Catalytic carbonylation of ethylene in the presence of the $Pd(acac)_2 - m - Ph_2PC_6H_4SO_3Na(H) - AcOH system$

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Catalytic systems based on phosphine complexes of palladium have been developed for synthesizing propionic acid (monocarbonylation) and alternating (1:1) ethylene—carbon monoxide copolymers, *i.e.*, polyketones (polycarbonylation). *m*-(Diphenylphosphino)benzenesulfonic acid or its sodium salt were used as ligands. Monocarbonylation proceeds at atmospheric pressure in dioxane or acetic acid solvents. Under high pressure, the reaction pathway can change from monocarbonylation, which occurs in the presense of the sodium salt of the ligand, to polycarbonylation when the sodium ion at the sulfo group is completely replaced by a proton. This change in reaction selectivity is observed when the process is performed in acetic acid. When the ligand is present both in the acid and the neutral form, products of di- and oligocarbonylation are formed along with propionic acid and the polyketone. These products were characterized by ¹H and ¹³C NMR spectra as alternating keto acids $C_2H_5(COCH_2CH_2)_nCOOH$, where $n = 1\div3$. Kinetic equations were derived for the selective synthesis of propionic acid and polyketones.

Key words: carbonylation of ethylene; propionic acid; polyketone; Pd-based catalysts.

The catalytic carbonylation of ethylene results in technologically important products such as propionic acid, its anhydride and esters, 1-3 diethyl ketone, 4 and copolymers of carbon monoxide with ethylene.^{5,6}

$$C_2H_4 + CO + ROH \longrightarrow C_2H_5COOR$$
 (1)

$$2C_2H_4 + 2CO + H_2O \longrightarrow (C_2H_5)_2CO + CO_2$$
 (2)

$$nC_2H_4 + nCO + ROH \longrightarrow H(C_2H_4CO)_nOR$$
 (3)

According to the type of compounds formed, reaction (1) can be labeled as monocarbonylation and reaction (3) as polycarbonylation.⁷ The polycarbonylation of ethylene gives polyketones, *i.e.*, copolymers of carbon monoxide with ethylene. The strictly alternating (1:1) structure of polyketones and some of their properties have been reported previously.⁸ Polyketones are promising materials possessing a combination of important properties.⁹ However, their thorough study has been prevented by the absence of well-developed synthetic procedures. Monocarbonylation has been known for over 50 years, whereas catalytic polycarbonylation was discovered rather recently and is being intensely investigated at present.^{6-8,10-12}

Previously we reported mono- and polycarbonylation of ethylene in the presence of a palladium-tertiary phosphine—acidic promoter catalytic system.^{2,6} The present paper reports the results of studying a system in which the functions of the ligand and the acid promoter are combined in one molecule, m-(diphenylphosphino)benzenesulfonic acid.

Experimental

Pd(acac)₂ was synthesized by the procedure reported previously.¹³ PPh₃ was recrystallized from a diethyl ether—ethanol mixture. m-Ph₂PC₆H₄SO₃Na · 2H₂O was obtained by sulfonation of PPh₃ with oleum (*cf.* Ref. 14). m-Ph₂PC₆H₄SO₃H was obtained from the sodium salt by cation exchange on a column with KU-23. Carbon monoxide (99.5 %) and ethylene (99.8 %) were used without further purification. The admixtures were monitored by mass spectrometry. "Chemically pure" grade acetic acid, "pure" propionic acid, and "chemically pure" dioxane were distilled, and the content of water in these reagents was determined by GLC.

The starting solutions and the catalysates were analyzed on a Khrom-5 chromatograph with an Interkhrom integrator (standard grade *n*-hexane as the internal reference, Separon CHN column (3 mm × 1.5 m), T = 180 °C, and a katharometer detector, v(He) = 30 mL min⁻¹, I = 80 mA). The gas phase was chromatographed on a LKhM-8 MD-5 chromatograph using a katharometer as the detector, helium as the carrier gas, isothermal mode (-40 °C), columns with 5 Å molecular sieves (3 mm × 1 m) and Porapak Q (3 mm × 2 m). ¹H and ¹³C NMR spectra were recorded on Tesla PS-587 A (80 MHz) and Bruker CXP-200 spectrometers.

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¹H and ¹³C NMR spectra of ketoacids. The reaction mixtures were analyzed by a specially developed NMR spectroscopic procedure. As a result, propionic acid and ketoacids of the general formula $C_2H_5(COC_2H_4)_nCOOH$ ($n = 1\div 3$) were identified in the acetic acid solution. The composition of the reaction mixture was quantitatively determined by comparing the areas of ¹H NMR peaks for functional groups of the reaction products using the ¹H-¹³C satellite signal of acetic acid. No other possible products such as diethyl ketones of lactones were found. The ¹H and ¹³C NMR spectra are interpreted below.

AcOH (solvent). ¹H NMR, δ : 2.05 (s, 3 H, H₃C(2)); 10.56 (s, 1 H, OH). ¹³C NMR, δ : 20.78 (C(2)); 178.2 (C(1)).

EtCOOH. ¹H NMR, δ : 1.09 (t, 3 H, H₃C(3), J = 7.4 Hz); 2.35 (q, 2 H, H₂C(2), J = 7.4 Hz). ¹³C NMR, δ : 9.30 (C(3)); 27.96 (C(2)); 181.20 (C(1)).

CH₃CH₂COCH₂CH₂COOH. ¹H NMR, δ : 1.02 (t, 3 H, H₃C(6), J = 7.2 Hz); 2.48 (br.q, 2 H, H₂C(5), J = 7.2 Hz); 2.74 (br.m, 4 H, H₂C(2)–C(3)H₂). ¹³C NMR, δ : 8.23 (C(6)); 28.67 (C(5)); 36.33 (C(2)); 37.15 (C(3)); 179.20 (C(1)); 212.70 (C(4)).

CH₃CH₂(COCH₂CH₂)₂COOH. ¹H NMR, δ : 1.00 (t, 3 H, H₃C(9), J = 7.2 Hz); 2.49 (br.q, 2 H, H₂C(8), J = 7.2 Hz); 2.70 (br.m, 4 H, H₂C(5)–C(6)H₂); 2.74 (br.m, 4 H, H₂C(2)–C(3)H₂). ¹³C NMR, δ : 8.13 (C(9)); 28.57 (C(8)); 36.39 (C(2)); 36.82 (C(3), C(5)); 37.58 (C(6)); 178.2 (C(1)); 211.0 (C(4)); 213.7 (C(7)).

CH₃CH₂(COCH₂CH₂)₃COOH. ¹H NMR, δ : 1.005 (t, 3 H, H₃C(12), J = 7.2 Hz); 2.49 (br.q, 2 H, H₂C(11), J =7.2 Hz); 2.70 (br.m, 8 H, H₂C(5)—C(6)H₂, H₂C(8)—C(9)H₂); 2.74 (br.m, 4 H, H₂C(2)—C(3)H₂). ¹³C NMR, δ : 8.13 (C(12)); 28.57 (C(11)); 36.39 (C(2)); 36.82 (C(3), C(5), C(6), C(8)); 37.58 (C(9)); 178.2 (C(1)); 210.1 (C(7)); 211.0 (C(4)); 213.7 (C(10)).

Catalytic experiments at atmospheric pressure were performed in a thermostatted glass reactor with a magnetic stirrer. The reaction rate was determined volumetrically. The experiments at enhanced pressures were performed in a thermostatted apparatus made of stainless steel ($V = 125 \text{ cm}^3$) mounted on a rocker and connected to the gas system by a flexible pipe. The reaction rate was found from the decrease in pressure.

Results and Discussion

The study of the effect of acidoligands on the catalytic properties of palladium phosphine complexes in reactions involving carbon monoxide showed that the reaction of aqueous gas efficiently occurs in the presence of these complexes if hydrohalogen acids are added, whereas the carbonylation of olefins is hindered by halide ions.² This agrees with the literature data:¹⁵ halocontaining complexes (e.g., (PPh₃)₂PdCl₂) catalyze carbonylation under drastic conditions. It can be assumed that the differences in the behavior of systems containing and not containing halide ions are due to different mechanisms of their action. As follows from the data presented in Table 1, the carbonylation of ethylene to propionic acid can be conducted at atmospheric pressure. The reaction was carried out in dioxane or acetic acid. The replacement of the sodium ion in the phosphine ligand by a proton increases the reaction rate in dioxane. Up to 30 % propionic acid was accumulated

Table 1. Carbonylation of ethylene at atmospheric pressure*

Solvent	<i>T</i> /°C	Phosphine (Ps)	$[Ps] \cdot 10^2/M$	a**
Dioxane	80	m-Ph ₂ PC ₆ H ₄ SO ₃ Na	7.5	9.8
	80	m-Ph ₂ PC ₆ H ₄ SO ₃ H	7.5	20.1
Acetic acid	70	m-Ph ₂ PC ₆ H ₄ SO ₃ Na	6.25	13.1
	70	m-Ph ₂ PC ₆ H ₄ SO ₃ H	6.25	15.8
Propionic acid	80	<i>m</i> -Ph ₂ PC ₆ H ₄ SO ₃ H	6.25	28.3

* $p_{CO} = p_{C_2H_4}$, $[Pd(acac)_2] = 1.25 \cdot 10^{-2} M$, $[H_2O] = 5 \%$ v/v. ** This column contains the values of $a/(mol EtCOOH) \cdot (g-at Pd h)^{-1}$.

after prolonged experiments. In acetic acid, the rate and selectivity of the reaction almost do not change when a proton is introduced in the sulfo group of the phosphine ligand, but the stability of the catalytic system increases.

If the pressure of the reagents is increased in the presence of the acidic form of the phosphine, the reaction changes its direction to give polyketone in quantitative yield instead of the anticipated propionic acid (Fig. 1). This change in selectivity is observed only if the reaction is performed in the lowest carboxylic acids. A decrease in the ratio of the acidic and neutral forms of



Fig. 1. Effect of the content of the phosphine acidic form on the overall reaction rate (1) and the yields of propionic acid (2) and polyketone (3). $[Ps]_{\Sigma} = 8 \cdot 10^{-2} M$, $[Pd(acac)_2] = 8 \cdot 10^{-3} M$, $[H_2O] = 0.42 M$, $p_{C_2H_4} = 2.0$ MPa, $p_{CO} = 3.0$ MPa, T = 90 °C).

the ligand when its overall concentration remains constant results in a decrease in the polyketone yield. At $[m-Ph_2PC_6H_4SO_3H] = 0$, the copolymer is not formed, but monocarbonylation occurs to give propionic acid in 96-97 % yield. The product of ethylene dicarbonylation, 4-ketocaproic acid, makes up the remaining 3-4 %.

$$2C_2H_4 + 2CO + H_2O \longrightarrow C_2H_5COC_2H_4COOH$$
(4)

It should be noted that the change in selectivity occurs at a practically constant overall reaction rate with respect to gas absorption. Decreasing the pressure from 5 to 2.5 MPa and increasing the temperature to 110−120 °C ensures \geq 99 % selectivity with respect to propionic acid. Within an intermediate acidity range, ketoacids of the general formula Et(COCH₂CH₂)_nCOOH $(n = 1 \div 3)$ are formed in addition to the polyketone. The increase in acidity resulting in the change in selectivity from mono- to polycarbonylation can also be achieved by increasing the content of water in the acetic acid.¹⁶ Hence, it was important to clarify the effect of the concentration of water on the reaction pathway under similar conditions using an equimolar ratio of the neutral and acidic forms of the phosphine ligand, when products of all types are formed. As follows from Fig. 2, the copolymer yield increases to 50 % at $[H_2O] = 0.5$ M and then levels off at a practically constant overall carbonylation rate with respect to gas absorption.

The monocarbonylation kinetics were studied at $p_{C_2H_4} = 0.5 \div 2$ MPa, $p_{CO} = 0.5 \div 3$ MPa, $T = 90 \div 135$ °C, [Pd(acac)₂] = $(2-8) \cdot 10^{-3}$ M, ratio



Fig. 2. Effect of water concentration on the yield of the copolymer (1) and the reaction rate with respect to gas consumption (2). ([Pd(acac)_2] = $8 \cdot 10^{-3}$ M, $[m-Ph_2PC_6H_4SO_3Na] = 4 \cdot 10^{-2}$ M, $[m-Ph_2PC_6H_4SO_3H] = 4 \cdot 10^{-2}$ M, T = 90 °C, $p_{C_2H_4} = 2.0$ MPa, $p_{CO} = 3.0$ MPa).



Fig. 3. Linear anamorphosis of the dependence of the reaction rate in the synthesis of propionic acid on the pressure of carbon monoxide ([Pd(acac)₂] = $8 \cdot 10^{-3} M$, $p_{C_2H_4} = 2.0$ MPa, T = 90 °C).

 $m-Ph_2PC_6H_4SO_3Na$: Pd = 10 : 1. Water (2-12 *M*) has almost no effect on the rate of reaction (1). Moreover, when the water is totally consumed, a mixed anhydride is formed by reaction (5) but at a lower rate.

$$CH_{3}COOH + C_{2}H_{4} + CO \longrightarrow (CH_{3}CO)O(OCC_{2}H_{5})$$
(5)

$$CH_{3}COOH + (CH_{3}CO)O(OCC_{2}H_{5}) \longrightarrow$$
$$\longrightarrow (CH_{3}CO)_{2}O + C_{2}H_{5}COOH \qquad (6)$$

In excess acetic acid, reaction (6) can partially occur. In this case propionic acid was found among the products. Since it appeared to be difficult to determine the content of anhydrides in the acetic acid, the GLC analysis was performed after hydrolysis with a strictly defined amount of water. The mass balance in each experiment was ensured to within ± 5 % on the basis of the GLC analyses and the consumption of gases. 2-3 % CO₂ was found in the gas phase after prolonged experiments. When the reactions were performed under static conditions, CO₂ accumulated as an admixture in the original carbon monoxide.

First order reactions with respect to the concentration of the catalyst and ethylene pressure were observed under the above conditions. The linear anamorphosis of the dependence of the reaction rate on the pressure of carbon monoxide is presented in Fig. 3. The effective activation energy is 63 ± 5 kJ mol⁻¹. The simplest equation fitting the experimental data has the form

$$r = \frac{k[\mathrm{Pd}] \cdot p_{\mathrm{C2H4}} \cdot p_{\mathrm{CO}}}{1 + K \cdot p_{\mathrm{CO}}} , \text{ mol } \mathrm{L}^{-1} \mathrm{min}^{-1}.$$
(7)

The constants of Eq. (7) are $K = 0.12 \text{ atm}^{-1}$, $k = 2.0 \cdot 10^{-2} \text{ atm}^{-2} \text{ min}^{-1}$ at 90 °C, as calculated from the data of Fig. 3 and the dependences of the reaction rate on catalyst concentration and ethylene pressure.

The polycarbonylation reaction was studied under the same conditions as monocarbonylation, but at $[H_2O] =$ 0.42 M and in the presence of $m-Ph_2PC_6H_4SO_3H$. The kinetic data are also described by Eq. (7) but with somewhat differing constants (K =0.13 atm⁻¹, $k = 1.9 \cdot 10^{-2}$ atm⁻² min⁻¹). The almost complete similarity of the kinetics for mono- and polycarbonylation makes it possible to assume that the stages of activation and introduction of CO and ethylene have similar mechanisms. The tendency of the reaction rate to approach a constant value as the pressure of CO increases implies that the stage of its activation is reversible. The mechanisms of these reactions and the role of the acid form of sulfophosphine in the change in selectivity are now under study.

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