

Hydroformylation, Hydrogenation, and Isomerization of Olefins over Polymer-Immobilized Rhodium Complexes

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The rhodium complex $(-\text{RhCl}(\text{CO})_2)$ coordinatively bonded to the phosphine group on polystyrene-coated silica gel is prepared and its catalytic activity is tested for hydroformylation, hydrogenation, and isomerization of olefins in the vapor phase. The dependence of rates and product yields on the partial pressures of hydrogen, carbon monoxide, and olefins is examined. The reaction mechanisms have been elucidated by applying the transient response method. The results thus obtained are compared with those of homogeneous catalysis.

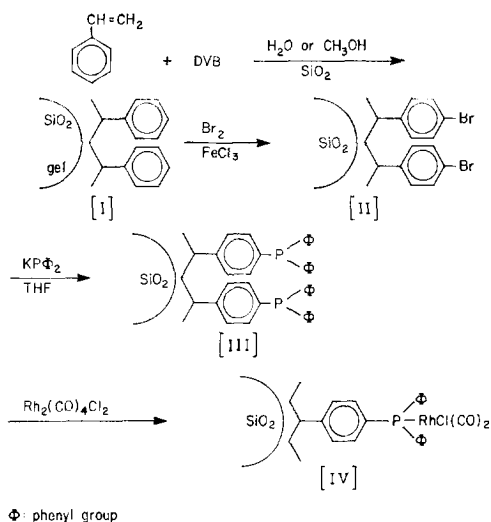
INTRODUCTION

Homogeneous catalysts are, in many cases, more active and more selective than heterogeneous ones (1, 2). However, homogeneous catalysts sometimes pose the problems of product contamination and of catalyst loss unless the catalyst is readily separated from the products. Self-aggregation of active species is another problem. A great advantage would be secured if the high activity and selectivity which homogeneous systems exhibit would be preserved in heterogeneous systems. Immobilized homogeneous catalysts on polymers or other supports could be an example of such devices (3, 4). These attempts have recently been the object of several research groups (5-10). When the reactants have to diffuse through a swollen organic polymer matrix to reach a bound catalyst site, the reaction rates may be limited by the rate of diffusion. Hence a catalyst is developed in which active species are anchored to ceramic of large surface area to eliminate the bottleneck of diffusion.

Arai *et al.* previously reported that the rhodium complex coordinatively bonded to the phosphine group on polystyrene-coated silica gel is an efficient catalyst for hydroformylation of olefins under mild reaction conditions (11). This coating method can be generally applied to most of the organic polymers containing functional groups. Moreover, the inorganic support is generally very stable toward solvent, heat, and mechanical shock.

EXPERIMENTAL

The copolymers of styrene and divinylbenzene (DVB) were prepared in the presence of azobisisobutyronitrile (AIBN) and silica gel (BET surface area, 293 m²/g). For preparation of Catalyst A emulsion polymerization in an aqueous solution was adopted, and for Catalyst B, polymerization in methanol solution was applied, the silica gel being coated with the copolymer. The polymer was brominated by using bromine and an iron catalyst under nitrogen atmosphere (12).



A reaction of the brominated copolymer with an H_4 folate solution of potassium diphenylphosphide yielded polymeric ligand [III]. A treatment of polymer [III] with a benzene solution of $Rh_2(CO)_4Cl_2$, which was made from $RhCl_3 \cdot 3H_2O$ and carbon monoxide under nitrogen (13), afforded substance [IV], in which the rhodium was fixed via Rh-P coordination to the polymer (14). The rhodium content was determined by atomic absorption spectroscopy.

Catalytic reactions were performed in a 50-cm Pyrex glass tubular reactor, 18 mm in diameter. The reactor was positioned vertically in an electric furnace and was usually loaded with 1.0 or 1.5 g of catalyst, and 2 mm of Pyrex glass beads were packed above and below the catalyst bed. The gaseous reactants, olefin, hydrogen, and carbon monoxide, were supplied from their respective cylinders. After being purified and measured separately, the reactant gases were thoroughly mixed at room temperature. The reaction temperature was controlled to an accuracy of $\pm 1^\circ C$. The reactions were normally performed at temperatures between 100 and $150^\circ C$ under atmospheric pressure. W/F was ranged between 5 and 17 g-cat·hr/mol, where W is the catalyst weight (grams) and F is the total gas flow rate (moles per hour). The order of the reaction was determined by

varying the partial pressures of olefin, carbon monoxide, and hydrogen with nitrogen as a diluent. The gaseous products were cooled in a small water condenser annexed to the bottom of the reactor. The condensed aldehyde products were periodically collected in a glass flask containing water and were analyzed by gas chromatography, using a 3-m PEG column at $110^\circ C$ for aldehydes. Small quantities of gas were sampled periodically during the reaction and analyzed with a gas chromatograph using a 5-m sebaconitrile column at $25^\circ C$ for paraffins. The steady state was attained 1.5 hr after the reaction was started. Therefore, the reaction rate data observed between 2 and 5 hr were averaged and employed for kinetic analysis. The reaction orders were determined for overall reaction from the plots of $\log v$ against $\log P$, where v is the rate of product formation per unit weight of catalyst (mol/hr·g-cat), and P is the partial pressure (atmospheres) of each reactant gas. The activation energies were calculated from the plot of $\log v$ vs $1/T$ (100 – $150^\circ C$).

The infrared spectroscopic observation of the catalysts was made by the KBr method using a JASCO-2A spectrophotometer. Rhodium contents, BET surface area, and ν_{CO} of these catalyst are summarized in Table 1.

RESULTS AND DISCUSSION

The hydroformylation of ethylene to propionaldehyde can be expressed by Eq. (1):



Catalysts A and B both demonstrated considerable catalytic activity for hydroformylation under mild reaction conditions, and the deactivation of the catalysts was negligible during the reaction periods for the kinetic studies. In order to compare these activities with those of the other rhodium catalysts, the reactions using $RhCl(CO)(PPh_3)_2$ on silica gel, $RhCl_3$ on

TABLE 1
Properties of Catalysts

Catalyst	Rh content (wt %) ^a	Surface area (m ² /g) ^b	ν_{CO} (cm ⁻¹)
Catalyst A ^c	3.1	42	2080–2020
Catalyst B ^d	6.5	10	2075–1995
Organic polymer-P Φ_2 -RhCl(CO) ₂	5.2	1	2085–2030

^a RhCl(CO)(PPh₃)₂-SiO₂, 10.3 wt%; RhCl₃-SiO₂, 7.9 wt%; Rh metal-SiO₂, 9.0 wt%.

^b SiO₂ gel, 293 m²/g.

^c Immobilized catalyst A: emulsion polymerization.

^d Immobilized catalyst B: solution polymerization.

silica gel, and Rh metal on silica gel were attempted under the same conditions. These catalysts are far less active in hydroformylation and the activities decreased gradually (1). Organic polymer (polystyrene)-P Φ_2 RhCl(CO)₂ catalyst had little activity for hydroformylation under such mild conditions because of the small surface area of the polymer. Catalyst A was about four times more active than Catalyst B. The

ratio was about proportional to that of the surface areas indicated in Table 1. The contact time (W/F) was varied from 6 to 17 g-cat·hr/mol by regulating the total flow rate at a constant feed composition (C₂H₄:H₂:CO = 1:2:2). As one would expect, the yield increased with contact time (1).

Hydroformylation, hydrogenation, and isomerization products from various olefins are shown in Table 2. The reactivity of olefins toward hydroformylation under the same reaction conditions is in the decreasing order: ethylene > propylene > 1-butene. However, neither *cis*- nor *trans*-2-butene was converted into the corresponding aldehyde.

The straight-chain aldehyde was obtained more frequently than was the branched one from a given olefin, which is analogous to the homogeneous system and also to other polymer-loaded catalysts. The activation energy of straight-chain aldehyde formation was lower than that of branched-chain aldehyde for propylene and butene hydroformylation, presumably because *n*-alkyl complexes are more stable than those of

TABLE 2
Reactivity of Olefins over Immobilized Catalyst^a

Olefin	Product	Reaction order ^b		Rate (10 ⁻⁵ mol/hr·g-cat)	Activation energy ^c (kcal/mol)
		Olefin	H ₂ CO		
C ₂ H ₄	C ₂ H ₅ CHO	1.1	0.8 -0.5	43.1	10.2
	C ₂ H ₆	1.1	0.8 -1.3	181.0	8.9
C ₃ H ₆	CH ₃ (CH ₂) ₂ CHO	1.0	1.0 -0.6	2.79	5.7
	(CH ₃) ₂ CHCHO	1.0	1.0 -0.6	0.46	11.3
	C ₃ H ₈	1.0	0.0 -1.1	9.2	9.7
1-C ₄ H ₈	CH ₃ (CH ₂) ₃ CHO	0.8	0.8 -0.5	2.11	8.5
	C ₂ H ₅ (CH ₂) ₂ CHCHO	0.9	0.9 -0.6	0.39	10.4
	C ₄ H ₁₀	0.9	0.6 -1.2	13.9	12.0
	<i>cis</i> -2-C ₄ H ₈	0.9	0.4 -1.3	26.0	16.9
	<i>trans</i> -2-C ₄ H ₈	0.9	0.4 -1.5	12.8	28.2

^a Catalyst A: 1.5 g; W/F = 10.0 g-cat·hr/mol; feed mole ratio, olefin:H₂:CO = 3:3:1; reaction temperature, 130°C; total pressure, 1 atm.

^b Nitrogen gas was used as diluent,

^c At 100–150°C.

isoalkyl ones. The dependence of the reaction rate on the partial pressures of hydrogen, carbon monoxide, and olefins are summarized in Table 2. The formation of each of the products followed a first-order kinetics to olefin pressure. Moreover the rate of aldehyde formation was nearly proportional to hydrogen partial pressure.

The immobilized catalyst was similar in structure to a homogeneous catalyst, except that the triphenylphosphine ligand was attached to the polymer. The kinetic equations for hydroformylation were the same as those for the corresponding homogeneous catalyst $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ (1). Accordingly, the heterogeneous reaction scheme can be speculated from the mechanism proposed for the homogeneous system (1, 2): The hydride is transferred to the coordinated olefin to give an alkyl group, which reacts with carbon monoxide ligand to form acyl complex. The hydride, which is formed through hydrogen molecule coordination, reacts with acyl complex to produce aldehyde.

The hydrogenation and isomerization were not observed in the absence of carbon monoxide and only hydrogenation occurred. The yield of hydrogenation product was 100% at 100°C. Carbon monoxide strongly inhibited the adsorption of hydrogen.

The reaction orders, summarized in Table 2, with respect to carbon monoxide were $-0.5 \sim -0.6$ for hydroformylation, $-1.1 \sim -1.3$ for hydrogenation, and $-1.3 \sim -1.5$ for isomerization. The results indicate that all these reactions are strongly inhibited by carbon monoxide. As the formation of aldehydes requires carbon monoxide, the reaction order for hydroformylation with respect to carbon monoxide is larger than those for hydrogenation and isomerization.

The catalytic hydrogenation of the olefins by the rhodium-hydride complex may take place through a reaction sequence similar to that proposed for the hydrogenation of olefins using $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ cata-

lyst in solution (15), since the reaction orders with respect to hydrogen and olefin are the same over the heterogeneous catalysts. The first step may be equilibration of the catalyst with the olefins, followed by metal hydride transfer to the coordinated olefins to form alkyl intermediates, and then molecular hydrogen activation to produce paraffin, regenerating the metal hydride. The fact that the rate of propane formation is independent of hydrogen pressure indicates that the coordination step of hydrogen is much faster than that of propylene (16).

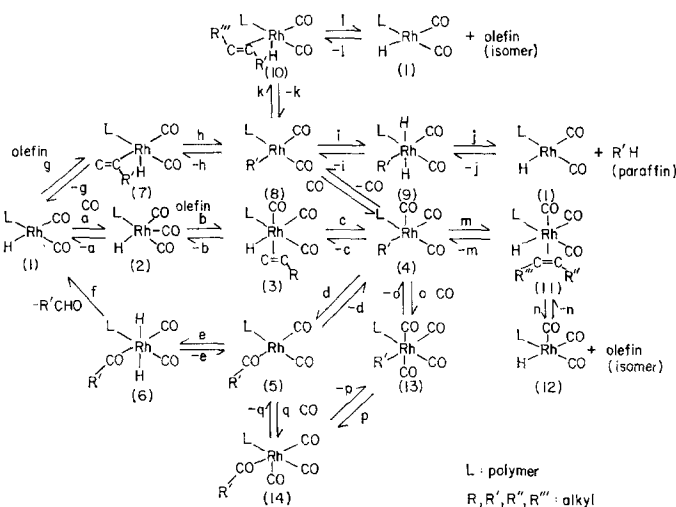
The same rate equations apply to both straight- and branched-chain aldehydes, suggesting that the same reaction mechanism holds, except for the structure of the σ -alkyl complex. The ratio of the rates for the straight- to branched-chain aldehydes was 6.1 for propylene and 5.4 for 1-butene. The *n*-alkyl metal complex is more stable than the isoalkyl complex due to steric or electronic factors (17).

The rate of isomerization of 1-butene to *cis*- or *trans*-2-butene increased as hydrogen pressure increased, which suggests that the reaction proceeds via a hydride intermediate (18) that reacts with the coordinated olefin to give an alkyl and comes back to a hydride- π -olefin complex to lead to isomerization. The isomerization catalyzed by palladium or iron complex proceeds through a dissociative π -allyl mechanism (19), while an associative hydride addition-elimination mechanism was proposed for rhodium catalyst in solution (18).

Trans-2-butene is favored thermodynamically in the isomerization of 1-butene. However, the *cis* isomer was formed preferentially from 1-butene and not directly to the *trans* isomer under the reaction conditions. *Cis*-2-butene is formed in super-equilibrium amounts probably due to the displacement step being faster than the conversion of *cis*- to *trans*-2-butene. The activation energy was 16.9 kcal/mol for *cis*-2-butene and 28.2 kcal/mol for *trans*-

2-butene formation. A remarkable difference in the *cis/trans* ratio and the activation energy, as such, showed that the *cis*- complex is more stable in the form of the metal- π complex than is the *trans* complex, due to steric hindrance of other ligands (20).

The reaction schemes proposed for hydroformylation, hydrogenation, and isomerization of olefin using the immobilized $\text{Rh}(\text{CO})_2\text{ClPPh}_3$ -polymer as catalyst are shown below as compared with homogeneous catalysis (1, 2, 15, 18, 21).



A transient method (22) was applied to the heterogeneous catalytic reaction. Figure 3 shows the characteristic behavior of propionaldehyde formation from ethylene, carbon monoxide, and hydrogen. When carbon monoxide was substituted by a nitrogen stream in the steady state, the rate of aldehyde formation increased sharply by four fold and then rapidly decreased to zero as the concentration of carbon monoxide fell to zero, whereas the rate of ethane formation increased sharply to 100% yield. In the absence of carbon monoxide, alkyl complex cannot react with the coordinated carbon monoxide to give an acyl complex, which is the most important intermediate of aldehyde formation. The alkyl complex reacted with the hydride ion to produce paraffin (hydrogenation) or the hydrogen atom of the alkyl complex was abstracted by rhodium to produce olefin (isomerization). The hydride ion was formed from the coordinated hydrogen molecule, but

this coordination was strongly inhibited by carbon monoxide.

Carbon monoxide was fed again and the reactant supply was restored to the initial state. The rate of propionaldehyde formation increased sharply by 20% as compared with the rate at the steady state and gradually decreased to the initial rate. This indicates that the rate is dependent on the concentration of carbon monoxide, which poisons the active sites. Because of the low concentration of carbon monoxide and the high concentration of σ -alkyl complex just before carbon monoxide is introduced again, the rate of aldehyde formation upon carbon monoxide introduction is a little faster than at the steady state. Such behavior is consistent with the observation that the rate of hydroformylation in the steady state is -0.5 order with respect to carbon monoxide (Fig. 1). The rate of ethane formation decreased sharply and rapidly with carbon monoxide, which indicates that

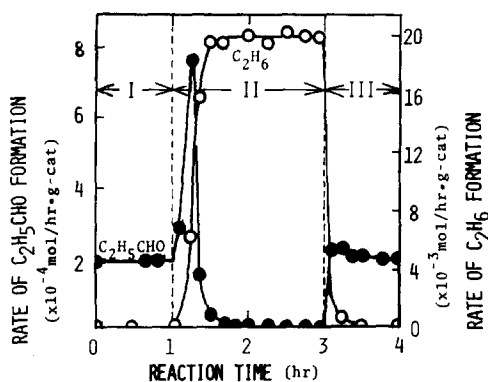


Fig. 1. Response of hydroformylation and hydrogenation in carbon monoxide stop-flow experiment. $W/F = 10$ g-cat·hr/mol; 100°C ; total pressure, 1 atm; mole ratio I and III, $\text{C}_2\text{H}_4:\text{H}_2:\text{CO} = 1:2:2$; mole ratio II, $\text{C}_2\text{H}_4:\text{H}_2:\text{N}_2 = 1:2:2$; (●) $\text{C}_2\text{H}_5\text{CHO}$; (○) C_2H_6 .

hydrogenation is strongly inhibited by carbon monoxide.

When the hydroformylation and hydrogenation proceeded in a steady state with a flow of ethylene, carbon monoxide, and hydrogen, the stream of ethylene was switched to that of nitrogen. The rates of both aldehyde and ethane formation decreased sharply and fell to zero, but, as the stream was restored to the initial condition, the rates returned immediately to their initial levels in both cases.

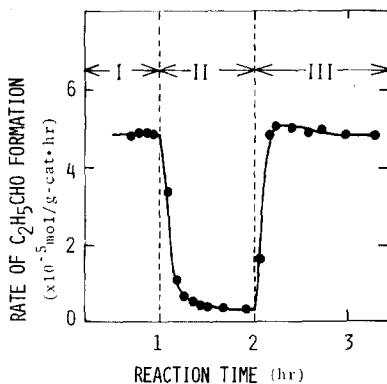


Fig. 2. Response of hydroformylation in ethylene stop-flow experiment. $W/F = 10$ g-cat·hr/mol; 100°C ; total pressure, 1 atm; mole ratio I and III, $\text{H}_2:\text{CO}:\text{C}_2\text{H}_4 = 2:2:1$; mole ratio II, $\text{H}_2:\text{CO}:\text{N}_2 = 2:2:1$.

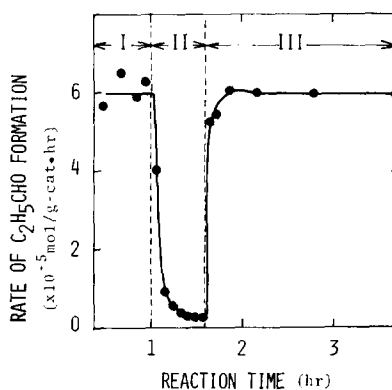


Fig. 3. Response of hydroformylation in hydrogen stop-flow experiment. $W/F = 10$ g-cat·hr/mol; 100°C ; total pressure, 1 atm; mole ratio I and III, $\text{C}_2\text{H}_4:\text{CO}:\text{H}_2 = 1:2:2$; mole ratio II, $\text{C}_2\text{H}_4:\text{CO}:\text{N}_2 = 1:2:2$.

In a hydrogen stop-flow experiment, a rate response similar to that for the ethylene stop-flow experiment was obtained. However, the characteristic overshoot-type curve of aldehyde formation, as shown in Fig. 2, was observed in the ethylene stop-flow experiment. On the other hand, this phenomenon was not observed in the hydrogen stop-flow experiment (Fig. 3). These facts indicate that the rates of ethylene coordination and acyl formation are faster than those of either hydrogen coordination or reaction with the acyl complex.

Immediately after stopping the carbon monoxide feeding, the rate of *n*-aldehyde formation increased sharply from 6×10^{-6} to 15×10^{-6} mol/hr·g-cat and then rapidly decreased to zero as shown in Fig. 4. This phenomenon indicates that the formation of the intermediate (acyl complex) is strongly inhibited by the coordination of carbon monoxide and cannot proceed easily to the next step; in other words, the concentration of the complex (5) increases rapidly from complex (14) through reaction (step -q), when the partial pressure of carbon monoxide becomes zero. The hydrogen can easily coordinate to complex (5) to form complex (6), and, therefore, the rate of the aldehyde formation increases rapidly. Com-

plexes (13) and (14) change readily to the intermediate complex (5) and, moreover, the acyl complex cannot be formed any more without carbon monoxide in the feed gas. Consequently, the rate of aldehyde formation is reduced.

The alkyl complex containing only one vacant site [complex (4)] cannot activate the hydrogen molecule to give the alkyl-hydrido complex, which is required to produce paraffin. However, the single vacant site of the complex can accommodate a hydrogen atom from the alkyl ligand and this complex changes to form the coordinate olefin-hydrido complex and produce olefin. Shortly after the cessation of carbon monoxide supply, the existence of a single-vacant site complex has a higher probability than that of a double-vacant site complex. During the initial period, isomerization proceeded more rapidly than hydrogenation, exhibited a maximum rate 4 min later, as shown in Fig. 4, and then decreased while the yield of butane formation was gradually raised to 100% in 60 min. The result showed that, in the absence of carbon monoxide, the rate of hydrogen abstraction from alkyl ligand (step k) was much slower than that of hydrogen attack on alkyl ligand to give paraffin (step i), and that carbon monoxide occupied the vacant site for adsorption of hydrogen to inhibit hydrogenation. The observations in the transient response experiments suggest that: (A) The increase in concentration of complex (5) through complexes (13) and (14) favors hydroformylation. (B) The increase of complex (4) and decrease of complex (5) favor isomerization over hydroformylation. (C) The increase of complex (9) favors hydrogenation, since the rate of step k is much faster than that of step i.

In the presence of carbon monoxide, the rate of *cis*-2-butene formation was much faster than that of the *trans* isomer, as indicated in Table 2. However, when nitrogen in the feed was substituted by carbon monoxide, the ratio of the rate of

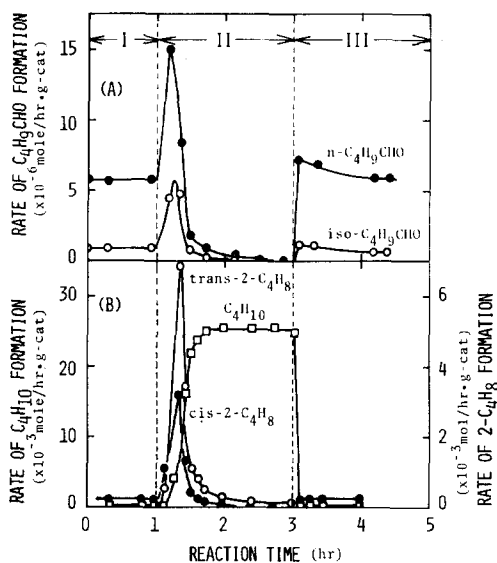


FIG. 4. Response of hydroformylation, hydrogenation, and isomerization in carbon monoxide stop-flow experiment. $W/F = 10$ g-cat·hr/mol; 100°C ; total pressure, 1 atm; mole ratio I and III, $1\text{-C}_4\text{H}_8:\text{H}_2:\text{CO} = 1:2:2$; mole ratio II, $1\text{-C}_4\text{H}_8:\text{H}_2:\text{N}_2 = 1:2:2$. (A) ●: $\text{CH}_3(\text{CH}_2)_3\text{CHO}$; ○: $\text{C}_2\text{H}_5(\text{CH}_2)\text{CHCHO}$. (B) ●: *cis*-2- C_4H_8 ; ○: *trans*-2- C_4H_8 ; □: C_4H_{10} .

cis- to *trans*-2-butene formation from 1-butene was reversed, as shown in Fig. 4. Since both isomerization rates were measured at low conversion, the isomerization of *cis*- to *trans*-2-butene did not occur during the reaction. The *trans* form of the π complex was generally thermodynamically more stable than the *cis* form of the π complex. However if the number of carbon monoxide ligands on rhodium decreases in the absence of carbon monoxide, the *cis* form of the π complex becomes more stable than the *trans* form. Therefore, a preference for the formation of *cis*-olefin during isomerization has not been observed in the absence of carbon monoxide in the feed.

The reaction orders summarized in Table 2 were rounded off to two decimal places. The reaction rate equations for isomerization were $V(\textit{trans}\text{-2-butene}) = k[1\text{-butene}]^{0.91}[\text{H}_2]^{0.38}[\text{CO}]^{-1.47}$ and $V(\textit{cis}\text{-2-butene}) = k[1\text{-butene}]^{0.92}[\text{H}_2]^{0.37}[\text{CO}]^{-1.25}$.

These equations also indicated that the adsorbed carbon monoxide inhibits the formation of the *trans* isomer more than that of the *cis* isomer.

In 1-butene, the reaction order with respect to the total pressure of the three reactants was 1.1 ($0.8 + 0.8 - 0.5$) for hydroformylation (valeraldehyde), 0.3 ($0.9 + 0.6 - 0.5$) for hydrogenation (butane), and 0 ($0.9 + 0.4 - 1.3$) for isomerization (*cis*-2-butene), respectively. Therefore, if the total pressure is increased at the same reactant composition (1-C₄H₈: H₂: CO = 3:3:1), the yield of hydroformylation product may be larger than the yields of hydrogenation and isomerization. Consequently, the value of the partial pressure of carbon monoxide plays an important role in determining the selectivity for hydroformylation.

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