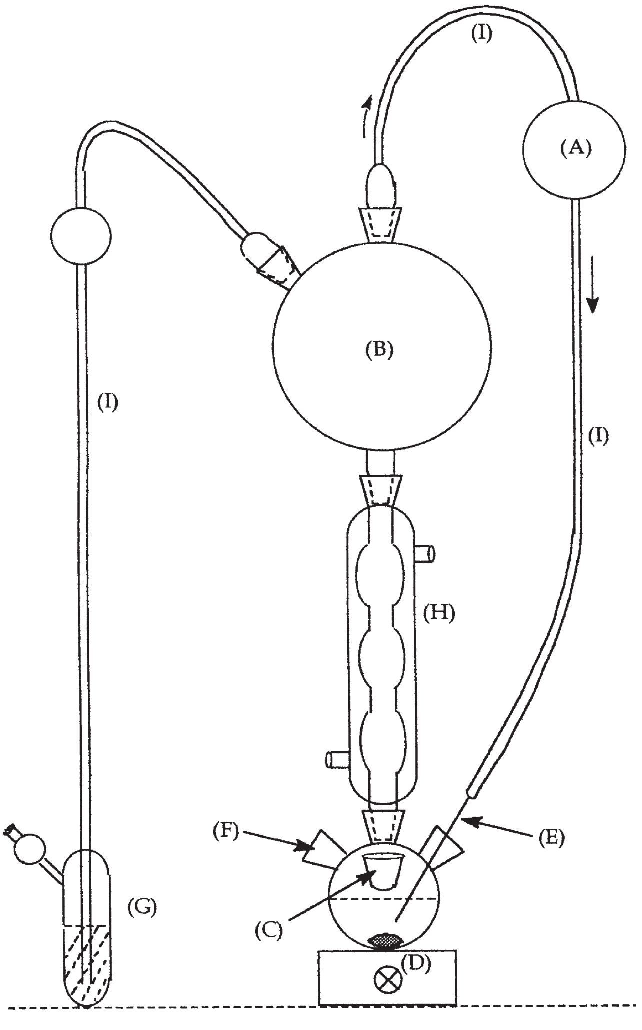


Figure 1. Glass reactor for propene hydroesterification at atmospheric pressure.

to connect the various parts. Gas mixture circulation was achieved with a single-head pump (A) (Air Cadet – Cole Parmer Instruments) equipped with a Fluorel diaphragm. The gas flow rate during the reaction course was 5 l/min. Accurate amounts of propene, oxygen and carbon monoxide were introduced into the reactor via the (C) inlet by using a flow meter/totalizer (Aalborg instrument). The liquid reaction mixture was added via the (C) inlet by using syringes.

Experiments under pressure were carried out in a 100 ml stainless steel autoclave reactor supplied by Autoclave Engineers and equipped with arrangements for automatic temperature control, pressure regulation and variable stirrer speeds. A safety rupture disk was also fitted to the reactor.

Gas–liquid chromatography analyses were carried out on a Chrompack 9001 or 9000 apparatus equipped with a CP Sil 5-CB column (25 m × 0.32 mm) and a FID detector or with a Poraplot Q column (25 m × 0.53 mm) and a micro TCD detector, respectively. Carrier gases were nitrogen and helium, respectively. UV spectra were recorded at 20 °C on a Perkin-Elmer 15 UV/VIS spectrophotometer (resolution of 0.25 nm) using quartz cells.

2.3. Catalytic runs

In a typical atmospheric pressure test, $PdCl_2$ (0.6 mmol), $CuCl_2$ (4 mmol) and HCl (12 mmol) were stirred in 50 ml of methanol until total dissolution under a nitrogen atmosphere. The resulting solution was then introduced in the glass apparatus which has been filled beforehand with propene (20 mmol), carbon monoxide (20 mmol) and oxygen (5 mmol). Magnetic stirring (1000 rpm) and pump (5 l/h) were then started.

The reactions under pressure were performed as follows: a methanol solution (50 ml) containing 0.6 mmol of $PdCl_2$, 4 mmol of $CuCl_2$ and 12 mmol of HCl was charged in the autoclave under an atmosphere of N_2. After pressurization with 4 or 20 bar of a gas mixture of propene, O_2 and CO (1/2/1) provided from a gas reservoir which was initially pressurized with 8 bar of C_3H_6, 8 bar of CO and 16 bar of O_2, mechanical stirring (1000 rpm) was started.

Products were identified by comparison of GLC retention times and spectral characteristics with authentic samples and in all experiments, the reaction was monitored by quantitative gas chromatographic analysis by using ethylbenzene as an internal standard. These analyses allow one to draw the curves depicting the variation of the amount of total C_4 esters obtained as a function of time. From the slope of the curves at the initial time and at $t = 5$ h, the initial turnover frequency ($TOF_{(0)}$) and the turnover frequency at 5 h ($TOF_{(5)}$) were respectively calculated as mole number of propene converted per mole of palladium and per hour.

3. Results and discussion

Preliminary experiments were carried out under the reaction conditions previously described by Alper et al. [5],

Table 1
Hydroesterification of propene catalyzed by multicomponent catalytic systems.[a]

Run	Catalytic system (mmol)				$TOF_{(0)} \times 10$	$TOF_{(5)} \times 10$	i/n
	$PdCl_2$	$CuCl_2$	HCl	O_2	(h^{-1})	(h^{-1})	ratio[b]
1	0	4	12	5	0	0	–
2	0.6	0	12	5	2	0.7	6.5
3	0.6	4	0	5	0.3	0.1	8
4	0.6	4	12	0	5.5	0.9	11
5	0.6	4	12	5	11.5	7.1	11

[a] Experimental conditions: $PdCl_2$: 0.6 mmol; $CuCl_2$: 4 mmol; HCl: 12 mmol; CH_3OH: 50 ml; C_3H_6: 20 mmol; CO: 20 mmol; O_2: 5 mmol.
[b] Methyl 2-methylpropanoate to methyl butanoate ratio.

by bubbling the different gases (propene, carbon monoxide and oxygen) with the convenient flow rate, into a solution of $PdCl_2$, $CuCl_2$ and HCl in methanol at room temperature. The lack of reproducibility of the results, probably due to the difficulty to keep the gas flows constant throughout the reaction course and/or to the variation of the liquid phase composition by HCl stripping by the gas flow, led us to use a totally closed vessel described in figure 1. This apparatus was initially filled with the gas mixture under atmospheric pressure and a circulation pump provided a continual bubbling of the gas mixture in the liquid phase (see section 2). Using this procedure, excellent reproducibility between the different runs was observed. Therefore, this experimental protocol was adopted for all the afterward experiments. In a typical run conducted at 20 °C with a gas mixture consisting of propene = 20 mmol, carbon monoxide = 20 mmol and oxygen = 5 mmol, the $PdCl_2$–$CuCl_2$–HCl catalytic system (1 : 6.6 : 20) dissolved in 50 ml of methanol gave selectively butyric esters with an initial turnover frequency ($TOF_{(0)}$) of 1.15 h^{-1}. As expected, the ratio branched (i) to normal (n) isomer is high ($i/n > 10$, table 1, run 5) and no other product than C_4 methyl esters was detected by chromatographic analysis.

Table 1 shows that all components of the catalytic system are needed to obtain both a good activity and selectivity of the system. Particularly relevant is the role of oxygen which is required to avoid the catalyst decay. From this observation the influence of various reoxidants typically used in the Wacker process was examined (table 2).

The performances of $CuCl_2$, CuCl and $CuSO_4$ are quite similar after 5 h of reaction although with $CuSO_4$ the initial $TOF_{(0)}$ was lower. The finding that Cu^{I} and Cu^{II} induce practically the same results can be explained by the existence of an equilibrium between the two species rapidly reached under CO–O_2 atmosphere. This assumption is confirmed by UV studies of reaction samples taken in the earlier stages of the reaction. Figure 2 shows the spectra of pure $CuCl_2$, $PdCl_2$ and CuCl in methanol and those of reaction samples. It appears that the signal at about 270 nm characteristic of $CuCl_2$ rapidly diminishes and has almost disappeared after only 2 min of bubbling of gas mixture in the reaction solution. In the same way the signal ascribable to $PdCl_2$ slightly decreases, whereas the one of CuCl, in comparison, increases. It should be noticed that the concentration of $CuCl_2$ tends to decrease just from contact of the gas and liquid phases (i.e., at $t = 0$), even without bubbling of the gas in the reaction solution.

Table 2
Hydroesterification of propene in the presence of various reoxidants.[a]

Run	Reoxidant	$TOF_{(0)} \times 10$ (h^{-1})	$TOF_{(5)} \times 10$ (h^{-1})	i/n ratio[b]
1	Benzoquinone	2.4	1.2	6
2	Chloranil	10.2	1	7
3	$CuSO_4$	7.3	6.1	15
4	CuCl	11.5	6.5	14
5	$CuCl_2$	11.5	7.1	11
6	Chloranil + $CuCl_2$[c]	17.5	5.2	12
7	$H_3PMo_{12}O_{40}$	9	3	7
8	$H_4PVMo_{11}O_{40}$	20	4	8
9	$H_5PV_2Mo_{10}O_{40}$	28	4	5
10	$H_4PVW_{11}O_{40}$	7	1.5	8
11	$H_5PV_2Mo_{10}O_{40}/CuCl_2$	20	1	4

[a] Experimental conditions: $PdCl_2$: 0.6 mmol; reoxidant: 4 mmol, except run 11: $H_5PV_2Mo_{10}O_{40}$: 4 mmol–$CuCl_2$: 4 mmol; HCl: 12 mmol; CH_3OH: 50 ml; C_3H_6: 20 mmol; CO: 20 mmol; O_2: 5 mmol.
[b] Methyl 2-methylpropanoate to methyl butanoate ratio.
[c] Chloranil: 2.8 mmol, $CuCl_2$: 1.2 mmol.

Benzoquinone and 1,4-tetrachlorobenzoquinone (chloranil) [7] were found as being practically inefficient although the latter exhibited an initial TOF almost similar to the one of $CuCl_2$ but rapidly the activity dropped. Moreover, the selectivity into the branched isomer is not as good as with the Cu system. Addition of a small amount of $CuCl_2$ to chloranil (Cu^{II}/chloranil = 0.4) with the same total concentration in potential oxidant, had as effect to increase significantly the initial TOF, the $TOF_{(5)}$ and to restore the selectivity (run 6). Finally, different heteropolyacids which had been successfully used in the Wacker process [8] were tested. At the same molar concentration as $CuCl_2$, $H_4PVMo_{11}O_{40}$ and $H_5PV_2Mo_{10}O_{40}$ exhibited a better initial activity than $CuCl_2$ (table 1, runs 8 and 9, respectively) but their efficiency quickly dropped and in the two cases, the overall conversion was significantly lower than the one observed with $CuCl_2$. The addition of $CuCl_2$ to $H_5PV_2Mo_{10}O_{40}$, in contrast with chloranil, had rather a detrimental influence on the $TOF_{(0)}$ and the $TOF_{(5)}$ (run 11).

As copper salts were found as the most efficient reoxidants, the influence of their concentrations was checked. In the range studied ($0 < \mathrm{Cu/Pd} < 24$), the initial activity increased with the amount of Cu^{II} initially introduced. However, the overall activity ($TOF_{(5)}$) and selectivity behaved in a totally different way: the activity reaches a maximum and remains almost constant for a Cu/Pd ratio >6, whereas an excess of copper chloride decreases the selectivity of methyl isobutanoate (figure 3). The high values of $TOF_{(0)}$ and the low i/n ratio observed with the heteropolyacids are probably in connection with the results obtained at high $CuCl_2$ concentration. Indeed, the heteropolyacids possess several oxidation states and for a same molar concentration as the one of $CuCl_2$ the oxidant power is much higher.

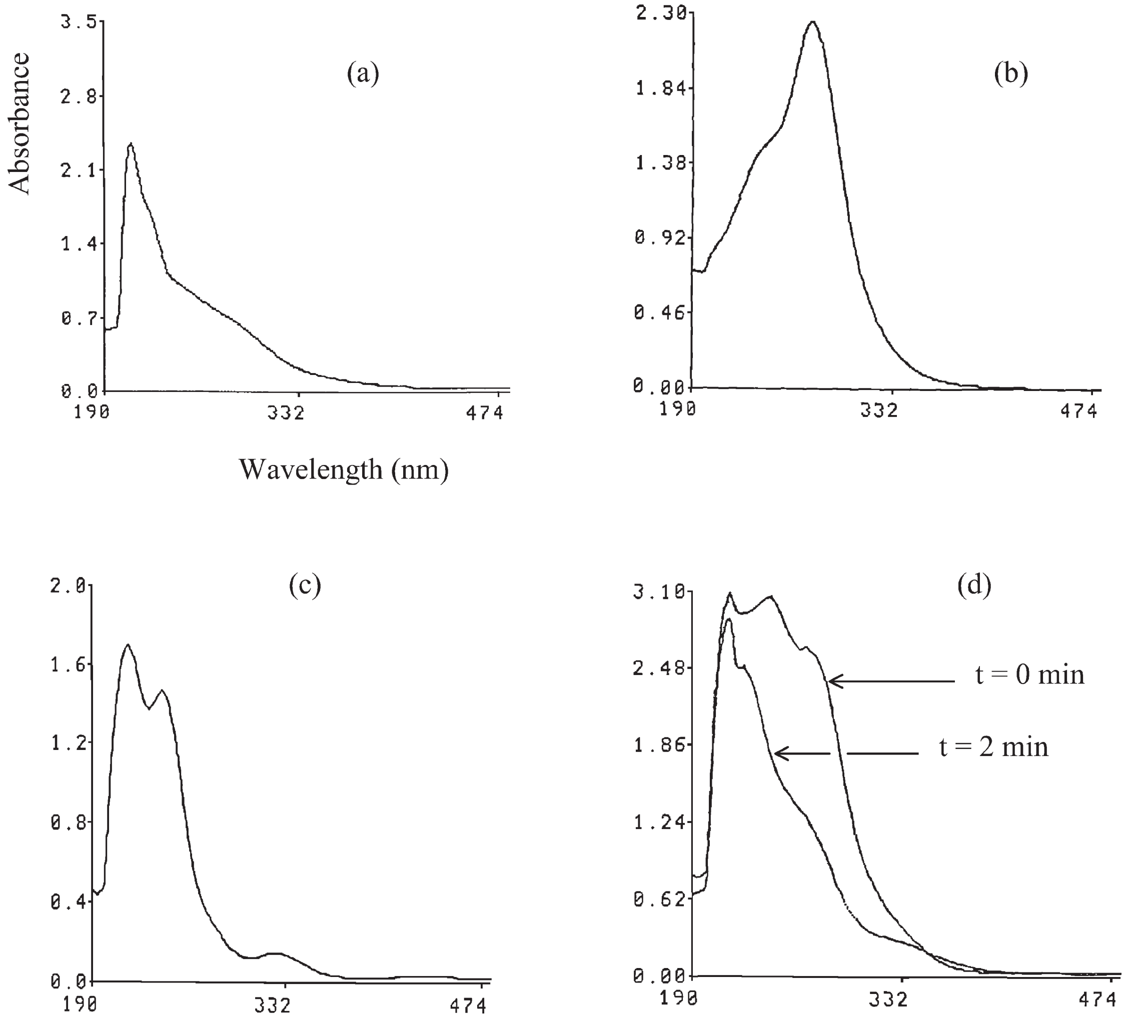


Figure 2. (a)–(c) UV spectra of CuCl (0.8 mmol/l, $\lambda_{\max} = 210$ nm), $CuCl_2$ (0.8 mmol/l, $\lambda_{\max} = 273$ nm) and $PdCl_2$ (0.12 mmol/l, $\lambda_{\max\ 1} = 220$ nm, $\lambda_{\max\ 2} = 243$ nm) in methanol, respectively; (d) UV spectra of catalytic solution at various times. Conditions identical to those used in table 1, run 5 after 100 times dilution before analysis. $t = 0$ min: $\lambda_{\max\ 1} = 215$ nm, $\lambda_{\max\ 2} = 245$ nm, $\lambda_{\max\ 3} = 267$ nm; $t = 2$ min: $\lambda_{\max} = 215$ nm.

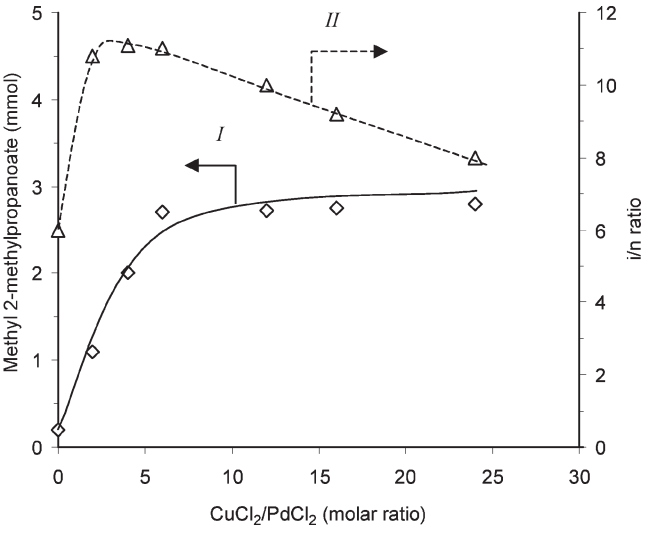


Figure 3. Influence of the copper to palladium ratio on the amount of methyl 2-methylpropanoate (I) and the i/n ratio (II) obtained after 5 h of reaction. HCl: 12 mmol; methanol 50 ml; CO: 20 mmol; O_2: 5 mmol; $CH_3CH{=}CH_2$: 20 mmol; T: 20 °C.

As the gas phase contains both an oxidant and a reductor and as the amount and the nature of the Pd reoxidant in the liquid phase have a great influence on the efficiency of the reaction, the gas phase composition must also have an effect on the reaction course. The influence of this parameter has been examined by using a gas tank of higher capacity than in standard experiments (3 l instead of 1 l, see figure 1). A suitable molar fraction of CO was obtained by adding to a variable quantity of this component the amount of nitrogen needed to maintain the atmospheric pressure in the reactor (at constant amounts of propene and oxygen). For standard contents of C_3H_6 and O_2 (corresponding to a molar fraction of 0.16 and 0.04, respectively), figure 4 shows that the quantity of methyl propanoate obtained after 5 h of reaction passed though a maximum for a molar fraction of CO of about 0.5. Above this value, an increase of the CO concentration strongly inhibited the reaction. In the same way the activity fell very quickly for CO molar fractions inferior to 0.4. This last observation is not ascribable to a lack of CO with respect to the stoichiometry, since even for a CO molar fraction of 0.2 the mole number of CO introduced

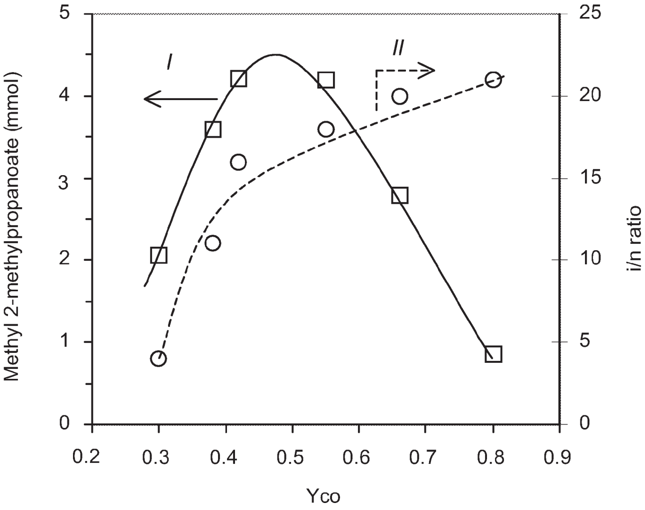


Figure 4. Influence of the mole fraction of carbon monoxide ($Y_{CO} = [n_{CO}/(n_{CO} + n_{propene} + n_{O_2} + n_{N_2})]$) on the amount of methyl 2-methylpropanoate (I) and on the i/n ratio (II) obtained after 5 h of reaction. $PdCl_2$: 0.6 mmol; $CuCl_2$: 4 mmol; HCl: 12 mmol; methanol 50 ml; T: 20 °C; mole fraction of propene: 0.16; mole fraction of oxygen: 0.04; various amounts of nitrogen were introduced to keep the total number of moles in the gas phase constant.

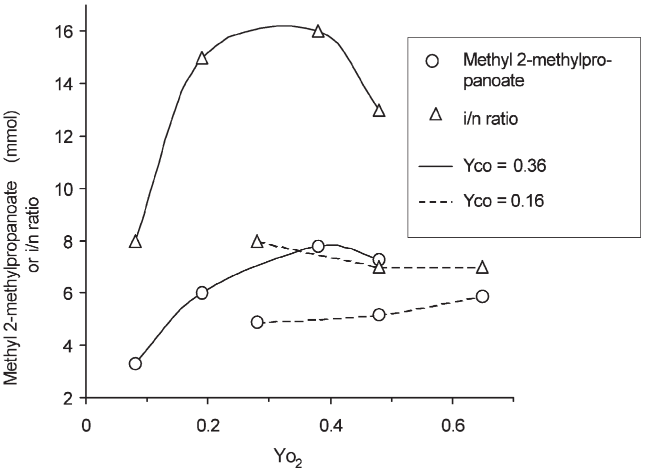


Figure 5. Influence of the mole fraction of oxygen on the amount of methyl 2-methylpropanoate and the i/n ratio obtained after 5 h of reaction. Conditions identical to those used in figure 4, except mole fraction of propene = 0.16; mole fraction of carbon monoxide = 0.16 and 0.36; various amounts of nitrogen were introduced to keep the total number of moles in the gas phase constant.

was higher than that of propene, but is rather due to the formation of inactive catalytic species. In contrast with the activity, the selectivity into the branched isomer continually increased with the molar fraction of CO. Nevertheless, this variation was not regular. The main part occurred for Y_{CO} varying between 0.3 and 0.5 which corresponds to a i/n ratio going from 5 to about 15.

The influence of the O_2 concentration has been examined, on the one hand, in a molar fraction range of 0.04–0.5 with a CO molar fraction of 0.36 (near to the optimum) and, on the other hand, of 0.25–0.68 with a CO molar fraction of 0.16 (figure 5). In both cases, significant improvement in the conversion of propene was observed upon increasing O_2 concentration.

Table 3

Hydroesterification of propene in the presence of various acids.[a]

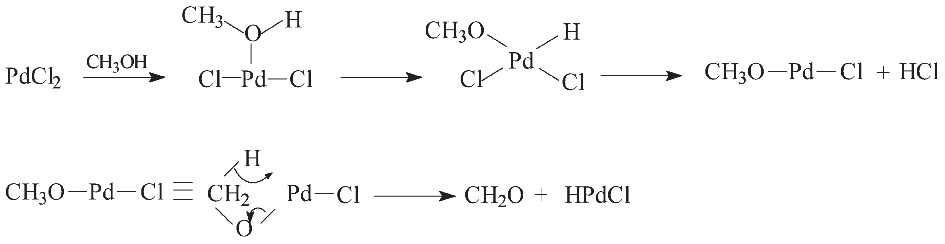
Run	Acid	$TOF_{(0)} \times 10$ (h^{-1})	$TOF_{(5)} \times 10$ (h^{-1})	i/n ratio[b]
1	HCl (aq.)	11.5	7.1	11
2	HCl (gas)	11.6	10.2	17
3	HCl (gas)[c]	17	10.1	15
4	p-$CH_3C_6H_4SO_3H$	17.1	8.5	14
5	CF_3CO_2H	3.1	1.5	10
6	CH_3SO_3H	16.4	3.2	21
7	CH_3SO_3H + LiCl[d]	15.7	7.4	15
8	HCl (aq.) + LiCl[d]	6.1	4.6	11
9	HCl (aq.) + NaCl[d]	8.1	5.4	12
10	H_2SO_4	17	5	13
11	HBF_4	8	3	18

[a] Experimental conditions: $PdCl_2$: 0.6 mmol; $CuCl_2$: 4 mmol; acid: 12 mmol; CH_3OH: 50 ml; C_3H_6: 20 mmol; CO: 20 mmol; O_2: 5 mmol.
[b] Methyl 2-methylpropanoate to methyl butanoate ratio.
[c] MeOH dried over Mg and addition of molecular sieves in the reaction medium.
[d] LiCl or NaCl: 8 mmol.

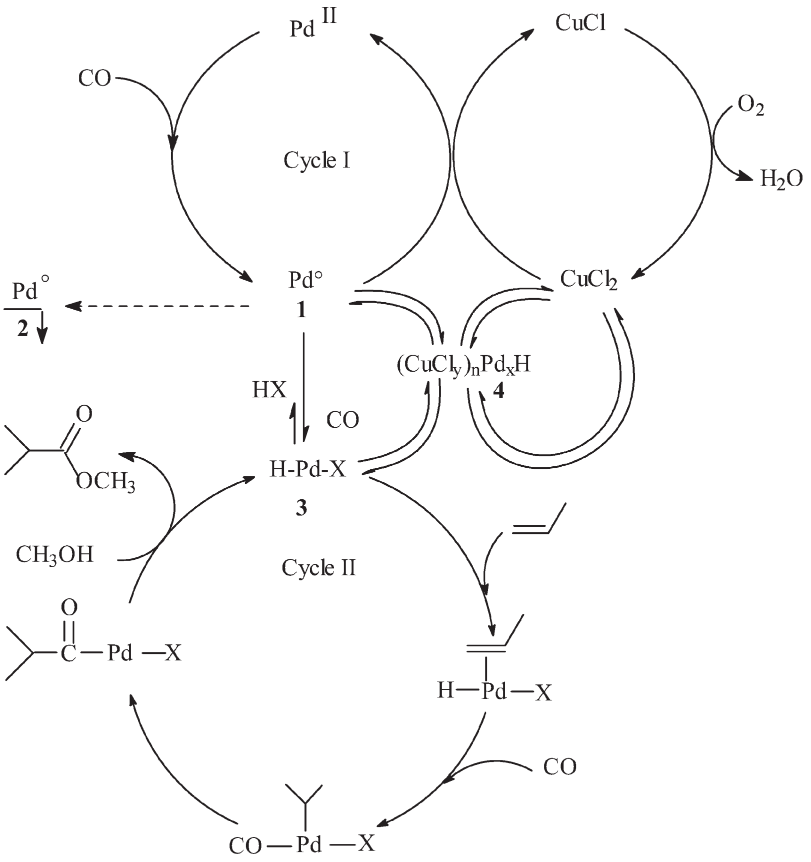
Finally, in order to determine the limitations of the process the influence of higher total pressure than in standard experiments on the efficiency of the reaction was also studied. The experiments were performed in an autoclave which was filled with the optimized gas mixture ($CO/O_2/C_3H_6$ v/v/v 1/2/1) under 4 and 20 bar. Unfortunately, in these cases no reaction took place and a large amount of a black metallic precipitate covering the walls of the autoclave was observed at the end of the experiments. Noteworthy similar results are obtained at higher temperature (50 °C). These results seem to indicate that, despite the presence of oxidants, under high CO partial pressure, Cu and Pd are under their reduced forms leading, in the absence of other ligands, to the formation of inactive colloidal or more probably metallic palladium. Indeed, hydroesterification of olefins under high CO pressure (>50 bar) is a well known process but it is operative only in the presence of phosphine or arsine ligands [9] and at room temperature this system proved to be also inactive in hydroesterification of propene [10].

Hydrochloric acid is necessary as undoubtedly indicated by run 3 in table 1. However, although numerous reports have described its promoter effect in hydrocarboxylation or in hydroesterification reactions, its role is not yet well understood. It was proposed that the acidity of the proton is important, particularly towards the selectivity. It could also act as a source of Cl^- ligand that stabilizes the Pd species [11]. It should be noticed that the addition of $CuCl_2$ to chloranil was found to maintain the activity of the system (table 2); this effect could be in connection with this role of Cl^-. To clarify this point different acids were tested (table 3).

Gaseous HCl gave better activity and selectivity than its aqueous form, especially using very dry conditions (table 3, run 3). Sulfuric acid and methane or p-toluenesulfonic acids



Scheme 3.



Scheme 4.

induced better initial activities than gaseous HCl but those decreased more rapidly. In the case of methanesulfonic acid, addition of Cl^- ions in the reaction medium led to a $TOF_{(5)}$ close to that obtained with HCl (aq). It should also be noticed that further Cl^- addition to aqueous HCl medium, whatever the nature of the cation, had rather a detrimental effect on the initial and overall activity and this effect was all the more marked as the Cl^- addition was high. Finally, CF_3COOH was practically inactive and HBF_4 weakly active. In conclusion, strong acids provide high initial activity and this one decreases with the strength of the acid, but coordinating anions are needed to stabilize the catalytic system. In their absence deactivation rapidly occurs.

Mechanistic aspects

Upon the basis of these results, it is difficult to delineate a detailed catalytic cycle. Nevertheless, some key points must be underlined: (i) Obviously the presence of an oxidizing agent is absolutely necessary and the activity increases with the amount of oxidant initially introduced ($CuCl_2$ and O_2). Among the oxidants tested the couple $CuCl_2$–O_2 is the most efficient. (ii) The activity decreases with the concentration of the reductor and drops towards zero for a partial CO pressure reaching 1–1.5 bar. (iii) A strong acid and Cl^- anions are also needed.

This last remark leads to thinking that the active catalytic species could be a palladium hydride such as H–Pd–X (X = Cl, solvent, CO, ...), **3**, resulting from the action of methanol on $PdCl_2$ (according to scheme 3) or more probably from the oxidative addition of HCl on a Pd^0 species arising from the reduction of $PdCl_2$ by carbon monoxide.

This palladium hydride **3**, co-ordinatively unsaturated, is expected to be very reactive towards olefins. The olefin insertion into the H–Pd bond followed by alkyl insertion into the CO–Pd bond and subsequent attack of CH_3OH should lead to the ester (scheme 4, cycle II).

The role of $CuCl_2$ could be to reoxidize the inactive metallic palladium into Pd^{II} (see scheme 2, cycle I). Indeed, in the absence of phosphorus ligands, the palladium species **1** which is only stabilized by CO, the solvent and Cl^- is very unstable, giving rapidly metallic palladium. Thus without $CuCl_2$, cycle I does not occur and all palladium quickly precipitates. In contrast, in the presence of phosphines L (such as PPh_3), **1** is stabilized as PdL_2 avoiding the precipitation of **2** and, therefore, the presence of $CuCl_2$–O_2 is not required as previously reported [9].

$CuCl_2$ could also stabilize the HPdCl species under the form of a $(CuCl_y)_nPd_xH$ complex (where $y = 1$ or 2) [12] such as **4** and/or could limit the reduction of HPdCl by CO ($CuCl_2$ should be reduced in the first time: see figure 3 and the comments in the text referring to this figure).

As the hydride **3** is the presumed catalytic active species for the hydroesterification of propene, the activity must be only function of its concentration at the steady state. This one depends not only on the amount of $PdCl_2$ initially introduced in the reactor but also on the conditions of the cycle I (P_{CO}, P_{O_2}, amount of $CuCl_2$, $\ldots$). For example, when the CO partial pressure is too high (experiments performed in autoclave) the concentration of **3** drastically decreases and the catalyst becomes inefficient.

The high selectivity in branched ester obtained with this catalytic system, as well as it high activity in comparison with the results reported in the literature with PPh_3, can be explained by the fact that the active species is coordinatively unsaturated. Actually, it is well known (for example, in hydroformylation) that phosphorus ligands produce a steric hindrance that directs the olefin insertion in a [M]–H bond towards the formation of the linear alkyl-metal.

Finally, it is also known that a related catalytic system Pd^{II}, Cu^{II} (catalytic or stoichiometric), CO (and O_2 when Cu^{II} is used in catalytic amounts) induces oxidative carbonylation of alkenes [13] to give mainly methoxyesters, diesters and unsaturated esters and this even under very mild conditions (room temperature and 3 bar CO pressure [13a]).

Nevertheless, it is noteworthy that in our reaction conditions the formation of these products was never observed. This difference of behavior is probably due to the fact that oxidative carbonylation is performed under neutral or basic conditions (in the presence of alkaline carboxylate). Thus it is generally accepted that the reaction proceeds via the formation of a palladium methoxy or methoxycarbonyl species followed by the insertion of the olefin in the metal methoxy or carbomethoxy bond. New CO insertion and alcoholysis or β-H elimination leads to the final products. In our case, in the presence of a strong acid the formation of a Pd–H species such as **3** instead of Pd–OMe or Pd–CO_2Me species is much more likely and as the consequence the reaction course proceeds differently.

4. Conclusion

In the presence of methanol and under atmospheric pressure of carbon monoxide and oxygen, the system $Pd^{II}/Cu^{II}/HCl$ catalyses the hydroesterification of propene into methyl 2-propanoate with a high selectivity. Actually, the C_4 methyl esters are the sole products of the reaction and the branched to linear ratio can reach values up to 20. All the components of the catalytic systems are required to perform the reaction with a high activity in comparison with other palladium phosphine-based catalysts previously reported. However, the activity is yet too weak to be compatible with industrial applications, as various attempts performed under harder conditions with the aim to increase the TOF have failed. The reduction of Pd^{II} into inactive palladium black under CO pressure higher than about 1 bar even in the presence of oxygen is the cause of this failure.

Acknowledgement

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