Hydroformylation of Olefins Using Rhodium Complex Catalysts (Part 1)*

—Effects of Reaction Variables on Reactivity and Selectivity—

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Summary: A new catalyst system is described for producing normal aldehydes predominantly from α -olefins. The catalyst consists of a rhodium compound, triphenyl phosphite and sodium acetate. Effects of various reaction parameters on the ratio of *n*- to iso-aldehyde are reported. Sodium acetate has been found to be highly selective production of normal isomer and for maintaining the activity of the catalyst for a long period of time.

The rate of aldehyde formation depends on the concentration of rhodium as follows:

$$\frac{d[\text{aldehyde}]}{dt} \propto [\text{Rh}]^{1.0} \quad (\text{at initial state}) \quad \frac{d[\text{aldehyde}]}{dt} \propto [\text{Rh}]^{0.7} \quad (\text{at stationary state})$$

However, the concentration of rhodium has little effect on the *n*/*i* ratio.

1 Introduction

Hydroformylation ("OXO") reaction is an important commercial route for production of aldehydes and alcohols. The best known hydroformylation catalysts comprise simple carbonyls of Group VIII transition metals such as $\text{Co}_2(\text{CO})_8$.

But, the $\text{Co}_2(\text{CO})_8$ catalyst system generally leads to the formation of large amounts of branched aldehydes besides the desirable linear aldehydes. Typical reaction conditions to prevent catalyst decomposition are temperatures from 100 to 180°C and CO/H_2 ratios from 1/1 to 1/1.3 at total pressures from 200 to 300 atm.

This reaction has been extensively reviewed.^{1),2)} Ten years ago, Slaugh et al.³⁾ reported use of modified cobalt catalysts containing organic ligands, e. g., $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$ ("Shell process") for hydroformylation. These catalysts permit lower pressure operations, although requiring somewhat higher reaction temperatures. This process is capable of giving high ratios of straight-chain to branched-chain products, and the main products are alcohols containing but small amounts of aldehydes.

However, a new generation of hydroformylation catalysts, comprising phosphine, phosphite and arsine complexes of rhodium active under mild

reaction conditions, has been reported in the past ten years^{4),10)}. It has also been reported that hydridocarbonyltris(triphenylphosphine) rhodium, $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, is one of the most active catalysts for hydroformylation of olefins and selectivity for aldehyde production is better than 99%⁹⁾.

Such high aldehyde selectivity can also be attained with the rhodium-triphenyl phosphite-sodium acetate catalyst system of the present study. Moreover, the ratio of straight-chain to branched-chain isomers is high and the catalyst life is very long¹⁷⁾.

The purpose of this paper is to report the results of the detailed investigation of olefin hydroformylation employing the rhodium-triphenyl phosphite-sodium acetate catalyst system.

2 Experimental

2.1 Materials

Triphenyl phosphite was purified by vacuum distillation and stored under nitrogen atmosphere. Triphenylphosphine was purified by recrystallization. Other ligands and reagents from Wako Pure Chemical Co. were used without further purification. Commercially available ethylbenzene was distilled in a 35 tray Oldershaw distillation column. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Engelhard Co. The rhodium complexes, *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ¹²⁾, $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ ¹³⁾, $\text{Rh}_6(\text{CO})_{16}$ ¹⁴⁾ and

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$\text{RhH}(\text{CO})(\text{PPh}_3)_3^{18}$ were prepared by the methods cited in the literature. Octene-1, butene-1, *cis*-butene-2, *trans*-butene-2 and propylene were purchased from Phillips Petroleum Co. ("technical" grade). Isobutylene was a commercial product of Maruzen Oil Co. 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

Experiments were performed in a 100ml stainless steel autoclave or a 50ml pressure glass reactor fitted with a magnetic stirrer, a temperature control system, a liquefied olefin charger, and a synthesis gas inlet line.

In the case of experiments with liquid olefins, the olefin in ethylbenzene was charged into the autoclave and then appropriate amounts of ligand, dehalogenation agent and rhodium catalyst were added. The autoclave was purged several times with the synthesis gas and it was further added until the desired reaction pressure was attained. The autoclave was then heated with an electric furnace whose temperature was automatically and electronically controlled. In the case of using gaseous olefins, the autoclave was charged with a solution containing the catalyst, the ligand and the dehalogenation agent. The autoclave was purged several times with the synthesis gas, and the olefin liquefied under high pressure was charged into it, which was then pressurized with the synthesis gas to the desired level. The reaction was usually carried out under constant pressure. During the reaction, the pressure in the autoclave was maintained at any desired level by intermittently charging fresh gas ($\text{H}_2/\text{CO}=1$) from the

synthesis gas inlet.

For relatively low pressure reactions, the 50ml pressure glass reactor was used instead of the stainless steel autoclave.

2.3 Analysis

Quantitative analyses of nonylaldehydes and valeraldehydes were carried out with a Shimadzu model IA gas chromatograph using a thermal conductivity detector and a $2.25\text{m} \times 5\text{mm}$ stainless steel column filled with 20% PEG 6000 on Chromosorb-P at $80\sim 130^\circ\text{C}$.

Quantitative analyses of butyraldehydes were carried out with a Hitachi model K-53 gas chromatograph using a flame ionization detector and a $45\text{m} \times 0.25\text{mm}$, capillary column coated with Carbowax 1,500 at 80°C .

Analyses of carbon monoxide, hydrogen and nitrogen were carried out with a Hitachi model K-23 gas chromatograph using a thermal conductivity detector and a $2\text{m} \times 3\text{mm}$ stainless steel column filled with 60 to 80-mesh active carbon at 100°C .

3 Results and Discussion

3.1 Effects of Ligands

It is known that rhodium complex catalysts allow hydroformylation reaction of olefins to proceed under rather mild conditions.

We studied reactivity and selectivity for normal aldehyde production of various rhodium-ligand complexes, using octene-1 as the raw material. The results obtained are shown in **Table 1**. The use of triphenyl phosphite gave high selectivity for straight-chain aldehyde production, but its reaction rate was lower than that of triphenylphosphine.

Table 1 Hydroformylation of Octene-1 with Various Ligands

Catalyst	Ligand	Reaction Temp. ($^\circ\text{C}$)	Reaction Press. (kg/cm^2)	Reaction Time (min)	Conversion (%)	Normal Isomer (%)
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	—	154	75	160	71	34.1
	$\text{P}(\text{OPh})_3$	120	69	120	65	76.5
	Ph_3N	165	90	40	44	32.3
$\text{Rh}_2\text{Cl}_2(\text{CO})_4$	—	90	33	60	38	63.5
	$\text{P}(\text{OPh})_3$	89	32	55	40	80.0
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	PPh_3	120	70	60	69	74.2
$\text{Rh}_5(\text{CO})_{16}$	—	90	34	90	27	63.6
	$\text{P}(\text{OPh})_3$	90	34	30	54	80.3
	PPh_3	96	60	30	85	77.8
	PBu_3	118	62	30	77	70.7
	$\text{P}(\text{OBu})_3$	90	32	30	37	74.5
	SbPh_3	113	32	120	20	79.4
	SbBu_3	150	34	60	32	72.1

Octene-1 10g, ethylbenzene 20g, Rh 0.13wt% vs. olefin, ligand/Rh=10, $\text{H}_2/\text{CO}=1/1$.

Although hydroformylation with rhodium-triphenylphosphine complex has been studied by many workers, only few papers have been reported on rhodium-triphenyl phosphite complexes⁷⁾ and the details of the reactions have not been discussed. Since triphenyl phosphite is cheaper than triphenylphosphine, some characteristics of the rhodium-triphenyl phosphite catalyst system were investigated by the authors in this series of papers with emphasis directed to industrial applications.

As shown in **Fig. 1**, excess of triphenyl phosphite is required to obtain high selectivity for normal aldehyde production. Selectivity for normal aldehyde formation increases to about 83% at the ratio of triphenyl phosphite ligand to rhodium atom of about 5 (excess ligand); but the selectivity does not significantly change at higher ratios. Similar results were observed by Craddock⁸⁾ and Olivier¹¹⁾ in the case of triphenylphosphine.

3.2 Effects of Dehalogenation Agents

Long induction periods were observed in the hydroformylation reactions catalyzed by rhodium complexes containing a halogen. It is considered

Catalyst: $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Rh 0.13 wt% vs. olefin), octene-1 10g, ethylbenzene 20g, AcONa 500mg, $\text{H}_2/\text{CO}=1/1$.

Fig. 1 Effect of $\text{P(OPh)}_3/\text{Rh}$ Molar Ratio on Normal Isomer in the Hydroformylation of Octene-1

that the active catalytic species is a hydrido-species^{7),9),21)}. The long induction periods suggest the slow formation of catalytically active hydrido-species by hydrogenolysis of the halide complex.

On the other hand, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ are easily available rhodium compounds. The addition of a dehalogenation agent to the catalyst system should be effective when the above compounds are used directly. Evans⁹⁾ has reported that the induction period of hydroformylation reaction was removed by the addition of Et_3N .

Effects of various dehalogenation agents were investigated, and the results are shown in **Table 2**. Induction periods were eliminated by addition of an agent such as AcONa, AcOK, Cu-powder and Zn-powder. Moreover, the *n/i* ratio of aldehydes is somewhat increased by the addition of AcONa.

In **Fig. 2**, the influence of the amount of AcONa added on *n/i* ratio is illustrated. Amines and KOH have proved to be also effective as dehalogenation agents¹⁷⁾. As shown in **Table 3**, the basic agents such as alkali acetates, amines and KOH capable of maintaining the high selectivity for normal isomer production during continuous reaction extending over a considerable period of time. In contrast, the selectivity drops relatively in a short period when the metal powders such as Cu and Zn are employed. Therefore, these bases seem not only to be the dehalogenation agents but also stabilizers of the catalyst. It is speculated that these bases prevent the degradation products of ligand from forming coordinate complexes with rhodium.

3.3 Effect of H_2/CO Molar Ratio

The influence of H_2/CO molar ratio on the selectivity for normal isomer formation was investigated using propylene as a raw material. Reactions were carried out in the 100ml stainless steel autoclave under 30kg/cm^2 at 90°C ; the conversion of propylene ranged from 91 to 97%.

Table 2 Effect of Dehalogenation Agents on the Hydroformylation of Octene-1

Catalyst	Agent	Reaction Temp. ($^\circ\text{C}$)	Reaction Press. (kg/cm^2)	Reaction Time (min)	Conversion (%)	Normal Isomer (%)
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	—	122	69	120	65	76.5
	AcONa	95	67	40	84	82.6
	AcOK	90	78	60	81	80.0
	Zn	122	68	50	65	81.6
	Mg	122	70	90	25	77.7
	Cu	73	62	60	78	84.3
$\text{Rh}_2\text{Cl}_2(\text{CO})_4$	—	71	31	130	45	84.4
	AcONa	72	31	40	47	85.9

Octene-1 10g, ethylbenzene 20g, Rh 0.13 wt % vs. olefin, ligand: P(OPh)_3 , $\text{P(OPh)}_3/\text{Rh}=10$, $\text{H}_2/\text{CO}=1/1$.

Catalyst: $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Rh 0.13 wt% vs. olefin), octene-1 10 g, ethylbenzene 20 g, $\text{P}(\text{OPh})_3/\text{Rh}=10$, $\text{H}_2/\text{CO}=1/1$.

Fig. 2 Effect of AcONa/Cl Molar Ratio on Normal Isomer in the Hydroformylation of Octene-1

Table 3 Effect of Additive on the Life of Catalyst*

Catalyst	Additive	Life of Catalyst (hr)
$\text{RhCl}(\text{CO})-(\text{P}(\text{OPh})_3)_2 + \text{P}(\text{OPh})_3$	—	2
	AcONa	>10
	KOH**	>10
	Cu	5
$\text{RhH}(\text{CO})(\text{PPh}_3)_3 + \text{P}(\text{OPh})_3$	—	4
	AcONa	>10
	$\text{N}(\eta\text{-Oct})_3$	>10
	$\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ **	>10
	NBu_3	>10
$\text{Rh}_2\text{Cl}_2(\text{CO})_4 + \text{P}(\text{OPh})_3$	—	2
	AcONa	>10
	Cu	4
	Zn	3

*Hydroformylation of butene-1.

Reaction temp. 90°C, reaction press. 15 kg/cm².

Rh 6.7mg., added ligand: $\text{P}(\text{OPh})_3$, $\text{P}(\text{OPh})_3/\text{Rh}=20$. Additive 500mg

**KOH 200mg, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ 150mg.

As shown in Fig. 3, the selectivity for normal isomer formation was enhanced as the molar ratio of H_2/CO increased. On the other hand, the yield of aldehyde decreased and that of propane increased steeply when H_2 was increased to 80% and above. The same tendency was observed in the case of rhodium-triphenylphosphine complex¹⁸.

In contrast, in the hydroformylation of propylene using $\text{Co}_2(\text{CO})_8(\text{PBu}_3)_2$, Tucci found that H_2/CO molar ratio had essentially no effect on the selectivity for normal isomer production although a decrease in conversion was observed at very high partial pressures of carbon monoxide¹⁵.

Catalyst: $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ (Rh 0.13 wt% vs. olefin), $\text{P}(\text{OPh})_3$ ($\text{P}(\text{OPh})_3/\text{Rh}=10$), AcONa 500 mg in ethylbenzene (20 g).

Propylene 10 ml, Reaction Temp. 90°C, Reaction Press. 30 kg/cm².

Fig. 3 Effect of H_2/CO Molar Ratio on the Hydroformylation of Propylene

Catalyst: $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ (Rh 0.13 wt% vs. olefin), $\text{P}(\text{OPh})_3$ ($\text{P}(\text{OPh})_3/\text{Ph}=10$), AcONa 500 mg in ethylbenzene (20 g).

Propylene 10 ml, Reaction Press. 30 kg/cm², $\text{H}_2/\text{CO}=60/40$.

Fig. 4 Effect of Reaction Temperature on the Hydroformylation of Propylene

3.4 Effect of Reaction Temperature

Reaction temperatures have a significant influence upon hydroformylation of olefins and product selectivity. As shown in Fig. 4, an increase in reaction temperature above 90°C favored the hydrogenation of propylene. The maximum selectivity and yield of aldehyde appeared in the range 80~100°C. Alcohol was not formed in this system. A similar tendency was observed in the reaction catalyzed by $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ⁸.

3.5 Effect of Total Pressure

The selectivity for normal aldehyde production decreased with increasing total pressures as shown

Table 4 Hydroformylation of Butene-1 with Various Catalyst Concentration

Butene-1	(g)	12.8	12.8	12.2	12.8
RhH(CO)(PPh ₃) ₃	(mg)	59.5	30.3	10.7	5.6
P(OPh) ₃	(mg)	422	213	73	33
Rh wt % × 10 ⁴ (vs. butene-1)		522	266	98	49
Reaction Time	(min)	90	109	166	126
Reaction Temp.	(°C)	90	90	90	90
Reaction Press.	(kg/cm ²)	10–15	10–15	10–15	10–15
Yield of Aldehyde	(g)	16.7	16.1	15.1	4.3
	(%)	84.9	81.9	80.9	21.9
Reaction Rate	(g/hr)				
Initial		21.6	11.3	4.9	1.9
Stationary		21.6	14.7	8.7	3.5
Normal Isomer	(%)	78	77	75	79

Catalyst: RhH(CO)(PPh₃)₃, ligand: P(OPh)₃ in 50ml. pressure glass reactor.

Catalyst: Rh₂Cl₂(CO)₄ (Rh 0.13 wt% vs. olefin), P(OPh)₃ (P(OPh)₃/Rh=10), AcONa 500 mg in ethylbenzene (20 g). Propylene 10 ml. Reaction Temp. 90°C, H₂/CO = 60/40.

Fig. 5 Effect of Total Pressure on the Hydroformylation of Propylene

in Fig. 5. The hydrogenation of propylene increased as the total pressure decreased. The yield of aldehyde was almost independent of the total pressure. A similar tendency was observed by Pruett.⁷⁾

3.6 Effect of Catalyst Concentration

Effects of catalyst concentration on the selectivity for normal isomer formation and the reaction rate were investigated with the hydroformylation of butene-1. Reaction were carried out in the 50ml pressure glass reactor at 90°C and 15kg/cm². The results are shown in Table 4. The *n/i* ratio scarcely depended on the concentration of rhodium in the hydroformylation of butene-1. However, the rate of aldehyde formation was depended on the concentration of rhodium.

At prescribed time intervals, the amounts of synthesis gas consumed were measured and the yields of aldehyde obtained were calculated, and the time-conversion curves are shown in Fig. 6. Reaction rates were calculated from these curves,

Concentration of rhodium (vs. butene-1):
1. 5.22×10^{-2} wt%, 2. 2.66×10^{-2} wt%
3. 9.8×10^{-3} wt%, 4. 4.9×10^{-3} wt%

Fig. 6 Time-Conversion Curves in the Hydroformylation of Butene-1

Fig. 7 The Relationships between Reaction Rate and Concentration of Rhodium

and the plots of relationship between the reaction rate and the concentration of rhodium are illustrated in Fig. 7. The following relationships between the rate of aldehyde formation and the

$\text{Rh}_2\text{Cl}_2(\text{CO})_4$ 25 mg, $\text{P}(\text{OPh})_3$ 420 mg, AcONa 500 mg in ethylbenzene (20 g).
Reaction temp. 90~94°C, reaction press. 25~30 kg/cm².

Fig. 8 Absorption of the Synthesis Gas in the Hydroformylation of Butenes

concentration of rhodium at the initial and stationary state were derived from the slopes of the plots shown in Fig. 7.

The rates are:

$$\frac{d[\text{aldehyde}]}{dt} \propto [\text{Rh}]^{1.0} \quad (\text{at the initial state})$$

$$\frac{d[\text{aldehyde}]}{dt} \propto [\text{Rh}]^{0.7} \quad (\text{at the stationary state})$$

The same results have been reported by Olivier¹⁰⁾, Yamaguchi¹⁹⁾ and Heil²⁰⁾ at the initial state of aldehyde formation. However, the rate of aldehyde formation at the stationary state has not been mentioned.

3.7 Reaction Rate of Butenes

Reaction rates of butene-isomers were compared in Fig. 8. The order of reaction rates is as follows: butene-1 $\gg$ cis-butene-2 $>$ trans-butene-2 $\gg$ isobutylene

Hindered olefins are much less reactive. For example, isobutylene reacts 20~30 times slower than butene-1 and yields 100% iso-valeraldehyde.

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