ELSEVIER

Journal of Molecular Catalysis A: Chemical 144 (1999) 295–306

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Hydroformylation of olefins with formaldehyde in the presence of $RhHCO(PPh_3)_3$

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Received 18 July 1998; accepted 23 October 1998

Abstract

Olefins, such as allyl alcohol, propylene, 1-hexene, styrene, methyl acrylate and acrolein, were hydroformylated with formaldehyde to form corresponding aldehydes. Allyl alcohol and methyl acrylate which have oxygen at β position to double bond showed higher reactivities and selectivities to *n*-products than those of olefins without oxygen such as propylene, 1-hexene and styrene. 4-Hydroxybutanal was formed as a major product from the reaction of allyl alcohol with formaldehyde under nitrogen atmosphere at 100°C and 5 h (yield: 26%, *n-/iso-* = 21). The addition of syn-gas or excess phosphine to the reaction mixture inhibited hydroformylation with decreasing *n-/iso*-ratio. The hydroformylation of olefins without oxygen gave better yield to aldehydes under syn-gas condition. From in situ IR experiments, the formation of formyl ligand coordinated to metal center was observed. Variable temperature NMR experiment was also performed to verify the mechanism. Based on those observations, a plausible reaction mechanism was proposed.

Keywords: Hydroformylation; $RhHCO(PPh_3)_3$; Formaldehyde

1. Introduction

Hydroformylation of unsaturated compounds with syn-gas has been an important industrial process to produce aldehyde from olefin [1–3]. The reactions generally occurred under high pressure in the presence of rhodium catalysts with phosphine ligand. However, the use of formaldehyde instead of syn-gas has several advantages over the syn-gas hydroformylation of olefins (Eqs. (1) and (2)). The hydroformylation with formaldehyde enables the reaction under atmospheric pressure of nitrogen or low pressure of syn-gas. Such a low pressure operation of hydroformylation does not need high-pres-

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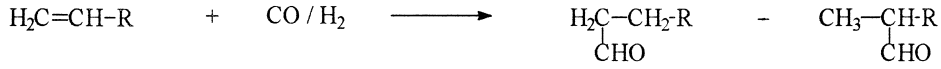
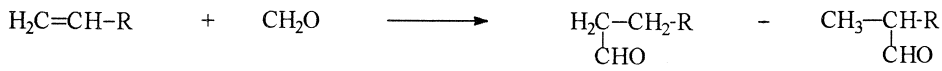
PII: S1381-1169(99)00002-3

sure equipments but could be performed even with glasswares, which would facilitate small scale hydroformylation reactions for the fine chemical industry.



(1)



(2)

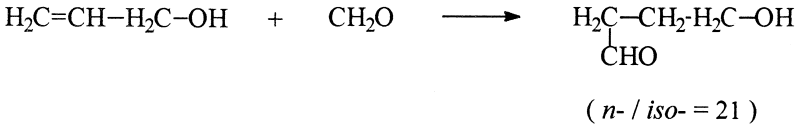
normal *iso*

Although it has several advantages, the hydroformylation of olefins with formaldehyde has been poorly investigated [4–9]. Here, we report the reaction of olefins with formaldehyde under nitrogen atmosphere or reduced pressure of syn-gas in the presence of Rh–phosphine catalytic systems. Especially, the high conversions and selectivities to *n*-isomer were monitored with the olefins, which have oxygen at β position to double bond. A plausible reaction mechanism is discussed.

2. Results

Hydroformylation of olefins with formaldehyde in THF was performed. The reaction was carried out under four different reaction conditions (Fig. 1): reaction condition 1, with formaldehyde under nitrogen atmosphere; reaction condition 2, with formaldehyde under atmospheric syn-gas; reaction condition 3, with formaldehyde under 5 atm syn-gas pressure; and reaction condition 4, without formaldehyde under 5 atm syn-gas pressure.

The formation of *n*- and *iso*-aldehyde was strongly dependent on the reaction conditions. The reaction of olefins containing oxygen at β position to double bond with formaldehyde yielded *n*-product in excellent reactivities and high selectivities (Fig. 1(a,b)). Especially, the reaction of allyl alcohol with formaldehyde gave the highest reactivity to form *n*-product, 4-hydroxybutanal with high selectivity of *n-/iso*-ratio of 21 (Eq. (3)).



(3)

The yield of 4-hydroxybutanal reached up to 23.4% (Fig. 1(a), condition 1). The turnover number for Rh catalyst was 75/atom h. The addition of 1 atm syn-gas to the reaction system slightly decreased the yield of *n*-product to 20.2% (Fig. 1(a), condition 2). As syn-gas pressure increased to 5 atm in the presence of formaldehyde, the yield of *n*-product further decreased to 12.3% (Fig. 1(a), condition 3). The formation of *iso*-product 3-hydroxy-2-methylpropanal was promoted to give 10%

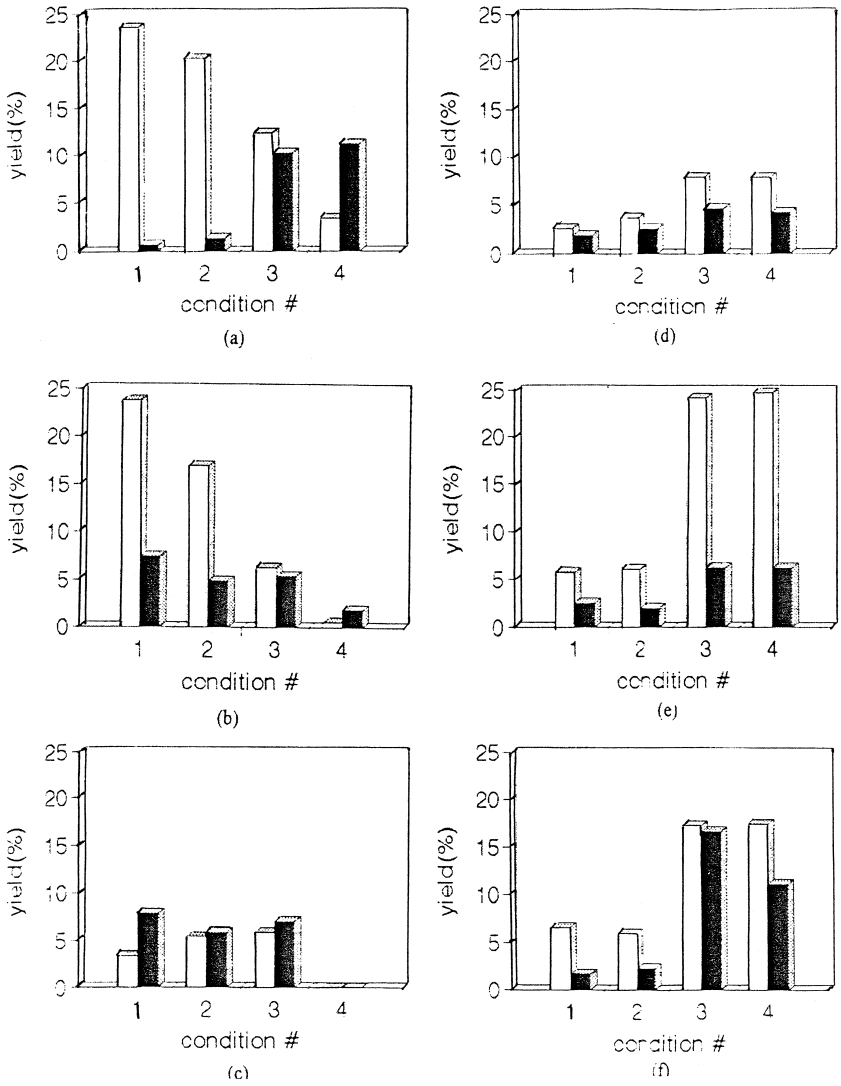
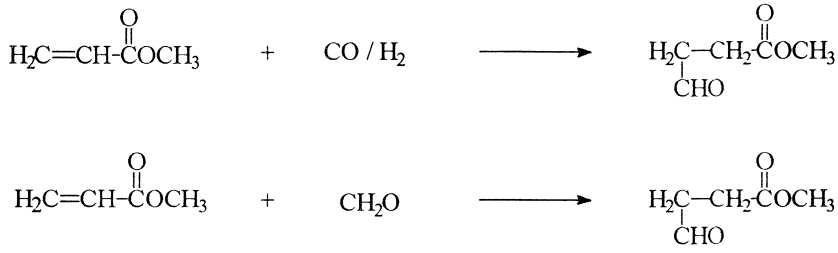


Fig. 1. Hydroformylation with formaldehyde: (a) allyl alcohol, (b) methyl acrylate, (c) acrolein, (d) propylene, (e) 1-hexene, (f) styrene; condition 1, w/ CH_2O under N_2 1 atm; condition 2, w/ CH_2O under CO/H_2 1 atm; condition 3, w/ CH_2O under CO/H_2 5 atm; condition 4, w/o CH_2O under CO/H_2 5 atm ($CO:H_2$ = 1:1, reaction time = 7 h, temperature = 100°C; white column = *n*-product, black column = *iso*-product).

yield in 5 atm syn-gas pressure, while reactions under conditions 1 and 2 gave negligible yields of *iso*-product. It is important to note that the yield of 4-hydroxybutanal was reduced to 3.3% without formaldehyde under 5 atm syn-gas pressure (Fig. 1(a), condition 4) with similar yield of *iso*-product. These experiments indicated that the formation of *n*-product, 4-hydroxybutanal, resulted from the reaction of olefin with formaldehyde and was inhibited by syn-gas. On the other hand, the *iso*-product, 3-hydroxy-2-methylpropanal, was mainly produced from the reaction of allyl alcohol with syn-gas.

The same trend was observed for the hydroformylation of methyl acrylate under the same reaction conditions mentioned above (Eq. (4)).



(4)

Methyl 3-formylpropanoate, *n*-isomer, was the major product from the reaction of methyl acrylate with formaldehyde. The reaction was inhibited by the addition of syn-gas as was allyl alcohol reaction. Without formaldehyde, the yield of *n*-isomer was negligible. The yield of *iso*-product, methyl 2-formylpropanoate, showed small change in the presence of syn-gas and decreased without formaldehyde (Fig. 1b, conditions 3 and 4). Same reaction was performed with acrolein, which has oxygen of carbonyl group at β position to double bond. Interestingly, there was no preference for the *n*-product or *iso*-product indicating that the carbonyl oxygen has little effects on the reactivity of olefins. Hydrogenation of olefin was another major reaction pathway during the hydroformylation of methyl acrylate and acrolein. The reactivity pattern showed that the presence of β oxygen to double bond of olefin was an important factor for the high reactivity and selectivity toward *n*-aldehyde product for the hydroformylation reaction with formaldehyde.

Hydroformylation of olefins without oxygen in the substituent, propylene, 1-hexene and styrene, was performed under the same reaction conditions. The reaction of these olefins with formaldehyde showed poor reactivity and selectivity toward aldehydes (in the case of propylene, yield: 4.4%, selectivity: 70%, *n-/iso-*: 1.45) (Fig. 1(d), (e), (f), condition 1). As syn-gas was introduced to the reaction mixture, reactivities to both *n*-product and *iso*-product increased compared to the reactions of allyl alcohol. The yield of *n*-product from propylene, *n*-butanal, improved from 2.6% to 4.7% as the system pressurized with 5 atm syn-gas (Fig. 1(d), conditions 2 and 3). Under the 5 atm syn-gas pressure, the yield of *n*-product was not affected by the presence of formaldehyde (Fig. 1(d), conditions 3 and 4). The selectivities were not much changed in four reaction conditions. The same trend was observed for the reactions of 1-hexene under four reaction conditions showing strong dependence on the pressure of syn-gas. The yield of *n*-product, *n*-heptanal, increased four times from 6% to 24% as the syn-gas pressure increased from 1 atm to 5 atm (Fig. 1(e), condition 3). The yield of *n*-product from styrene, 3-phenylpropanal, was 6.5%, and increased to 17.3% in atmospheric syn-gas and 5 atm (Fig. 1(f), conditions 2 and 3). For olefins such as propylene, 1-hexene, and styrene which do not have β oxygen in common, showed similar reactivity changes under the four reaction conditions. They gave higher productivities of aldehyde under syn-gas than formaldehyde.

2.1. Hydroformylation of 4-hydroxy-1-butene

The presence of oxygen at β position to double bond improved reactivity and selectivity to *n*-product indicating strong participation of oxygen atom during catalytic reaction with the formation of 5-membered metallacyclic ring compound. To investigate the positional effect of oxygen in the side group of olefin, a homo allylic compound, 4-hydroxy-1-butene, which has oxygen at γ position to double bond, was used to perform the hydroformylation reaction with formaldehyde and/or syn-gas.

As shown in Fig. 2, the reaction of 4-hydroxy-1-butene with formaldehyde showed similar reactivity pattern to that of propylene instead of allyl alcohol with negligible effect of γ oxygen. The

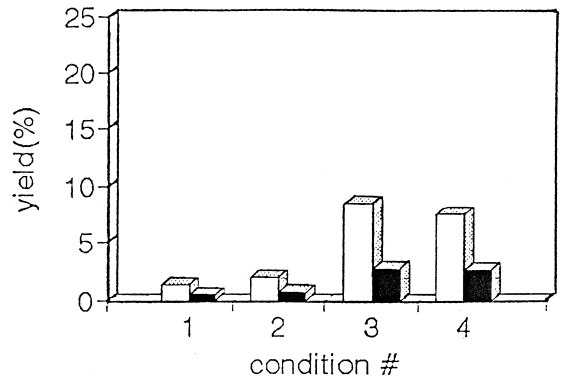


Fig. 2. Hydroformylation of 4-hydoxy-1-butene: condition 1, w/ CH_2O under N_2, 1 atm; condition 2, w/ CH_2O under CO/H_2 1 atm; condition 3, w/ CH_2O under CO/H_2 5 atm; condition 4, w/o CH_2O under CO/H_2 5 atm ($CO:H_2 = 1:1$, reaction time = 7 h, temperature = 100°C; white column = *n*-product, black column = *iso*-product).

yield of *n*-product from the hydroformylation reaction with formaldehyde (condition 1) was very poor and increased by the addition of syn-gas. The yield of *n*-aldehyde increased from 2.0% to 8.5% as syn-gas pressure increased from 1 atm to 5 atm (Fig. 2, conditions 2 and 3). The presence of formaldehyde did not noticeably affect for the reaction under syn-gas (Fig. 2, conditions 3 and 4). The reaction pattern of 4-hydroxy-1-butene was rather similar to that of propylene.

2.2. In situ ir spectroscopy study

In situ IR spectra of the reaction mixture were obtained (Fig. 3). The reaction of propylene with formaldehyde in IR cell was performed under the same reaction conditions as the batch reactions

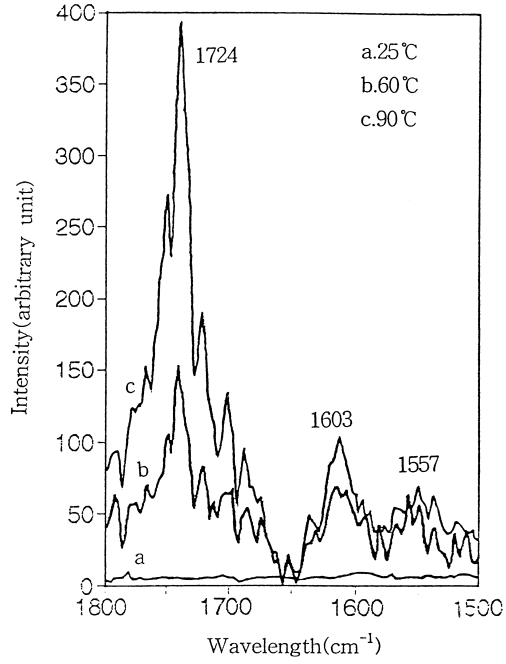


Fig. 3. In situ high-pressure IR spectra of hydroformylation of propylene with formaldehyde.

described above. As the temperature increased, formaldehyde was generated from paraformaldehyde with a characteristic peak at 1724 cm^{-1}. Along with the increase of the concentration of formaldehyde, the peak at 1603 cm^{-1} started to increase. The peak at 1603 cm^{-1} was assigned to the stretching frequency for the formyl group coordinated to the metal center, which is similar to the reported value of formyl ligand coordinated to iridium metal center, $IrClH(CHO)(P(CH_3)_3)_3$ which appeared at 1600 cm^{-1} [10–12].

As the reaction proceeded, the peak at 1760 cm^{-1} from the product for butyraldehyde increased. At region between 1800 and 2100 cm^{-1}, there was no detectable peak increase due to the formation of metal carbonyl ligand, indicating no significant decomposition of formaldehyde to syn-gas in the course of hydroformylation reaction with formaldehyde. It was difficult to monitor the formation of Rh–H bond due to the presence of the starting material Rh complex and the high noise level of the IR spectra of the reaction mixture. Rhodium carbonyl peak did not increase very much in the course of reaction indicating no significant decomposition of formaldehyde to syn-gas.

2.3. Excess phosphine effects

Phosphine has been one of the essential components for hydroformylation of olefin with syn-gas. In the presence of excess phosphine, hydroformylation reaction generally showed saturation kinetics under syn-gas. The reaction of propylene with syn-gas yielding aldehyde in the presence of excess phosphine showed saturation kinetics after 1 h (Fig. 4(a)). On the other hand, the hydroformylation of allyl alcohol with formaldehyde showed the maximum yield at 5 molar equivalents of phosphine to rhodium catalyst (Fig. 4(b)). Hydroformylation of allyl alcohol with formaldehyde was inhibited by the excess phosphine. The difference in reactivity using excess phosphine suggested different reaction pathway of formaldehyde hydroformylation from syn-gas reaction.

2.4. Variable temperature ^{1}H-NMR study

Although the reaction conditions were quite different from those described above, variable temperature ^{1}H-NMR studies of reaction mixture containing Rh complex, paraformaldehyde, allyl

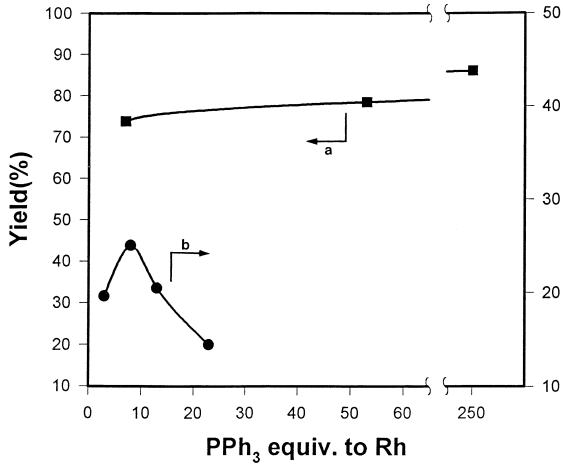


Fig. 4. Excess phosphine effect: (a) hydroformylation of propylene with syn gas 13.5 atm (reaction time = 1 h, temperature = 100°C), (b) hydroformylation of allyl alcohol with formaldehyde under N_2 1 atm (reaction time = 5 h, temperature = 100°C).

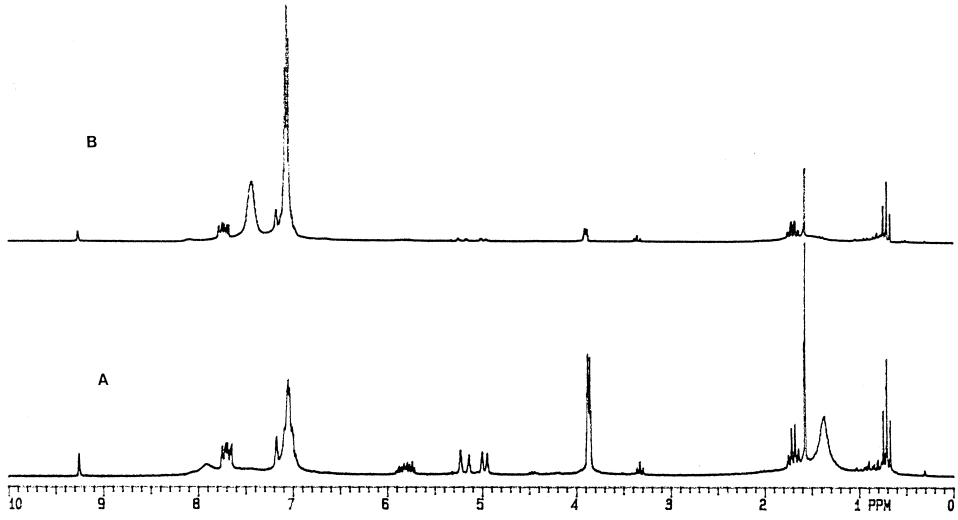


Fig. 5. ^{1}H-NMR spectra of reaction mixture of $RhH(CO)(PPh_3)_3$ and allyl alcohol in C_6D_6 at 65°C (A) without PPh_3 and (B) with PPh_3.

alcohol, and triphenylphosphine in C_6D_6 were performed to detect the possible reactive species and to understand the reaction mechanism in the course of hydroformylation reaction. As the temperature was raised up to 45°C, paraformaldehyde was decomposed to formaldehyde, which showed the characteristic peak at 8.75 ppm. Propanal was detected as the major product from two NMR spectra of the reaction mixture of Rh complex and allyl alcohol with and without triphenylphosphine at 65°C as shown in Fig. 5.

The loss of one of three triphenylphosphine ligands in $RhHCO(PPh_3)_3$ complex was characterized by the disappearance of the peak around 7.4 ppm, while the peak at 9.27 ppm for aldehydic proton of

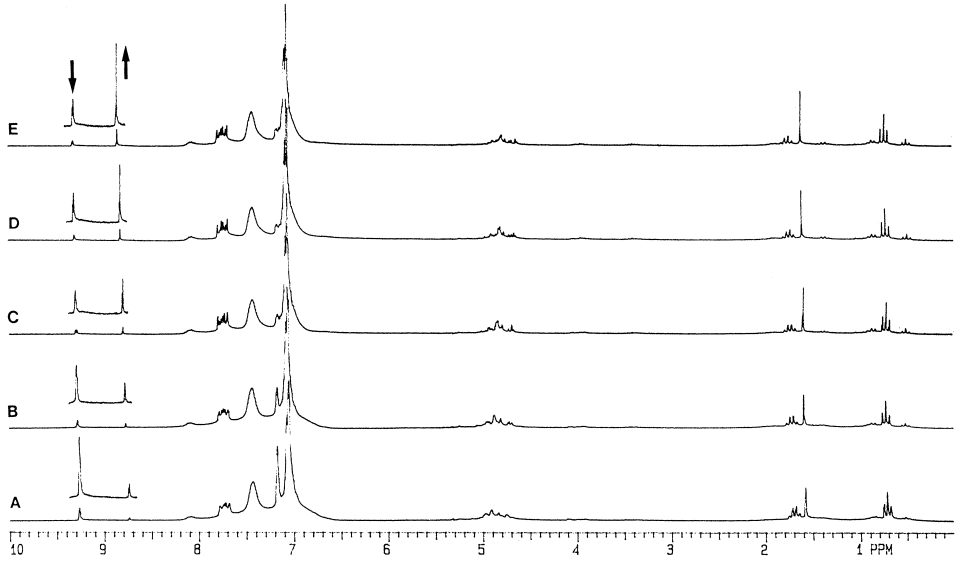


Fig. 6. ^{1}H-NMR spectra of reaction mixture of $RhH(CO)(PPh_3)_3$, allyl alcohol, PPh_3, and $(CH_2O)_X$ in C_6D_6 at the temperature of (A) 25°C, (B) 35°C, (C) 45°C, (D) 55°C, (E) 65°C.

the organic product appeared. Propanal may be formed by the isomerization of double bond in allyl alcohol, followed by the corresponding tautomeric isomerization. We also found out that the Rh–H peak at −9.27 ppm disappeared, which might be ascribed to the change in the environment of the Rh metal center.

Fig. 6 showed the variable NMR spectra of the reaction mixture of Rh complex, allyl alcohol, triphenylphosphine, and paraformaldehyde which resulted in hydrogenated and tautomerized products in catalytic amounts.

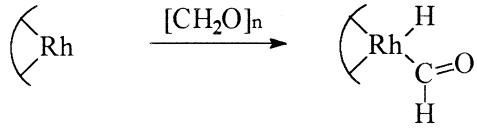
The interesting fact was that the peak at 8.75 ppm for the aldehydic proton of paraformaldehyde increased as the peak at 9.27 ppm for the aldehydic peak for propanal decreased. This fact suggested that the consumption of formaldehyde was necessary to continue the reaction. For several hydrido formyl complexes of Ir(III), π-bound aldehyde complexes have not been observed. Rather the peak for the formyl group coordinated to Ir metal was observed at 15.0 ppm [10–12]. However, the corresponding peak for Rh-formyl complex was not detected in the reaction conditions mentioned above.

3. Discussion

3.1. Formation of formyl ligand

The use of formaldehyde as a source of syn-gas could give us several advantages such as simple reaction system without using high pressure equipments and control of *n-/iso*-selectivity. Hydroformylation reaction could be even performed in a glass reactor if formaldehyde substituted syn-gas. However, the study on the use of formaldehyde instead of syn-gas has not received much attention. Among the tested olefins, allyl alcohol showed excellent reactivity with formaldehyde to form 4-hydroxybutanal, *n*-product, with excellent *n-/iso*-ratio of 21 under mild reaction conditions.

In the course of hydroformylation with formaldehyde, there are two kinds of reaction pathway. Syn-gas is formed from the decomposition of formaldehyde which participates in the hydroformylation reaction. The other possibility is the formation of formyl ligand to metal center followed by the addition of formyl group to olefin. The experimental results strongly supported the latter route for formaldehyde hydroformylation. If syn-gas was generated from formaldehyde decomposition and became reactant to hydroformylation, the formation of metal carbonyl could be expected and monitored in IR spectroscopy. However, the formation of Rh carbonyl was not observed in in-situ IR study. There was no detectable peak increase between 1800 cm^{-1} and 2100 cm^{-1} in IR spectrum ascribed to the formation of Rh carbonyl complexes. However, the formation of formyl ligand coordinated to Rh center was observed at 1604 cm^{-1} in in situ IR spectrum (Eq. (5)).



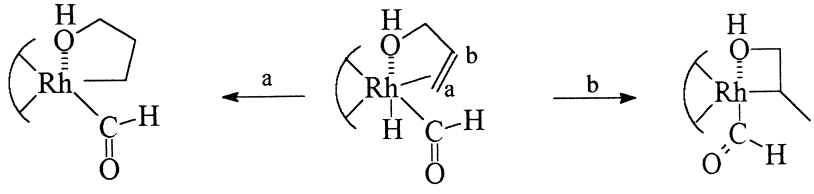
(5)

The oxidative additions of aldehyde C–H bond to d^8 and d^{10} transition metal centers have been reported [10–16]. The presence of formyl group without syn-gas formation during the reaction

suggested that formaldehyde was oxidatively added to metal center to form formyl ligand followed by the coupling of formyl group with olefin to form aldehyde.

3.2. Oxygen participation to form metallacyclic complex

As was observed from the hydroformylation of allyl alcohol with formaldehyde, the presence of β oxygen in side group was an important part for the high reactivity and selectivity to form 4-hydroxybutnal, *n*-product. The origin of the oxygen effects would be the coordination of oxygen atom to Rh metal center along with the olefin coordination to form a metallacyclic compound (Eq. (6)). This fact was verified from the ^{1}H-NMR spectra of the reaction mixture of Rh complex with allyl alcohol, which showed the coordination of allyl alcohol to the Rh metal with the disappearance of Rh–H peak. Furthermore, the formation of cyclic ligand to rhodium center was closely related to the high selectivity toward *n*-product, 4-hydroxybutanal. The next step following the cyclic formation was the hydride transfer to olefin to form σ-bonded cyclic ligand. The selectivity could be controlled in this step as depicted in Eq. (6).



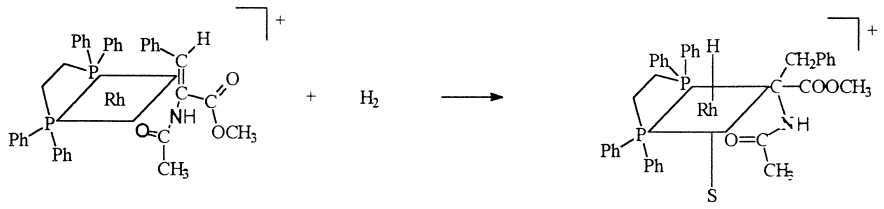
(6)

If hydride is transferred to α carbon of olefin, it will form 5-membered metallacyclic ring compound. The formation of 5-membered metallacyclic ring complex is a thermodynamically stable process and will lead to *n*-product. On the other hand, if the hydride is transferred to β carbon of olefin, the product will be 4-membered metallacyclic ring complex with large ring strain to give *iso*-product. The participation of β oxygen was further supported by the inhibition of syn-gas. It is necessary to open empty coordination sites to participate oxygen and double bond to metal center. At high pressure of CO, however, the formation of empty coordination site on rhodium metal would be hindered, and the coordination of allyl alcohol be suppressed. It is also important to note that hydroformylation of allyl alcohol with formaldehyde was inhibited by high concentration of phosphine (Fig. 4(b)). The excessive phosphine would block the coordination site on Rh metal center and inhibit the coordination of allyl alcohol. The blocking of coordination site would also prohibit the oxidative addition of formaldehyde to form formyl and hydride ligand.

The position of oxygen in olefin was also an important factor for the hydroformylation reaction. The reaction of 4-hydroxy-1-butene with γ oxygen to double bond with formaldehyde did not give oxygen promotion effect. Interestingly, its reactivity was rather similar to that of propylene and 1-hexene. The same 5-membered ring compound was expected to be formed after hydride migration to β carbon of double bond. Nevertheless, the reactivity of 4-hydroxy-1-butene became close to those of propylene and 1-hexene. One of the possible explanation was the presence of steric hindrance of cyclic compound with phosphine ligand. The 5-membered ring compound thus formed has the methyl group on α carbon in Rh metal, and it might have steric hindrance with triphenylphosphine ligands.

The neighboring oxygen group participation in olefin hydrogenation was observed in many reactions with metal complexes [17,18]. The coordination of oxygen in methylacetamidocinnamate

was reported to be a key step for the hydrogenation of olefin, especially for asymmetric catalytic hydrogenation (Eq. (7)).



(7)

Methylacetamidocinnamate was coordinated to rhodium metal via oxygen of acetyl as well as double bond, and after hydride migration into β carbon of olefin it formed stable 5-membered metallacyclic ring compound. The formation of cyclic compound was a driving force for high reactivity.

3.3. Proposal of plausible reaction mechanism

From the experiments described above, two mechanistic aspects were identified: the first was the formation of formyl group coordinated to metal center from in situ IR experiments, and the second

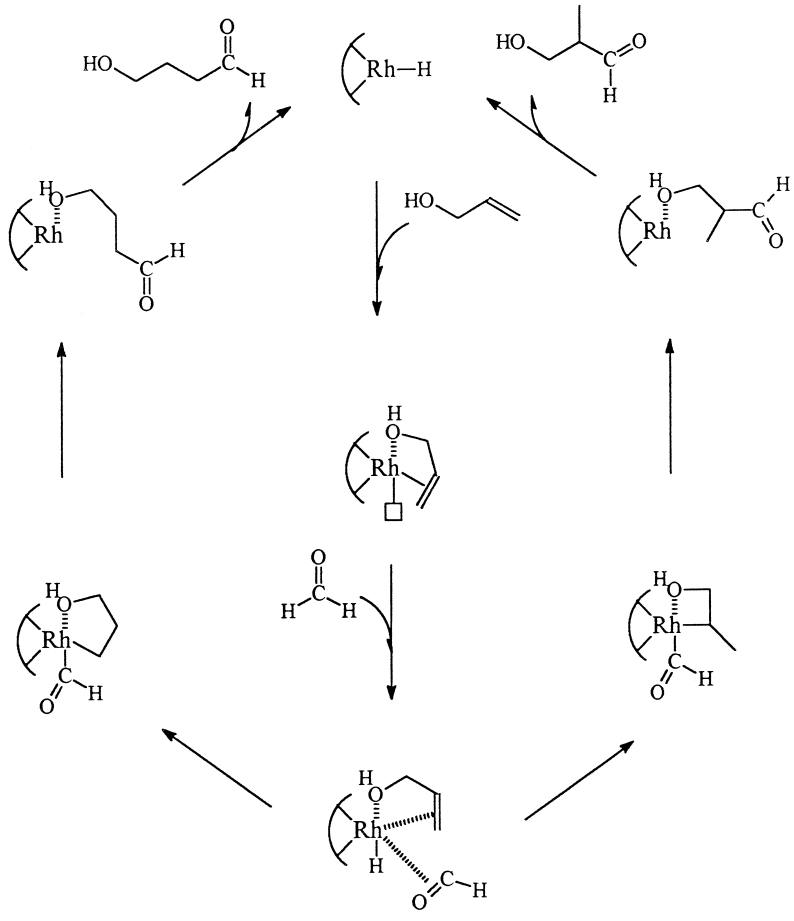


Fig. 7. Proposed mechanism of hydroformylation with formaldehyde.

was the β oxygen participation to form a metallacyclic ring compound in allyl alcohol hydroformylation. Based on the two major observations, a plausible mechanism was proposed in Fig. 7.

Allyl alcohol was coordinated to Rh metal center to form π-bonded metallacyclic complex, then formaldehyde reacted with rhodium complex to give formyl ligand and hydride coordinated to the Rh metal. Then, hydride was migrated to the double bond to form metallacyclic compound. If the hydride was transferred to the α carbon of the double bond, the product would be a 5-membered metallacyclic ring compound, and if transferred to the β carbon, a 4-membered ring compound [19]. The metallacyclic ring compounds coupled with formyl ligand to give aldehyde products and catalytically active Rh species were regenerated. However, it is possible that formaldehyde was activated to form formyl ligand followed by the coordination of allyl alcohol. Experiments to understand the detail mechanism are under investigation.

4. Conclusions

The hydroformylation reaction of olefin was performed with formaldehyde and compared with the reaction with syn-gas. Olefins with oxygen at β position to double bond in side group, such as allyl alcohol and methyl acrylate, showed excellent reactivity toward hydroformylation with high *n-/iso*-ratio. Especially, the selectivity to *n*-product from allyl alcohol was extremely high with *n-/iso*-ratio of 21. The additions of syn-gas and excess phosphine inhibited the formation of *n*-product. It was suggested that olefin with β oxygen would form metallacyclic ring compound in the course of the reaction. Formyl ligand coordinated to metal center was observed at 1604 cm^{-1} from in situ IR experiments. Based on the experimental observations above, the activation of formaldehyde to form formyl ligand and the direct coupling of formyl ligand with olefin after hydride migration were discussed.

5. Experimental

5.1. Materials

Reagents were the extra pure grade and used as received. Solvents were distilled from appropriate drying agents.

5.2. General procedure for hydroformylation of olefins

In a 10 ml of autoclave were placed $RhHCO(PPh_3)_3$ (8.2 mg, 8.90 mmol), PPh_3 (11.8 mg, 45 mmol) and paraformaldehyde (225 mg, 7.5 mol), to which allyl alcohol (174 mg, 3.0 mol) in THF (2.66 g) was added. The autoclave was purged with nitrogen or syn-gas several times. The reactor was heated in an oil bath under the reaction conditions of 100°C and 7 h. Paraformaldehyde was in situ decomposed to form formaldehyde under the reaction conditions which were monitored by IR spectroscopy. Four different types of reactions were performed: condition 1, atmospheric pressure of nitrogen with formaldehyde; condition 2, atmospheric pressure of syn-gas with formaldehyde; condition 3, 5 atm of syn-gas at room temperature with formaldehyde; and condition 4, 5 atm syn-gas at room temperature without paraformaldehyde. In addition to allyl alcohol, different types of olefins such as methyl acrylate, acrolein, propylene, 1-hexene, styrene, and 4-hydroxy-1-butene were tested. After reaction was completed, the autoclave was cooled down to room temperature, and the product

were analyzed by a gas chromatography (Hewlett Packard 5880, FID detector, Capillary column FFAP 50 m). Each component was identified by comparing gas chromatogram with authentic materials and/or GC/MSD spectrometer (Hewlett Packard 5890/5971 with FFAP 50 m capillary column). The effects of excess phosphine were performed under the same conditions described above in two cases: propylene with syn-gas and allyl alcohol with formaldehyde varying phosphine/rhodium ratio.

5.3. In situ infrared spectroscopy

In situ IR spectra were obtained from a home made high pressure IR reactor with CaF_2 windows. All the reaction conditions and procedure were same as the autoclave reaction. After the reactants were charged, the IR reactor was heated in a rate of 1°C/min up to a desired temperature. IR spectra were recorded at every 10°C with IR spectrometer (Midac model 101025).

5.4. Variable temperature ^{1}H-NMR study

^{1}H-NMR spectra of a reaction mixture of $RhHCO(PPh_3)_3$ (4.5 mg, 5.5 mmol), allyl alcohol (20 mg, 340 mmol), paraformaldehyde (20 mg, 670 mmol), and triphenylphosphine (7.0 mg, 27 mmol) were measured in 5 mm NMR tubes in saturated solution with 1 ml of deuteriated benzene as a solvent at various temperatures and were referenced to tetramethylsilane (TMS) with Varian Gemini-200 MHz spectrometer. Variable temperature studies were carried out by using a Varian variable temperature accessory calibrated by the Van Geet method [20].

Acknowledgements

We thank KOSEF(96-0501-01-01-3) for financial support and STEPI for its fund to Dr. G.A. Korneeva.

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