

# Palladium catalysed hydroxycarbonylation of 1-phenylethanol in molten salt media

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Received 11 January 2006; received in revised form 15 February 2006; accepted 16 February 2006

## Abstract

Hydroxycarbonylation of 1-phenylethanol (PE) in molten salt media was studied systematically. Phosphine-free palladium catalysts are active in bromide-containing molten salts such as tetrabutylammonium bromide and [BMIM][Br]. The nature of the anion, CO pressure and the presence of PPh<sub>3</sub> affect the reaction rate and selectivity. A two-route reaction scheme is proposed to explain the regularities of the process. The catalytic system can be used repeatedly by simple extraction of products with diethyl ether. Nine cycles were carried out without loss of activity. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Carbonylation; Palladium catalysis; Molten salts

## 1. Introduction

Palladium-catalysed hydroxycarbonylation of alcohols and olefins is a very promising and clean route for the synthesis of carboxylic acids and esters [1–10]. In particular, commercial non-steroidal anti-inflammatory drugs ibuprofen and naproxen [11,12] may be synthesised by hydroxycarbonylation of 1-arylethanol and derivatives [13–15]. The separation of the product from the catalyst is a serious problem in hydroxycarbonylation as well as in other homogeneous transition-metal-catalysed reactions. A number of ways of overcoming this drawback have been proposed, in particular, immobilising catalyst in water [16], perfluorated solvents [17], the use of scCO<sub>2</sub> [18]. Another promising class of new media are molten salts or ionic liquids. They are good solvents for transition metal complexes and are poorly miscible with non-polar organics such as paraffins and ethers, allowing the formation of two-phase systems. Ionic liquids are generally thermally stable and chemically resistant. Being composed entirely of ions, they possess negligible vapour pressures. This makes them environmentally benign media for industrial use. Wide range of possible cations and anions means that their properties may be directly controlled. Despite short history of ionic liquids in chemistry, there have been numer-

ous publications on their employment in diverse organic and catalytic reactions such as alkylation, nitration of aromatics, isomerisation and cracking of paraffins, Diels–Alder reaction, Wittig reaction, dipolar cycloadditions, hydroformylation, Suzuki cross-coupling, Heck reaction, allylic substitution, Trost–Tsuji coupling [19–27].

There are some examples of catalytic carbonylation in molten salt media. Palladium-catalysed carbonylation of aryl and benzyl halides [28–32], carbonylation of terminal 3-alkyn-1-ols and 1-alkyn-4-ols into *exo-α*-methylene  $\gamma$ - and  $\delta$ -lactones [33], hydroesterification of styrene derivatives [34,35], have been performed. Recently we found that styrene and olefins can be converted into the corresponding acids in a tetrabutylammonium bromide melt (TBAB) in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or Pd(OAc)<sub>2</sub> [36,37]. Somewhat unexpectedly, the phosphine-free catalyst seemed to be more active than traditional Pd–phosphine systems when reaction is carried out in a molten salt. These results forced us to study hydroxycarbonylation of 1-phenylethanol (PE) in molten salt media.

## 2. Results

### 2.1. Hydroxycarbonylation of 1-phenylethanol

The hydroxycarbonylation of 1-phenylethanol proceeds in the presence of palladium catalyst and acidic promoter

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Table 1  
Hydroxycarbonylation of 1-phenylethanol<sup>a</sup>

Entry	Catalyst	Ionic liquid	Acid yield, GLC (%)	1:2 ratio	Styrene yield, GLC (%)
1	Pd(OAc) <sub>2</sub>	TBAB	81.2	1.1	0.4
2 <sup>b</sup>	Pd(OAc) <sub>2</sub>	TBAB	87.4	1.0	0.2
3 <sup>c</sup>	Pd(OAc) <sub>2</sub>	TBAB	55.5	1.7	19.5
4 <sup>d</sup>	Pd(OAc) <sub>2</sub>	TBAB	82.4	1.4	7.2
5 <sup>e</sup>	Pd(OAc) <sub>2</sub>	TBAB	8.2	2.3	5.3
6 <sup>f</sup>	Pd(OAc) <sub>2</sub>	TBAB	0	–	2.0
7	Pd(OAc) <sub>2</sub>	TBAC	tr.	–	4.0
8	Pd(OAc) <sub>2</sub>	[BMIM][Br]	86.3	0.4	0
9	Pd(OAc) <sub>2</sub>	[BMIM][Cl]	4.3	0.3	0.1
10	Pd(OAc) <sub>2</sub>	[BMIM][BF <sub>4</sub> ]	tr.	–	34.5 <sup>g</sup>
11	Pd(OAc) <sub>2</sub>	[BMIM][PF <sub>6</sub> ]	tr.	–	12.9 <sup>g</sup>
12	PdCl <sub>2</sub> (PhCN) <sub>2</sub>	TBAB	84.5	2.2	1.0
13	PdCl <sub>2</sub> (Py) <sub>2</sub>	TBAB	77.3	2.2	2.3
14	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TBAB	42.3	2.5	35.8
15	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TBAC	17.9	16.9	0
16 <sup>h</sup>	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TBAC	44.5	12.9	0
17	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	[BMIM][Br]	7.6	0.7	56.9
18	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	[BMIM][Cl]	6.5	9.8	4.2
19	Pd(PPh <sub>3</sub> ) <sub>4</sub>	TBAC	15.9	16.7	0

<sup>a</sup> Run conditions: 4 mmol 1-phenylethanol, 0.02 mmol catalyst, 0.8 mmol TsOH·H<sub>2</sub>O, 2 g ionic liquid; *T* 110 °C, *P* 50 bar, 2 h.

<sup>b</sup> 20 mmol H<sub>2</sub>O were added.

<sup>c</sup> 5 mL heptane were added.

<sup>d</sup> HBr as an acidic promoter instead of TsOH.

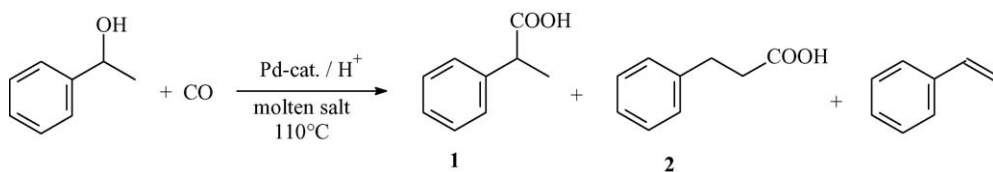
<sup>e</sup> CCl<sub>3</sub>COOH as an acidic promoter.

<sup>f</sup> HCOOH as an acidic promoter.

<sup>g</sup> Polymers were found in the reaction products.

<sup>h</sup> Run time 4 h.

in molten salt media affording branched (**1**) and linear (**2**) phenylpropionic acids. Styrene can be formed as a by-product.



Acid yield and reaction regioselectivity strongly depend on both the molten salt nature and the catalyst composition (Table 1). The phosphine-free catalyst derived from palladium acetate seemed to be very active in TBAB (mp 103 °C). The 81.2% yield of acids was reached in the presence of TsOH as an acidic promoter (entry 1). Adding five equivalents of water to the initial mixture increased the yield to 87.4% (entry 2). When heptane was added, the yield decreased, likely due to lower concentration of the reagent. At the same time, considerable amount of styrene was found in the reaction mixture (entry 3). Hydrobromic acid is also an efficient acidic promoter providing a high yield of target acids and a minor amount of styrene (entry 4). On the contrary, weak acids such as CCl<sub>3</sub>COOH and HCOOH gave little or no carbonylation activity (entries 5 and 6).

Replacing TBAB with tetrabutylammonium chloride (TBAC, mp 41 °C) totally inactivated the catalyst. Only trace amounts

of carboxylic acid were found in the reaction mixture. Styrene yield was 4% (entry 7). In this run black precipitate was formed indicating decomposition of the palladium compound into the bulk metal. Similar observations were done when 1-butyl-3-methylimidazolium bromide and chloride were tested as reaction media and palladium acetate was a precursor. In [BMIM][Br], a 86% yield of acid was found. In [BMIM][Cl], the yield was only 4%. No styrene formed in both cases. Remarkably, the selectivity to branched acid **1** was lower in [BMIM][Hal] solutions than in the TBAB medium (entries 8 and 9).

Two ionic liquids containing complex anions, [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>], seemed to be unsuitable for hydroxycarbonylation of PE. However, the substrate was completely converted in these media yielding styrene and unidentified polymers (entries 10 and 11). Considerable amount of Pd-black was found in the autoclave.

Palladium complexes bearing weakly coordinating ligands such as PhCN and pyridine seemed to be as active as Pd(OAc)<sub>2</sub> in TBAB media. Somewhat higher selectivity to the branched acid was observed: **1:2** ratio was 2.2 versus 1.1 for Pd(OAc)<sub>2</sub> (entries 12 and 13). On the contrary, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> possesses moderate hydroxycarbonylation activity in TBAB, judging by low-acid yield and considerable amount of styrene formed (entry 14). Replacing TBAB with TBAC decreased the activity of phosphine-containing catalysts but sharply increased the regioselectivity to **1** (entries 15 and 19). Remarkably, the **1:2** ratio decreased when the reaction was prolonged for 4 h (entry 16).

Finally, the activity PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in both [BMIM][Cl] and [BMIM][Br] was only a little but regioselectivity was sharply different. Branched acid **1** was a major product in the [BMIM][Cl] media while in [BMIM][Br] both isomeric acids were formed in approximately equal amounts. Dehydration of PE into styrene seemed to be the predominant reaction in

the [BMIM][Br] medium but not in [BMIM][Cl] (entries 17 and 18).

In Pd(OAc)<sub>2</sub>–TsOH–TBAB catalytic system the total yield of phenylpropionic acids was almost independent of the carbon monoxide pressure in the range of 10–50 bar. A pressure lower than 10 bar is obviously insufficient for hydroxycarbonylation. Styrene was formed predominantly (Fig. 1). Qualitatively the same effect was found for PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as a catalyst. However, higher CO pressure is needed for reaction to proceed. At CO pressure of 10 bar, no hydroxycarbonylation occurred at all, styrene being the only product. Only a 42% yield of acids was obtained at a 50 bar CO pressure (entry 14, Fig. 1). Pressure strongly affected the reaction regioselectivity.

The higher the pressure, the higher the **1:2** molar ratio (Fig. 2). This result agrees with known data on higher regioselectivity to branched acid at elevated pressures in the carbonyla-

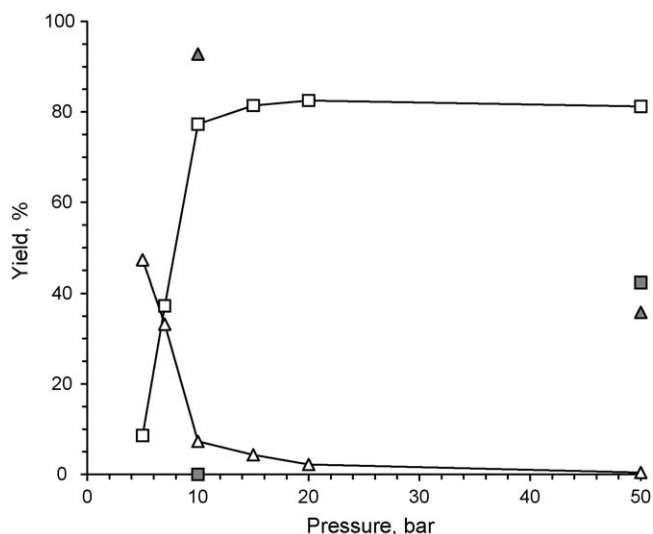


Fig. 1. Effect of pressure on acid yield (squares) and styrene yield (triangles). Catalyst: Pd(OAc)<sub>2</sub> (empty symbols), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (filled symbols). Run conditions: see footnote a of Table 1, excepting pressure.

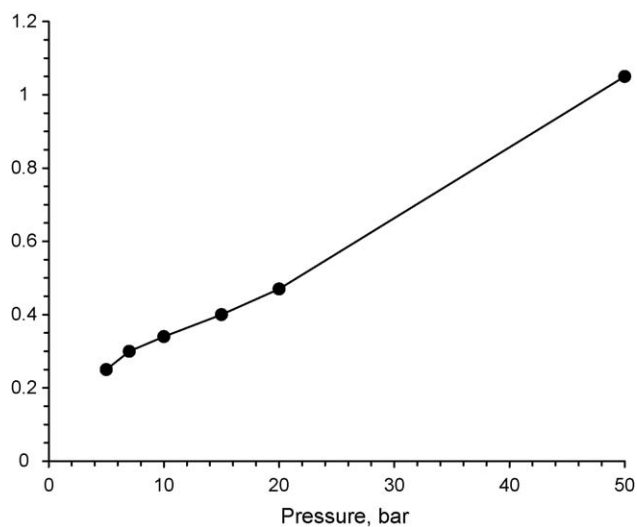


Fig. 2. Effect of pressure on the 1:2 ratio. Run conditions: see Table 1, entry 1, except pressure.

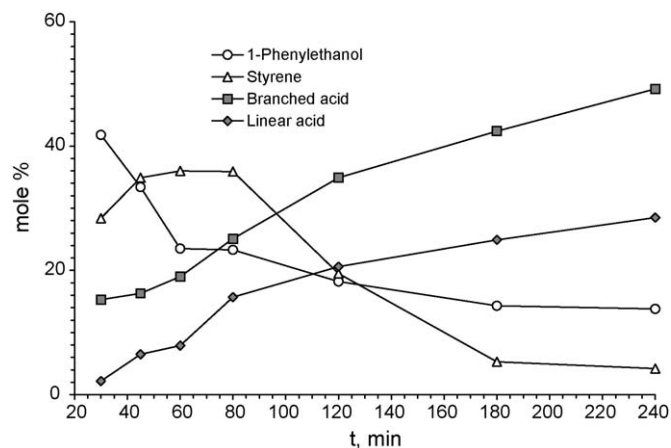


Fig. 3. Time-concentration curves in 1-phenylethanol hydroxycarbonylation. Run conditions: see Table 1, entry 1, except the run time.

tion of styrene [7,9,34] and 1-(4-isobutylphenyl)ethanol [14].

The time-concentration dependences for the Pd(OAc)<sub>2</sub>-TsOH-TBAB-heptane system are shown in Fig. 3. The general shape of the curves indicates that styrene is the main reaction intermediate. Similar curves were obtained by Jang et al. in IBPE carbonylation using traditional catalyst and solvent [14]. Although the catalyst activity is higher in our case, the selectivity to **1** is much lower. Notably, the 1:2 ratio decreased from 7 in the first 30-min run to ~1.7 in 80 min. This fact contradicts the consecutive scheme PE → styrene → **1** + **2**. It is more likely that the two mechanisms operate simultaneously.

An important advantage of ionic liquids as media for catalytic reactions is the simple procedure for catalyst recovering. The reaction products are generally weakly soluble in the ionic liquid and may be separated from the catalyst by decantation. We used extraction with ether followed by decantation. The catalyst remained in the crystallised TBAB and could be used repeatedly upon adding a new portion of PE. However, the acid promoter was partly extracted too, so that we had to add it in every run. To prevent gradual replacement of bromide by another anion (this is essential for catalyst activity, see Table 1) we used HBr as the acidic promoter. As a result, Pd(OAc)<sub>2</sub>-HBr-TBAB catalytic system maintains the initial activity and selectivity for at least nine runs (Fig. 4). Notably, all reloading operations were carried out in air.

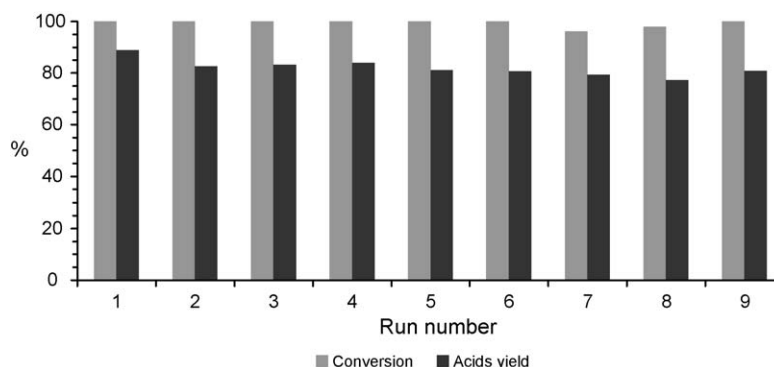


Fig. 4. Catalyst recycling.

Table 2  
Hydroxycarbonylation of styrene<sup>a</sup>

Entry	Catalyst	Ionic liquid	Conversion, GLC (%)	Acid yield, GLC (%)	1:2 ratio
20	Pd(OAc) <sub>2</sub>	TBAB	97.1	87.2	0.8
21 <sup>b</sup>	Pd(OAc) <sub>2</sub>	TBAB	93.5	83.0	1.0
22	Pd(OAc) <sub>2</sub>	TBAC	22.2	16.0	6.3
23	Pd(OAc) <sub>2</sub>	[BMIM][Br]	60.8	52.3	0.4
24	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TBAB	33.3	29.2	1.0
25 <sup>b</sup>	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TBAB	76.1	69.2	1.4
26	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	TBAC	100	89.5	7.2
27	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	[BMIM][Br]	12.9	9.7	1.0
28	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	[BMIM][Cl]	26.2	21.6	10.4

<sup>a</sup> Run conditions: 4 mmol styrene, 20 mmol H<sub>2</sub>O, 0.02 mmol Pd catalyst, 0.8 mmol TsOH·H<sub>2</sub>O, 2 g ionic liquid, 5 mL heptane; *T* 110 °C, *P* 50 bar, 2 h.

<sup>b</sup> HCl as an acidic promoter.

## 2.2. Dehydration of phenylethanol

Styrene seems to be the primary product in PE hydroxycarbonylation in the Pd(OAc)<sub>2</sub>–TsOH–TBAB catalytic system. However, only a little amount of styrene was formed when reaction was conducted in a chloride-containing molten salt (Table 1). Complicated dependences of the reaction rate and selectivity on the molten salt nature forced us to study styrene formation and conversion under the reaction conditions, namely, 110 °C and a CO pressure of 50 bar.

The first question is whether or not PE eliminates water under the reaction conditions. 1-phenylethanol, TsOH, molten salt and heptane were heated under reflux in an argon atmosphere for 2 h. Styrene was formed in the presence of TBAB. Surprisingly, no reaction occurred in the TBAC medium. A possible explanation of this outcome is insufficient acidity of the TBAC–TsOH melt to provide PE dehydration. This fact was taken into account while drawing up the scheme of PE hydroxycarbonylation.

## 2.3. Hydroxycarbonylation of styrene

Table 2 contains representative results on styrene hydroxycarbonylation. In TBAB medium, the Pd(OAc)<sub>2</sub> catalyst was more active than PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (entries 20 and 24). A reverse order was found in the TBAC media (entries 22 and 26). The selectivity to **1** was higher in TBAC regardless the presence of PPh<sub>3</sub>. These regularities were confirmed when the chloride anion was added in the reaction mixture with HCl as an acidic promoter. The activity of Pd(OAc)<sub>2</sub> decreased (entries 20 and 21), while the activity of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> increased (entries 24 and 25) upon the adding of Cl<sup>−</sup>.

The same effects of the anion nature were obtained in [BMIM]-containing ionic liquids. Namely, replacing bromide by chloride increased the activity of the phosphine-containing catalyst and greatly enhanced the selectivity to the branched acid (entries 27 and 28). The phosphine-free palladium catalyst was more active but less selective to **1** than PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the [BMIM][Br] medium (entries 23 and 27).

## 3. Discussion

Our results clearly demonstrate that hydroxycarbonylation of PE and styrene successfully occurs in molten salt media. Remarkably, the reaction proceeds smoothly in the absence of phosphine ligands if bromide-containing ionic liquid is used. In the TBAB and [BMIM][Br] media Pd(OAc)<sub>2</sub> as well as palladium complexes bearing weakly coordinating ligands are suitable catalyst precursors. Another effective catalytic system for styrene hydroxycarbonylation is PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>–TsOH–TBAB.

A strong acid as a promoter is an essential part of the catalytic system, which is in line with the generally accepted Pd-hydride mechanism of olefin carbonylation [38–40]. Weak acids such as CCl<sub>3</sub>COOH and HCOOH make the catalyst ineffective (entries 5 and 6). The effect of acidity on the catalyst activity and regioselectivity in styrene hydroxycarbonylation in TBAB is discussed elsewhere [36].

An increase in the carbon monoxide pressure promotes the formation of the branched isomer in carbonylation of styrene or 1-arylethanol [7,9,14,34]. Our observations confirm this rule (Fig. 2). The effect of pressure on the regioselectivity can be attributed to the small size and strong π-acceptor nature of the CO ligand. As the concentration of CO in solution increases, CO replaces other ligands in the H–Pd complex, thus making it more compact and more acidic. Both factors favour the formation of the branched alkyl-palladium complex according to the Markovnikov's rule.

The effect of the counter anion on the activity and regioselectivity of palladium catalysts in the carbonylation of styrene derivatives is widely discussed in the literature [8,9,14,15,41]. Neutral palladium hydride complexes are formed in the presence of halide anion and act as true catalysts [40]. Similar complexes are likely to be involved when halide containing ionic liquids are used as the reaction media. We discovered that the chloride anion greatly enhances the selectivity to branched isomer **1**. This is in line with literature data [8,13,14]. Jang et al. [14] reported that the branched/linear ratio decreased when Cl<sup>−</sup> was replaced by Br<sup>−</sup>, which is in agreement with our results.

The efficiency of different ionic liquids in carbonylation is reported to depend on the cation nature. This point is closely discussed in [42]. The bulky tetrahedral ammonium ion forces the halides anions away from the cation, thus making them more nucleophilic and available for the catalyst activity as compared with the planar [BMIM<sup>+</sup>] [29,42]. In line with this consideration, the yield of methoxycarbonylation of iodobenzene is higher in ammonium salts of the [NR<sub>4</sub>]X type than in imidazolium ionic liquids [30]. It should be noted that these data relate to essentially basic conditions, while PE and styrene hydroxycarbonylation proceeds in the presence of strong mineral acids. Nevertheless, our results also indicate that NBu<sub>4</sub><sup>+</sup> is more effective than [BMIM<sup>+</sup>] in styrene hydroxycarbonylation (Table 2) and in PE hydroxycarbonylation with the PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> catalyst (Table 1). On the contrary, Pd(OAc)<sub>2</sub>–TBAB and Pd(OAc)<sub>2</sub>–[BMIM][Br] systems provide almost the same yield of carboxylic acid in PE hydroxycarbonylation (entries 1 and 8). The reason is obscure

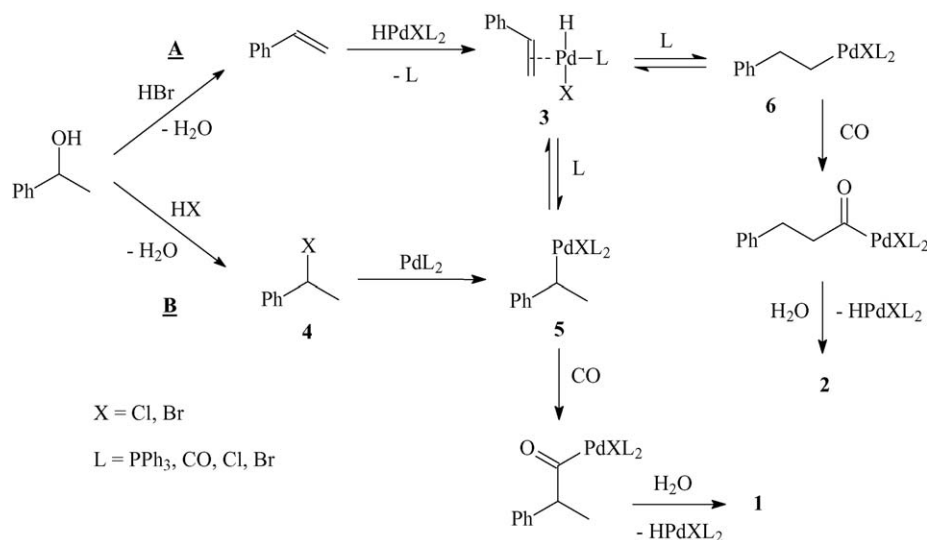


Fig. 5. Proposed scheme of hydroxycarbonylation of 1-phenylethanol.

for us and calls for further studies. The hydroxycarbonylation of PE is a more complex process than that of styrene, as far as dehydration step and nucleophilic substitution of the halogen for OH can be involved. Therefore, the effect of the cation on the carbonylation step may be masked.

How can the homogeneous palladium catalyst work in the absence of the stabilising phosphine ligand? The literature data attest to involvement of intermediate palladium nanoparticles as colloids in these systems [43,44]. PdNPs were supposed to serve as “reservoirs” for catalytically active species or to be themselves active in the Heck coupling and in some other transition metal-catalysed reactions [44,45]. However, in hydroxycarbonylation the effect of CO pressure on the regioselectivity indicates that a single Pd atom is likely the catalytic site. One can assume that palladium atoms are detached from the surface of the nanoparticle and form species such as HPdXL<sub>2</sub> where non-phosphine ligands L can be easily replaced by olefin or CO, thus providing higher activity in carbonylation. Due to the existence of the colloid some of the metal is not involved in the catalytic events. However, this is compensated by the enhanced reactivity of hydride–palladium species. Phosphine ligands as well as the chloride anion provide an ambiguous effect on the catalyst activity, depending on the molten salt nature. Phosphine can replace CO in the coordination sphere of palladium and thus it hampers the formation of the acyl–Pd complex. As a result, higher CO pressure is needed for carbonylation to proceed in TBAB (Fig. 1). However, TBAC and [BMIM<sup>+</sup>]-containing ionic liquids stabilise palladium less efficiently, judging by the black precipitate observed in the reactor. Therefore, PPh<sub>3</sub> is needed to sustain Pd in these reaction media.

We assume that at least two reaction pathways are involved in PE hydroxycarbonylation (Fig. 5). The first one (A) includes PE dehydration followed by the formation of the styrene  $\pi$ -complex with hydride–Pd species (3). Then the migrating insertion of olefin gives branched (5) or linear (6) alkyl–Pd complex. The insertion of CO and the subsequent hydrolysis of acyl–Pd complexes give acids 1 and 2 and release the hydride–Pd com-

plex. The regioselectivity depends on the ligand nature in 3. As pointed above, the ligands L = Cl, CO favour the formation of 5 and therefore 1. Phosphine inhibits CO addition to 5 and 6 (and probably styrene addition to hydride–Pd species), thus decreasing the reaction rate. Styrene is not formed in TBAC–TsOH medium under the reaction conditions. Therefore, in this medium 5 appears via the formation of 1-halo-1-phenylethane (4) followed by its oxidative addition to Pd<sup>0</sup> complex (route B). The intermediacy of 1-chloro derivatives was supposed in hydroxycarbonylation of IBPE [14,46]. Bromide is less nucleophilic than chloride in polar aprotic solvents [47]. Therefore, route B can be realised more easily for X = Cl than for X = Br. This is why the selectivity to 1 increases in chloride-containing molten salts or when Cl<sup>−</sup> is added in the reaction mixture. Of course, 5 and 6 can partly interconvert via  $\beta$ -elimination of styrene. A high 1:2 ratio in an early period of the reaction in the Pd(OAc)<sub>2</sub>–TsOH–TBAB system (Fig. 3) may be explained by significant contribution of route B to the product distribution when the concentration of PE in the system is large.

#### 4. Conclusion

The hydroxycarbonylation of PE and styrene into phenylpropionic acid proceeds in molten salt media such as TBAB, TBAC, [BMIM][Br], and [BMIM][Cl]. Phosphine-free palladium compounds are suitable precursors if the reaction is carried out in bromide-containing molten salts. Another effective catalytic system for styrene hydroxycarbonylation is PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>–TsOH–TBAC. Notably, this system is much more selective to branched acid 1 than phosphine-free systems. The reaction rate and selectivity depend on the molten salt nature, CO pressure and the presence of PPh<sub>3</sub>. A two-route reaction scheme is proposed to explain the observed complex regularities of the process. Pd(OAc)<sub>2</sub>–HBr–TBAB catalytic system can be used repeatedly without loss of activity and selectivity. All reloading operations are carried out in air.



## 5. Experimental

### 5.1. Materials

Catalytic precursors  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{PdCl}_2(\text{PhCN})_2$ , and  $\text{PdCl}_2(\text{Py})_2$  were prepared as previously described [48–51]. Molten salts were purchased from Acros Organics and Fluka. Carbon monoxide, 99.7% purity, was purchased from the Redkino plant. Solvents and PE were distilled before use.

### 5.2. Analysis

The products were identified by  $^1\text{H}$  NMR spectroscopy on a Bruker WM-250 spectrometer. GLC was performed on an Avtokhrom UE5 PID instrument (Alltech<sup>TM</sup> quartz capillary column 30 m  $\times$  0.25 mm, stationary phase SE 30, helium as the carrier gas). The reaction mixture was extracted with 2  $\times$  20 mL ether and the extracts were combined, washed with water and dried over  $\text{Na}_2\text{SO}_4$ . Then ether was removed in vacuum and the residue was analysed by  $^1\text{H}$  NMR and GLC. Carboxylic acids were converted into the corresponding methyl esters by treating the sample with diazomethane before GLC analysis.

### 5.3. Procedure for hydroxycarbonylation

Hydroxycarbonylation of PE and styrene was carried out in a pressurized 50 mL Hastelloy lined steel reactor equipped with a magnetic stirrer, arrangements for automatic temperature control and pressure regulation. The reactor was charged with reagents, solvent(s), the catalyst and the acid promoter, as indicated in the tables, flushed three times with 5 bar of CO and heated to 110 °C. Then CO was introduced up to desirable pressure and stirring was switched on. The pressure was maintained constant as CO consumption by pressure regulator. After 2 h the reactor was cooled to ambient temperature and depressurized. In time-dependence experiments, the reaction was sharply quenched at the specified time instant by cooling the reactor with water. The reaction mixture was extracted with ether and analysed.

In catalyst recycling experiments, the reactor charged with PE (4 mmol),  $\text{Pd}(\text{OAc})_2$  catalyst (0.02 mmol), HBr (0.8 mmol), and TBAB (2 g) and heated at 110 °C and a CO pressure of 50 bar for 2 h. After cooling and releasing the excess of pressure, the reactor was opened up and the mixture was extracted with 2  $\times$  20 mL of ether. New portions of PE (4 mmol) and HBr (0.8 mmol) were added to the residue and the reaction was carried out again. The same procedure was repeated nine times.

### 5.4. Dehydration of phenylethanol

Phenylethanol (0.25 mL),  $\text{TsOH}\cdot\text{H}_2\text{O}$  (80 mg), TBAB (2 g) and heptane (5 mL) were stirred and heated under reflux in argon atmosphere for 2 h. Styrene was formed in 45% yield based on GLC analysis. The same run conducted in the TBAC–heptane medium gave no reaction.

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