

# Hydroformylation of Olefins Using Rhodium Complex Catalysts (Part 2)\*

## —Deterioration of Phosphorous Ligands in the Rhodium Complex Catalyst System—

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**Summary:** Chemical changes of phosphorous ligands in the rhodium complex catalyst system were studied using  $^{31}\text{P}$  NMR analysis. Triphenyl phosphite was readily oxidized by the small amount of oxygen contained in the synthesis gas to triphenyl phosphate in the course of hydroformylation. It is conceivable that this oxidation reaction is the cause of deactivation of the catalyst. The treatment of the synthesis gas with triisobutyl aluminum in toluene solution was effective in preventing the oxidation of triphenyl phosphite to triphenyl phosphate and in prolonging the activity of the catalyst for a long period.

A 191-hr continuous run was made to establish catalyst activity, and 3,220 g of aldehyde was obtained using only 6.5 mg of rhodium.

### 1 Introduction

Hydroformylation reactions using rhodium complex catalysts have been studied by many workers<sup>1)</sup>. However, almost all of them are concerned with the reactivity of newly found rhodium complex, with the mechanism of the reaction and with the discussion of the reaction conditions. And the stability of the catalysts has scarcely been reported except the studies of Olivier<sup>2),3)</sup> and Roth<sup>4),5)</sup>. Chemical changes of phosphorous ligands during hydroformylation reaction have not been reported.

In the preceding paper<sup>6)</sup>, it was made clear that the rhodium-triphenyl phosphite complex catalyst allowed both high yields of aldehyde and high selectivity for normal isomer formation in the hydroformylation of olefins, and that the selectivity was affected by various reaction conditions.

It was found that continuous use of several hours caused a sharp drop in the catalytic activity which, however, was recovered by the addition of fresh triphenyl phosphite.

In this paper, chemical changes of phosphorous ligands of rhodium complexes were examined using NMR analysis to elucidate the mechanism of deactivation.

### 2 Experimental

#### 2.1 Materials

Triphenyl phosphite was purified by vacuum

distillation and stored under nitrogen atmosphere. Other phosphorous ligands and reagents from Wako Pure Chemical Co. were used without further purification. Commercially available ethylbenzene (EB) was distilled in a 35-tray Oldershaw distillation column. Propylene and butene-1 were purchased from Phillips Petroleum Co., ("technical grade").

$\text{Rh}_2\text{Cl}_2(\text{CO})_4$  was prepared as described in the preceding paper<sup>6)</sup>.

$\text{RhCl}(\text{CO})((\text{C}_6\text{H}_5\text{O})_2\text{POH})_2$  was prepared by the following method. Addition of an ethanol solution of diphenyl phosphite (4 mmoles) to dichlorotetracarbonyldirrhodium ( $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ ) (1 mmole) in petroleum ether produced an orange precipitate. Recrystallization of the precipitate from ethanol formed orange crystals, (Found C, 45.6%; H, 3.4%. Calc. for  $\text{C}_{25}\text{H}_{22}\text{ClP}_2\text{Rh}$ : C, 47.3%; H, 3.5%). The synthesis gas of any desired composition was prepared by mixing pure grade hydrogen and carbon monoxide (from Takachiho Trading Co.).

#### 2.2 Apparatus and Procedures

##### 2.2.1 Hydroformylation Reaction

For testing the reactivity of catalysts, batch experiments were performed in the same autoclave used in the preceding work<sup>6)</sup>.

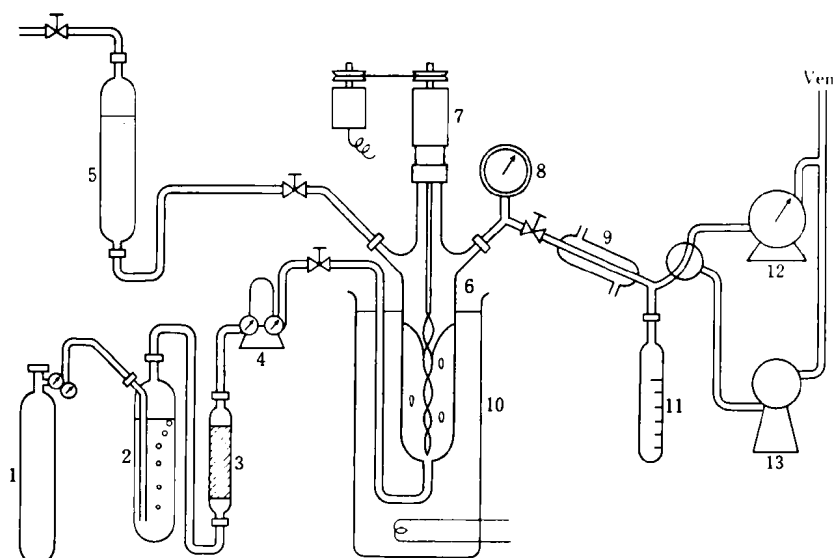
Experimental procedures and analyses of products were carried out as described in the preceding paper<sup>6)</sup>.

##### 2.2.2 Life Test of Catalyst

Hydroformylation reactions were carried out in

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1 Synthesis gas cylinder 2 TIBA solution 3  $\text{CaCl}_2$  4 Automatic pressure controller 5 Olefin reservoir  
6 50 ml. Pressure glass reactor 7 Magnetic stirrer 8 Pressure gauge 9 Cooler 10 Oil bath  
11 Product receiver 12 Gas meter 13 Vacuum pump

Fig. 1 Apparatus and Flow Diagram of the Life Test of Catalyst

a "continuous-batch" system. The apparatus and flow diagram employed are shown in **Fig. 1**.

Twenty grams of ethylbenzene containing a rhodium compound, a phosphorous ligand and sodium acetate was charged into the 50 ml pressure glass reactor (Taiatsu Glass Industry Co., Ltd.). After purging the reactor several times with the synthesis gas, liquid butene-1 was added from the olefin reservoir and then the synthesis gas introduced to desired pressure. The reactor was heated to  $90^\circ\text{C}$  while the mixture was stirred magnetically. The pressure of the reactor was maintained at  $15 \text{ kg/cm}^2$  by supplying as required the synthesis gas from the bottom of the reactor through the automatic pressure controller (Tama-seiki Kogyo Co.) during the reaction. After prescribed reaction time (30 min) had elapsed, the supply of the synthesis gas was stopped and the products were distilled under vacuum. Then, a second batch reaction was performed by introducing fresh butene-1 and synthesis gas into the reactor, and stirring the mixture at  $90^\circ\text{C}$ . These batch reactions were repeated until such changes appeared as decrease in the selectivity for normal aldehyde formation or decrease in the product yields.

### 2.2.3 NMR Analysis

$^{31}\text{P}$  NMR analysis was carried out to determine the type and concentration of phosphorous compounds.  $^{31}\text{P}$  NMR spectra at 24.29 MHz were obtained with a Hitachi R-20 high resolution spec-

Table 1 Hydroformylation of Butene-1

Raw Material		Butene-1 9.3g
Reaction Press.	$\text{kg/cm}^2$	15~20
$\text{H}_2/\text{CO}$ Ratio		1/1
Reaction Temp.	$^\circ\text{C}$	95
Reaction Time	min.	70
Aldehyde		
Yield	%	ca. 100
Normal Isomer	%	73
Space Time Yield		
Av. g/l/hr		263
Max. g/l/hr		1,600

$\text{Rh}_2\text{Cl}_2(\text{CO})_4$  25mg,  $\text{P}(\text{OPh})_3$  420mg,  $\text{AcONa}$  500mg, ethylbenzene 20 g.

trometer at  $34^\circ\text{C}$  and a PDP-8/I computer (Digital Equipment Corp.) for spectrum accumulation when necessary. Chemical shifts were reported in parts per million of the applied field using 85%  $\text{H}_3\text{PO}_4$  as an external standard.

### 2.2.4 Analysis of Oxygen

Quantitative analysis of oxygen was carried out with a Hitachi RMU-5B mass spectrometer.

## 3 Results and Discussion

The homogeneous catalyst system used in this study is composed of  $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ , triphenyl phosphite and sodium acetate (insoluble in ethylbenzene). Ethylbenzene was selected as the solvent, because it is a good solvent for  $\text{Rh}_2\text{Cl}_2(\text{CO})_4$  and  $\text{P}(\text{OPh})_3$ , and it does not undergo any changes under usual hydroformylation reaction conditions and its boiling point is higher than that of valeraldehydes.

Using this catalyst system, the hydroformyla-

Table 2 NMR Spectra of Standard Reagents

Compound	$\delta^*$ (ppm)	Obsd. Spin-Spin Splitting		Area	Remarks
		No. peaks	$J$ (Hz)**		
P(OPh) <sub>3</sub>	-126.4	Singlet	0	19	0.53 wt% as P in EB 0.50 wt% as P in EB
O=P(OPh) <sub>3</sub>	+18.0	Singlet	0	13	
PPh <sub>3</sub>	+5.7	Triplet	ca. 7		
O=PPh <sub>3</sub>	-30.6				
(PhO) <sub>2</sub> POH	-15.8	Doublet	739		
	+14.6				
PhPCl <sub>2</sub>	-159.4	Triplet	9		

\*Chemical shift from 85% H<sub>3</sub>PO<sub>4</sub> external standard.

\*\*Spin-Spin coupling constant.

Table 3 NMR Spectra of Stability Test Samples (under N<sub>2</sub> and Air Atmosphere)

Condition	$\delta$ (ppm)	Obsd. Spin-Spin Splitting		Area	Remarks
		No. peaks	$J$ (Hz)		
Fresh Catalyst*	-126.3	Singlet	0	41	Unchanged
N <sub>2</sub> , 25°C, 1 atm. (for 4 days)	-126.3	Singlet	0	44	Unchanged
N <sub>2</sub> , 110°C, 1 atm. (for 9 hrs.)	-126.3	Singlet	0	41	Unchanged
Air, 25°C, 1 atm. (for 4 days)	-126.4	Singlet	0	14	Unchanged
	-15.1	Doublet	736	17	Formed (PhO) <sub>2</sub> POH
	+15.2			16	
Air, 25°C, 1 atm. (without AcONa) (for 3 days)	-126.2	Singlet	0	9	Unchanged
	-14.9	Doublet	736	18	Formed (PhO) <sub>2</sub> POH
	+15.2			16	

\*It was prepared from Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub> (25mg), P(OPh)<sub>3</sub> (5g), AcONa (500mg) and ethylbenzene (20g).

Table 4 Hydroformylation of Propylene

Catalyst	Ligand	Reaction Temp. (°C)	Reaction Press. (kg/cm <sup>2</sup> )	Reaction Time (min)	Conversion (%)	Normal Isomer (%)
Rh <sub>2</sub> Cl <sub>2</sub> (CO) <sub>4</sub>	—	110	47	60	17	41.0
	(PhO) <sub>2</sub> POH	95	61	42	26	57.1
	(PhO) <sub>3</sub> PO	100	55	27	18	43.6
	(PhO) <sub>3</sub> P	90	40	60	22	74.4

Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub> 25 mg, ligand 500 mg, AcONa 500 mg, Propylene 10 g, ethylbenzene 20 g, in 100 ml. stainless steel autoclave.

tion reaction of butene-1 proceeded rapidly and smoothly under mild conditions and the valeraldehydes obtained contained a large amount of normal aldehyde. The results are shown in **Table 1**.

The reaction was repeated in the continuous-batch system, as shown in **Fig. 3**. It was observed that the selectivity for normal isomer formation gradually decreased as the number of repeated reactions increased. However, the selectivity was recovered by addition of fresh triphenyl phosphite.

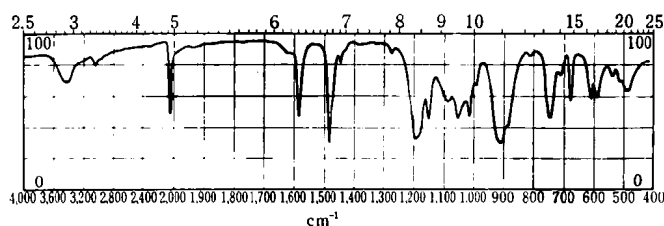
Therefore, any changes in triphenyl phosphite that took place during the course of hydroformylation reaction were examined using <sup>31</sup>P NMR analysis. Chemical shifts of several phosphorous compounds in the catalyst solution were measured directly and shown in **Table 2**.

These data are in good agreement with those of pure phosphorous compounds obtained by

Moedritzer<sup>8</sup>). These data suggest that if the concentration of phosphorous compounds is about 0.5 wt% or more as atomic phosphorus, determination of their types and concentrations is possible.

Chemical changes of triphenyl phosphite were examined by exposing the catalyst solution to air or nitrogen atmosphere. The catalyst solution was prepared from ethylbenzene (20 g), Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub> (25 mg), AcONa (500 mg) and triphenyl phosphite (5 g). The concentration of triphenyl phosphite is about 10 times higher than that of the usual catalyst solution. The results are shown in **Table 3**.

Triphenyl phosphite does not change under nitrogen atmosphere even at high temperatures, but it undergoes hydrolysis in the presence of air. The cause of hydrolysis of triphenyl phosphite to diphenyl phosphite is probably the moisture in the air. Sodium acetate seems to have but slight ef-

Fig. 2 IR Spectrum of  $\text{RhCl}(\text{CO})((\text{PhO})_2\text{POH})_2$ Table 5 NMR Spectra of Stability Test Samples (under  $\text{H}_2$  and  $\text{CO}$  Atmosphere)

Condition	$\delta$ (ppm)	Obsd. Spin-Spin Splitting		Area	Remarks
		No. peaks	$J$ (Hz)		
$\text{H}_2/\text{CO}$ , 110°C, 12-13 kg/cm <sup>2</sup> (for 9 hr)	—	—	—	—	No signal was detected
$\text{H}_2/\text{CO}^*$ , 110°C, 11-12 kg/cm <sup>2</sup> (for 9 hr)	-126.2	Singlet	0	37	Unchanged
$\text{H}_2^*$ , 90°C, 1 atm. (for 9 hr)	-125.9	Singlet	0	38	Unchanged
$\text{CO}^*$ , 90°C, 1 atm. (for 9 hr)	-125.9	Singlet	0	37	Unchanged

 $\text{H}_2/\text{Co}=1/1$ \* Gas was treated with TIBA-toluene solution and  $\text{CaCl}_2$ .

fect on this kind of hydrolysis.

The effects of diphenyl phosphite, triphenyl phosphate and triphenyl phosphite ligands were examined in the hydroformylation of propylene, and the results obtained are shown in **Table 4**. Diphenyl phosphite and triphenyl phosphate have only little influence on the selectivity for normal isomer production.

A new complex,  $\text{RhCl}(\text{CO})((\text{PhO})_2\text{POH})_2$  was formed when diphenyl phosphite was added to a solution of  $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ . Its IR spectrum is shown in **Fig. 2**.

The catalyst solution was exposed in the synthesis gas atmosphere, and the results are shown in **Table 5**. Triphenyl phosphite did not change in the synthesis gas which was treated with a triisobutyl aluminum (TIBA)toluene solution and granular calcium chloride, but it disappeared in the synthesis gas untreated with the TIBA solution. It was found that this synthesis gas originally contained 300 ppm oxygen, that diminished to less than 100 ppm by this TIBA-solution treatment.

Longevity of this catalyst system was examined, and the results obtained are shown in **Fig. 3**. It was observed that the selectivity for normal isomer formation gradually decreased as the reactions were repeated, but the selectivity was recovered by the addition of fresh triphenyl phosphite.

The activity of the catalyst was maintained for a considerable period of time when the synthesis gas was treated with the TIBA-toluene solution. Any change in triphenyl phosphite may be due to

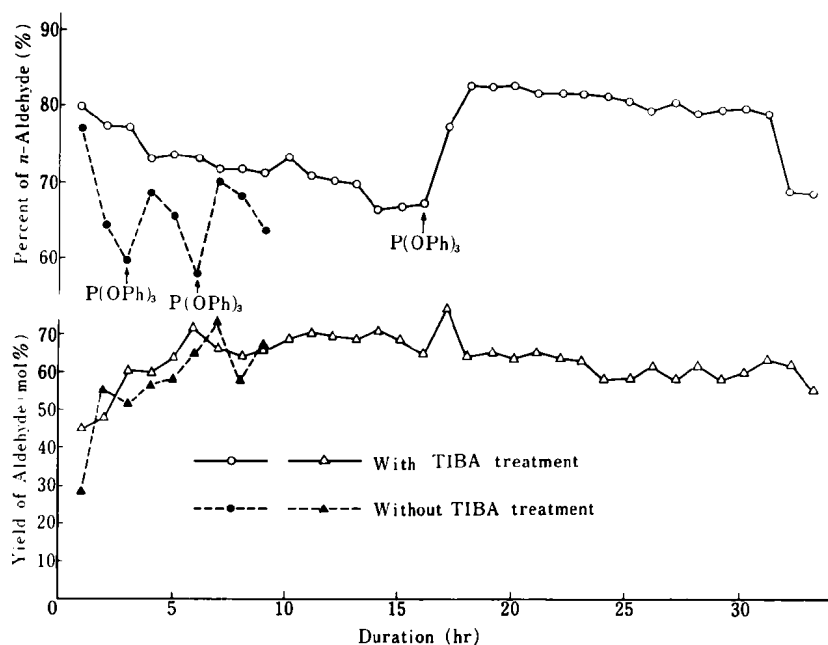
its oxidation to triphenyl phosphate, and to clarify this assumption,  $^{31}\text{P}$  NMR analysis of the used catalyst solution was carried out\*).

The results obtained are shown in **Table 6**. Triphenyl phosphite was oxidized to triphenyl phosphate with a deactivated catalyst and with a catalyst of decreased selectivity. Triphenyl phosphite completely remained unchanged when the synthesis gas was treated with the TIBA-toluene solution. This shows that the change in triphenyl phosphite is due to its oxidation to triphenyl phosphate by the small amount of oxygen found in the synthesis gas. As shown in **Table 4**, triphenyl phosphate has but little effect as ligand.

The treatment of the synthesis gas with the TIBA-toluene solution was effective in preventing the oxidation of triphenyl phosphite to triphenyl phosphate, and the activity of the catalyst was kept unchanged for a long period by this treatment. Thus it was concluded that deactivation of the catalyst is mainly due to the oxidation of triphenyl phosphite to triphenyl phosphate.

Furthermore, additional examination was carried out in which 1% of water was added to this catalyst system. However, its addition had no effects on the activity of the catalyst. On the other hand, triphenyl phosphite was hydrolyzed to diphenyl phosphite in the presence of air as shown

\* In these hydroformylation reactions high content of triphenyl phosphite was used for the purpose of  $^{31}\text{P}$  NMR analysis. The molar ratio of rhodium to triphenyl phosphite was about 1 : 128.



Butene-1 20 ml,  $\text{Rh}_2\text{Cl}_2(\text{CO})_4$  25 mg,  $\text{P}(\text{OPh})_3$  420 mg,  $\text{AcONa}$  500 mg in ethylbenzene (20 g).  
Reaction temp.  $90^\circ\text{C}$ , Reaction press.  $15 \text{ kg/cm}^2$ .

Fig. 3 Effect of TIBA Treatment on the Life Test of Catalyst

Table 6 NMR Spectra of Used Catalyst

Condition	$\delta$ (ppm)	Obsd. Spin-Spin Splitting		Area	Remarks
		No. peaks	$J$ (Hz)		
Deactivated Catalyst	+18.2	Singlet	0	20	Formed $\text{O}=\text{P}(\text{OPh})_3$
Catalyst of Decreased Selectivity (after 8.5 hr reaction)	+18.3	Singlet	0	24	Formed $\text{O}=\text{P}(\text{OPh})_3$
Active Catalyst (after 2 hr reaction)	-126.3	Singlet	0	17	Unchanged
Active Catalyst*	+18.3	Singlet	0	13	Formed $\text{O}=\text{P}(\text{OPh})_3$
Active Catalyst* (after 2 hr reaction)	-126.3	Singlet	0	56	Unchanged

\*  $\text{H}_2/\text{CO}$  gas was treated with TIBA-toluene and  $\text{CaCl}_2$ . Butene-1 was passed through Molex-3A.

in Table 3. It is speculated that hydrolysis of triphenyl phosphite is accelerated by the presence of oxygen. However, it seems that degradation of triphenyl phosphite is due to oxidation rather than to hydrolysis under the hydroformylation conditions.

Moreover, it was found that alkali acetates and amines as dehalogenation agents were effective in sustaining the activity of the catalyst<sup>7)</sup>. It was assumed that these bases prevented the degradation products of ligand from forming a coordinate complex with rhodium.

A 191-hr continuous run was made to establish the catalyst activity of the system, and 3,220 g of aldehyde was obtained using only 6.5 mg of rhodium.

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