Hydroalkoxycarbonylation of Isobutylene with Polyhydric Alcohols in the Presence of Catalytic Systems Based on Palladium Compounds and Tertiary Phosphines

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Abstract—The reaction of isobutylene hydroalkoxycarbonylation at low carbon monoxide pressures (≤ 2.0 MPa) with ethylene glycol and glycerol in the presence of catalytic systems based on Pd and mono- and bidentate organic phosphines has been studied. The effect of different conditions of the reaction in the presence of the Pd(Acac)₂–PPh₃–TsOH catalyst system on the ratio of the products, mono- and diglycolides (mono-, di-and triglycerides) of isovaleric acid has been investigated. The relative catalytic activity of a number of binary and ternary systems based on synthesized Pd(Acac)₂, Pd(PPh₃)₄, and PdCl₂(PPH₃)₂ complexes has been determined.

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Hydroalkoxycarbonylation of isobutylene with carbon monoxide and alcohols under conditions of homogeneous catalysis by transition metal complexes is an efficient method for the synthesis of isovaleric acid esters, which find wide practical application.

Note that the hydroalkoxycarbonylation reaction of olefins with CO and monohydric alcohols has been widely studied [1]. Of course, the extension of this method to polyols for obtaining polyol esters of carboxylic acids, which are widely used as plasticizers, components of pharmaceuticals and cosmetics, wetting agents, and emulsifiers, is of practical interest [2]. The esters of polyhydric alcohols are also used in the manufacture of synthetic lubricants [3].

There are patent data [2, 4, 5] on the synthesis of polyol esters of carboxylic acids by the hydroalkoxycarbonylation reaction of olefins with carbon monoxide and polyols in the presence of two-component catalyst systems consisting of Co, Ni or Rh compounds (octanoates, stearates, chlorides, or carbonates) and pyridine (or its derivatives).

We previously showed the feasibility of the synthesis of glycolides (glycerides) of isovaleric acid by the isobutylene hydroalkoxycarbonylation reaction at low CO pressures (≤ 2.0 MPa) in the presence of ethylene glycol (glycerol) and the Pd(Acac)₂-PPh₃-TsOH system [6]. The aim of this work was to study the effect of various reaction conditions on the ratio of the products mono- and diglycolides (mono-, di-, and triglycerides) of isovaleric acid and to determine the catalytic activity of other systems based on Pd phosphine complexes.

EXPERIMENTAL

The coordination complexes $PdCl_2(PPh_3)_2$, $Pd(Acac)_2$, and $Pd(PPh_3)_4$ and the ligands PPh_3 , $Ph_2PCH_2PPh_2$, and $Ph_2PCH_2CH_2PPh_2$ were obtained according to the procedures described in [7–10]. Commercial reagent-grade ethylene glycol and glycerol were used without special purification. *n*-Toluenesulfonic acid was recrystallized from 96% ethanol and dried to have the TsOH \cdot H₂O composition. The experiments were carried out in the solvent-free mode.

A steel autoclave of 150 mL capacity was charged with 0.035 g $(1.1 \times 10^{-4} \text{ mol})$ of Pd(Acac)₂, 0.212 g $(8.085 \times 10^{-4} \text{ mol})$ of PPh₃, 0.263 g $(1.386 \times 10^{-3} \text{ mol})$ of TsOH, and 3.94 g (6.35×10^{-2} mol) of ethylene glycol or 5.975 g (6.35×10^{-2} mol) of glycerol. The autoclave was sealed, purged twice with CO to remove air from the system, and then filled with CO to a pressure of 1.0–1.1 MPa. After that, the calculated amount of isobutylene (one or two equivalents relative to ethylene glycol or one, two, or three equivalents relative to glycerol) was introduced, and the CO pressure was brought to the desired value. After that, stirring and heating were turned on. The reaction mixture was stirred for varying durations of the process at different temperatures, reactant ratios, and catalyst component ratios. Then, the autoclave was cooled to room temperature and left to stay overnight. After releasing the pressure to an atmospheric value, the reaction mixture was fractionated in a vacuum (1 mmHg). From the resulting product mixture, the desired products were isolated by column adsorption chromatography on silica gel (0.005-0.04 mm) with a 9 : 1 (by volume) chlo-

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No.	Molar ratio of reactants and components of the catalytic system					Reaction conditions			Yield of glycolides, wt %		
	Isobuty- lene	Ethylene glycol	Pd(Acac) ₂	PPh ₃	TsOH	T, ℃	$P_{\rm CO}$, atm	τ, h	Mono-	Di-	Total
1	550	550	1	7	12	80	20	3	9.9	3.1	13.0
2	550	550	1	7	12	90	20	3	10.0	6.1	16.1
3	550	550	1	7	12	100	20	3	25.0	16.8	41.8
4	550	550	1	7	12	110	20	3	10.7	5.4	16.1
5	550	550	1	7	12	100	10	3	19.6	3.3	22.9
6	550	550	1	7	12	100	15	3	31.2	5.6	36.8
7	550	550	1	7	12	100	25	3	26.0	9.0	35.0
8	550	550	1	7	12	100	30	3	25.8	8.1	33.9
9	550	550	1	7	12	100	20	1	0.8	1.8	2.6
10	550	550	1	7	12	100	20	2	2.5	4.7	7.2
11	550	550	1	7	12	100	20	4	16.2	17.8	34.0
12	550	550	1	7	12	100	20	5	8.1	7.3	15.4
13	550	183.3	1	7	12	100	20	3	17.4	9.4	26.8
14	550	275	1	7	12	100	20	3	17.9	20.1	38.0
15	550	825	1	7	12	100	20	3	17.6	4.1	21.7
16	550	1100	1	7	12	100	20	3	11.0	3.9	14.9
17	550	550	1	6	12	100	20	3	10.9	2.2	13.1
18	550	550	1	8	12	100	20	3	11.4	15.6	27.0
19	550	550	1	7	11	100	20	3	10.5	2.2	12.7
20	550	550	1	7	13	100	20	3	13.9	16.8	30.7
21	450	450	1	7	12	100	20	3	24.8	9.2	34.0
22	650	650	1	7	12	100	20	3	4.5	0.1	4.6

Table 1. Isobutylene hydroalkoxycarbonylation with CO and ethylene glycol in the presence of the $Pd(acac)_2 - PPh_3 - TsOH$ catalytic system. Quantity of loaded $Pd(acac)_2$, 0.035 g (1.1 × 10⁻⁴ mol)

roform : methanol solvent blend as the eluent. The identity of the products was determined by thin-layer chromatography, elemental analysis, IR spectroscopy, and ¹H and ¹³C NMR techniques. The purity of the products was determined by thin layer chromatography on Silufol (Czech Republic) in chloroform or in the 9 : 1 (by volume) chloroform : methanol solvent system. The ¹H and ¹³C NMR spectra were taken on a Bruker DPX-400 instrument.

RESULTS AND DISCUSSION

It was found that isobutylene carbonylation with CO and ethylene glycol (glycerol) in the presence of the $Pd(Acac)_2$ -PPh₃-TsOH system proceeds regioselectively at the terminal atom of the reactant olefin to give products with the linear structure (isovalerates). Table 1 presents the results of examining the effect of various reaction conditions on the yield of mono- and diglycolides of isovaleric acid. As is seen, the dependences of the product yields on the reaction temperature (entries 1-4), CO pressure (entries 3, 5-8), and the reaction time (entries 3, 9-12) are nonmonotonic in character. The optimal conditions were as follows: temperature, 100° C; CO pressure, 2.0 MPa; and reaction time, 3 h. Under these conditions, the total yield of mono- and diglycolides of isovaleric acid reached 41.8% (Table 1, entry 3).

The reactants (isobutylene, ethylene glycol) ratio is of considerable importance (Table 1, entries 3, 13-16). The optimal [isobutylene] : [ethylene glycol] ratio was 1 : 1; the increase in the ratio from 1 to 3 reduced

No.	Molar ratio of reactants and components of the catalytic system					Reaction conditions			Yield of glycerides, wt %			
	Isobuty- lene	Glycerol	Pd(Acac) ₂	PPh ₃	TsOH	<i>T</i> ,°C	P _{CO} , atm	τ, h	Mono-	Di-	Tri-	Total
1	1100	550	1	7	12	100	20	2	2.5	13.3	_	15.8
2	1100	550	1	7	12	100	20	3	16.2	13.1	_	29.3
3	1100	550	1	7	12	100	20	4	11.3	10.4	_	21.7
4	1100	550	1	7	12	90	20	3	_	10.8	3.8	14.6
5	1100	550	1	7	12	110	20	3	7.1	8.8	_	15.9
6	1100	550	1	7	12	100	15	3	_	9.3	5.5	14.8
7	1100	550	1	7	12	100	25	3	6.3	7.6	_	13.9
8	550	550	1	7	12	100	20	3	6.7	6.4	_	13.1
9	1650	550	1	7	12	100	20	3	4.6	9.7	8.6	22.9

Table 2. Isobutylene hydroalkoxycarbonylation with CO and glycerol in the presence of the $Pd(acac)_2$ -PPh₃-TsOH catalytic system. Quantity of loaded Pd(acac)_2, 0.035 g (1.1 × 10⁻⁴ mol)

the total yield of mono- and diglycolides of isovaleric acid to 26.8%. The highest yield (20.1%) of isovaleric acid diglycolide was obtained at an [isobutylene] : [ethylene glycol] ratio of 2 : 1. Note that the highest yield of isovaleric acid monoglycolide (25.0%) is observed at an [isobutylene] : [ethylene glycol] ratio of 1 : 1 and a CO pressure of 2.5 MPa.

The reactant to catalyst ratio has a noticeable effect on the yield of the products, as well as the ratio between the components of the catalytic system. The dependences of the product yields on the component ratio of the catalytic system are nonmonotonic in character (Table 1, entries 3, 17–20), the optimal $[Pd(Acac)_2]$: $[PPh_3]$: [TsOH] ratio is 1 : 7 : 12. The optimal ratio of the reactants and catalyst is [isobutylene] : [ethylene glycol] : [Pd] = 550 : 550 : 1.

It was found that the carbonylation of isobutylene with CO and glycerol in the presence of the $Pd(Acac)_2$ -PPh₃-TsOH system yields a mixture of mono- and diglycerides or mono-, di-, and triglycerides of isovaleric acid depending on the ratio between the reactants (isobutylene, glycerol).

Table 2 shows the results of study of the influence of different reaction conditions for isobutylene hydroesterification with CO and glycerol in the presence of the $Pd(Acac)_2$ -PPh₃-TsOH system on the yield of mono-, di-, and triglycerides of isovaleric acid. It can be seen that the dependences of the product yields on the reaction conditions (temperature, carbon monoxide pressure, and reaction time) are nonmonotonic. The ratio of the reactants (isobutylene, glycerol) is of considerable importance (entries 2, 8, 9). The optimal ratio was found to be [isobutylene] : [glycerol] = 2 : 1 (total yield of mono- and diglycerides of isovaleric acid, 29.3%) (2). The highest yield of diglyceride (13.3%) is observed at an [isobutylene] : [glycerol] ratio of 2 : 1 (100°C; 2.0 MPa; reaction time, 2 h) (entry 1). The highest yield of isovaleric acid triglyceride (8.6%) was found at a reactant ratio of 3 : 1 (100°C; 2.0 MPa; reaction time, 3 h) (entry 9).

Note that at reactants (isobutylene, glycerol) ratios of 1 : 1 ($T = 100^{\circ}$ C, $p_{CO} = 2.0$ MPa, $\tau = 3$ h) (entry 8) and 2 : 1 ($T = 100-110^{\circ}$ C, $p_{CO} = 2.0-2.5$ MPa, $\tau = 2-4$ h) (entries 1–3, 5, 7), the formation of only mono- and diglycerides of isovaleric acid was observed. It is interesting that a mixture of di- and triglycerides of isovaleric acid formed at the 2 : 1 ratio of the reactants under different conditions of the process— $T = 90^{\circ}$ C, $p_{CO} = 2.0$ MPa, $\tau = 3$ h (entry 4) and $T = 100^{\circ}$ C, $p_{CO} = 1.5$ MPa, $\tau = 3$ h (entry 6). At the 3 : 1 ratio ($T = 100^{\circ}$ C, $p_{CO} = 2.0$ MPa, $\tau = 3$ h) (entry 9), the triglyceride with a yield of 8.6% is produced along with the mono- and diglycerides.

The elemental analysis and IR data for the synthesized mono- and diglycolides and mono-, di-, and triglycerides of isovaleric acid were reported in [6]. Tables 3 and 4 present the ¹ H and ¹³C NMR data for the obtained isovaleric acid glycolides (1) and (2) and glycerides (3)–(5), which are completely consistent with their structure [11, 12].

The catalytic activity of the $Pd(Acac)_2$, $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ complexes and a number of binary and ternary systems based on the complexes in the isobutylene hydroalkoxycarbonylation reaction with CO and ethylene glycol under the found optimal conditions ([isobutylene] : [ethylene glycol] : [Pd] = 550 :

	¹ H NMR, δ, ppm (J, Hz)										
Compound	С <u>Н</u> 3	С <u>Н</u>	о с <u>н</u> 2-С	С <u>Н</u> 2-О	С <u>Н</u> 2-ОН	С <u>Н</u> –О	С <u>Н</u> –ОН	О <u>Н</u>			
1	0.81 d (6.5)	1.97 m	2.07 d (7.0)	4.03 t (4.9)	3.63 t (4.9)	_	—	3.90 br.s			
2	0.82 d (6.4)	1.98 m	2.07 d (7.0)	4.06 t (4.8) 4.05 t (4.8)	_	_	_	_			
3	0.86 d (6.5)	2.00 m	2.13 d (6.9)	4.02 d (5.4)	3.48 dd (11.8; 6.5) 3.57 dd (11.2; 3.2)	_	3.82 m	3.6 d 3.66 t			
4	0.85 d (6.4)	1.99 m	2.11 d.(7.0)	3.97 dd. (11.3; 4.9) 4.10 dd (10.8; 6.5)	_	_	4.04 t (4.8)	3.61 d			
5	0.84 d (7.4) 0.85 d (6.5)	2.00 m	2.09 d (7.0) 2.12 (6.9)	4.05 dd (4.8; 5.9) 4.22 dd (11.8; 4.3)	_	5.17 um.	_	_			

 Table 3. ¹H NMR data for glycolides and glycerides of isovaleric acid

Table 4. ¹³C NMR data for glycolides and glycerides of isovaleric acid

	¹³ C NMR, δ, ppm										
Compound	0 — <u>C</u> —	<u>С</u> Н ₂ –О	<u>С</u> Н ₂ –ОН	<u>C</u> H ₃	<u>С</u> Н	о <u>с</u> н ₂ -сн	<u>С</u> Н–О				
1	173.85	65.85	60.73	22.55	27.66	43.45	_				
2	172.89	62.12	_	22.59 22.54	27.63	43.38	_				
3	173.92	65.21	63.72	22.65	25.92	43.48	70.48				
4	173.46	65.13	—	22.60	25.91	43.42	72.30				
5	172.73 172.30	62.35	-	22.57 22.53	25.86 25.90	43.33 43.40	65.14				

550 : 1, $T = 100^{\circ}$ C, $p_{CO} = 2.0$ MPa, $\tau = 3$ h) for this reaction in the presence of the Pd(Acac)₂-PPh₃-TsOH system was determined. Note that higher yields of diglycolides are observed in the presence of the systems based on Pd(PPh₃)₄. Their yield in the presence of the Pd(PPh₃)₄-PPh₃-TsOH system reaches 19.9% (at a total yield of glycolides of 31.4%).

In summary, studying the effect of the conditions of the reaction of isobutylene hydroalkoxycarbonylation with CO and ethylene glycol (glycerol), we have determined the relative catalytic activity of a number of binary and ternary systems based on Pd(Acac)₂, Pd(PPh₃)₄ and PdCl₂(PPh₃)₂ complexes. Only the Pd(Acac)₂-PPh₃-TsOH (1 : 7 : 12), Pd(PPh₃)₄-PPh₃-TsOH (1 : 3 : 12) and Pd(PPh₃)₄-TsOH (1 : 12) systems exhibit a high activity; the total yields of glycolides are 41.8, 31.3 and 21.4%, respectively. A low catalytic activity was shown by the PdCl₂(PPh₃)₂-PPh₃-TsOH system (yield of glycolides, 4.3%) and PdCl₂-PPh₃-TsOH (yield of glycolides, 0.4%). The PdCl₂-dppm-TsOH and PdCl₂-dppe-TsOH (dppm = bis-(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane) catalytic systems did not display the catalytic activity in the reactions in question.

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