ELSEVIER

Reaction intermediates in the Pd/tppts-catalyzed aqueous phase hydrocarboxylation of olefins monitored by NMR spectroscopy (tppts = P(C$_6$H$_4$-m-SO$_3$Na)$_3$)$^{☆}$

Göran Verspui, Ilya I. Moiseev [1], Roger A. Sheldon *

Laboratory for Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, NL-2826 BL, Delft, The Netherlands

Abstract

The involvement of water-soluble Pd–hydride, Pd–alkyl and Pd–acyl complexes as intermediates in the catalytic cycle of the Pd-catalyzed aqueous phase hydrocarboxylation of olefins was demonstrated. Kinetic investigations have shown that the conversion of a Pd–acyl to a Pd–hydride complex is a rate-determining, pseudo first-order reaction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aqueous-phase catalysis; Palladium; tppts; Hydrocarboxylation

1. Introduction

Organometallic catalysis in aqueous–organic two-phase systems combines the advantages of selective conversions under mild reaction conditions with efficient catalyst separation from the product phase and the use of water as a safe and environmentally friendly solvent. The increasing demand for environmentally benign processes has spawned considerable interest in such systems [1].

We, and others, previously reported that the Pd/tppts-catalyzed hydrocarboxylation of olefins [2], as well as the alternating copolymerization of CO and ethene [3], proceeds rapidly in neat water. Although there was no direct evidence for their existence, the involvement of Pd–hydride, Pd–alkyl and Pd–acyl complexes in the hydrocarboxylation reaction was proposed.
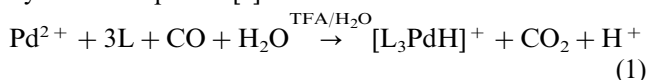
By following the course of the hydrocarboxylation of ethene with ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy, we have now successfully characterized all three types of

water-soluble Pd complexes in an aqueous solution (see Scheme 1, [4]).

2. Results and discussion

2.1. Preparation and characterization of [Pd(H)(tppts)$_3$]$^+$

When a solution of Pd(OAc)$_2$ and tppts (1×10^{-2} and 4×10^{-2} M) in 60% (v/v) aqueous trifluoroacetic acid (TFA) was subjected to a CO atmosphere, the cationic hydride [Pd(H)(tppts)$_3$]$^+$ (**1**) was formed quantitatively in 2.5 h. The formation of **1** is considered to proceed via reduction of a Pd(II) complex with CO and H$_2$O to [Pd(tppts)$_3$] (Eq. (1)) [5] and subsequent protonation by TFA (Eq. (2)). At room temperature (r.t.), under an inert atmosphere, **1** is stable for at least 3 days. However, when a coordinating anion is added (aqueous NaCl) the hydride complex decomposed instantaneously, with concomitant formation of gas bubbles (presumably H$_2$). This result is consistent with the generally higher stability of cationic versus neutral Pd-hydride complexes [6].

$$Pd^{2+} + 3L + CO + H_2O \xrightarrow{TFA/H_2O} [L_3PdH]^+ + CO_2 + H^+ \quad (1)$$

0022-328X/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S 0 0 2 2 - 3 2 8 X (9 9) 0 0 2 6 5 - X

$$Pd(tppts)_3 + HX \rightarrow [PdH(tppts)_3]^+ X^- \qquad (2)$$

At 25°C, broad adsorptions are observed in the ^{1}H- and ^{31}P-NMR spectra, indicating facile ligand exchange between **1** and the 1 equivalent of non-coordinated tppts. The resonances sharpened up to a doublet of triplets at −6.55 ppm ($^2J_{PH} = 174$ Hz, *trans*; $^2J_{PH} = 15$ Hz, *cis*) in the ^{1}H-NMR and a doublet and a triplet ($^2J_{PP} = 29$ Hz) in the ^{31}P-NMR spectrum when the sample was cooled to 0°C. Selective coupling with the hydride signal resulted in a doubled signal for both *cis*- and *trans*-phosphines in the ^{31}P-NMR spectrum (dt, 1P, $^2J_{HP} = 168$ Hz, *trans*; dd, 2P, $^2J_{HP} = 15$ Hz, *cis*), consistent with the presence of a hydride and three phosphines in a square planar structure.

These NMR-characteristics are similar to those observed for [PdH(PPh$_3$)$_3$]$^+$ [7]. In the presence of CO this compound transforms into the dinuclear [L$_2$Pd(μ-H)(μ-CO)PdL$_2$]$^+$. In contrast, during the preparation of **1** in a CO atmosphere, we did not observe the formation of any dinuclear compound.

2.2. Reaction of [Pd(H)(tppts)$_3$]$^+$ with ethene and CO

The reaction of **1** with ethene (1 atm, −20°C) gave two new compounds, **2a** and **2b** (46 and 51%, respectively). Upon addition of an extra amount of tppts (10 equivalents), the equilibrium shifted to **2a**. From the ^{1}H- and ^{31}P-NMR spectra we conclude that **2a** is a square planar complex with three phosphines and one ethyl ligand in the coordination sphere, [Pd(Et)(tppts)$_3$]$^+$. Compound **2b** was identified as *trans*-[Pd(Et)(tppts)$_2$]$^+$ by comparing the spectra with those of *trans*-[[Pd(Et)(PPh$_3$)$_2$]$^+$ [7].

The coordination of a third phosphine at the *trans*-position in **2a** has not been observed for *trans*-[Pd(Et)(PPh$_3$)$_2$]$^+$, suggesting a stronger Pd–P bond in the Pd/tppts complexes which might be attributed to a stronger back donation as a result of a larger π-acidity of tppts compared to PPh$_3$. This also might explain the absence of a dinuclear complex when **1** is treated with CO (vide supra). The stronger coordination ability of tppts in comparison with PPh$_3$ has also been observed in [Rh(H)(CO)(tppts)$_3$] [8].

The sample containing both Pd–alkyl complexes, **2a** and **2b**, (and 3% of **1**) reacted readily with CO (1 atm, −20°C) to afford *trans*-[Pd(COEt)(tppts)$_2$]$^+$ (**3**). When a mixture of ethene and CO is applied at r.t., **3** is obtained from **1** quantitatively. Addition of 10 equivalents of tppts to complex **3** did not result in the coordination of a third phosphine to the metal center. From these observations we can deduce that the *trans*-influence in these Pd/tppts complexes is increased in the order of hydride < ethyl < propionyl. It is still unclear if the coordination sites *trans* to the Pd–alkyl bond in **2b** and the Pd–acyl bond in **3** remain vacant or are being occupied by a solvent molecule or an anion. The ethene and CO insertion
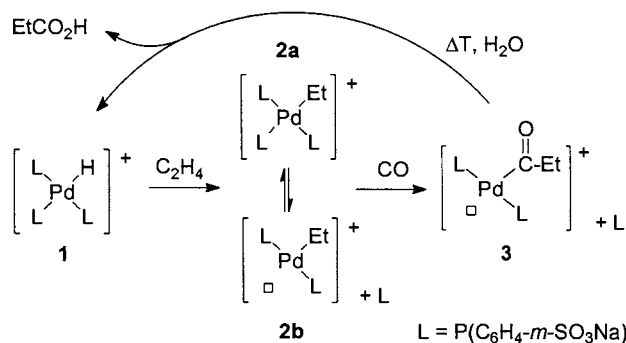
Scheme 1. The stepwise hydrocarboxylation of ethene.

reactions are assumed to proceed via an associative mechanism since no isomers of **2b** and **3** with *cis* coordination were observed.

The Pd–acyl complex is stable at r.t. for a few hours, but undergoes hydrolysis at elevated temperatures to form **1** and propanoic acid (detected by GC) quantitatively. Complex **3***, which is obtained from the reaction of **1** with ethene and ^{13}CO, gives a slightly broadened signal at 235.0 ppm in the ^{13}C-NMR spectrum which is assigned to Pd-^{13}COEt. After the hydrolysis of the Pd–acyl bond, this signal disappeared and a new adsorption was observed at 181.8 ppm (Et^{13}COOH). The hydrolysis may proceed via an associative coordination of a hydroxy ligand and a subsequent reductive elimination of the product, or more likely under acidic conditions, via a nucleophilic attack of a water molecule on the metal-bonded carbon in **3**.

2.3. Kinetic investigations

Whereas ethene and CO are readily inserted at −20°C in a Pd–hydride and a Pd–ethyl bond, respectively, the hydrolysis of the Pd–acyl bond proceeds at elevated temperatures. Obviously this latter reaction is the rate-determining step in the catalytic cycle. The conversion of **3** into **1** was found to exhibit pseudo first-order kinetics, the rate being dependent on the amount of water in the solution. At 50°C, reaction rate constants of 7.2×10^{-3}, 4.2×10^{-3} and 3.1×10^{-3} min^{-1} were measured in 50, 60 and 70% TFA solutions, respectively (Fig. 1). The faster hydrolysis in mixtures with a higher water content is in agreement with the higher catalytic activity of this water-soluble catalyst compared to its organic counterpart, Pd/PPh$_3$, which is not soluble in neat water [2a].

2.4. Hydrocarboxylation in a bi-phasic system

Having identified the key intermediates in the mechanism of the hydrocarboxylation of olefins in the aqueous phase, we are now in a position to explain characteristic features of this system.
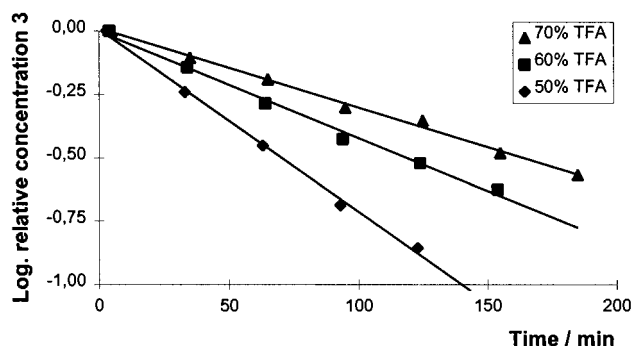
Fig. 1. The conversion of **3** into **1** at 50°C at different TFA concentrations.

As previously reported [2], the hydrocarboxylation reaction proceeds optimally in the presence of a Brønsted acid cocatalyst, derived from a weakly coordinating anion. Under these conditions Pd(tppts)$_3$ is formed by reduction of a [PdX(tppts)$_3$]$^+$ complex (X = anion) with CO and water [5]. In an acidic medium Pd(tppts)$_3$ is in equilibrium with the cationic hydride, compound **1** (Eq. (2)). A fast reaction with an olefin and CO takes place to afford **3**. In neutral or basic solutions, or in the presence of a strongly coordinating anion, no hydrocarboxylation takes place, owing to the absence of the initial hydride complex.

In the case of a sufficiently water-soluble olefin the conversion of **3** into **1** is rate determining, which implies that **3** is the most abundant complex. In the final stage of the reaction (after ca. 70% conversion) the catalyst starts to decompose. Furthermore, the catalyst has low stability when olefins which are sparingly soluble in the aqueous phase are used as substrates. Apparently, at very low olefin concentrations in the aqueous phase the insertion of the olefin into the Pd–hydride bond becomes rate determining. This leads to an increase of the concentration of **1**, which is in equilibrium with Pd(tppts)$_3$ and lower ligated Pd(0) complexes that, at higher reaction temperatures, are less stable than Pd(II) complexes such as **3**.

A better transport of poorly soluble olefins to the aqueous phase, which could possibly be achieved by adding surfactants or by making use of a supported aqueous phase system [9], would facilitate the coordination of the olefin, followed by a fast insertion in the hydride bond, and thus lead to a significantly more stable catalyst system for the hydrocarboxylation of these substrates.

3. Conclusions

In conclusion, we have identified the key intermediates of the hydrocarboxylation of olefins in the aqueous phase, catalyzed by water-soluble Pd/tppts complexes.

It is for the first time that a water-soluble Pd–hydride complex was observed. This Pd–hydride reacts readily with ethene and CO, to give a Pd–acyl complex. The hydrolysis of this Pd–acyl derivative is the rate determining step in the catalytic cycle.

Further investigations are aimed at additional characterization of complexes **2a**, **2b** and **3** by alternative techniques and revealing the identity of other possibly coordinated ligands (H$_2$O, anion or CO at higher pressure). The determination of the basicity of Pd(tppts)$_3$ and a study of the reactivity of **1** and related hydride complexes towards various substrates is in progress.

4. Experimental

All manipulations were done under an argon atmosphere using standard Schlenk techniques. Tppts was prepared according to a previously described method [10]. The synthesis of **1**, **2a**, **2b**, and **3** occurred in a stirred solution consisting of TFA, H$_2$O and D$_2$O (60, 20 and 20% (v/v), respectively) by bubbling through the reactant gasses (CO, ^{13}CO, ethene) at the chosen temperatures. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a 300 MHz Varian Inova spectrometer. ^{13}CO (99% labeled) is obtained from Cambridge Isotope Laboratories.

1: ^{1}H-NMR (300.2 MHz, D$_2$O, 0°C) δ (ppm): -6.55 (dt; $^{2}J_{PH} = 174$ Hz, *trans*; $^{2}J_{PH} = 15$ Hz, *cis*). ^{31}P-NMR (121.5 MHz, D$_2$O, 0°C) δ (ppm): 27.0 (d, $^{2}J_{PP} = 29$ Hz, 2P, *cis*), 20.3 (t, $^{2}J_{PP} = 30$ Hz, 1P, *trans*).

2a: ^{1}H-NMR (300.2 MHz, D$_2$O, 0°C) δ (ppm): 1.4 (broad, CH$_2$), -0.1 (broad, CH$_3$); ^{31}P-NMR (121.5 MHz, D$_2$O, 0°C) δ (ppm): 31.1 (d, $^{2}J_{PP} = 40$ Hz, 2P, *cis*), 15.2 (t, $^{2}J_{PP} = 39$ Hz, 1P, *trans*).

2b: ^{1}H-NMR (300.2 MHz, D$_2$O, 0°C) δ (ppm): 1.6 (broad, CH$_2$), 0.1 (broad, CH$_3$); ^{31}P-NMR (121.5 MHz, D$_2$O, 0°C) δ (ppm): 26.6 (s, 2P).

3: ^{1}H-NMR (300.2 MHz, D$_2$O, 0°C) δ (ppm): -0.1 (broad signal); ^{31}P-NMR (121.5 MHz, D$_2$O, 0°C) δ (ppm): 18.9 (s, 2P).

3* ^{13}C-NMR (75.5 MHz, D$_2$O, 0°C) δ (ppm): 235.1 (s, Pd-^{13}COEt); ^{31}P-NMR (121.5 MHz, D$_2$O, 0°C) δ (ppm): 18.9 (s, 2P).

Kinetics: **3** was prepared in situ in 60% (v/v) aqueous TFA (without D$_2$O) as described in the text. Diluting the mixture (3 × 7.5 ml) at 0°C with H$_2$O, TFA or not at all, gave 50, 70 and 60% TFA solutions, respectively. The three mixtures were heated in a preheated oilbath (50°C) simultaneously. Samples were taken at regular time intervals, inserted in a cooled (-20°C) NMR tube under argon and analyzed with ^{31}P-NMR (unlocked) immediately. The relative concentration of **3** was calculated from the intensity of the phosphine signals of **3** and **1**. (Apart from tppts and some tppts–oxide no other signals are observed.)

Acknowledgements

References

[1] See for recent reviews: (a) F. Joó, A. Kathó, J. Mol. Cat. A. 116 (1997) 3. (b) G. Papadogianakis, R.A. Sheldon, Catalysis, Vol. 13, Senior reporter, J.J. Spivey, Specialist Periodical Report, Royal Soc. Chem. (1997) 114–193. (c) B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, Wiley–VCH, Weinheim, Germany, 1998.

[2] (a) G. Papadogianakis, G. Verspui, L. Maat, R.A. Sheldon, Catal. Lett. 47 (1997) 43. (b) G. Verspui, G. Papadogianakis, R.A. Sheldon, Catal. Today 42 (1998) 449. (c) G. Verspui, J. Feiken, G. Papadogianakis, R.A Sheldon, J. Mol. Cat. A, accepted for publication. See also: (d) E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, G.N. Boiko, Russ. Chem. Bull 43 (1994) 360. (e) B. Xie, Y. Kou, Y.Ying, Fenzi Cuihua 11 (1997) 81. (f) S. Tilloy, E. Monflier, F. Bertoux, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 529.

[3] (a) G. Verspui, G. Papadogianakis, R.A. Sheldon, Chem. Commun. (1998) 401. See also: (b) C. Bianchini, A. Meli, F. Vizza, Patent appl. WO 98/22482 (1998) (Consiglio Internationale Delle Richerche).

[4] The neutral *trans*-[PdBr(Ph)(tppts)$_2$] and *trans*-[Pd(Br)(COPh)(tppts)$_2$] have been prepared previously: F. Monteil, P. Kalck, J. Organomet. Chem. 482 (1994) 45.

[5] (a) G. Papadogianakis, J.A. Peters, L. Maat, R.A. Sheldon, J. Chem. Soc. Chem. Commun. (1995) 1105. (b) G. Papadogianakis, R.A. Sheldon, Inorg. Synth. 32 (1998) 25.

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

[7] (a) V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Likholobov, Yu. I. Yermakov, J. Organomet. Chem. 289 (1985) 425. (b) V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Rogov, V.A. Likholobov, Yu. I. Yermakov, J. Mol. Cat. 52 (1989) 27.

[8] I.T. Horvath, R.V. Kastrup, A.A. Oswald, E.J. Mozeleski, Catal. Lett. 2 (1989) 85.

[9] K.T. Wan, M.E. Davis, Nature 370 (1994) 449.

[10] R. Gärtner, B. Cornils, H. Springer, P. Lappe, GE 3235030 A1 (1982) to Ruhrchemie AG, Chem. Abstr. 120, 55331t (1984).