2564 Russian Chemical Bulletin, International Edition, Vol. 53, No. 11, pp. 2564—2567, November, 2004

Carboxylation of styrene in the $N(C_4H_9)_4Br$—heptane system

A. L. Lapidus,* O. L. Eliseev, N. N. Stepin, and T. N. Bondarenko

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5303. E-mail: oleg@ioc.ac.ru

The carboxylation of styrene into carboxylic acids in the $N(C_4H_9)_4Br$—heptane system in the presence of phosphine complexes and palladium acetate was studied. In the absence of phosphine, the Pd catalyst seems to be stabilized in solution by forming anionic complexes with NBu_4Br; the stabilization depends on the acidity of the reaction medium. The catalytic system can be used repeatedly, its activity being reduced only slightly.

Key words: styrene, palladium catalysts, carboxylation; ionic liquids.

Carbonylation of organic substrates with carbon monoxide is an important domain in metal complex catalysis.[1—4] In particular, Pd-catalyzed carboxylation of styrenes affords derivatives of hydratropic acid, which is the structural fragment of nonsteroidal antipyretics such as ibuprofen and its analogs.[5,6]

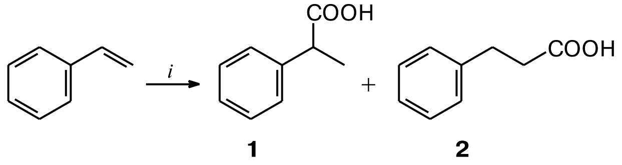
The essential problem in homogeneous catalysis by metal complexes is their recycling. A catalyst is dissolved in one (usually, polar) phase, while both reagents and products are dissolved in another phase. In this case, the products and the catalyst are separated because the reaction mixture forms two immiscible layers. Most often, water serves as a polar solvent and water-soluble ligands are used.[7,8] Recently,[9,10] ionic liquids were proposed as "liquid carriers" for homogeneous catalysts; such liquids require no special water-soluble ligands and thus common usual metal complexes are suitable.

Two-phase carboxylation of olefins is poorly investigated. In the only study dealing with ionic liquids as reaction media for styrene carboxylation,[11] the formation of α-arylpropionates was found to be highly selective; however, a low activity of the catalyst prevented it from being used repeatedly.

The present work was aimed at developing a stable Pd-based catalyst for styrene hydrocarboxylation. Use of a mixture of tetrabutylammonium bromide (TBAB) and heptane as a reaction medium allows the reaction products to be easily separated from the homogeneous catalyst.

Results and Discussion

The hydrocarboxylation of styrene in the presence of a Pd catalyst and a strong inorganic acid as a promoter yields hydratropic (**1**) and hydrocinnamic acids (**2**).



i. $[Pd]/H^+$, CO, H_2O, TBAB/n-C_7H_{16}

Let us consider the effects of the pressure, the temperature, and the concentration of the promoter (HCl) on the main reaction parameters in the presence of $PdCl_2(PPh_3)_2$ as a catalyst. With an increase in the pressure of CO from 1 to 7 MPa, the conversion of styrene increased from 46 to 98%, while the yield of the acids increased from 37 to 91%. Both the conversion and the yield depend on the pressure in a nearly linear fashion. An insignificant amount of ethylbenzene was detected among the reaction products. At a pressure below 1.5 MPa, the major product was unbranched acid **2**; with an increase in the pressure, the ratio of **1** to **2** grows (Table 1). This result agrees with the reported[11,12] data on higher yields of isomeric carboxylation products at elevated pressures. Apparently, the effect of the pressure on the regioselectivity can be associated with reduced steric hindrances. As the concentration of CO in solution increases, the bulky PPh_3 molecules in the Pd catalyst are replaced by CO through ligand exchange. Accordingly, the resulting catalytic complex is more compact and favors the formation of isomeric product **1**.

With an increase in the reaction temperature, the conversion of styrene increased. Up to a temperature of 120 °C, the yield of the acids and the styrene conversion increased in a parallel manner, styrene being insignificantly hydrogenated into ethylbenzene. With a further

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2458—2461, November, 2004.

Table 1. Effect of the pressure on the styrene carboxylation catalyzed by 0.5% $PdCl_2(PPh_3)_2$—40% HCl (110 °C)

P/MPa	Conversion of styrene (%)	Yield (%)			
		1	**2**	the acids	ethylbenzene
1.0	45.7	9.2	28.1	37.3	1.3
1.5	52.2	16.3	31.2	47.5	2.2
2.0	56.5	26.2	23.1	49.3	0.9
5.0	91.3	53.1	25.0	78.1	2.2
7.0	97.8	66.1	24.6	90.7	0.0

increase in the temperature, the yield of ethylbenzene increased dramatically, with a respective decrease in the acid yields. At 150 °C, the conversion of the substrate was complete and the yields of the acids and ethylbenzene were 43 and 36%, respectively (Fig. 1).

The ratio between acids **1** and **2** is also temperature-dependent. At 130 °C, the selectivity to hydratropic acid **1** was reduced, which correlates with the literature data.[12] However, with further increase in the temperature, the concentration of hydrocinnamic acid **2** became higher (Fig. 2).

These results suggest that the nature of the catalytic system changes at $t > 120$—130 °C. Apparently, the catalytic complex decomposes to give metallic palladium. This is evident from the sharply enhanced hydrogenating ability of the catalyst. In addition, the heated reaction mixture turned from yellow-orange (this color is characteristic of a dissolved palladium phosphine complex) to greenish black, which also indicates the formation of finely divided palladium.

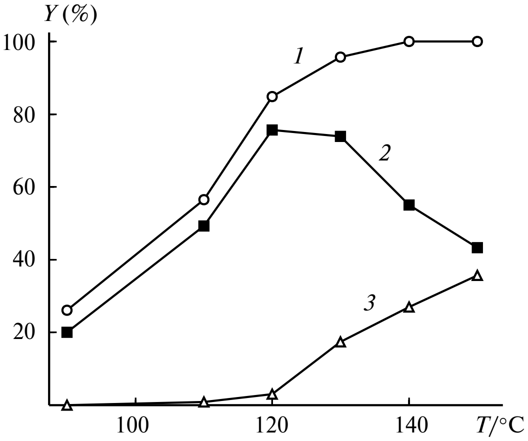


Fig. 1. Effect of the temperature on the styrene carboxylation catalyzed by 0.5% $PdCl_2(PPh_3)_2$—40% HCl (P = 2.0 MPa): (*1*) the conversion of styrene, (*2*) the yield of the acids, and (*3*) the yield of ethylbenzene.

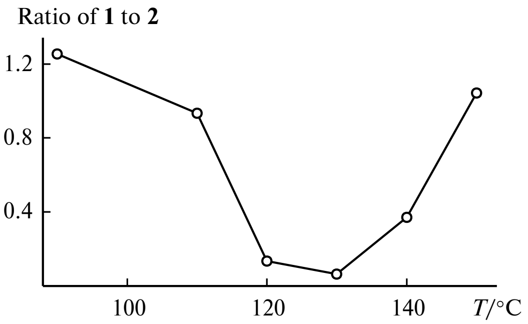


Fig. 2. Effect of the temperature on the ratio between acids **1** and **2** (0.5% $PdCl_2(PPh_3)_2$—40% HCl, 2.0 MPa).

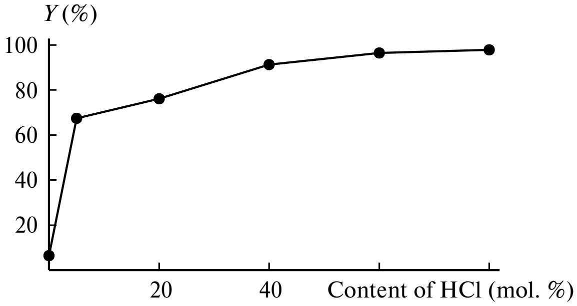


Fig. 3. Effect of the concentration of HCl on the styrene conversion (0.5% $PdCl_2(PPh_3)_2$—HCl, 5.0 MPa, 110 °C).

An acid promoter is a necessary component of this catalytic system. In the absence of an acid, the conversion of styrene was only 6.5% and the yield of the acids was 6%. With an increase in the concentration of HCl, the catalyst became much more effective (Fig. 3).

In weakly acidic media, products **1** and **2** were formed in nearly equal amounts. With an increase in the concentration of HCl, the ratio **1** : **2** increases (Fig. 4). The total selectivity to both acids was reduced from 99 to 80% as [HCl] increased from 5 to 80%. For [HCl] $\geq$40%, the yield of ethylbenzene was 2%.

Palladium complexes with such bidentate ligands as 1,2-diphenylphosphinoethane (dppe) and 1,4-diphenylphosphinobutane (dppb) proved to be less effective in styrene carboxylation. Under the same conditions, the yields of the acids were 78, 20, and 18% for $PdCl_2(PPh_3)_2$,

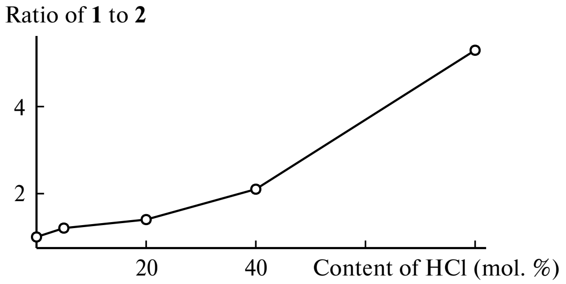


Fig. 4. Effect of the concentration of HCl on the ratio between acids **1** : **2** (0.5% $PdCl_2(PPh_3)_2$—HCl, 5.0 MPa, 110 °C).

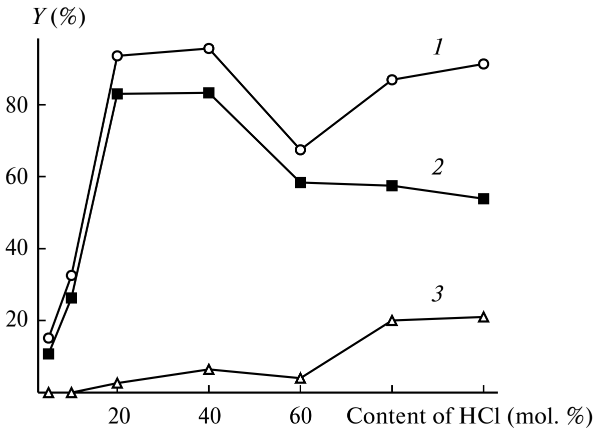


Fig. 5. Effect of the concentration of HCl on the styrene carboxylation catalyzed by 0.5% $Pd(OAc)_2$—HCl (5.0 MPa, 110 °C): (*1*) the conversion of styrene, (*2*) the yield of the acids, and (*3*) the yield of ethylbenzene.

$PdCl_2$(dppe), and $PdCl_2$(dppb), respectively. A similar reduction in the catalyst efficiency was noted for diphosphine ligands.[13]

The phosphine ligand is not a necessary component of the catalytic system. With palladium acetate as a catalytic precursor, carboxylation products were also obtained in high yields. The activity and selectivity of such a catalytic system strongly depend on the concentration of an acid promoter (Fig. 5).

In conventional solvents such as ethanol or acetone, a palladium catalyst should include ligands (most often, phosphines) to prevent precipitation of palladium metal.[1—4] However, when a phosphine-free catalyst is used, palladium black is not detected up to high concentrations of HCl, with the catalyst remaining highly effective. Apparently, such stability of the catalyst is due to a TBAB melt used as a reaction medium. Based on available literature data, one can assume that palladium is stabilized by forming 16-electron complexes of the type $[NBu_4]^+[L_2PdBr]^-$, which are effective in carbonylation.[14] The stability of such complexes seems to be dependent on the acidity of the medium. An increase in the concentration of HCl above 40% makes the catalyst less effective. With further increase in acidity, the complex decomposes completely to produce metallic palladium. Under these conditions, the increase in the conversion of styrene is due to its hydrogenation to ethylbenzene (see Fig. 5).

Ionic liquids are used in homogeneous catalysis mainly to ensure catalyst recycling. The catalyst can be used repeatedly, with nearly no loss in its activity or selectivity to acids (Fig. 6). After each cycle, organic material (carboxylation products + unreacted styrene) was extracted from the reaction mixture with ether. When new portions of styrene, water, and heptane were added to the system, the catalyst proved to be still effective (see Fig. 6).

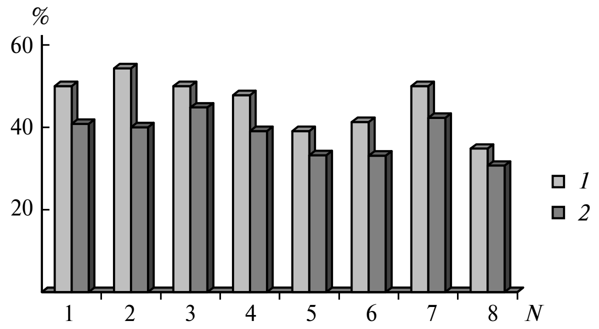


Fig. 6. Recycling of the catalytic system 0.5% $PdCl_2(PPh_3)_2$—40% TsOH in the two-phase TBAB—heptane medium (2.0 MPa, 110 °C): (*1*) the conversion of styrene and (*2*) the yields of the acids; *N* is the number of cycles.

Thus, the carboxylation of styrene into carboxylic acids can be successfully conducted in a two-phase TBAB—heptane system. Either palladium phosphine complexes or palladium acetate can be used as effective catalysts. In the absence of phosphine, palladium seems to be stabilized in solution through the formation of anionic complexes with TBAB. This catalytic system can be recycled.

Experimental

Carboxylation of styrene was carried out in a pressurized 50-mL Hastelloy-lined steel reactor fitted with a magnetic stirring bar. The reactor was heated with an electric furnace. The reactor was charged with styrene (0.5 mL, 4.35 mmol), the catalyst (0.022 mmol, 0.5% with respect to styrene), heptane (5 mL), NBu_4Br (1 g), 37% aqueous HCl, and water. Water was added in such an amount that its total volume (added water + water in the solution of HCl) was 0.39 mL (21.8 mmol, 500% with respect to styrene). The reactor was purged with CO several times and closed and the temperature was controlled. Then CO was introduced to a required pressure and the stirrer was switched on. After 2 h, the reactor was cooled to ambient temperature and the reaction mixture composed of two liquid layers was withdrawn and analyzed by GLC. In catalyst recycling experiments, the organic material was extracted from the reaction mixture with ether (20 mL). New portions of styrene and heptane and a required amount of water were added to the residue and the reaction was carried out again. Ethereal extracts were concentrated, treated with diazomethane, and analyzed by GLC.

GLC was performed with an Avtokhrom UE5 PID instrument (quartz capillary column 30 m × 0.25 mm, stationary phase SE-30, helium as a carrier gas, *n*-octane as the internal standard).

References

1. H. M. Colguhoun, D. J. Thompson, and M. V. Twigg, *Carbonylation. Direct Synthesis of Carbonyl Compounds*, Plenum Press, New York, 1991.

2. G. W. Parshall and S. D. Itell, *Homogeneous Catalysis, The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed., Wiley-Interscience, New York, 1992.
3. Yu. V. Gulevich, N. A. Bumagin, and I. P. Beletskaya, *Usp. Khim.*, 1988, **57**, 529 [*Russ. Chem. Rev.*, 1988, **57** (Engl. Transl.)].
4. A. L. Lapidus and S. D. Pirozhkov, *Usp. Khim.*, 1989, **58**, 197 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
5. J.-P. Rieu, A. Boucherle, H. Cousse, and G. Mouzin, *Tetrahedron*, 1986, **42**, 4095.
6. H. R. Sonawane, N. S. Bellur, J. R. Ahuja, and D. G. Kulkarni, *Tetrahedron: Asymmetry*, 1992, **3**, 163.
7. B. Cornils and E. Wiebus, *CHEMTECH*, 1995, **25**, 33.
8. F. Bertiux, E. Monflier, Y. Castanet, and A. Morteux, *J. Mol. Catal. A: Chem.,* 1999, **143**, 11.
9. C. M. Gordon, *Appl. Catal. A: General*, 2001, **222**, 101.
10. H. Olivier-Bourbigou and L. Magna, *J. Mol. Catal. A: Chem.,* 2002, **182—183**, 419.
11. D. Zim, R. F. de Souza, J. Dupont, and A. L. Monteiro, *Tetrahedron Lett.*, 1998, **39,** 7071.
12. E. J. Jang, K. H. Lee, J. S. Lee, and Y. G. Kim, *J. Mol. Catal. A: Chem.*, 1999, **138**, 25.
13. I. del Ro, N. Ruiz, C. Claver, L. A. van der Veen, and P. W. N. M. van Leeuwen, *J. Mol. Catal. A: Chem.*, 2000, **161**, 39.
14. V. Calo, P. Giannoccaro, A. Nacci, and A. Monopoli, *J. Organomet. Chem.*, 2002, **645**, 152.

Received March 25, 2004;
in revised form October 11, 2004