Doklady Chemistry, Vol. 401, Part 2, 2005, pp. 59–61. Translated from Doklady Akademii Nauk, Vol. 401, No. 4, 2005, pp. 486–488.
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Phosphine-Free Catalytic System for the Carboxylation of Olefins with Carbon Oxide

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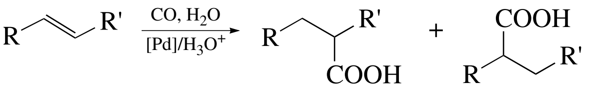
Received December 2, 2004

The carboxylation of olefins with carbon oxide in the presence of palladium catalysts can result in the corresponding acids. The reaction proceeds under CO pressure and requires an acid promoter [1–3]:



In particular, the carboxylation of styrenes allows one to obtain the derivatives of hydratropic acid, which is a structural fragment of the nonsteroidal anti-inflammatory pharmaceutical ibuprofen and its analogues [4].

One of the reasons restricting the applicability of this reaction is the necessity to use ligands stabilizing palladium in solution [5]. Phosphines are the most widely used ligands. However, they are rather expensive and toxic. Moreover, they gradually decompose under the reaction conditions. Another problem inherent not only in the carboxylation reactions but also generally in metal complex catalysis is the necessity to separate and reuse the homogeneous catalyst. A promising way to solve this problem is to carry out syntheses in two-phase systems with the reaction products and the catalyst being in two liquid phases, polar and nonpolar. Water usually serves as the polar phase [6]. This requires the use of water-soluble metal complexes as the catalysts. When ionic liquids serve as the polar phases, common complex compounds of Pd, Rh, and other metals can be used as the catalysts [7, 8]. Information on the carboxylation of olefins in the medium of ionic liquids is extremely limited. A paper is available [9].

When studying the carboxylation of olefins in an ionic liquid medium, namely, tetrabutylammonium bromide (TBAB), we found unexpectedly that not only palladium phosphine complexes but also “ligand-free” palladium shows high catalytic activity.

The carboxylation of olefins under pressure was carried out in a 50-mL steel reactor equipped with a magnetic stirrer. The reactor was heated with an electric furnace. The reactor was charged with an olefin (4 mmol), a catalyst (0.5 mol %), NBu_4Br or NBu_4Cl or their mixture (2 g), an acid (TsOH or 37% aqueous HCl solution), and water. Water was added in an amount to reach a total content of 500 mol % with respect to the olefin taking into account the presence of HCl. The reactor was purged several times with CO, sealed, and kept at the required constant temperature. Then, CO was admitted up to the required pressure and the stirrer was turned on. The pressure in the reactor was maintained automatically with a control valve. After 2 h, the reactor was cooled to ambient temperature and the reaction mixture was unloaded, extracted with ether, and analyzed by GLC.

The use of $Pd(CH_3COO)_2$ as the catalyst led to high, up to quantitative, conversion of olefins and high general selectivity toward the target carboxylic acids (table). The reaction with aliphatic olefins in most cases resulted in more than two isomeric acids. This is due to the migration of the double bond in the substrate molecule in the presence of strong mineral acids. The resulting isomeric olefins also undergo carboxylation.

Primary olefins are the most reactive. Their conversion was 97% and higher, and styrene conversion was 93.5%. The yield of acids was 83–91%. The conversion of octene-2 was slightly lower (86%) at a total acid yield of 82%. Tetradecene-7 was the least reactive: its conversion was 62% at an acid yield of 57%. This feature, i.e., the decrease in the olefin reactivity as the number of substituents at the double bond rises, is explained by steric hindrances at the stage of olefin coordination to palladium.

We used HCl and TsOH as acid promoters. The yields of acids are somewhat higher in the presence of HCl. Thus, upon the carboxylation of decene-1, the yield of acids was 90.5 and 86% in the presence of HCl and TsOH, respectively, whereas the carboxylation of tetradecene-7 led to 57 and 49.5% yields, respectively (table). The role of the anion of the promoter acid in the presence of strongly coordinated bromide ion is unclear. This requires further studies.

On the basis of available literature data, we can suppose that palladium is stabilized in a ionic liquid due to the formation of 16-electron complexes of type $[NBu_4]^+[L_2PdHal]^-$ [10]. The nature of the halide ion should affect the catalytic activity of the complex.

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Carboxylation of olefins in the presence of $Pd(CH_3COO)_2$ in a TBAB medium (P = 5.0 MPa, T = 383 K, 2 h)

Olefin	Acid promoter	Conversion, %	Yield of acids, %			Selectivity toward acids, %		
			linear	α-methyl-substituted	total	linear	α-methyl-substituted	overall
Heptene-1	HCl	100	41.8	40.0	91.1	41.8	40.0	91.1
Octene-1	″	100	42.2	38.2	88.4	42.2	38.2	88.4
Octene-2	″	86.2	14.9	42.9	81.9	17.3	49.8	95.0
Nonene-1	″	98.6	42.4	38.4	91.1	43.0	38.9	92.4
Decene-1	″	99.7	44.2	37.8	90.5	44.3	37.9	90.8
″	TsOH	98.6	41.0	34.0	86.0	41.6	34.5	87.2
Hexadecene-1	HCl	97.4	37.6	39.8	88.9	38.6	40.9	91.3
Tetradecene-7	″	61.8	–	55.9*	57.2	–	90.5*	92.6
″	TsOH	55.3	–	47.5*	49.5	–	85.9*	89.5
Styrene**	HCl	93.5	41.0	42.0	83.0	43.9	44.9	88.8

* α-Hexylpelargonic acid.

** Heptane was added to the reaction mixture.

To verify this assumption, we conducted a series of experiments in the presence of tetrabutylammonium chloride (TBAC) and TBAB–TBAC mixtures of different composition. Indeed, the yield of acids upon the carboxylation of decene-1 turned out to depend on the content of bromide ion in the system (Fig. 1). The conversion of olefin in the presence of TBAC was only 15 wt %, and the yield of acids was 12.5%. When TBAB was added to the system (the total weight of the ionic liquid was the same), the conversion and the yield increased, reaching a maximum value at a mole fraction of Br^- of 0.7 (Fig. 1).

In the experiments on styrene carboxylation, we showed that the $Pd(CH_3COO)_2$–TBAB–HCl catalytic system can be used many times with no loss of activity. After each cycle, the reaction mixture was extracted with ether. The extract contained the carboxylation products and the unreacted styrene. The catalyst remained in the system and retained its activity during seven or eight runs after the addition of a fresh portion of styrene, water, and heptane (Fig. 2).

Thus, we showed that the carboxylation of olefins proceeds in high yields in an ionic liquid medium in the presence of a Pd catalyst containing no phosphine ligands. The advantage of the suggested catalytic system is the possibility of easy separation of the products from the catalyst and multiple use of the system.

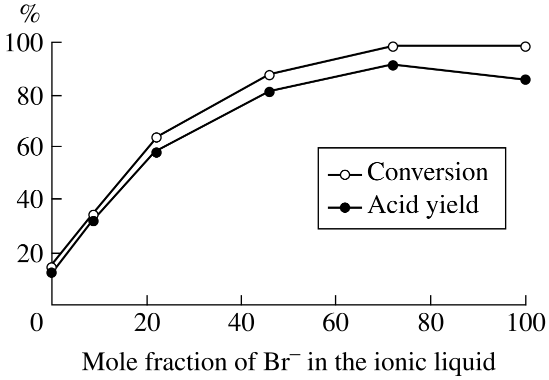

Fig. 1. Carboxylation of decene-1 in a TBAB–TBAC mixture.

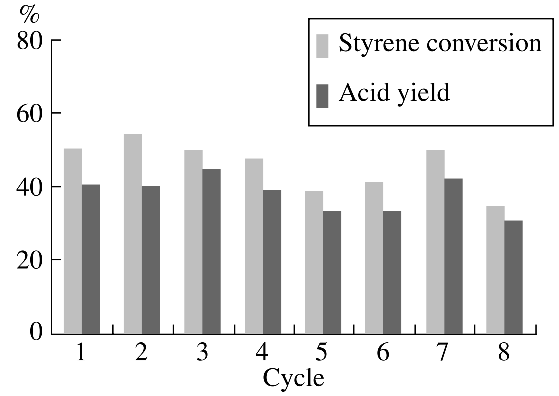

Fig. 2. Multiple use of the catalytic system for styrene carboxylation.

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