

Hydroesterification of cyclohexene using the complex $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2$ as catalyst precursor Effect of a hydrogen source (TsOH, H_2O) on the TOF and a kinetic study (TsOH: *p*-toluenesulfonic acid)

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Abstract

The hydroesterification of cyclohexene is catalyzed by a preformed $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2$ complex **I** in methanol as solvent. The effect of PPh_3 , TsOH, and water on the TOF has been evaluated. The system **I**/ PPh_3 /TsOH = 1/6/8, in the presence of 800 ppm of H_2O , at 373 K and under 2.0 MPa of CO leads to a TOF as high as 850 h^{-1} . The increase of TOF observed adding a hydride source such as TsOH and H_2O suggests that Pd-hydride species plays a key role in the first step of the catalytic cycle. The initial reaction rate increases linearly with the concentration of cyclohexene and of MeOH and passes through a maximum with increasing the pressure of CO. The rate equation $r_0 = k_1 P_{\text{CO}} (1 + k_2 P_{\text{CO}} + k_3 P_{\text{CO}}^2)^{-1}$ fits well the experimental data. The values of k_1 , k_2 , and k_3 have been evaluated at different temperatures. From the plot $\ln k$ versus $1/T$, $E_1 = 19.4 \text{ kcal/mol}$, $E_2 = 20.6 \text{ kcal/mol}$ and $E_3 = 6.5 \text{ kcal/mol}$ have been evaluated. On the basis of experimental evidences and of the kinetic study, a catalytic cycle mechanism has been proposed.

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1. Introduction

It is widely reported that palladium complexes catalyze the reaction of an olefin with carbon monoxide to give carboxylic acids and esters in the presence of water or alcohol, respectively [1,2]. These are important chemicals used for the manufacture of several products such as solvents, flavorings and perfumes.

Particularly interesting appear the results obtained using palladium complexes containing phosphine ligands [3–14]. With regard the hydroesterification of cyclohexene, it is reported that using the $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ catalyst, at 120°C and 50 atm, a yield of 95% is obtained in 5 h, with a TOF (mol/mol Pd h) of ca. 15 h^{-1} (average TOF in the first hour of reaction), in benzene/methanol = 1/4 as solvent [3].

In recent years, Pd-catalysts having, in addition to phosphine, weakly coordinating ligands so that the metal cation has easily available coordination sites capable of activating the reacting molecules, have attracted much interest both in academic and industrial

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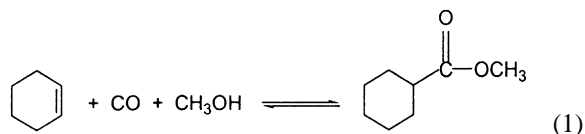
studies [5–14]. For instance, the catalyst precursor $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2$ has been successfully employed in the carbonylation of ethylene and styrene [15,16]. This precursor can be formed in situ by combination of palladium acetate, phosphine and TsOH.

This paper deals with the hydroesterification of cyclohexene catalyzed by preformed $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2$ (**I**), in methanol as solvent. The effect of PPh_3 , TsOH, and water on the TOF has been studied, together with the kinetics of the reaction.

2. Results and discussion

2.1. On the catalyst

Precursor **I** is highly active in the hydroesterification of cyclohexene when employed in the presence of added PPh_3 and TsOH



The effect of added PPh_3 is shown in Fig. 1 ($\text{TsOH}/\text{Pd} = 10/1$). The TOF increases up to a maximum of 850 h^{-1} at $\text{PPh}_3/\text{I} = 6/1$. At higher concentration of PPh_3 the TOF is depressed, probably due to the competition with the reagents for the coordination to the metal center. In the absence of TsOH and PPh_3 , precursor **I** is reduced to inactive Pd metal. In the presence of PPh_3 , and without TsOH, the precursor is reduced to a soluble $\text{Pd}(0)$ complex (for instance $[\text{Pd}(\text{PPh}_3)_3(\text{CO})]$), which is also inactive. This complex is readily reactivated by addition of TsOH, probably through formation of Pd-hydride species [16] (reaction (2)). As a matter of fact, when this $\text{Pd}(0)$ complex is employed in place of precursor

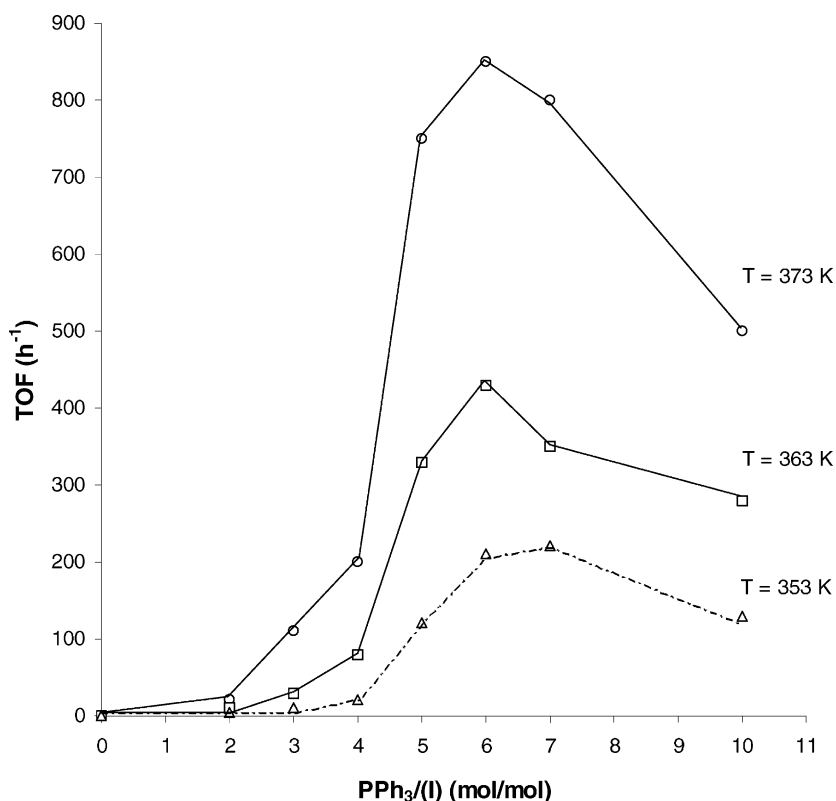


Fig. 1. Effect of PPh_3 addition on the TOF at different temperatures. Run conditions—**I**: $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2 = 0.1 \text{ mmol}$; $\text{Pd}/\text{TsO} = 1/10$ molar ratio; $\text{CH}_3\text{OH} = 40 \text{ ml}$; cyclohexene = 10 ml; $\text{H}_2\text{O} = 800 \text{ ppm}$; $P_{\text{CO}} = 2.0 \text{ MPa}$; reaction time = 1 h.

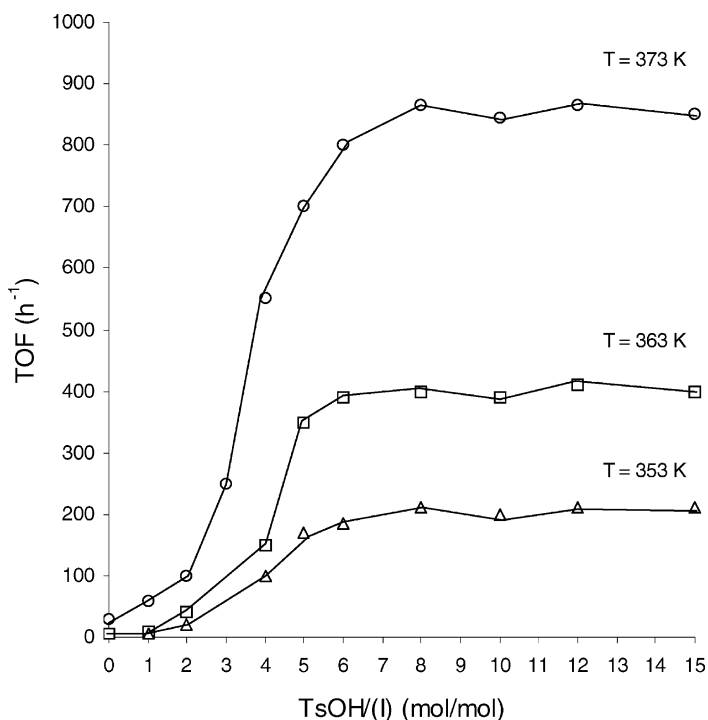


Fig. 2. Effect of *p*-toluenesulfonic acid on the TOF at different temperatures. Run conditions—I: Pd(PPh₃)₂(TsO)₂ = 0.1 mmol; Pd/PPh₃ = 1/8 molar ratio; CH₃OH = 40 ml; cyclohexene = 10 ml; H₂O = 800 ppm; P_{CO} = 2.0 MPa; reaction time = 1 h.

I, under the same conditions, i. e. in the presence of PPh₃ and TsOH in the ratio Pd/PPh₃/TsOH = 1/8/10, the hydroesterification occurs with comparable rate.



L = PPh₃, CO, H₂O, MeOH and TsO⁻.

The effect of added TsOH is shown in Fig. 2 (PPh₃/Pd = 8/1). There is a significant increase in the activity upon addition of TsOH. For example, at 373 K, the TOF increases from ca. 20 h⁻¹ in the absence of TsOH to ca. 850 h⁻¹ when TsOH/Pd = 10/1.

In the absence of TsOH, the Pd-hydride species may be formed also by reaction with the solvent itself (reaction (3)) [11], but in the present case formation of Pd metal (or Pd(0) complex by adding PPh₃) is observed probably due to reduction by the hydride (reaction (4))

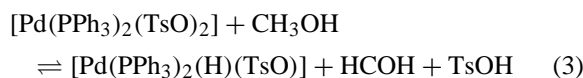
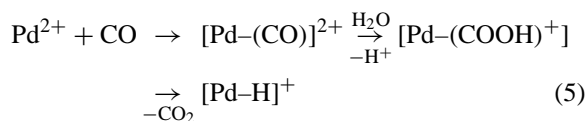


Fig. 3 shows that also H₂O plays a significant role in promoting the catalyst activity. At low water content, obtained by adding a water scavenger like trimethylorthoformate to methanol [17], the TOF is significantly low, ca. 200 h⁻¹, but increasing the water content up to 500–800 ppm, a maximum value of TOF is observed (850 h⁻¹). Since it is known that water can act as a source of hydride species through a reaction strictly related to the water gas shift [18], it is reasonable to suppose that water favors the formation of Pd-hydride species [16].



At higher concentration of water the TOF decreases, suggesting that water competes with the coordination of cyclohexene and carbon monoxide, slowing down the insertion of the olefin into a Pd-hydride species (see the proposed mechanism). A further increase of

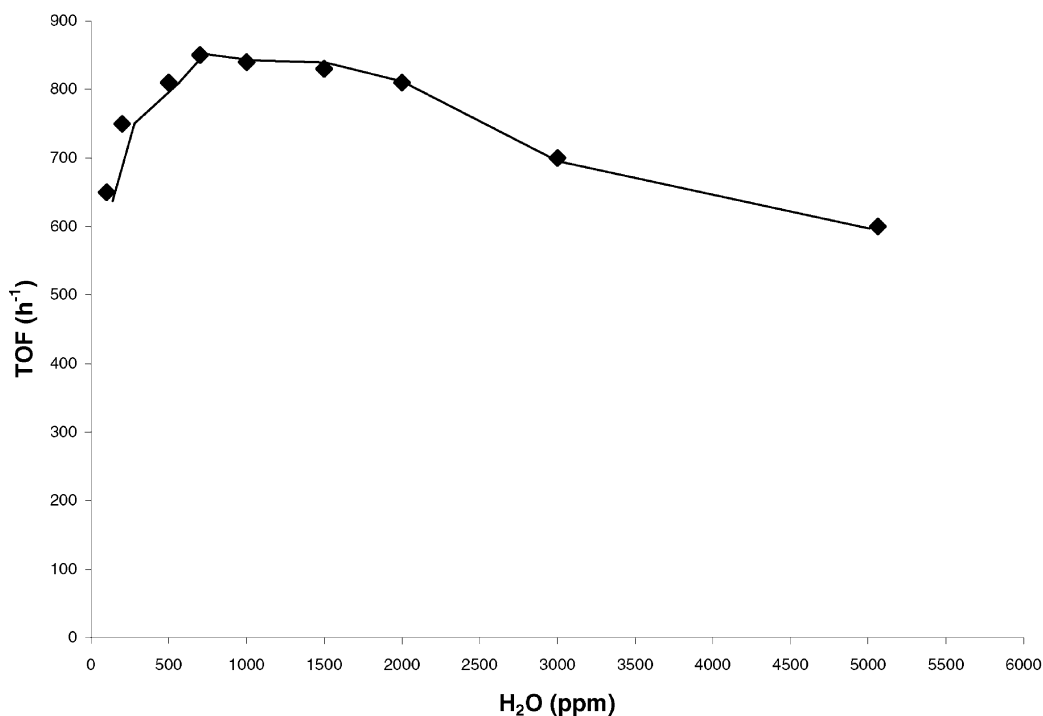


Fig. 3. Effect of water on the TOF. Run conditions: $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2 = 0.1 \text{ mmol}$; $\text{Pd}/\text{PPh}_3/\text{TsO} = 1/8/10$ molar ratio; $\text{CH}_3\text{OH} = 40 \text{ ml}$; cyclohexene = 10 ml; $T = 373 \text{ K}$; $P_{\text{CO}} = 2.0 \text{ MPa}$; reaction time = 1 h.

water (>3000 ppm) causes also decomposition to Pd metal



These observations suggest that when water is present in optimal concentration the insertion of the olefin into the Pd–H bond is faster than the decomposition of the hydride to Pd metal.

Experiments have been carried out also using acetone as a solvent in the presence of variable amounts of MeOH. Fig. 4 shows that the TOF increases almost linearly with increasing of the concentration of MeOH. It shows also that the TOF depends on the bulkiness of the alcohol employed for the hydroesterification, being in the order $\text{MeOH} > \text{EtOH} > n\text{-PrOH} > iso\text{-PrOH}$. This trend has been formed also in the hydroesterification of styrene using the same catalytic system [15].

In the catalytic mechanism proposed below, the slow step is the nucleophilic attack of the alcohol on an acyl intermediate (see reaction (19)). The accelerating effect of water may have also another origin. It

is reasonable to suppose that the cleavage of the acyl intermediate by water is faster than by the alcohols.

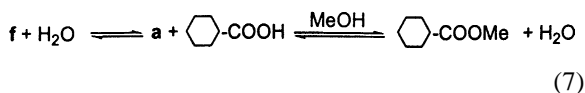


Fig. 5 shows that the TOF increases up to 850 h^{-1} upon increasing the temperature to 373 K. At higher temperature the TOF decreases because the catalyst decomposition to inactive Pd metal.

In conclusion, the best TOF is obtained using the catalyst system $\text{I}/\text{PPh}_3/\text{TsOH} = 1/6/8$, in the presence of 800 ppm of H_2O . This catalyst system has been used for the kinetic study.

2.2. Reaction kinetic

2.2.1. Check of kinetic regime

The system involves a gas–liquid reaction. It is important to ensure that the rate data used for kinetic analysis are obtained under condition of chemical

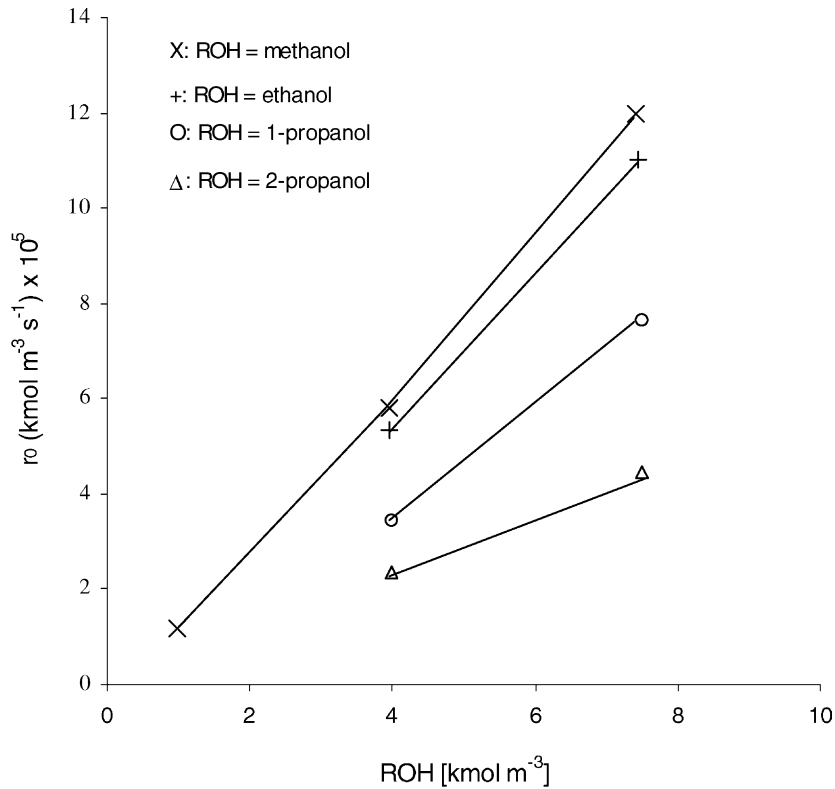


Fig. 4. Hydroesterification with different alkanols at different concentrations. Run conditions—I: Pd(PPh₃)₂(TsO)₂ = 0.1 mmol; I/PPH₃/TsO = 1/6/8 molar ratio; (ROH + acetone) = 40 ml; cyclohexene = 10 ml; H₂O = 800 ppm; T = 373 K; P_{CO} = 2.0 MPa; reaction time = 1 h.

reaction control and that mass transfer limitation (gas–liquid) is not significant. If

$$\frac{r_0}{k_{L,a}C_{CO}^*} < 0.1 \quad (8)$$

the gas–liquid mass transfer resistance is negligible [19]; r_0 : initial reaction rate (kmol m⁻³ s⁻¹); C_{CO}^* : concentration of CO in liquid in equilibrium with the gas phase (kmol m⁻³); $k_{L,a}$ = volumetric gas–liquid mass transfer coefficient (s⁻¹). The $k_{L,a}$ can be calculated by the correlation [20]

$$k_{L,a} = 1.48 \times 10^{-3} N^{2.18} \left(\frac{V_g}{V_L} \right)^{1.88} \left(\frac{d_1}{d_T} \right)^{2.16} \times \left(\frac{h_1}{h_2} \right)^{1.66} \quad (9)$$

where N is the agitation speed (Hz), d_1 the impeller diameter (m), d_T the tank diameter (m), h_1 the height of the impeller from the bottom (m), h_2 the liquid height in the reactor from the bottom (m), V_g the volume of gas phase (m³), and V_L the volume of liquid phase (m³). Since the ratio (8) is <0.01 at all temperatures (353–373 K), the reaction rate is not mass transfer controlled.

In addition, the effect of stirring speed on the reaction rate has been considered. Fig. 6 shows that the stirring speed variation between 5 and 24 Hz has no effect on the rate at all temperatures, indicating gas–liquid mass transfer resistance is unimportant. In this study, all the reactions have been carried out at 12 Hz.

Moreover, in order to ensure that the rate data obtained are in the kinetic regime, the effect of catalyst concentration and the apparent activation energy have

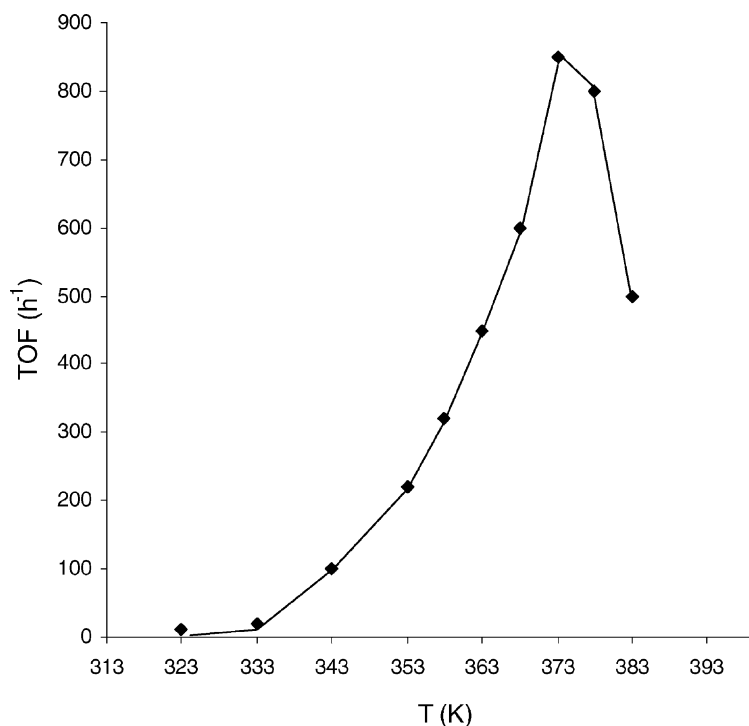


Fig. 5. Effect of temperature on the TOF. Run conditions—I: Pd(PPh₃)₂(TsO)₂ = 0.1 mmol; I/PPh₃/TsO = 1/6/8 molar ratio; CH₃OH = 40 ml; cyclohexene = 10 ml; H₂O = 800 ppm; P_{CO} = 2.0 MPa; reaction time = 1 h.

been evaluated also. Fig. 7 shows that the rate of reaction is first order with respect to the catalyst concentration. From the Arrhenius plot shown in Fig. 8, an observed activation energy of 19.5 kcal/mol has been evaluated, confirming the reaction is not limited by CO adsorption.

2.2.2. Rate equation

In the range of concentration studied, the reaction rate is first-order both with respect to catalyst (Fig. 7) and with respect to cyclohexene (Fig. 9). The dependence of the rate on P_{CO}, shown in Fig. 10, indicates a non-linear variation of the initial reaction rate with CO pressure. The following rate equation fits satisfactorily the experimental data of Fig. 10 (the error between the predicted and the observed rates is less than 4%)

$$r_0 = k_1 P_{\text{CO}} (1 + k_2 P_{\text{CO}} + k_3 P_{\text{CO}}^2)^{-1} \quad (10)$$

where P_{CO} is the partial pressure of CO (MPa); k₁, k₂ and k₃ are constants, respectively units in

kmol m⁻³ s⁻¹ MPa⁻¹, MPa⁻¹, MPa⁻². In Table 1 are reported the calculated values of k₁, k₂ and k₃ at four different temperatures. The equation constants k₁, k₂ and k₃ have been evaluated (Table 1) at different temperatures, by fitting the experimental data in Fig. 10.

2.3. Proposed mechanism

The Pd-catalyzed hydroesterification of olefins has been proposed to proceed through either a Pd-hydride

Table 1
Values of k₁, k₂ and k₃ at different temperatures

T (K)	k ₁ × 10 ⁴ (kmol m ⁻³ s ⁻¹ MPa ⁻¹)	k ₂ × 10 ² (MPa ⁻²)	k ₃ × 10 ¹ (MPa ⁻²)
373	5.07	1.59	2.61
368	3.53	1.33	2.39
363	2.29	0.76	2.05
353	1.20	0.29	1.75

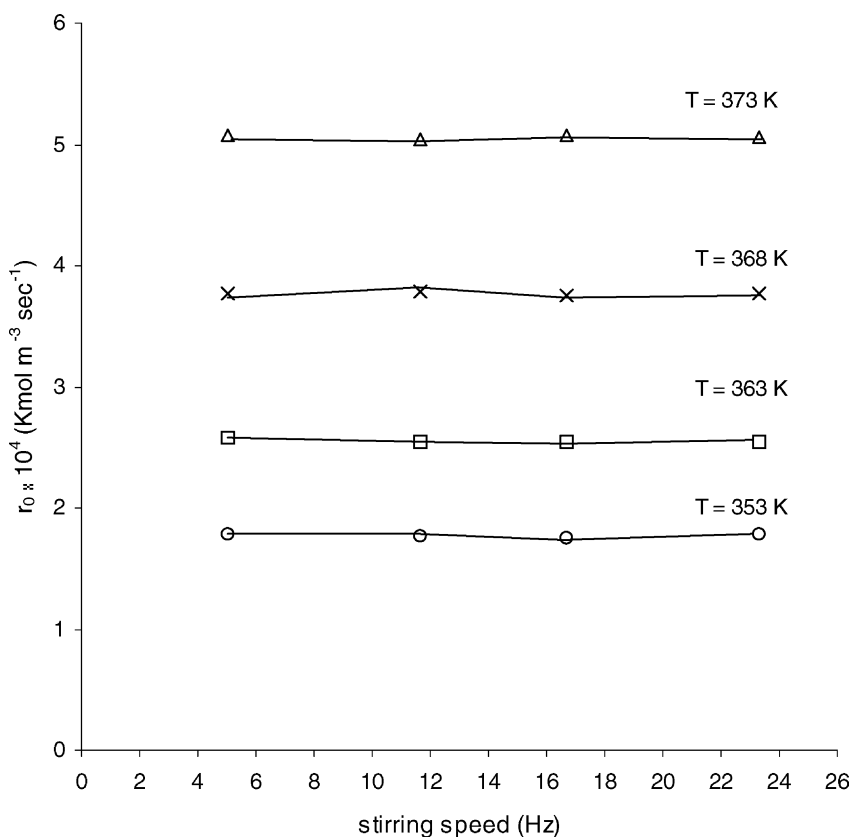
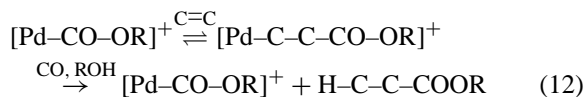
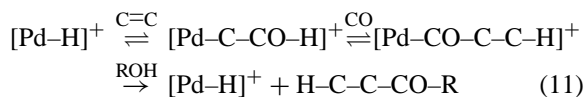


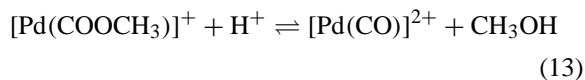
Fig. 6. Effect of stirring speed variation on the initial reaction rate. Run conditions—I: Pd(PPh₃)₂(TsO)₂ = 0.1 mmol; I/PPh₃/TsO = 1/6/8; CH₃OH = 40 ml; cyclohexene = 10 ml; H₂O = 800 ppm; T = 373 K; P_{CO} = 2.0 MPa.

or a Pd-carboalkoxy intermediate [19,21–30]

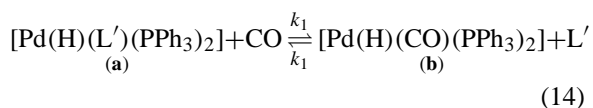


The Pd-hydride species forms from the precursor and a hydrogen source, while the Pd-carboalkoxy species forms by interaction of a Pd-carbonyl species with the alkanol. In the present case, on the basis of the promoting effect of a hydride source such as TsOH and water, reported in the previous discussion,

it is likely that the Pd-hydride pathway plays a major role. The Pd-carboalkoxy pathway may also be operative, however not in the case when an excess of TsOH is used because the formation of the carboalkoxy species is not favored



According to the kinetic results (Eq. (10)), we propose the following mechanism (where L' = PPh₃, H₂O, CH₃OH, TsO⁻)



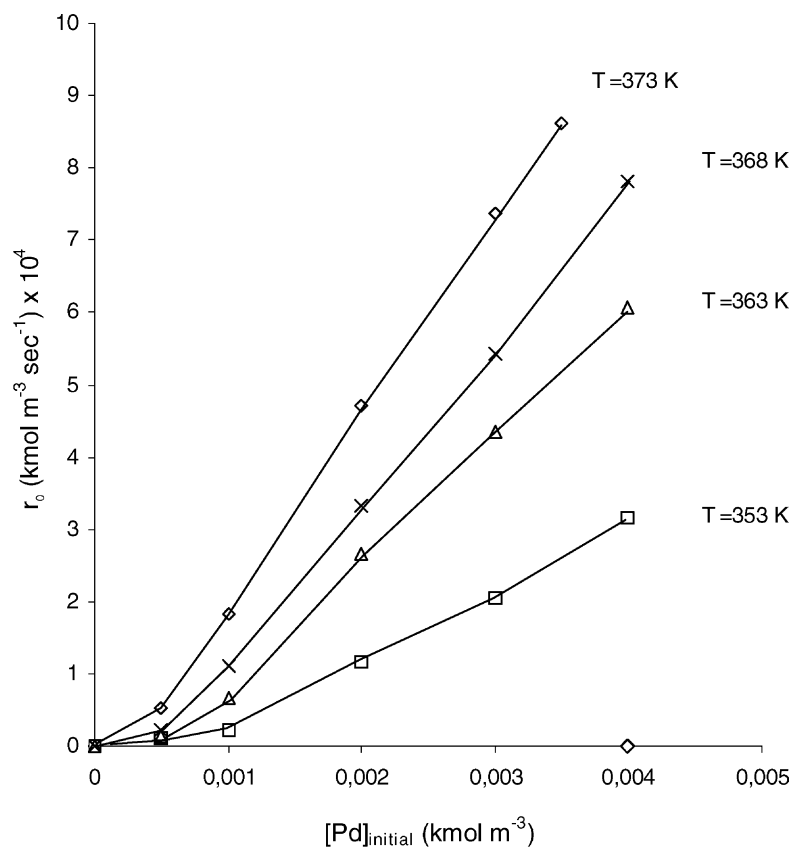
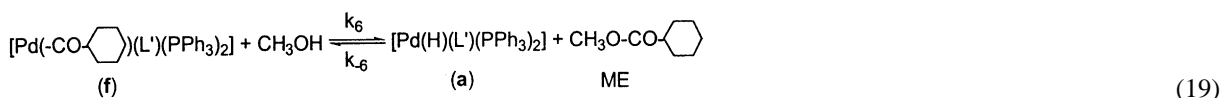
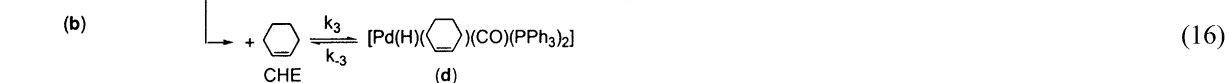


Fig. 7. Effect of catalyst loading on the initial reaction rate at different temperatures. Run conditions: Pd/PPh₃/TsO = 1/8/10 molar ratio; CH₃OH = 40 ml; cyclohexene = 10 ml; H₂O = 800 ppm; P_{CO} = 2.0 MPa.



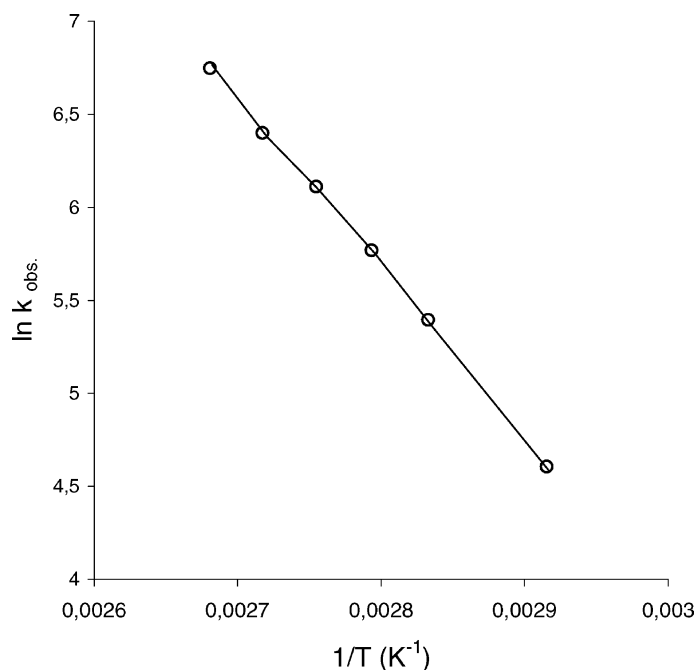


Fig. 8. Arrhenius plot. Run conditions—I: $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2 = 0.1 \text{ mmol}$; $\text{I}/\text{PPh}_3/\text{TsO} = 1/6/8$ molar ratio; $\text{CH}_3\text{OH} = 40 \text{ ml}$; cyclohexene = 10 ml; $\text{H}_2\text{O} = 800 \text{ ppm}$; $P_{\text{CO}} = 2.0 \text{ MPa}$; reaction time = 1 h.

This scheme is over-simplified since only the species (four or five coordinated) that appear in the scheme are considered to be involved in the catalytic cycle, whilst it is likely that, for example, hydride (**a**) is at equilibrium with several other hydrides (depending on L in Eq. (2)). The reactions that afford intermediate (**a**) are assumed to proceed rapidly. The Pd-hydride (**a**) reacts with carbon monoxide to form the intermediate (**b**) (reaction (14)). Carbon monoxide and the olefin compete for coordination to intermediate (**b**) (reactions (15) and (16)). Only the species (**d**) continues the catalytic cycle, whilst the five-coordinated dicarbonyl (**c**) must dissociate a CO molecule to give back (**b**) in order to continue the catalytic cycle. The penta-coordinate Pd-hydride species (**d**) gives the tetra-coordinate Pd-cyclohexyl species (**e**) by insertion of the olefin into the Pd-hydride bond (reaction (17)). The intermediate (**e**) is converted into Pd-carbonylcyclohexyl intermediate (**f**) by the insertion of carbon monoxide (reaction (18)). Complex (**f**) reacts with methanol to give methyl cyclohexanecarboxylate (ME) and the

Pd-hydride complex (**a**) (reaction (19)), which re-starts the cycle.

Considering reaction (19) as slow step and reactions (14)–(18) fast, the rate of formation of the ester is

$$r = k_6[\mathbf{f}][\text{CH}_3\text{OH}] - k_{-6}[\mathbf{a}][\text{ME}] \quad (20)$$

To consider the attack of CH_3OH to the Pd-acyl intermediate (**f**) as slow step is reasonable since, during the course of hydroesterification of propylene and 1-hexene catalyzed by the precursor $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, it has been possible to isolate the active intermediate acyl complexes $\text{Pd}(\text{PPh}_3)_2(\text{COR})\text{Cl}$ ($\text{R} = n\text{-propyl}$, $n\text{-hexyl}$) [29,30]. Their isolation suggests that all the steps that lead to their formation are fast compare to the subsequent step that lead to the product, the ester. The fact that the TOF depends on the concentration of MeOH and on the bulkiness of the alkanol (see Fig. 4) also supports the suggestion that the slow step is the nucleophilic attack of the alkanol to the acyl intermediate (**f**).

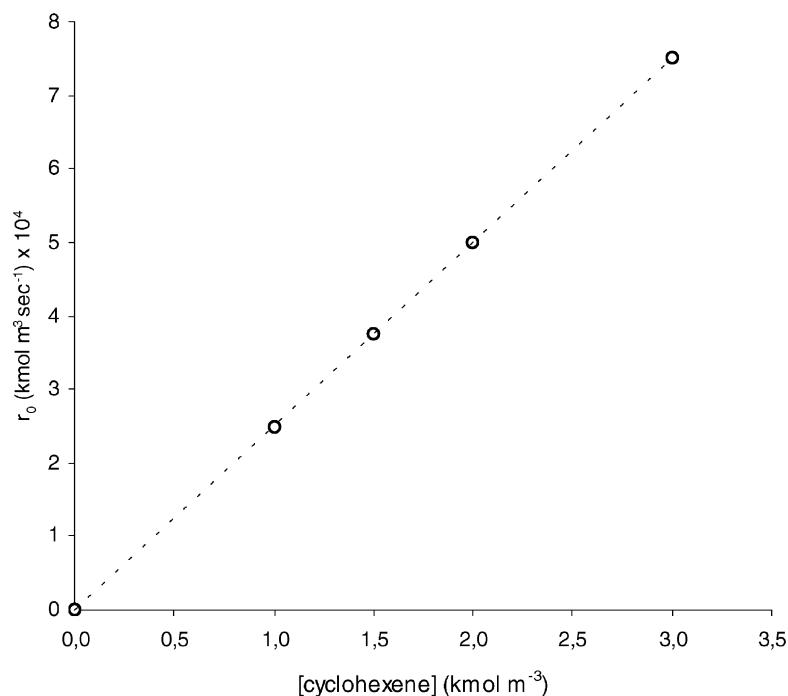


Fig. 9. Effect of cyclohexene concentration on the initial rate. Run conditions—I: $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2 = 0.1 \text{ mmol}$; $\text{I}/\text{PPh}_3/\text{TsO} = 1/6/8$ molar ratio; $\text{CH}_3\text{OH} + \text{cyclohexene} = 50 \text{ ml}$; $\text{H}_2\text{O} = 800 \text{ ppm}$; $T = 373 \text{ K}$; $P_{\text{CO}} = 2.0 \text{ MPa}$.

If reaction (19) is the slow step, all the others are at equilibrium. Thus,

$$K_1 = \frac{[\mathbf{b}][\text{L}']}{[\mathbf{a}][\text{CO}]}, \quad K_2 = \frac{[\mathbf{c}]}{[\mathbf{b}][\text{CO}]}, \quad K_3 = \frac{[\mathbf{d}]}{[\mathbf{b}][\text{CHE}]},$$

$$K_4 = \frac{[\mathbf{e}]}{[\mathbf{d}]}, \quad K_5 = \frac{[\mathbf{f}]}{[\mathbf{e}][\text{L}']} \quad (21)$$

Considering that at the initial time $[\text{ME}] = 0$, the initial reaction rate r_0 can be expressed by Eq. (24) (where H is the Henry constant for CO, $H_{373\text{K}} = 4.5$, $H_{363\text{K}} = 4.6$, $H_{353\text{K}} = 4.8 \text{ MPa m}^3 \text{ kmol}^{-1}$ for a MeOH/CHE mixture in the ratio 4/1 (v/v); $[\text{CHE}] = 2.0 \text{ kmol m}^{-3}$), which is in agreement with Eq. (10).

$$r_0 = \frac{k_6 K_1 K_3 K_4 K_5 [\text{Pd}_{\text{tot}}][\text{CH}_3\text{OH}][\text{CHE}]H^{-1}P_{\text{CO}}}{1 + (K_1[\text{L}']^{-1} + K_1 K_3[\text{L}']^{-1}[\text{CHE}] + K_1 K_3 K_4[\text{L}']^{-1}[\text{CHE}] + K_1 K_3 K_4 K_5[\text{CHE}]H^{-1}P_{\text{CO}} + K_1 K_2[\text{L}']^{-1}H^{-2}P_{\text{CO}}^2)} \quad (24)$$

Taking into account also the mass balance,

$$[\text{Pd}_{\text{tot}}] = [\mathbf{a}] + [\mathbf{b}] + [\mathbf{c}] + [\mathbf{d}] + [\mathbf{e}] + [\mathbf{f}] \quad (22)$$

the rate Eq. (19) can be re-written as

$$r = \frac{k_6 K_1 K_3 K_4 K_5 [\text{Pd}_{\text{tot}}][\text{CH}_3\text{OH}][\text{CHE}][\text{CO}](1 - [\text{ME}])}{K_1 K_3 K_4 K_5 K_6 [\text{L}'] [\text{CH}_3\text{OH}][\text{CHE}][\text{CO}]} \quad (23)$$

$$1 + (K_1[\text{L}']^{-1} + K_1 K_3[\text{L}']^{-1}[\text{CHE}] + K_1 K_3 K_4[\text{L}']^{-1}[\text{CHE}] + K_1 K_3 K_4 K_5[\text{CHE}][\text{CO}] + K_1 K_2[\text{L}']^{-1}[\text{CO}]^2)$$

Under the conditions reported in Fig. 10, the term in parenthesis at denominator of Eq. (24) is negligible compared to the others two, thus Eq. (24) is in agreement also with the finding that the reaction rate

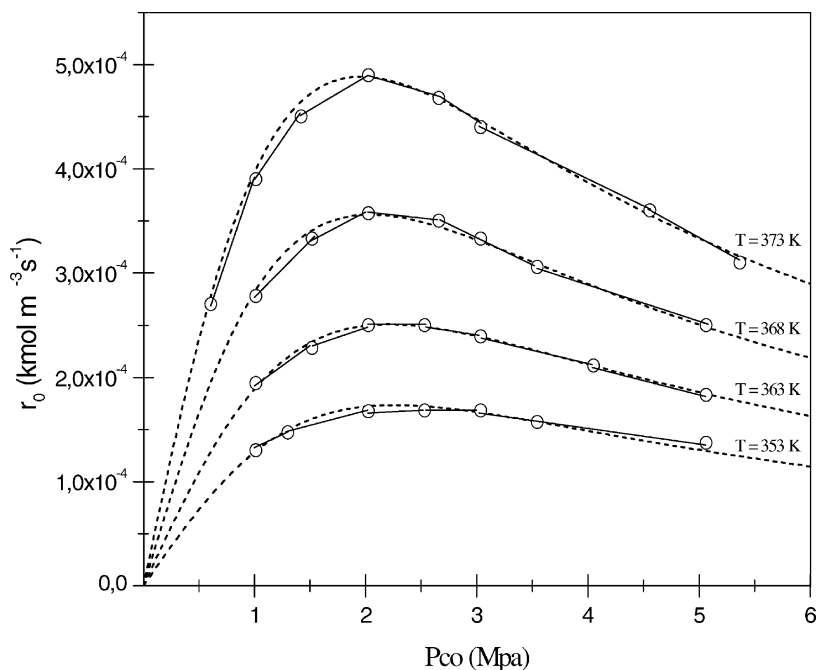


Fig. 10. Effect of CO pressure on initial rate at different temperatures. (○): Experimental values; (dotted curves): predicted by Eq. (10). Run conditions—I: Pd(PPh₃)₂(TsO)₂ = 0.1 mmol; I/PPh₃/TsO = 1/6/8 molar ratio; CH₃OH = 40 ml; cyclohexene = 10 ml; H₂O = 800 ppm.

increases linearly with the concentration of cyclohexene (see Fig. 9).

The data of Fig. 10 have been obtained at [CHE] = 2.0 kmol m⁻³ = constant (note that in Eq. (24) the first member is the initial rate r_0). Thus, by comparing Eq. (10) with Eq. (24) and since [L'] is constant

$$\begin{aligned} k_1 &= k_6 K_1 K_3 K_4 K_5 [\text{Pd}_{\text{tot}}][\text{CH}_3\text{OH}][\text{CHE}]H^{-1} \\ k_2 &= (K_1[\text{L}']^{-1} + K_1 K_3 [\text{L}']^{-1} [\text{CHE}] \\ &\quad + K_1 K_3 K_4 [\text{L}']^{-1} [\text{CHE}] \\ &\quad + K_1 K_3 K_4 K_5 [\text{CHE}])H^{-1} \\ k_3 &= K_1 k_2 [\text{L}']^{-1} H^{-2} \end{aligned} \quad (25)$$

By plotting $\ln k_1$, $\ln k_2$ and $\ln k_3$ versus $1/T$ (Fig. 11) it is possible to calculate energy activations $E_1 = 19.0$ kcal/mol, $E_2 = 23.6$ kcal/mol and $E_3 = 5.5$ kcal/mol. The k_2 is the sum of four terms, in spite of this the plot $\ln k_2$ versus $1/T$ fits well with a straight line, its slope gives $E_2 = 23.6$ kcal/mol (probably one of the four terms prevails).

3. Experimental section

3.1. Materials

Carbon monoxide (purity higher than 99%) was supplied by SIAD Spa (Italy). Methanol was purchased from Baker (purity higher than 99.5%, 0.01% of water) and Pd(OAc)₂ (98%), triphenylphosphine, *p*-toluenesulfonic acid, cyclohexene from Aldrich. The Pd(PPh₃)₂(TsO)₂ complex was prepared according to the method reported in the literature [15].

3.2. Experimental setup

All the experiments were carried out in a stainless steel autoclave of ca. 250 cm³ of capacity, provided with a self-aspirating turbine. The reagents were added in a ca. 150 ml Pyrex glass beaker placed into the autoclave in order to prevent contamination by metallic species because of corrosion of the internal surface of the autoclave.

Carbon monoxide was supplied from a gas reservoir (260 cm³) connected to the autoclave through a

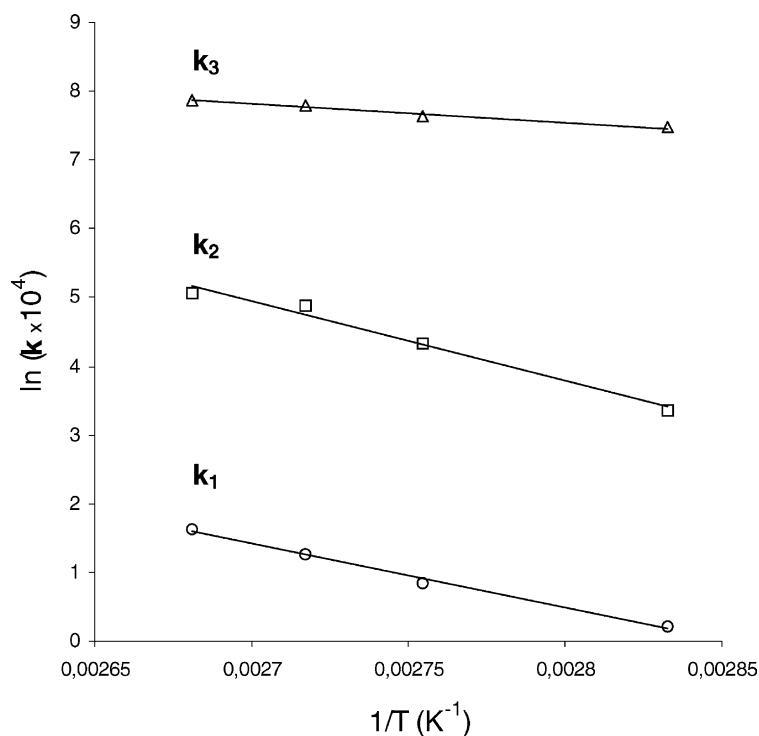


Fig. 11. $\ln k_1$, $\ln k_2$ and $\ln k_3$ vs. $1/T$.

constant pressure regulator. The autoclave was provided with a temperature control ($\pm 0.5^\circ\text{C}$).

3.3. Experimental procedure

Typical reaction conditions were: $T = 373\text{ K}$, $P = 2.0\text{ MPa}$, \mathbf{I} : $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2 = 0.1\text{ mmol}$, reaction time = 1 h. PPh_3 and TsOH was also added to the reaction mixture so that total molar ratio was $\mathbf{I}/\text{PPh}_3/\text{TsOH} = 1/6/8$.

In a typical experiment, known quantities of \mathbf{I} , PPh_3 and TsOH along with 40 ml of methanol and 10 ml of cyclohexene were charged into the glass bottle placed in the autoclave. Then, the autoclave was washed and pressurized ($P < 5\text{ atm}$) at room temperature with carbon monoxide. The autoclave was then heated to the working temperature while stirring. At this temperature the pressure in the autoclave was adjusted at 2.0 MPa and maintained constant through the pressure regulator connected to the gas reservoir. The gas consumption was measured by monitoring the pres-

sure drop of the reservoir. After 1 h, the autoclave was cooled to room temperature and vented.

Products were characterized by GC analysis on a HP 5890 series II apparatus equipped with a $30\text{ m} \times 0.53\text{ mm} \times 0.1\text{ }\mu\text{m}$ HP 5 column. Initial rate was calculated by plotting the pressure drop of CO in the gas reservoir versus time.

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