

Highly selective transfer hydrogenation from formates to the C=C double bond of γ -keto- α, β -unsaturated carboxylic acids catalyzed by Pd/C

G. Cavinato ^a, L. Toniolo ^{b,*}

^a Department of Inorganic Chemistry, University of Padua, Via F. Marzolo, 4, 35131 Padova, Italy

^b Department of Chemistry, University of Venice, Calle Larga-S. Marta 2137, 30123 Venezia, Italy

Abstract

A Pd/C catalytic system is highly active and selective at 80–90°C in the hydrogen transfer reaction from sodium formate to the C=C double bond of PhCOCH=CHCOOH to yield the corresponding γ -keto acid PhCOCH₂CH₂COOH. When the substrate is allowed to react with a defect of formate salt and in the presence of a relatively large amount of catalyst, the yield, with respect to the formate, is practically quantitative. Since it is known that Pd/C catalyzes the decomposition of alkali formates, this result suggests that the hydrogen transfer to the substrate is much faster than the hydrogen evolution or that there are no catalytic sites able to absorb only the formate anions and water, and that the chemisorption of the substrate PhCOCH=CHCOOH is relatively fast and occurs in the first step of the catalytic cycle. Moreover, water, at low concentration, has a beneficial effect on the reaction rate, which passes through a maximum with changes in its concentration. The reaction rate increases also with the increasing concentration of formate and of substrate. These results suggest that water competes with the other reacting molecules for activation on only one type of active centers. It is also proposed that the catalytic cycle then proceeds through the adsorption of the hydrogen donors, followed by a hydride abstraction from absorbed formate. Hydrogen transfer from this hydride and water to the substrate yields the products and regenerates the catalyst, after the desorption steps.

Keywords: Hydrogen transfer; Formates; Keto acids; Palladium

1. Introduction

Very recently, we reported that, on attempting the carbonylation of the γ -keto- α, β -unsaturated acid PhCOCH=CHCOOH with the aim of synthesising a ketomalonic acid derivative, instead of the desired product, the reaction

yielded, in the presence of a PdCl₂(PPh₃)₂-HCl catalytic system, the corresponding γ -keto acid PhCOCH₂CH₂COOH, with concomitant evolution of CO₂. The reaction, which is quite selective, consists of a hydrogen transfer from H₂O-CO. It has been proposed that the catalytic cycle begins with (i) the activation of CO through coordination to the metal and proceeds with (ii) the nucleophilic attack of H₂O with formation of a palladium carboxylic acid, Pd-(COOH), and of proton; (iii) the metallo carboxylic acid

* Corresponding author.

intermediate undergoes decarboxylation with formation of a metal hydride, which is transferred to the α -C of the chloride $\text{PhCOCH}_2\text{CHClCOOH}$ which forms in situ through the addition of HCl to the C=C double bond of the starting substrate [1,2]. This reaction is closely related to the water gas shift reaction (WGSR) catalyzed by several transition metal complexes [3–6]. In this case the hydride which forms through steps i–iii is transferred to the proton which forms in step i with evolution of hydrogen. When the metal can give considerable electron density back donation to the CO ligand, then a stronger nucleophile such as OH^- may be necessary in order to give the intermediate that gives the hydride and CO_2 evolution. An alternative route to the WGSR begins with reaction of H_2O or OH^- with CO not coordinated to the metal, to yield formic acid or formate anion. Formic acid interacts with a metal with formation of a hydride–metallo–formate intermediate $\text{HM}(\text{O}_2\text{CH})$ which gives evolution of H_2 and CO_2 . The formate anion coordinates the metal with formation of a metallo–formate $\text{M}(\text{O}_2\text{CH})$, which evolves CO_2 and gives a metal–hydride which is transferred to a proton source to yield H_2 . It has been proposed also that metal formates and metalcarboxylic acid can interconvert via the intermediacy of a $\text{H-M}-(\eta^2\text{-CO}_2)$ species [6].

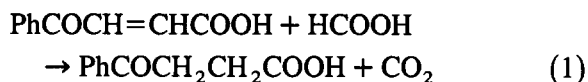
Thus, it appears that the H_2O –CO system can be equivalent to formic acid. The fact that formic acid or formates can give hydrogen transfer reactions to many types of organic substrates¹ with concomitant evolution of CO_2 stresses further this equivalence.

Recently, Alper et al. reported that the system formic acid/carbon monoxide can be used in the palladium catalyzed hydrocarboxylation of alkenes and alkynes to the corresponding

carboxylic acids [16–18]. These findings prompted us to undertake the study of the reactivity of HCOOH with $\text{PhCOCH}=\text{CHCOOH}$. In no case, in the presence of a Pd/C catalyst, the hydroxycarbonylation of the C=C double bond is observed. Rather, hydrogen transfer occurs selectively to the C=C double bond. Hereafter, we present the results of this investigation.

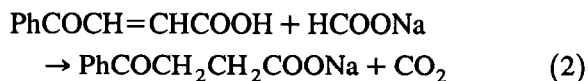
2. Results and discussion

The hydrogen transfer reaction from formic acid is schematized as follows:



Under typical reaction conditions in which a Pd/C catalytic system is normally employed, i.e. at 90–100°C, the yield is rather low. For example under the conditions reported in the experimental section, except using 0.5 ml of HCOOH in place of 0.680 g of sodium formate, the yield is < 5%.

The same catalyst is more active when employing sodium formate in place of formic acid. The reaction can be schematized as follows:



This result is in line with the observation made by several researchers who found that formic acid salts are more active hydrogen donors than formic acid itself both in catalytic [19] or non-catalytic reductions [20].

Figs. 1–3 show the influence of the temperature, of the reaction time and of the concentration of the catalyst on the yield. In 4 h, under the conditions reported in Fig. 1, the yield is practically quantitative.

Water, at low concentration, has a beneficial effect on the reaction rate. As a matter of fact, the yield passes through a maximum with changes in the amount of added water as shown in Fig. 4. Maximum yield is obtained when the water/formate molar ratio is ca. 2.8.

¹ Such as for example olefins and acetylenes [7,8], aromatic nitro compounds [9], aryl halides [10], aldehydes and ketones [11], α,β -unsaturated ketones or carboxylic acids [12,13], allylic esters [14] or to several other substrates [15].

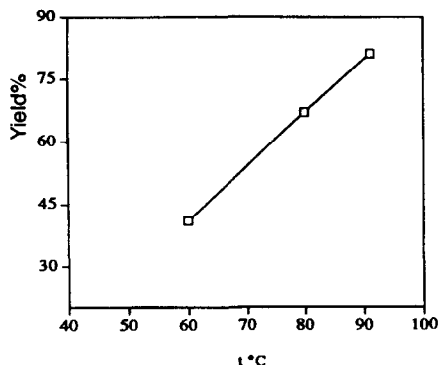


Fig. 1. Influence of the temperature. Run conditions: PhCOCH=CHCOOH 3.5 mmol; HCOONa 10 mmol; H₂O 55.5 mmol (1 ml); 10% Pd/C 8 mg; dioxane 8 ml (*V*_{tot} 10 ml); reaction time 2 h.

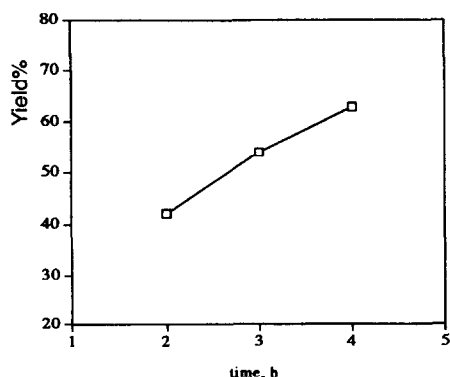


Fig. 2. Influence of the reaction time. Run conditions: PhCOCH=CHCOOH 5 mmol; HCOONa 10 mmol; H₂O 55.5 mmol (1 ml); 10% Pd/C 4 mg; dioxane 8 ml; temperature 90°C.

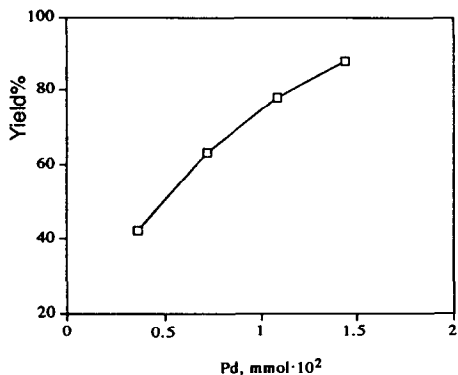


Fig. 3. Influence of the concentration of catalyst. Run conditions: PhCOCH=CHCOOH 5 mmol; HCOONa 10 mmol; H₂O 55.5 mmol (1 ml); dioxane 8 ml; temperature 90°C; reaction time 2 h.

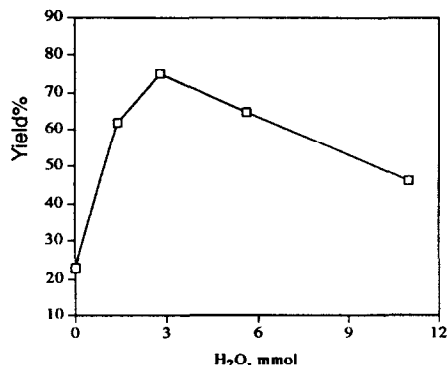
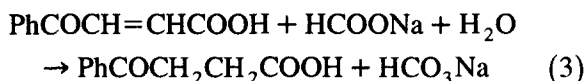


Fig. 4. Influence of the concentration of water. Run conditions: PhCOCH=CHCOOH 5 mmol; HCOONa 10 mmol; 10% Pd/C 8 mg; dioxane 7–9 ml; *V*_{tot} = 10.5 ml; temperature 90°C; reaction time 2 h.

A similar behaviour has been found for the reduction of nitroarenes [21] or of aryl halides [22], using potassium formate as hydrogen donor in the presence of a 10% Pd/C catalyst. In these cases the reactions are more sensitive to the amount of water than in the present case. Actually, it has been found that water is a reactant, as no reaction takes place when it is not present, and that the formate ion ends as bicarbonate, which eventually evolves carbon dioxide. Thus, in the presence of water, reaction (2) can be rewritten as:



The yield increases with increasing concentration of formate as shown in Fig. 5. Moreover, the reaction rate slightly increases with increas-

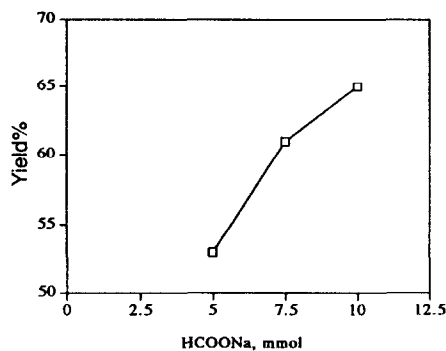


Fig. 5. Influence of the concentration of formate. Run conditions: PhCOCH=CHCOOH 5 mmol; H₂O = 55.5 mmol (1 ml); 10% Pd/C 8 mg; dioxane 8 ml; temperature 90°C; reaction time 2 h.

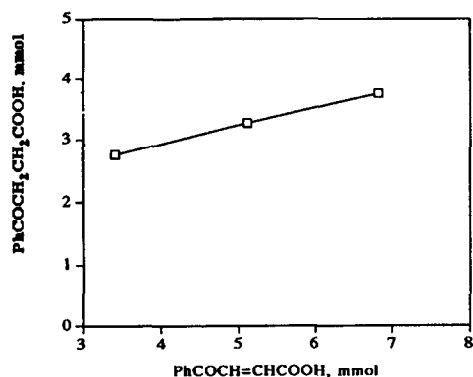


Fig. 6. Influence of the concentration of substrate. Run conditions: HCOONa 10 mmol; H₂O 55.5 mmol (1 ml); 10% Pd/C 8 mg; dioxane 8; temperature 90°C; reaction time 2 h.

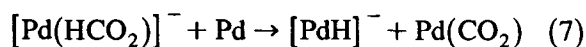
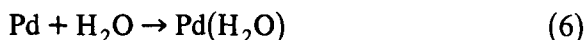
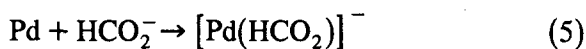
ing concentration of the substrate (Fig. 6). These results suggest that water competes with the other reacting molecules for coordination to the metal surface.

We have found also that when the substrate is allowed to react with a defect of formate salt, according to Eq. (3) (formate/substrate = 1/2), in the presence of a relatively large amount of catalyst (Pd/formate = 1/100), the yield, in 2 h, with respect to the formate is practically quantitative (for comparative purposes see the experimental section). Since aqueous alkali metal formates at 20–70°C, in the presence of a Pd/C catalyst, undergo decomposition into molecular hydrogen and bicarbonate [23], the result just reported suggests that the chemisorption of the substrate PhCOCH=CHCOOH is relatively fast and occurs in the first step of the catalytic cycle which is schematized by Eqs. (4–12), in which Pd represents an active site on the surface of the metal and S represents the substrate. Moreover, it suggests also that the hydrogen transfer to the substrate is much faster than the hydrogen evolution or that there are no catalytic sites able to absorb only the formate anions and water, which otherwise would yield molecular hydrogen:

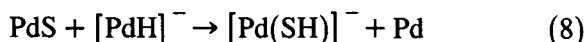


In addition, the trends shown in Figs. 4–6 suggest that the reactive molecules compete for

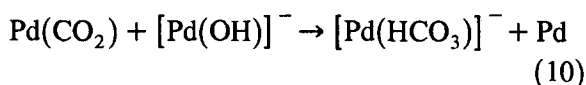
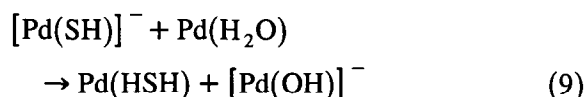
adsorption on only one type of active center. The catalytic cycle may then proceed:



Then the surface reaction between the adsorbed substrate and the hydride gives rise to the half-hydrogenated intermediate PdSH:



A proton transfer from coordinated H₂O to the intermediate Pd(SH) and interaction of CO₂ with OH⁻ yield the products and regenerate the catalyst, after the final desorption steps:

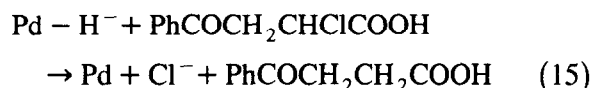
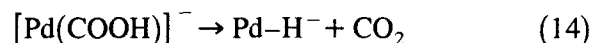
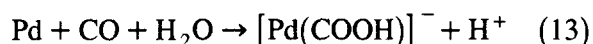


A similar mechanism has been proposed also for the transfer hydrogenolysis of aryl halides by formates promoted by a Pd/C catalyst [22].

In the absence of the substrate the formate anion decomposes with hydrogen evolution probably through absorption of formate anion, hydride abstraction, adsorption of water, evolution of hydrogen with formation of bicarbonate as proposed by Sasson et al. on the basis of kinetic evidence [23]. Steps (5–7) and (9) and (11).

As a final comment, it is worthwhile to outline the several important features that this chemistry has in common with the one relevant to the hydrogen transfer from CO/H₂O to PhCOCH=CHCOOH catalyzed by a Pd/C–HCl or a PdCl₂(PPh₃)₂–HCl system [1,2]. Also in these cases a Pd–H species plays a key role in the hydrogen transfer reaction. This takes place from the hydride to chloride PhCOCH₂CHClCOOH, which forms in situ

from the starting substrate and HCl. The hydride comes from the interaction of CO with H₂O on the metal center via a metal carboxylic acid:



Also in this case the reaction rate passes through a maximum with changes in the concentration of H₂O. Moreover, it should be underlined that HCl presents a beneficial effect on the catalytic activity, since it passes through a maximum with increasing concentration of the acid. It has been proposed that one important function of HCl is to increase the concentration of the hydride through oxidative addition to the metal:



Instead, in the present case, where formate is employed, the yield in PhCOCH₂CH₂COOH is quite unsatisfactory when Pd/C is used in the presence of HCl.

3. Experimental

3.1. Materials

Sodium formate was commercial grade. Dioxane was dried over sodium. PhCOCH=CHCOOH was prepared as reported in the literature [24]. 10% Pd/C was a JMC sample.

3.2. Product identification and analysis

Products were identified by NMR on a Bruker 200 AC spectrometer in CDCl₃ and by IR on a Perkin Elmer model 683 spectrometer. Yields were determined by HPLC, on a Perkin Elmer liquid chromatograph, model HPLC series 10, using a C18-SIL-X-10 column of 25 cm, sol-

vent: H₂O 70%, CH₃CN 30% containing 2% CH₃COOH.

3.3. General procedure for formate transfer hydrogenation catalyzed by Pd/C

In a typical experiment, to a 25 ml magnetically stirred two-necked flask, equipped with a reflux condenser and a thermometer, which was placed in a thermostat kept at 90°C, were added 8 ml of dioxane, an aqueous solution of sodium formate (1 ml of H₂O in which 680 mg of HCOONa, 10 mmol, were dissolved), 900 mg of PhCOCH=CHCOOH (5 mmol). When the solution was thermally equilibrated, 8 mg of 10 Pd/C was added. The system was stirred for 2 h, then was cooled to room temperature. The resulting system was analysed by HPLC. The yield in PhCOCH₂CH₂COOH was 65%.

Acknowledgements

The authors thank the Italian Ministry of Research (MURST) and the National Research Council (C.N.R. – ‘Progetto Finalizzato Chimica Fine II’) for sponsoring this research.

References

- [1] G. Cavinato, L. Ronchin and L. Toniolo, *J. Mol. Catal.*, 94 (1994) 173.
- [2] G. Cavinato and L. Toniolo, *J. Mol. Catal.*, in press.
- [3] P.C. Ford, *Acc. Chem. Res.*, 14 (1981) 31.
- [4] P. Escaffre, A. Thorez and Ph. Kalck, *J. Mol. Catal.*, 33 (1985) 87.
- [5] P.C. Ford and A. Rokicki, *Adv. Organomet. Chem.*, 28 (1988) 139.
- [6] R.M. Laine and E.J. Crawford, *J. Mol. Catal.*, 44 (1988) 357.
- [7] M.E. Volpin, V.P. Kukolev, V.O. Chernyshev and I.S. Kolomnikov, *Tetrahedron Lett.*, 26 (1894) 327.
- [8] T. Nishiguchi, H. Imai, Y. Hirose and K. Fukuzumi, *J. Catal.* 41 (1976) 249.
- [9] N.A. Cortese and R.F. Heck, *J. Org. Chem.*, 42 (1977) 3491.
- [10] P. Helquist, *Tetrahedron Lett.*, 22 (1978) 1913.
- [11] R. Bar, Y. Sasson and J. Blum, *J. Mol. Catal.*, 26 (1984) 327.
- [12] J. Blum, Y. Sasson and S. Iflah, *Tetrahedron Lett.*, 11 (1972) 1015.

- [13] H. Brunner and W. Leitner, *J. Organomet. Chem.*, 387 (1990) 209.
- [14] J. Tsuji and T. Yamakawa, *Tetrahedron Lett.*, (1979) 613.
- [15] S. Ram and R.E. Ehrenkanfer, *Synthesis*, (1985) 91.
- [16] B. El Ali and H. Alper, *J. Mol. Catal.*, 77 (1992) 7.
- [17] D. Zargarian and H. Alper, *Organometallics*, 12 (1993) 712.
- [18] B. El Ali, G. Vasapollo and H. Alper, *J. Org. Chem.*, 58 (1993) 4739.
- [19] J. Tsuji and T. Yamakawa, *Tetrahedron Lett.*, 613 (1979).
- [20] K. Nanjo, K. Suzuki and M. Sekiya, *Chem. Lett.*, 1169 (1976).
- [21] H. Wiener, J. Blum and Y. Sasson, *J. Org. Chem.*, 56 (1991) 4481.
- [22] H. Wiener, J. Blum and Y. Sasson, *J. Org. Chem.*, 56 (1991) 6145.
- [23] H. Wiener, Y. Sasson and J. Blum, *J. Mol. Catal.*, 35 (1986) 277.
- [24] O. Grummitt, E.I. Becker and C. Miesse, *Org. Synth. Collect.*, 3 (1955) 109.