Catalysis Letters 47 (1997) 43–46

Catalytic conversions in water. Part 6. A novel biphasic hydrocarboxylation of olefins catalyzed by palladium TPPTS complexes (TPPTS=P(C_6H_4-*m*-$SO_3Na)_3$) *

Georgios Papadogianakis, Göran Verspui, Leendert Maat and Roger A. Sheldon ‡

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Received 10 April 1997; accepted 3 June 1997

Dedicated to Professor F. Asinger on the occasion of his 90th birthday

Exceptionally high catalytic activities (TOF> 2500 h^{-1}) have been achieved in the biphasic hydrocarboxylation of propene catalysed by water-soluble Pd/TPPTS complexes. The activity was even higher than that exhibited by organic-soluble Pd/PPh_3 systems. This contrasts with the general perception that biphasic catalysis normally exhibits lower rates compared to analogous reactions in organic media. The hydrocarboxylation of 4-isobutylstyrene to ibuprofen and of styrene in a two-phase system is also reported.

Keywords: two-phase catalysis, hydrocarboxylation, olefin, palladium, TPPTS

1. Introduction

There is growing interest in catalysis in aqueous media using transition metal TPPTS and related complexes because of its far reaching applications in industrial organic synthesis [1]. The use of aqueous media circumvents the need for organic solvents, such as chlorinated hydrocarbons, and facilitates recovery and recycling of the catalyst which provides substantial environmental benefits [1]. Recently, we reported [2] that the water-soluble Pd(TPPTS)$_3$ complex [3] catalyses the carbonylation of 1-(4-isobutylphenyl)ethanol (IBPE) to 2-(4-isobutyl-phenyl)propanoic acid (ibuprofen), a nonsteroidal antiinflammatory drug, under relatively mild and noncorrosive reaction conditions in an aqueous/organic two-phase system. We now report the first example of the hydrocarboxylation of olefins catalyzed by Pd(TPPTS)$_3$ in an aqueous/organic two-phase system. Moreover, the higher activity of Pd/TPPTS compared to Pd/PPh_3 [4], observed in the hydrocarboxylation of propene, is unusual. An intrinsic limitation of biphasic catalysis is generally the significantly lower rates compared to analogous reactions in organic media [5].

2. Results and discussion

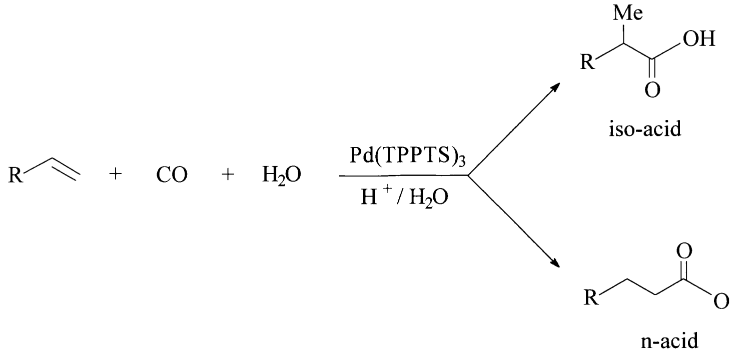
During our investigations of the carbonylation of IBPE to ibuprofen in organic media we observed that substantial amounts of 4-isobutylstyrene (IBS) were formed at short reaction times, especially at elevated temperatures. This suggested that IBS is probably an intermediate in this reaction and that the low catalytic activity of Pd/TPPTS (turnover frequency, TOF= 2.3 h^{-1}) observed in the biphasic carbonylation of IBPE [2] at 90°C was due to the low rate of formation of IBS under these conditions. A comparison of the biphasic carbonylation of IBPE and hydrocarboxylation of IBS (scheme 1; $R = 4\text{-}(CH_3)_2CHCH_2\text{-}C_6H_4\text{–}$) under the same conditions (Pd/TPPTS catalyst at 90°C in the presence of *p*-$CH_3C_6H_4SO_3H$, no organic solvent) confirmed that the latter reaction proceeds eight times faster than the former. We subsequently optimized the biphasic hydrocarboxylation of IBS by performing the reaction at lower temperatures in order to minimize competing polymerization of the IBS. In a typical experiment (table 1 , run 1), at 65°C and 50 bar CO pressure, in the presence of aqueous Pd/TPPTS and *p*-$CH_3C_6H_4SO_3H$ (no organic solvent), ibuprofen and its linear isomer were obtained in selectivities of 74% and 14%, respectively, at 62% IBS conversion. However, the activity remained low (TOF = 3 h^{-1}).

The assumption that the low rates observed in the biphasic hydrocarboxylation of IBS may be due to the very low water solubility of IBS led us to study styrene and propene, which are more water soluble. Indeed, the Pd/TPPTS-catalyzed hydrocarboxylation of styrene to a mixture of 2- and 3-phenylpropanoic acid (scheme 1; R = Ph–), was faster than that of IBS (runs 2 and 3 in table 1). At 65°C and a styrene/Pd molar ratio of 250 a TOF of 49 h^{-1} was observed. Interestingly, quantitative conversion of styrene to carboxylic acids was also observed (run 4) in the absence of added Brønsted acids at a styrene/Pd molar ratio of 50. However, we note that two equivalents of HCl per Pd are formed (scheme 2)

---

* For part 5 of this series see ref. [2].

‡ To whom correspondence should be addressed.



Scheme 1. $Pd(TPPTS)_3$-catalyzed hydrocarboxylation of IBS, styrene and propene. R = 4-$(CH_3)_2CHCH_2$-C_6H_4–; Ph–; CH_3–.

during the in situ generation of $Pd(TPPTS)_3$ from $PdCl_2$, TPPTS and CO in water [3c], which corresponds to a H^+/styrene molar ratio of 0.04. In contrast, the addition of external Brønsted acids was essential in the hydrocarboxylation of IBS or with styrene at higher styrene/Pd ratios ($\geqslant 250$), possibly because p-$CH_3C_6H_4SO_3H$ acts both as an acid and an amphiphilic reagent. The best result (90% selectivity to the branched isomer at 100% styrene conversion) was obtained with a TPPTS/Pd molar ratio of 4 at 140 bar CO pressure and 65°C (run 5).

We next turned our attention to the biphasic hydrocarboxylation of propene (scheme 1; R = CH_3–). Since propene is less reactive than styrene (propene was hydrocarboxylated under the conditions described in run 3 with a TOF of 34) and less susceptible to polymerization, reactions were carried out at higher temperatures (110–120°C). Under these conditions exceptionally high turnover frequencies were observed (see table 1). For example, with a propene/Pd molar ratio of 1000 and a p-$CH_3C_6H_4SO_3H$/propene molar ratio of 0.148, at 120°C and 50 bar CO, a TOF of 2507 h^{-1} was observed (run 9). The n/iso ratio of the carboxylic acid products was ca. 60/40. No reaction was observed in the absence of TPPTS and a lower activity resulted when no Brønsted acid was added (run 6). As expected, no reaction was observed when a base, such as sodium acetate or sodium hydroxide was added to neutralize the HCl formed in the catalyst generation. The activity of $Pd(TPPTS)_3$ was also strongly influenced by the nature of the anion of the added Brønsted acid. Acids of weakly coordinating anions, e.g. p-$CH_3C_6H_4SO_3H$ or CF_3CO_2H, were effective while with acids of strongly coordinating anions, e.g. HI, virtually no reaction was observed.

Table 1
Catalytic hydrocarboxylation of IBS (**1**), styrene (**2**) and propene (**3**)[a]

Run	Olefin	Olefin/Pd molar ratio	p-$CH_3C_6H_4SO_3H$ (mmol)	H^+/olefin molar ratio[b]	t (min)	T (°C)	Conv. (mol%)	Selectivity (mol%)		TOF[c] (h^{-1})
								iso	n	
1[d]	**1**	50	7	0.74	600	65	62	73.5	14.3[e]	3
2[d]	**2**	50	7	0.74	600	65	100	56.4	32.8[e]	5
3[d]	**2**	250	7	0.148	180	65	59	73.0	27.0	49
4[d]	**2**	50	0	0.04	600	65	100	71.2	28.8	5
5[d]	**2**	50	7	0.74	600	65	100	90.2	9.8	5
6[d,g]	**3**	1000	0	0.002	30	110	12	42.9	57.1	239
7[d,g]	**3**	1000	29.2	0.148	30	110	70	42.0	58.0	1390
8[d,g]	**3**	1000	59.6	0.3	30	110	64	42.5	57.5	1284
9[d,g]	**3**	1000	29.2	0.148	15	120	63	42.9	57.1	2507
10[f,g]	**3**	1000	29.2	0.148	30	110	12	43.1	56.9	246

[a] Reaction conditions: 0.2 mmol of $PdCl_2$ and TPPTS (TPPTS/Pd molar ratio= 4; except runs 1, 2 and 4, P/Pd= 8) were dissolved in 50 g of de-aerated distilled H_2O to give the complex $[PdCl(TPPTS)_3]^+$ within 25–30 min of complexation at room temperature (pH= 2.0–2.9), addition of deoxygenated distilled H_2O to give 141.9 g of aqueous reaction mixture, [Pd]= 150 ppm, Brønsted acid, amount of olefin without addition of organic solvents; P = 50 bar; except run 5, 140 bar.

[b] H^+ = added Brønsted acid and 0.4 mmol HCl formed during the in situ synthesis of $Pd(TPPTS)_3$ catalyst from $PdCl_2$, TPPTS and CO in H_2O [3c].

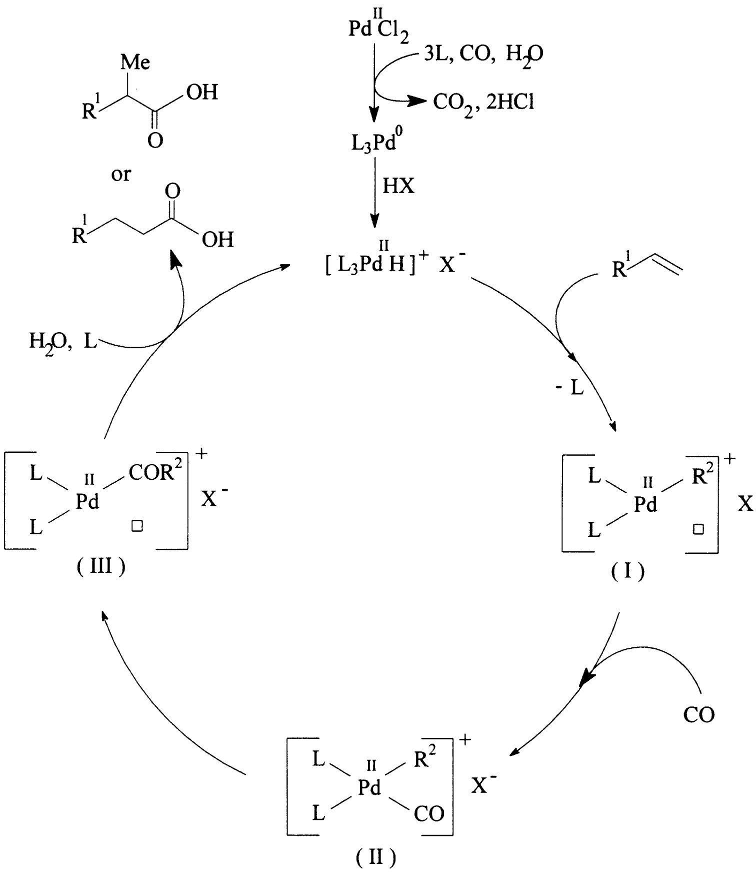
[c] Defined as mol of converted olefin per mol of palladium per hour.

[d] No metallic palladium formation.

[e] Formation of heavy ends, presumably polymers of olefin **1** or **2**.

[f] PPh_3 (0.8 mmol), 116.0 g of 1,4-dioxane and 18.7 g of H_2O; black precipitate, probably metallic palladium.

[g] One phase after the reaction.



L = TPPTS ; R^1= 4-$(CH_3)_2CHCH_2$-C_6H_4-, Ph-, CH_3-

Scheme 2. Proposed catalytic cycle in the $Pd(TPPTS)_3$-catalyzed hydrocarboxylation of olefins.

We subsequently compared our system with Pd/PPh_3 in aqueous dioxane. We found that Pd/TPPTS was significantly more active (TOF= 1390 h^{-1} vs. 246 h^{-1}). Furthermore, the $Pd(TPPTS)_3$ catalyst was stable whereas in the Pd/PPh_3-catalyzed reaction palladium black formation was observed indicating decomposition of the catalyst.

To explain the observed results we propose the catalytic cycle depicted in scheme 2. We previously showed that the $Pd(TPPTS)_3$ catalyst is generated in situ by complexation of $PdCl_2$ with TPPTS in H_2O and subjecting the formed $[PdCl(TPPTS)_3]^+$ to the appropriate CO pressure [3c]. By analogy with related palladium chemistry, we assume that oxidative addition of HX to L_3Pd^0 forms the cationic palladium TPPTS hydride $[L_3Pd^{II}H]^+$, which is the catalytically active species [6]. Dissociation of a TPPTS ligand is followed, successively, by olefin coordination, olefin insertion into the Pd–H bond to give intermediate I, CO coordination giving II, migratory insertion and nucleophilic attack of H_2O on the acyl intermediate III to give carboxylic acid and, after coordination of a TPPTS ligand, regenerate the initial hydride intermediate. *Markownikov* addition of Pd–H species to the olefin leads to the branched carboxylic acid and *anti-Markownikov* addition to the linear product. When X^- is a strongly coordinating anion, such as I^-, the free coordination site in I is occupied, inhibiting coordination of CO.

A possible explanation for the higher catalytic activity of Pd/TPPTS compared with Pd/PPh_3 is that the lower basicity of TPPTS facilitates nucleophilic attack of H_2O on the acyl intermediate III (scheme 2). Nucleophilic attack of ROH on organic soluble acyl palladium intermediates has been proposed to be the rate-limiting step in Pd-catalyzed carbonylations [7]. An alternative explanation is that the catalytically active cis-form of the TPPTS cationic Pd intermediate I is stabilized by intramolecular association of sulfonate groups of neighboring TPPTS ligands via hydrogen bonding in water [5a].

3. Conclusion

We have shown that Pd/TPPTS in a biphasic aqueous/organic system is more active than conventional

Pd/PPh_3 in organic solvents for the hydrocarboxylation of propene. The exceptionally high catalytic activities, coupled with the ease of recovery and recycling of the catalyst and the avoidance of organic solvents, have obvious economic and environmental benefits. Hence, we are currently investigating the scope of this synthetically useful system.

4. Experimental

$PdCl_2$ and TPPTS (purity: 99.3%; [8]) were dissolved in deoxygenated distilled H_2O to give the $[PdCl(TPPTS)_3]^+$ complex. The Brønsted acid was added and the resulting solution was diluted with deoxygenated distilled H_2O to give 141.9 g of aqueous solution containing 150 ppm of Pd. IBS or styrene was added and the mixture was charged into a Hastelloy C autoclave (300 ml) under an atmosphere of argon. After four pressurizing–depressurizing cycles with CO to remove the last traces of argon/air, the autoclave was pressurized and the contents were heated with mechanical stirring (645 rpm). In the hydrocarboxylation of propene a different procedure was used. The Hastelloy C autoclave was charged under an atmosphere of argon with the $[PdCl(TPPTS)_3]^+$ catalyst solution, Brønsted acid and deoxygenated distilled water to give 141.9 g of aqueous solution ([Pd]=150 ppm). After four pressurizing–depressurizing cycles with CO the autoclave was pressurized through a stainless-steel cylinder containing condensed propene (200 mmol) with CO and the contents were heated with mechanical stirring. After the reaction the autoclave was cooled to room temperature, slowly depressurized and the reaction mixture removed. The hydrocarboxylation mixture of IBS and styrene was extracted with ether after addition of octanoic acid as an internal standard. The ether layer was separated, dried and after evaporation and addition of methanol the hydrocarboxylation mixture of IBS was analyzed by HPLC (Novapak C_{18}, 25°C, mobile phase: CH_3OH/H_2O (70/30) containing 0.1 M buffer of CH_3COOH/CH_3COONa, pH= 4.7, flow= 1 ml/min) and the hydrocarboxylation products of styrene by ^1H NMR (300.20 MHz, 25°C, $CDCl_3$). The hydrocarboxylation products of propene were directly analysed by ^1H NMR (300.20 MHz, 25°C, D_2O) after addition of 2-hydroxyisobutanoic acid as standard.

Acknowledgement

Financial support of this research in part by the Hoechst Celanese Corporation, Dutch National Innovation Oriented Program on Catalysis (IOP-c) and the Foundation for Chemical Research in The Netherlands (SON) is gratefully acknowledged.

References

[1] (a) F. Joó and A. Kathó, J. Mol. Catal. A 116 (1997) 3;
(b) G. Papadogianakis and R.A. Sheldon, New J. Chem. 20 (1996) 175.

[2] G. Papadogianakis, L. Maat and R.A. Sheldon, J. Chem. Technol. Biotechnol. 68 (1997), in press.

[3] (a) G. Papadogianakis, L. Maat and R.A. Sheldon, Inorg. Synth. 32 (1997), in press;
(b) G. Papadogianakis, L. Maat and R.A. Sheldon, J. Chem. Soc. Chem. Commun. (1994) 2659;
(c) G. Papadogianakis, J.A. Peters, L. Maat and R.A. Sheldon, J. Chem. Soc. Chem. Commun. (1995) 1105;
(d) G. Papadogianakis, L. Maat and R.A. Sheldon, J. Mol. Catal. A 116 (1997) 179.

[4] (a) W.P. Shum and J.F. White, US 4612390 (1986) (Atlantic Richfield Co.); Chem. Abstr. 106 (1987) 35085r;
(b) E.N. Squire and F.J. Waller, US 4292437 (1981) (E.I. du Pont de Nemours and Co.); Chem. Abstr. 96 (1982) 6206a;
(c) G. Cavinato and L. Toniolo, J. Mol. Catal. 6 (1979) 111.

[5] (a) I.T. Horváth, R.V. Kastrup, A.A. Ostwald and E.J. Mozeleski, Catal. Lett. 2 (1989) 85;
(b) I.T. Horváth and F. Joó, in: *Aqueous Organometallic Chemistry and Catalysis*, Vol. 5, NATO ASI Ser., Ser. 3: High Technology, eds. I.T. Horváth and F. Joó (Kluwer, Dordrecht, 1995) p. 1.

[6] V.V. Grushin, Chem. Rev. 96 (1996) 2011, and references therein.

[7] D. Milstein, J. Chem. Soc. Chem. Commun. (1986) 817.

[8] R. Gärtner, B. Cornils, H. Springer and P. Lappe, DE 32 35 030 (1982) (Ruhrchemie AG); Chem. Abstr. 101 (1984) 55331t.