PROPERTIES OF TRIPHENYLPHOSPHITE-MODIFIED RHODIUM CARBONYL CATALYSTS FOR THE HYDROFORMYLATION OF 2-BUTENES

E. V. Slivinskii, N. A. Markova,
A. T. Teleshev, G. A. Korneeva,
O. L. Butkova, A. V. Shishin,
N. V. Kolesnichenko, S. M. Loktev,
and É. E. Nifant'ev

UDC 541.128.12:546.97: 547.558.1:547.313.4

The factor responsible for the deactivation of a carbonyl triphenylphosphite rhodium hydroformylation catalyst appears to be the formation of a chelate-structure complex with diphenylphosphite, which is the product of partial hydrolysis of the organophosphorus ligand. The deactivating effect of diphenylphosphite can be suppressed upon interaction of the $H(O)P(OPh)_2$ and $P(OPh)_3$ -modified complex with 2-butenes under hydroformylation reaction conditions.

Triphenylphosphite is an efficient modifier for rhodium carbonyl catalysts for the hydroformylation of olefins [1]. It is also known, however, that triphenylphosphite is susceptible to various reactions, both under hydroformylation process conditions, such as reaction with aldehydes [2], as well as outside of catalysis, for example, hydrolysis [3]. This may lead to changes in the catalytic function (activity, selectivity, and stability) of rhodium carbonyl catalysts modified with triphenylphosphite.

In the present paper we have examined the conversion of triphenylphosphite upon exposure to oxygen and moisture, and have also studied the effect of the resulting transformation products on the properties of triphenylphospite-modified rhodium carbonyl catalysts in the hydroformylation reaction of 2-butenes.

EXPERIMENTAL

The hydroformylation of 2-butenes was carried out in a 0.25 liter stainless steel autoclave equipped with a stirring apparatus, at 90°C, 6 MPa pressure, CO/H_2 ratio = 1, and a [Rh] concentration = $3.0 \cdot 10^{-4}$ g-atom/liter. The reaction rate was followed based on the amount of gas consumed, which was measured as the pressure drop in a calibrated volume from which the gas was transferred to the autoclave as a function of its consumption. The reaction products were analyzed by GLC on a "Khrom-5" chromatograph (50 m capillary column, PEG 20M phase, helium carrier gas, 110° C). ³¹P NMR spectra were recorded on a Bruker WP-80 spectrometer, with chemical shifts measured relative to 85% H₃PO₄ as external standardd. IR spectra were obtained on IKS-29 and Specord 75-IR spectrophotometers.

Carbon monoxide was prepared by dehydration of formic acid with sulfuric acid. Synthesis gas was obtained by mixing electrolytic hydrogen and carbon monoxide and was subjected to a two-stage purification procedure on Cu/SiO_2 catalyst and Cr_2O_3/SiO_2 sorbent, to give a final residual O_2 concentration of 10^{-6} %.

The following reagents were also used in this study: $Rh_4(CO)_{12}$, $acacRh(CO)_2$, prepared according to [4, 5]; triphenylphosphite [6], bp 183-184°C (1 mm), mp 21-23°C, n_D^{20} 1.5910, R_f 0.9 (Silufol UV-254, 3:1 benzene-dioxane eluent), δP 127.7 ppm; diphenylphosphite [6], bp 100°C ($8 \cdot 10^{-3}$ mm), n_D^{20} 1.5570, δP 1.3 ppm, ¹J_{PH} 749.7 Hz; triphenyl phosphate, mp 49-50°C, $\delta P - 17.8$ ppm; phosphorus acid [7], mp 74.4°C, δP 5.3 ppm, ¹J_{PH} = 676.0 Hz (water); phenol, mp 42°C.

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2712-2716, December 1990. Original article submitted September 25, 1989.



Fig. 1. Catalytic activity of triphenyl-modified $Rh_4(CO)_{12}$ catalyst after preliminary treatment of the complex with synthesis gas (90°C, P 6 MPa CO:H₂ = 1, τ 20 h), in a series of sequential experiments of 2-butenes hydroformylation.

Bis(diphenylphosphite)bis(diphenylphosphito)rhodiumhydrocarbonyl (III). To a solution of 0.1 g acacRh(CO)₂ in 10 ml absolute ether was added with stirring a solution of 0.9 g diphenylphosphite in 10 ml ether at 20°C (P/Rh mole ratio = 10). The color of the solution changed from yellow to red. After mixing the reaction solution for 2 h a white precipitate appeared, which was removed by filtration, washed with ether, and dried on the filter. Mp (dec.) 123-125°C, R_f 0.84 (Silufol UV-254, 5:1 benzene-dioxane); v_{CO} 2000 cm⁻¹ (KBr). ³¹P NMR: δP 96.4 ppm, ¹J_{Rh}, P = 127.8 Hz (benzene). Found: P 11.6%. C₄₉H₄₃O₁₃P₄Rh. Calculated: P 11.3%.

RESULTS AND DISCUSSION

In studing the hydroformylation reaction of 2-butenes in the presence of $Rh_4(CO)_{12}$ and $P(OPh)_3$ as catalyst precursors it was found thast preliminary treatment of the catalytic complex for an extended period of time with synthesis gas led in a series of sequential experiments to a reduction in the activity and selectivity with respect to 2-methylbutanal to 92% (Fig. 1).

It is known that one of the factors responsible for deactivation of rhodium carbonyl catalysts is the formation of polynuclear cluster complexes which are inactive with respect to hydroformylation [8]. Analysis of the principles governing the deactivatdion of the rhodium triphenylphosphite catalyst led us to assume that modification of rhodium carbonyl complexes by the products of chemical conversion of triphenylphosphite may be one of the factors responsible for the observed reduction in catalytic activity.

Using ³¹P NMR spectroscopy* we have shown that upon short exposure to air triphenylphosphite undergoes partial hydrolysis to give diphenylphosphite. Upon storage in air for four months triphenylphosphite is completely converted to diphenylphosphite (δ P 1.3 ppm, ¹J_{PH} = 749.7 Hz),[†] monophenylphosphite (δ P 3.9 ppm, ¹J_{PH} = 717.1 Hz), phosphorous acid (δ P 6.6 ppm, ¹J_{PH} = 672.8 Hz), and triphenylphosphate (δ P -17.9 ppm). The integrated intensity ratio for these signals was 30:15:1:2, respectively. In addition, phenol is accumulated in the rection mixture. Signal assignments were made based on the ³¹P NMR spectra of authentic reference compounds synthesized expressly for this purpose, and in the case of H(0)P(OH)Ph, based on literature data [9].

We have investigated the effects of these products (L) on the activity and selectivity of $Rh_4CO)_{12}$ + nL catalytic systems. The results are summarized in Table 1.

It is clear from the table that triphenylphosphate, phosphorus acid, and phenol do not exert a significant effect on the activity and selectivity of $Rh_4(CO)_{12}$ catalyst, while diphenylphosphite results in complete catalyst deactivation. The influence of the P/Rh mole

^{*}The presence of its chemical transformation products in triphenylphosphite can also be determined using IR: $\nu P=0$ 1260, $\nu P=H$ 2440 cm⁻¹.

[†]The absence or lack of an effect due to phosphorous acid may be due to its insolubility in p-xylene.

TABLE 1. Effect of the Nature of Organophosphorus Modifier (L) on the Catalytic Properties of $Rh_4(CO)_{12}$ + nL with respect to 2-Butene Hydroformylation (p-xylene solvent, 90°C, 6 MPa pressure, [Rh] = $3.0 \cdot 10^{-4}$ g-atom/liter, P/Rh mole ratio = 9)

Catalyst $Rh_4(CO)_{12} + nL$, where L is	Activity 10 ³ , moles CO/min	Selectivity for 2-methylbutanal, %	
OP(OPh) ₃	8,0	74	
H ₃ PO ₃	8,1	73	
PhOH	8,0	74	
H(O)P(OPh) ₂	0	-	
P(OPh) ₃	5,0	99	
Unmodified	8,0	74	

TABLE 2. Effect of $H(O)P(OPh)_2/Rh$ and $P(OPh)_3/Rh$ Mole Ratios on the Catalytic Properties of Complexes with respect to 2-Butene Hydroformylation (same reaction conditions as listed in Table 1)

P/Rh mole ratio in the system	Activity [•] 10 ³ , moles CO/min	Selectivi- ty for 2- methylbut- anal, %	P/Rh mole ratio in the system	Activity [.] 10 ³ ,moles CO/min	Selectivity for 2-meth- ylbutanal, %
Dipheny1- phosphite 0,5 1,0 2,0 4,0 9,0	3,1 3,2 0,6 0,05 0	75 74 	Triphenylphosphite 0,5 1,0 2,0 3,0 9	7,2 9,6 12,2 11,0 5,0	83 91 92 96 99

ratio on the catalytic properties of the system $Rh_4(CO)_{12} + nH(0)P(OPh)_2$ was examined. The resulting data (Table 2) reveal that the deactivating effect of diphenylphosphite arises sharply and distinctly at P/Rh mole ratios equal to two and higher. At low ratios (P/Rh = 0.5) the catalyst exhibits characteristic activity similar to the catalytic activity of a $P(OPh)_3$ catalyst at the same P/Rh ratio.

We have concluded, based on these results, that deactivation of the diphenylphosphitemodified rhodium catalyst is related to the formation of chelate-structure complexes of the type described in the literature [10] for rhodium compounds with dialkylphosphites. In order to confirm this assumption we have synthesized a model chelate complex, namely, bis(diphenylphosphite)bis(diphenylphosphito)rhodiumhydrocarbonyl (III), via reaction of diphenylphosphite with acacRh(CO)₂, and have examined its properties with respect to catalysis of 2-butenes hydroformylation.

The rhodium chelate complex was synthesized according to a published procedure [10], via reaction of ether solutions of acacRh(CO)₂ and excess diphenylphosphite.

acacRh(CO)₂ + H(O)P(OPh)₂
$$\longrightarrow$$
 H
O(PhO)₂P
H
O(PhO)₂P
CO
P(OPh)₂O

The composition and structure of the resulting complex were established based on IR and ³¹P NMR spectroscopy and elemental analysis. The IR spectrum of the complex contains absorption bands for vRh-H at 2110 and vCO at 2000 cm⁻¹. Bands due to vP=O and vP-H, which are characteristic of acidic phosphites, are absent. Assignment of the vRh-H absorption band was made based on the results of D \rightarrow H exchange in the complex. The ³¹P NMR spectrum provides evidence for the coordination and equivalence of all four phosphorus atoms, exhibiting a signal doublet at δ P 96.4 ppm with a ¹JRh, p spin-spin coupling constant = 127.7 Hz, which is characteristic of this type of complex [10].

TABLE 3. Effect of Triphenylphosphite and $P(OPh)_3-H(O)P(OPh)_2$ Mixtures on the Catalytic Properties of the Complex $Rh_4(CO)_{12} + nL$ (mole ratio diphenylphosphite/triphenylphosphite = 1:8; for reaction conditions, cf. Table 1)

Catalyst precursor	Techno- logical cycle	Treat. time for the catalyst with synthesis gas, h	Activity [.] 10 ³ , moles CO/min
¹ / ₄ Rh ₄ (CO) ₁₂ +9P (OPh) ₃	1 2	0 (20)	5,0(5,0) 5,0
¹ / ₄ Rh ₄ (CO) ₁₂ +8P (OPh) ₃ + + H (O) P (OPh) ₂	3 1 2	0	5,0 4,5 4,9
	3 1 2 3	20	5,2 3,7 3,1 2,2

Experiments with this chelated diphenylphosphite rhodium catdalyst in the hydroformylation of 2-butenes revealed that it possesses no catalytic activity (under reaction conditions the same as listed in Table 1).

 31 P NMR and IR spectral studies of the system $Rh_4(CO)_{12} + nH(0)P(OPh)_2$ further indicated an analogy between the complex formed from it and the model compound. We have therefore, concluded, based on these results, that deactivation of the diphenylphosphite-modified rhodium carbonyl catalyst results from the formation of chelate-structure complexes which are inactive with respect to hydroformylation catalysis.

In order to elucidate further the effect of acidic phosphorus acid esters on the catalytic properties of a rhodium-triphenylphosphite catalyst, we composed a mixture of $P(OPh)_3$ and $H(O)P(OPh)_2$ in concentrations approaching their actual values, and investigated its modifying properties on the hydroformylation of 2-butenes. The results of these experiments are summarized in Table 3.

As can be seen from the data in Table 3, prolonged pre-reaction treatment of the catalyst with synthesis gas (P = 6 MPa, 90°C) in the absence of olefins results in irreversible deactivation of the complex with loss of selectivity to 92.4%. In contrast, however, without this preliminary exposure a gradual increase in activity is observed and is stabilized at a level characteristic of the system $Rh_4(CO)_{12} + nP(OPh)_3$.

The IR spectrum of $Rh_4(CO)_{12}$ modified with a mixture of ligands does not contain bands due to vP=O and vP-H; the position of the carbonyl bands is also analogous to the IR spectrum of $Rh_4(CO)_{12}$ modified with triphenylphosphite. After treatment of the complex with synthesis gas, however, the IR spectrum contains bands at 2110 and 2000 cm⁻¹ analogous to those observed in the model compound and in the complex formed from the reaction of $Rh_4(CO)_{12}$ with diphenylphosphite. We assume, therefore, that under the reaction conditions disubstituted complexes $HRh(CO)_2[P(OPh)_3][P(OH)(OPh)_2]$ are formed, which are active with respect to hydroformylation. Treatment of the complex with synthesis gas results in the formation of chelate complexes and corresponding deactivation of the catalytic system.

The results obtained here in lead us to conclude that the factor responsible for the deactivation of the rhodium triphenylphosphite catalyst under conditions of partial ligand hydrolysis, and also in the case of diphenylphosphite-modified rhodium complexes, is the formation of catalytically inactive chelate complexes.

When the hydroformylation process is carried out under conditions of excess olefin the deactivating effect of $H(O)P(OPh)_2$ is suppressed; the catalytic system does not differ, indeed, in its activity and selectivity, from the normal or conventional catalytic system composed of $Rh_4(CO)_{12}$ and $P(OPh)_3$ (Table 2). We have hypothesized, therefore, that it is possible for alkylation of the coordinated diphenylphosphite ligand by olefin to take place, leading to reduction in the modifying properties of hydrolyzed $P(OPh)_3$. It is established however, that this reaction is catalytic in nature, since it occurs only in the presence of rhodium complexes.

This type of alkylation of acidic phosphites by unsaturated compounds in the presence of metal complex catalysts has been reported previously in the literature, for example, by acetylenic compounds [11].

LITERATURE CITED

- J. Matsui, H. Taniquchi, K. Terade, et. al., Bull. Jpn. Petrol. Inst., <u>19</u>, No. 1, 62 (1977).
- 2. Patent W085 03702; Chem. Abstr., <u>105</u>, 81142j (1986).
- 3. A. E. Arbuzov and M. G. Imaev, Izv. Akad. Nauk SSSR, No. 1, 171 (1959).
- 4. S. Maretinengo and P. Chini, J. Organomet. Chem., <u>27</u>, No. 3, 389 (1971).
- 5. Yu. S. Varshavskii and T. G. Cherkasova, Zh. Neorg. Khim., <u>12</u>, 1709 (1967).
- 6. E. N. Walsh, J. Am. Chem. Soc., <u>81</u>, 3023 (1959).
- 7. Yu. V. Karyakin and I. I. Angelov, Pure Chemical Reagents, GKhI, Moscow (1955), p. 290.
- 8. Yu. B. Kagan, E. V. Slivinskii, et al., Neftekhimiya, 25, No. 6, 791 (1986).
- 9. D. Ludewing, W. Eiserbeck, and E. Feike, Z. Chem., <u>24</u>, 290 (1984).
- E. E. Nifant'ev, T. S. Kukhareva, M. Yu. Antipin, and Yu. T. Struchkov, Zh. Obshch. Khim., 55, 289 (1985).
- 11. US Patent No. 3,681,481; RZhKhim 13N116P (1973).