Hydroformylation of Olefins Catalyzed by Rhodium Complexes with Phosphinitecalix[4]arenes

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Abstract—Hydroformylation of alkenes with various carbon chain lengths and arylalkenes in the presence of the catalytic system consisting of $Rh(acac)(CO)_2$ and phosphinitecalix[4]arenes was studied. The influence of the P/Rh and substrate/catalyst ratios, temperature, and pressure on the process and the product composition was examined.

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The hydroformylation of unsaturated hydrocarbons is currently one of the leading and dynamically developing branches of petrochemical synthesis. Intensive investigations into the use of compounds capable of molecular recognition and formation of host-guest inclusion complexes, such as calixarenes and cyclodextrins, in catalysis have been carried out in recent years. Inspection of the literature on the chemistry of phosphorus-containing calixarenes showed that considerable attention has been given to the synthesis of new cyclophanes and to the investigation of complexation of these compounds with various metals [1-3], whereas their use as ligands in the hydroformylation reaction has been poorly studied. The catalytic properties substantially depend on the nature of the organophosphorus ligand, with the influence of the structure on the ratio and yield of reaction products being rather complex in character and being determined, not only by electronic, but also steric factors [4]. Some examples of the use of phosphorus-containing calix[4,6]arenes in hydroformylation of linear alkenes-1 and styrene have been described in the literature [5–9].

The development of bifunctional catalysts that combine the properties of a metal complex with the capability of molecular recognition in one molecule is one of the promising lines of work on the design of new catalytic systems.

The objective of this study was to examine the catalytic properties of systems based on phosphinitecalix[4]arenes (I) and (II) in the hydroformylation reaction of linear alkenes and alkenylarenes.



EXPERIMENTAL

All operations were carried out in an argon atmosphere with the use of the standard technique of work in an inert atmosphere [10].

5,11,17,23-tetra (*tert*-butyl)-25,26,27,28-tetra (diphenylphosphinooxy)calix[4]arene (I) was synthesized with a yield of 67% from 5,11,17,23-tetra(*tert*-butyl)-25,26,27,28-tetrahydroxycalix[4]arene via the successive reactions with butyllithium and diphenylchlorophosphine [11]. There is only one singlet signal at δ 121.70ppm in the ³¹P NMR spectrum. (¹H NMR (CDCl₃), ppm: 1.03 (s., 36H, C(CH₃)₃), 2.13 (d, 4H, Ar–CH₂–Ar), 4.00 (d, 4H, Ar–CH₂–Ar), 7.05 (s, 8H, ArH), 7.07–7.44 (m, 40H, PPh₂)). A signal at *m*/*z* = 1385 [M⁺] was observed in the AP-ESI mass spectrum.

5,11,17,23-tetra(*tert*-butyl)-25,27-bis(diphenylphosphinooxy)-26,28-dimetoxycalix[4]arene (II) was obtained via a similar procedure from 5,11,17,23 tetra(*tert*-butyl)-25,27-dimetoxy-26,28-dihydroxycalix[4]arene with a yield of 81% [12.] (¹H NMR (CDCl₃), ppm: 0.89 (s,18H, C(CH₃)₃), 1.29 (s, 18H, C(CH₃)₃), 3.56 (br. s, 6H, OCH₃), 2.90 (br. d, 4H, Ar– CH₂–Ar), 3.88 (br. d, 4H, Ar–CH₂–Ar), 6.45 (br. s, 4H, *m*-H), 6.98 (s, 4H, *m*-H), 7.43–7.46 and 7.68–7.76 (m,



Fig. 1. Hydroformylation of nonene-1 at various P/Rh ratios. Toluene, 1.5 ml; 50° C; (a) Ligand I: nonene-1, 1.5 mmol; Rh(acac)(CO)₂, 0.01 mmol; 0.5 MPa; 2 h. (b) Ligand II: nonene-1, 0.75 mmol; Rh(acac)(CO)₂, 0.005 mmol; 1.0 MPa; 6 h.

20H, PPh₂)). (³¹P NMR (CDCl₃), ppm: 120.3). The AP-ESI mass spectrum: m/z = 1045 [M⁺].

The purity of the products was monitored by means of ¹H and ³¹P NMR spectroscopy and ESI-MS mass spectrometry.

Rhodium acetylacetonate dicarbonyl was obtained via a procedure described in [13].

The general procedure of hydroformylation is described in [14].

The reaction mixture was analyzed by means of gas–liquid chromatography on a Chrom-5 chromatograph with a flame ionization detector, a fused-silica capillary column 30 m \times 0.5 mm coated with the XE-60 phase, and temperature programming in the range 30–220°C.

ESI-MS spectra were obtained on an Agilent LC/MS 1100 SL instrument using atmospheric-pressure electrospray ionization (AP-ESI) in the positive-ion detection mode.

¹H and ³¹P NMR spectra were recorded in the stationary mode on a Bruker Avance 400 spectrometer with working frequencies of 400.13 and 161.9 MHz, respectively.

RESULTS AND DISCUSSION

Rhodium complexes with phosphorus-containing ligands were obtained in situ from $Rh(acac)(CO)_2$ and corresponding calixarene. In the products of the reaction of alkenes-1 with synthesis gas, corresponding aldehydes with both normal and branched carbon chains, as well as isomeric alkenes, were detected.

An analysis of published data on hydroformylation has shown that the maximal transformation of substrate is reached at the P/Rh ratio of its own for each organophosphorus ligand. With the use of nonene-1 as an example, it was found that the maximum value of the yield of aldehydes for ligand I is reached at a phosphorus : rhodium ratio of 4 : 1 (Fig. 1). Ligand II has a much lower solubility in most organic solvents; for this reason, all catalytic experiments with its participation were carried out at P : Rh = 2.

It was found that the conversion and the aldehyde yield substantially depend on temperature; a temperature of 50°C turned out to be the optimal value for both ligands. When the process is conducted at 70°C, an increase in the rate of isomerization reaction is observed and the yield of byproducts noticeably increases. The further elevation of temperature results



Fig. 2. Hydroformylation of octene-1 in the presence of ligand (I). $Rh(acac)(CO)_2$, 0.01 mmol; P/Rh = 4; octene-1, 1.5 mmol; 50°C; 0.5 MPa.

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Substrate	Octene-1						Decene-1		
Pressure	0.5 MPa			2.5 MPa			0.5 MPa		
Tempera- ture, °C	Conver- sion, %	Yield of al- dehydes, %	Regioselec- tivity, %	Conver- sion, %	Yield of al- dehydes, %	Regioselec- tivity, %	Conver- sion, %	Yield of al- dehydes, %	Regioselec- tivity, %
25	_	-	_	8	5	60	8	5	60
50	62	49	63	99	94	57	62	51	65
70	79	48	70	98	92	65	88	49	65
100	59	22	68				53	29	66

Table 1. Hydroformylation of octene-1 and decene-1 at various temperatures in the presence of ligand I

Reaction conditions: $Rh(acac)(CO)_2$, 0.01 mmol; P/Rh = 4; substrate, 1.5 mmol; 2 h; 0.5 MPa; regioselectivity is (the yield of *n*-alde-hyde/total aldehyde yield)100%.

in a significant decrease in both olefin conversion and the yield of aldehydes.

An increase in a gas pressure from 0.5 to 2.5 MPa resulted, not only in substantial acceleration of the catalytic reaction, but also in a sharp growth of chemoselectivity of the process even at a temperature of 70°C (Table 1).

As the synthesis gas pressure was increased, the olefin conversion became quantitative already at a gas pressure of 2.5 MPa, with the practically entire amount of the reactant alkene converting into aldehydes within 2 h (Table 2).

By the example of octene-1, it was shown that an increase in the reaction time leads to an insignificant growth of conversion (Fig. 2) and the yield of aldehydes remains practically constant with time.

The catalytic systems based on phosphinite ligands I and II have displayed a high activity in the hydroformylation of a number of linear alkenes C_7-C_{12} . As is

Table 2. Hydroformylation of nonene-1 at various pressuresin the presence of ligand I

P, MPa	Conversion, %	Yield of alde- hydes, %	Regioselectivity (decanal yield/total aldehyde yield)100%
0.5	69	56	64
1.0	91	82	65
2.5	99	98	60
5.0	98	98	61

Reaction conditions: $Rh(acac)(CO)_2$, 0.01 mmol; P/Rh = 4; nonene-1, 1.5 mmol; toluene, 1.5 ml; 50°C; 2 h.

evident from the data presented in Table 3, the conversion for 2 h was 60–80% for all investigated olefins and the yield of aldehydes was 50–60%. The ratio of the normal- to branched-chain aldehyde yields remained practically unchanged.

The substrate : catalyst ratio in the reaction mixture has an effect on the proceeding of the hydroformylation reaction. An increase in this ratio promotes the isomerization reaction, a result that may be caused by the hindered access of carbon monoxide molecules to the rhodium coordination sphere because of the growth in olefin concentration. We carried out the hydroformylation of linear substrates at a pressure of 2.5 MPa and ratios of 150 and 500. As is seen from the results presented in Table 4, practically complete conversion is observed for all alkenes at a substrate : catalyst ratio of 150, whereas the yield of aldehydes sharply decreases at a 500-fold excess of alkene.

Under the optimal conditions for the hydroformylation of linear alkenes, we studied the reaction of some alkenylarenes and cycloalkenes with synthesis gas. The data are presented in Table 5; it can be seen from these data that all of the substrates easily enter into the hydroformylation reaction and corresponding aldehydes are the main products of the reaction.

In the case of styrene and allyl phenyl ether, the prevailing formation of *iso*-aldehyde is observed. For allyl phenyl ether, its formation can be associated with the influence of the lone electron pair on the oxygen atom in the β -position to the double bond, and the prevalence of 2-phenylpropanal in the styrene hydroformylation products can be explained by the preferable formation in the catalytic cycle of the *iso*-acyl intermediate stabilized by conjugation of the double bond with the π -system of the aromatic ring.

Alkene	Ligand I, S : Cat = 150*			Ligand I, S : Cat = 500*			Ligand II, S : Cat = 150**		
	Conver- sion, %	Yield of al- dehydes, %	Regioselec- tivity, %	Conver- sion, %	Yield of al- dehydes, %	Regioselec- tivity, %	Conver- sion, %	Yield of al- dehydes, %	Regioselec- tivity, %
Heptene-1	68	50	66	27	13	62	75	57	63
Octene-1	62	49	63	33	25	68	70	60	63
Nonene-1	69	56	64	23	12	67	67	48	62
Decene-1	62	51	65	32	12	67	59	41	61
Dodecene-1	74	57	68	36	14	64	87	67	66

Table 3. Hydroformylation of linear alkenes

Reaction conditions: *-Rh(acac)(CO)₂, 0.01 mmol; 2 h; 50°C; 0.5 MPa; P : Rh = 4.

**-Rh(acac)(CO)₂, 0.005 mmol; 2 h; 50°C; 1.0 MPa; P : Rh = 2.

Table 4. Hydroformylation of linear alkenes in the presence of ligand I

Alkene		S : Cat = 150		S : Cat = 500			
	Conversion, %	Yield of aldehydes, %	Regioselectivity, %	Conversion, %	Yield of aldehydes, %	Regioselectivity, %	
Hexene-1	99	83	61	55	38	66	
Heptene-1	96	78	63	71	52	65	
Octene-1	95	93	59	82	74	61	
Nonene-1	99	98	60	76	61	64	
Decene-1	92	83	58	66	52	65	
Dodecene-1	94	84	58	68	49	65	

Reaction conditions: $Rh(acac)(CO)_2$, 0.01 mmol; P/Rh = 4; substrate, 1.5 mmol; toluene, 1.5 ml; 50°C; 2 h; 2.5 MPa.

Table 5. Hydroformylation of alkenylarenes and cycloalkenes

Ligand	Ligand I				Ligand II		
Pressure	0.5 MPa		2.5	MPa	2.5 MPa		
Substrate	TOF, h ⁻¹	n/i	TOF, h^{-1}	n/i	TOF, h^{-1}	n/i	
	22	0.3	42	0.1	44	0.1	
	27	1.2	74	1	32	0.9	
	24	0.6	105	0.5	75	0.4	
ОН	35	1.2	138	1.1	90	1.1	
	35	3.6	86	2.8	81	2.9	
	41	2.1	57	2.4	18	1.4	

Reaction conditions: *-Rh(acac)(CO)₂, 0.01 mmol; 50°C; P : Rh = 4; 1 h. **-Rh(acac)(CO)₂, 0.005 mmol; 50°C; P : Rh = 2; 1 h.

TOF, h^{-1} is the number of moles of the product per mole of catalyst per unit time.

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