## **OXIDATIVE CARBONYLATION OF STYRENE TO ETHYL CINNAMATE**

A. R. Él'man, O. V. Boldyreva, E. V. Slivinskii, and S. M. Loktev UDC 541.128:547.538.141:546.98-386

A detailed study was made of the products of oxidative carbonylation of styrene in the presence of the catalyst system  $PdCl_2-CuCl_2-Cu(OAc)_2-Mn(OAC)_2$  at 100°C and 3.2 MPa. The target product, ethyl cinnamate, reached a molar proportion of 95%. The principal side reaction products were acetophenone and diethylphenyl succinate. Investigation of the influence of the composition of the catalyst system on the yield of target product and the selectivity of the reaction showed that  $Mn(OAc)_2$  was of greatest importance as a co-catalyst in the multicomponent Pd catalyst system. The results are discussed with reference to an alcoholate mechanism for oxidative carbonylation of olefins.

**Keywords:** oxidative carbonylation, styrene, ethyl cinnamate, acetophenone, diethylphenyl succinate, catalysis, palladium, complex.

Oxidative carbonylation of styrene is a promising synthetic method for cinnamic acid esters (cinnamates), which are used in the production of pharmaceuticals, fragrances, light-sensitive and current-conducting materials, and agrochemicals [1].



The catalyst systems used ordinarily contain Pd and Cu salts as well as other metallic compounds as co-catalysts [2, 3]. The gas mixture includes CO and air [4] or CO,  $O_2$  and  $CO_2$  [5]; in the presence of large quantities of oxidizers an oxygen-free mixture is used: CO and  $N_2$  [6, 7], or CO alone [8].

The principal reaction product is an ester of cinnamic acid [4], while the main side products are a dialkyl ester of phenyl succinate [3-8] and acetophenone (AP) [2, 4, 7]. Until the present, information about the reaction has appeared mainly in the patent literature, while virtually no systematic investigations have been made (with the exception of [2], carried out with the heterogeneous catalyst Pd/C).

The purpose of this study was to clarify in detail the reaction-product composition of the oxidative carbonylation of styrene as well as the influence of the composition of the catalyst system on the yield of the target product and the selectivity of the reaction, using the model of ethyl cinnamate (EC) under conditions of homogeneous catalysis.

## **RESULTS AND DISCUSSION**

The oxidative carbonylation of styrene to EC was studied with the 4-component catalyst system  $PdCl_2(1)-CuCl_2(2)-Cu(OAc)_2$ (3)—Mn(OAc)<sub>2</sub>(4), the most active for this type of process [5]. The product compositions obtained with mole ratios of 1:2:3:4 = 1.0:18.9:16.0:25.9 are shown in Table 1. The mass spectra of most of them agree well with published data [9]. The principal products of the reactions were EC, AP, and diethylphenyl succinate (DEPS). Taking into account the published data, we may suppose that the minor quantities of most of the side products are results of styrene oxidation. In contrast, side reactions of styrene carbonylation lead to minor quantities of DEPS and ethyl-3-ethoxy-3-phenylpropionate (EEPP). In [2], with the heterogeneous catalyst 0.5% Pd/C, a similar product mixture was obtained, but with the addition of 2-phenylpropionate and 2-phenylacrylate. It should be noted that the side formation of substituted acrylates, propionates, and succinates is characteristic of many oxidative olefin carbonylation reactions carried out with Pd compounds [3].

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TABLE 1. Mass Spectra of the Reaction Products of Oxidative Carbonylation of Styrene

Reaction product	Mass spectrum* m/z (I <sub>rel</sub> , %)
Acetic acid † Ethyl-1-phenylethyl ester † Benzaldehyde† Acetophenone† Ethylphenyl acetate	$\begin{array}{l} 60[M]^+(53), \ 45[M-CH_3]^+(83), \ 43[M-OH]^+(100) \\ 150[M]^+(2), \ 135[M-CH_3]^+(100), \\ 107[M-C_2H_3+H]^+(80), \ 105[M-OC_2H_3]^+(71) \\ 106[M]^+(83), \ 105[M-H]^+(96), \ 77[M-CHO]^+(100) \\ 120[M]^+(25), \ 105[M-CH_3]^+(100), \ 77[M-COCH_3]^+(75) \\ 164[M]^+(22), \ 119[M-OC_2H_3]^+(4), \end{array}$
1-Phenylethyl alcohol†	$91[M-CO_2C_2H_3]^+(100)$ $122[M]^+(33), 107[M-CH_3]^+(100),$
Ethyl-3-phenylpropio- nate Ethyl cinnamate	77[M-CH <sub>3</sub> -CHOH] <sup>+</sup> (50) 178[M] <sup>+</sup> (23), 105[M-CO <sub>2</sub> C <sub>2</sub> H <sub>3</sub> ] <sup>+</sup> (45), 104[M-H-CO <sub>2</sub> C <sub>2</sub> H <sub>3</sub> ] <sup>+</sup> (100), 91[M-CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>3</sub> ] <sup>+</sup> (61) 176[M] <sup>+</sup> (27), 131[M-OC <sub>2</sub> H <sub>3</sub> ] <sup>+</sup> (100),
Diethylphenyl succinate (DEPS) Ethyl-3-ethoxy-3- phenylpropionate	$\begin{array}{l} 103[M-CO_2C_2H_5]^+(48)\\ 205[M-OC_2H_5]^+(35), \ 204[M-H-OC_5H_5]^+(100),\\ 176[M-H-CO_2C_2H_5]^+(79), \ 104[M-2CO_2C_2H_5]^+(85)\\ 177[M-OC_2H_5]^+(32), \ 149[M-CO_2C_2H_5]^+(41),\\ 135[M-CH_2CO_2C_2H_5]^+(100),\\ 107[M-CH_2CO_2C_3H_5-C_2H_5^+H]^+(33), \end{array}$
(EEPP)	$105[M - CH_2CO_2C_2H_3 - C_2H_3 - H] + (90)$

The principal ions including the molecular ion. †See [9].

TABLE 2. Influence of the Catalyst—System Composition on Yield of EC and the Selectivity of the Oxidative Carbonylation of Styrene

Experi- ment	Concentration, M·10 <sup>3</sup>			Yield of	C'EC-100	
	PdCl <sub>2</sub>	CuCl <sub>2</sub> *	Cu (OAc)2 *	Mn (OAc)2 *	theor.	$C_{EC} + C_{AP} + C_{DEPS}$
$ \begin{array}{c} 1\\2\\3\\4\\5\\6\\7\\8\\9\\10\\11\\12\\13\\14\\15\\7\end{array} $	$\begin{matrix} 0 \\ 1.2 \\ 1.4 \\ 1.5 \\ 1.3 \\ 1.4 \\ 1.5 \\ 1.3 \\ 1.5 \\ 1.3 \\ 1.5 \\ 1.3 \\ 1.5 \\ 1.3 \\ 1.5 \\ 1.3 \\ 1.5 \\ 1.3 \\ 1.5 $	22.7 64.9 0 23.0 22.6 22.7 22.6 22.7 22.6 22.7 22.5 22.7 22.5 22.7 22.6 22.6 22.6 22.6 22.6 22.6	0 0 66.0 22.7 9.4 19.2 43.4 79.7 0 0 0 0 0 0 0 0 0 0	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 0\\ 1.0\\ 5.8\\ 24.5\\ 0.4\\ 4.5\\ 15.4\\ 7.1\\ 1.3\\ 25.7\\ 50.2\\ 60.0\\ 41.7\\ 26.4\\ 36.1\\ 96.1\\ \end{array}$	0 40.0 90.2 94.7 - - 99.8 85.1 95.5 37.7 89.1 86.2 93.7 73.3 93.4 93.2 93.7 73.3 93.4 90.0
16 17 18 ‡	1.0 1.2 1.2	23.0 22.3	19.5 0	31.6 15.8	52.2 55.9	80.9 88.3 94.7

\*Crystal hydrates of  $CuCl_2 \cdot 2H_2O$ ,  $Cu(OAc)_2 \cdot H_2O$ , and  $Mn(OAc)_2 \cdot 4H_2O$  were used.

†Mn(II) acetate was replaced with Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O.

‡Anhydrous salts of CuCl<sub>2</sub>, Cu(OAc)<sub>2</sub>, and Mn(OAc)<sub>2</sub> were used.

The influence of the composition of the catalyst system on the yield of EC and the selectivity of the reaction was determined in a series of experiments with differing ratios of catalyst components — Pd, Cu, and Mn salts. Since the content of most side products, except for AP and DEPS, in the reaction mixture was extremely small (often less than 1%), the selectivity of the reaction was evaluated on the basis of the mole proportion (in %) of EC in a mixture of only AP and DEPS (Table 2).

As is well known, Pd is the main component of the catalyst systems used in the oxidative carbonylation of olefins [1]. There are, however, examples of such reactions proceeding in the absence of Pd compounds [10]. In our hands the reaction did not proceed in the absence of Pd salts (experiment 1). The binary systems  $PdCl_2$ —CuCl<sub>2</sub> and  $PdCl_2$ —Cu(OAc)<sub>2</sub> proved to have very low activity (experiments 2 and 3), while the simultaneous presence of CuCl<sub>2</sub> and Cu(OAc)<sub>2</sub> markedly increased the activity of the Pd—Cu system (experiments 2, 3, and 7). The introduction of Mn(OAc)<sub>2</sub> substantially increased the activity

as well as the use of a binary Pd—Mn catalyst (in the absence of Cu salts) confirmed the hypothesis that Mn compounds may, in the course of the oxidative carbonylation of styrene, participate in oxidation—reduction reactions (experiments 15 and 16) including the reoxidation of Pd (since in the absence of a reoxidant, a rapid reduction of active Pd to Pd black takes place, accompanied by a cessation of reaction). The activity of the binary PdCl<sub>2</sub>—Mn(OAc)<sub>2</sub> system was much higher than that of binary Pd—Cu systems (experiments 2, 3, and 16).

With increase in the concentration of Cu or Mn acetates in the ternary system  $PdCl_2-CuCl_2-M(OAc)_2$ , where M is Cu or Mn, the yield of EC varied between extremes (experiments 5-8 and 9-14). The activity of the Mn-containing system, however, was much higher (see, e.g., experiments 7 and 12). The reason for these extreme results was probably competition between the formation of active complexes and the deactivation of the catalyst with an increasing M/Pd ratio. Since at high values of these ratios precipitation was observed, one of the causes of catalyst deactivation may have been the formation of insoluble M·Pd complexes, reducing the concentration of Pd compounds in solution. Although some of the 3-component Pd-Cu-Mn systems possessed good activity in this reaction, the combined use of all four salts clearly gave the most active catalyst system for this reaction under the chosen conditions (cf. experiments 6, 13, and 17).

Carrying out the reaction with absolute ethyl alcohol and anhydrous salts led to an increased yield of EC (experiments 11 and 18), evidently as a result of inhibition of the oxidation of CO to  $CO_2$  [10, 11] (usually occurring parallel with the principal reaction under conditions of oxidative carbonylation of olefins [3]) and consequently of an increase in the concentration of catalytically active particles in solution as well as in the selectivity of the reaction giving EC.

The results show that in this reaction the activity of the  $PdCl_2$ —CuCl<sub>2</sub> catalyst system conventionally used in the oxidative carbonylation of olefins may be greatly increased by the addition of Cu and Mn as co-catalysts, where the determining role is played by Mn acetate. The principal reaction product in such cases (up to 95% of the mixture) is always EC, while AP with DEPS are the main side products.

The results show that along with its high selectivity with respect to EC, the oxidative carbonylation of styrene also proceeds with high regioselectivity: in this case the monocarbonylation of styrene occurred only at the  $\beta$ -carbon of the vinyl group (see Table 1). This suggests that the reaction of the starting olefin with the alkoxycarbonyl complex LnPd—COOR, a key intermediate of the alcoholate mechanism [12] usually occurring in similar cases, involves a sharing of charge distribution on the styrene double bond [13] and the bond of the Pd—C complex (probably by a synchronous route) through transition state 5:

$$\begin{array}{c} \delta^{-} & \delta^{+} \\ C_{6}H_{5}-CH & \overleftarrow{\mp} CH_{2} \\ \delta^{+} & \delta^{-} \\ L_{m}(GI)Pd - CO_{2}R \end{array} \xrightarrow{-1} \left[ \begin{array}{c} C_{6}H_{5}-CH = CH_{2} \\ L_{m-1}(GI)Pd & \cdots & OO_{2}R \end{array} \right]^{\ddagger} \underbrace{L} & C_{6}H_{5}-CH-CH_{2}-CO_{2}R \\ L_{m}PdGI \\ L_{m}PdGI \\ (5) \end{array} \right]$$

 $R = C_2 H_s$ .

The transformation of the  $\sigma$ -complex 6 by a  $\beta$ -hydride elimination reaction [14] results in the formation of EC, while the incorporation of CO at the Pd—C bond with subsequent alcoholysis of the resulting acyl complex is the probable source of phenyl succinate esters. It can be supposed [14] that under these experimental conditions the rate of  $\beta$ -hydride elimination in complex 6 is much higher than the rate of incorporation of CO, thus determining the observed ratio of EC to DEPS concentration in the reaction products.

## **EXPERIMENTAL**

The experiments on oxidative carbonylation of styrene were conducted in a glass reactor placed in a thermostated steel autoclave [15]. The apparatus permitted a constant forced passage of gas through the reaction during an experiment. First the components of the catalyst system (Pd, Cu, and Mn salts) were added to the reactor with benzoic acid (90 mg), 8 ml dioxane (solvent), 2 ml ethyl alcohol, and 3 ml styrene. The reactor was placed in the autoclave, which was then sealed, purged twice with a gas mixture of  $CO:O_2:CO_2$  (1:1:10), and filled with gas to the required pressure. The consumption of gas was then adjusted to the required 60 ml/min and stirring and heating were begun. The reaction temperature, 100°C, and pressure, 3.2 MPa, were held constant during the 3.5 h of the reaction.

The reaction mixture was analyzed by GLC on a LKhM-80 instrument with flame ionization detection and a glass 2 m  $\times$  3 mm column packed with Chromosorb W (60-80 mesh) with 3% H<sub>3</sub>PO<sub>4</sub> coated with 10% polyethylene glycol adipinate (PEGA). The carrier gas was helium (50 ml/min) and the internal standard, dimethyl phthalate.

Gas chromatography—mass spectrometry (GLC/MS) was carried out on a Kratos DS-90 instrument using a glass 2 m  $\times$  3 mm column packed with Chromosorb W with Carbowax 20 M, as well as on a Incos-50 instrument with a quadrupole mass filter, equipped with a fused silica capillary column (50 m) with a stationary phase of DB-5 (phenylvinylmethylsilicone elastomer). The ionization energy in both cases was 70 eV.

Mn(III) acetate was prepared by the conventional method [16]. The anhydrous salts  $CuCl_2$ ,  $Cu(OAc)_2$ , and  $Mn(OAc)_2$  were prepared by heating the crystal hydrates at 110°C for 3-4 h.

Benzoic acid was added to increase the solubility of the salts, producing a virtually homogeneous reaction mixture and increasing the yield of EC.

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