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Photochemical Hydroformylation of Olefins in the Cobalt-Phosphine Catalyst System

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Cobalt-catalyzed hydroformylation of olefins was found to proceed even at ambient temperature under UV irradiation in the presence of phosphine. Extremely high selectivity toward straight-chain aldehyde (99% in case of 1-hexene) was obtained by lowering the partial pressure of carbon monoxide at ambient temperature. A catalytic species different from the well-known species under high pressure of carbon monoxide and high temperature contributed to the highly selective formation of straight-chain aldehydes. Two photochemical processes were suggested to be involved in the photochemical hydroformylation reaction, that is, the formation of $HCo(CO)_3PBu_3$ from the cationic cobalt species, $[Co(CO)_3(PBu_3)_2]^+$, and then the formation of the coordinatively unsaturated hydride, $HCo(CO)_2PBu_3$.

Organometallic photochemistry is an area of growing interest in homogeneous transition-metal catalysis.[1] Photochemical hydroformylation of olefins was first reported by Mirbach and co-workers[2] They have examined the effects of UV irradiation on hydroformylation in some different cobalt catalyst systems. With $Co(OAc)_2$ or $Co_2(CO)_8$ as catalyst precursor in the presence of excess tributylphosphine, olefin hydroformylation proceeds photochemically under the conditions where no reaction could take place thermally (85 °C), and yields linear aldehydes in a relatively high selectivity.

$$\text{1-octene} \xrightarrow[\text{Co(OAc)}_2/\text{PBu}_3]{h\nu,\ \text{CO/H}_2,\ 85\,^\circ\text{C}} \underset{79\%}{\text{nonanal}} + \underset{9\%}{\text{2-methyloctanal}} + \underset{12\%}{\text{octane}}$$

In the absence of phosphine the thermal reaction with $Co(OAc)_2$ catalyst at 85 °C has a long induction period of 15 h, whereas the reaction under UV irradiation is initiated within 1 h. Based on the observed high pressure IR and UV absorption spectra, they have suggested the photogeneration of active catalytic species, $HCo(CO)_3PBu_3$ or $HCo(CO)_4$ in the presence or absence of phosphine, respectively.

Later, they found rhodium catalysts to be also photochemically active for the hydroformylation of olefins in the presence of norbornadiene.[3]

Recently E. M. Gordon and R. Eisenberg reported that Ru(0) complexes such as $Ru(CO)_3(PPh_3)_2$, $Ru(CO)_4PPh_3$ and $Ru_3(CO)_{12}$ are effective for the photochemical hydroformylation of ethylene and propene under mild conditions.[4]

We found the cobalt-catalyzed photochemical hydroformylation proceeds even at ambient temperature, and extremely high selectivity toward linear aldehyde is achieved at low CO partial pressure. Here we report the influence of reaction temperature and CO partial pressure on the reaction rate and selectivity toward straight-chain products, and discuss the photochemical processes and catalytic species.

Experimental

Photochemical Experiments. The photochemical reactions were performed in a 10 mL home-made UV autoclave as shown in Fig. 1. Inside of the autoclave is coated with Teflon to avoid the contact of the solution with stainless steel. If necessary, this can be used as a high-pressure UV cell for UV spectroscopy. Mixing of the liquid and gases was achieved by a magnetically driven up-and-down stirrer. The reaction solution in the autoclave was irradiated with an external high-pressure mercury lamp (500 W, Ushio USH500D) through a

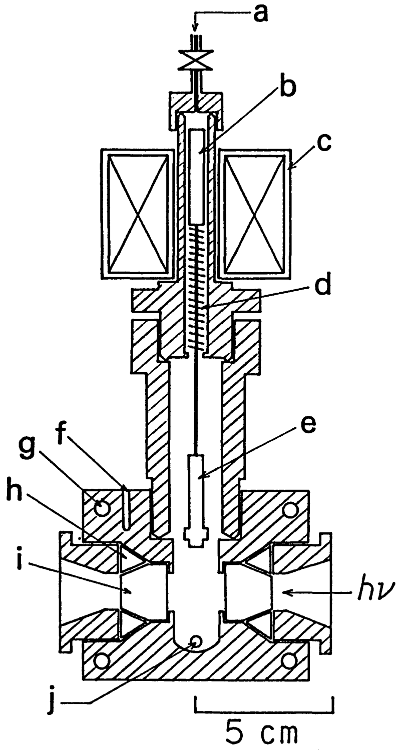


Fig. 1. High pressure UV autoclave (schematic).
a; gas inlet, b; magnet, c; solenoid, d; spring, e; up-and-down stirrer, f; thermocouple hole, g; heater or coolant, h; Teflon packing, i; quartz window, j; sample outlet.

quartz lens and a cooled water filter (2 cm thickness).

In a typical run, methanol solution (5 mL) of olefin (3.2 mol dm^{-3}), $Co(OAc)_2 \cdot 4H_2O$ (0.016 mol dm^{-3}), and PBu_3 (0.16 mol dm^{-3}) was introduced into the autoclave. The autoclave was flushed with synthesis gas ($CO/H_2=1/1$) three times and then pressurized to a desired pressure. The reaction mixture was stirred and then irradiated after the autoclave had been thermostated to a desired temperature. When the gas mixture of low CO content was employed, the fresh gas mixture was introduced continuously into the solution through the sample outlet portion (j in Fig. 1), and released from the gas inlet valve (a in Fig. 1) with keeping a constant pressure. The product solution was taken out through the sample outlet valve to a cooled bottle. Product analysis was performed by GLC with internal standards (Shimadzu GC-5A). A back flush system fitted with tandem column of PEG 20M and *n*-Octane/Poracil C was used for a concurrent analysis of hydrocarbons and hydroformylation products. GC-MS (NEVA TE-600) was also used to identify the products. UV absorption spectra of cobalt species such as Co^{2+}, $[Co(CO)_3(PBu_3)_2]^+$, and $Co_2(CO)_6(PBu_3)_2$ were measured by JASCO UVDEC-1 spectrometer.

Thermal Reaction with $HCo(CO)_3PBu_3$. $HCo(CO)_3PBu_3$ was prepared according to Piacenti and co-workers,[5] except for the addition of free phosphine which can avoid the concomitant formation of $HCo(CO)_4$.[6] Without isolating $HCo(CO)_3PBu_3$, a solution containing the hydride was used for the reaction, that is, $Co_2(CO)_6(PBu_3)_2$ (0.35 mmol), PBu_3 (0.35 mmol) and pentane (15 mL) were placed in a 50 mL rocking type autoclave and pressurized with 7 atm of CO and 22 atm of H_2. The autoclave was heated at 120 °C for 2 h, then cooled immediately at −70 °C. Two milliliter (16 mmol) of 1-hexene was injected into the autoclave by means of a plunger pump under −70 °C. The autoclave was rapidly heated to a desired temperature, and the reaction was started.

Materials. Commercially available $Co(OAc)_2 \cdot 4H_2O$, olefins and methanol were used without further purification. Tributylphosphine was distilled under vacuum. Hydrogen was obtained commercially. Carbon monoxide was prepared by decomposing formic acid in hot sulfuric acid. Its purity was above 98%, and impurity was mainly hydrogen. $Co_2(CO)_6(PBu_3)_2$ and $HCo(CO)_2(PBu_3)_2$ were prepared according to the procedures described in literatures.[7,8]

Results and Discussion

The results of the photochemical hydroformylation of 1-hexene with cobalt acetate and tributylphosphine in methanol are summarized in Table 1. The reaction proceeds even at ambient temperature and surprisingly the rate of hydroformylation at 30 °C is nearly the same at 80 °C and 120 °C. Heptanal via CO addition to the terminal carbon atom of 1-hexene is a principal product, and total of branched aldehydes (2-methylhexanal and 2-ethylpentanal) is about 1/10 of normal aldehyde ($n/i=10$, the ratio of straight-chain product to branched products is expressed by n/i hereafter). 2-Ethylpentanal is still less than 1/6 of 2-methylhexanal. The n/i ratio in isomeric aldehydes decreases slightly at 120 °C. Alcohols are minor products under these conditions, though a conventional hydroformylation with the phosphine-modified cobalt catalysts at higher temperature leads to the alcohol formation due to the highly reductive character of $HCo(CO)_3PBu_3$. Hydrogenation of olefinic substrate occurs in small extent and isomerization becomes significant only at higher temperature.

Total yield of hydroformylation products increases with the period of irradiation such as 13.6% for 18 h, 24% for 40 h, and 34% for 68 h at 30 °C, but the reaction ceases completely when the light is turned off. Thus the reaction is photocatalytic. Reactions of 1-pentene, 1-hexene, and 1-octene give almost the same results in the yield and the distribution of the corresponding

Table 1. Photochemical Hydroformylation of 1-Hexene[a)]

Temp	Product yield[b)]/%							
°C	*n*-Ald[c)]	*i*-Ald[d)]	*n*-Alc[e)]	*i*-Alc[f)]	Acetal[g)]	Ester[h)]	Hexane	2- and 3-Hexenes
30	11.9	1.12	0.17	0.03	0.01	0.35	1.3	0.1
80	13.4	1.27	0.78	0.07	0.11	0.32	1.6	2.3
120	10.3	1.30	1.83	0.13	1.79	0.15	1.5	15.1

a) Reaction conditions: $Co(OAc)_2 \cdot 4H_2O$, 0.0164 mol dm^{-3}; PBu_3, 0.163 mol dm^{-3}; 1-hexene, 3.20 mol dm^{-3}; solvent, methanol; total pressure, 80 atm ($CO/H_2=1/1$); reaction time, 18 h. b) Based on starting 1-hexene. c) Heptanal. d) Branched aldehyde: total of 2-methylhexanal and 2-ethylpentanal. e) 1-Heptanol. f) Branched alcohol: 2-methyl-1-hexanol. g) Heptanal dimethyl acetal. h) Methyl heptanoate.

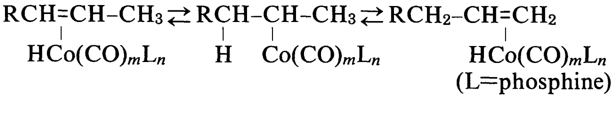
Table 2. Photochemical Hydroformylation of Hexene Isomers[a)]

Hexene	Product yield/%				
	Heptanal	2-Methylhexanal	2-Ethylpentanal	*n*-Alc[b)]	*i*-Alc[b)]
1-Hexene	23.6	1.96	0.31	0.39	0.08
trans-2-Hexene	18.4	2.18	0.58	0.53	0.23
trans-3-Hexene	17.4	1.86	1.41	0.61	0.31

a) Reaction conditions: Hexene, 1.60 mol dm^{-3}; temperature, 30 °C; others are the same as in Table 1. b) See footnotes in Table 1.

hydroformylation products.

In the hydroformylation of hexene isomers, the formyl group preferentially adds to the terminal carbon atom of each olefin, though the position of double bond in starting olefins affects slightly on the isomeric distribution of produced aldehydes as seen in Table 2. These results are similar to those in the conventional cobalt-catalyzed hydroformylation at higher temperature.[9] It has been assumed that fast isomerization of π-olefin complex via σ–π interconversion takes place without releasing isomerized olefins.



$$\underset{\mathrm{HCo(CO)}_m\mathrm{L}_n}{\mathrm{RCH{=}CH{-}CH_3}} \rightleftarrows \mathrm{R}\underset{\mathrm{H}}{\mathrm{CH}}{-}\underset{\mathrm{Co(CO)}_m\mathrm{L}_n}{\mathrm{CH}}{-}\mathrm{CH_3} \rightleftarrows \mathrm{RCH_2{-}}\underset{\mathrm{HCo(CO)}_m\mathrm{L}_n}{\mathrm{CH{=}CH_2}}$$

(L=phosphine)

On steric grounds, the preferable π-olefin complex is that involving the terminal olefins, thus the production of straight-chain aldehydes predominates. It is rather interesting that 2-propylhexanal was reported as the main product in the photochemical hydroformylation of 4-octene with $Co_2(CO)_8$ catalyst at 80 °C, CO/H_2=40 atm/40 atm,[10] though the thermal hydroformylation of 4-octene preferentially afforded nonanal (150 °C, CO/H_2=100 atm/100 atm).[9]

Influence of Phosphine Ligand. The influence of phosphine on the hydroformylation of 1-hexene is summarized in Table 3. At 30 °C both the presence of phosphine and UV irradiation are essential to initiate the hydroformylation reaction, and even at higher temperature (80 °C) the reaction in the presence of phosphine is still photochemical. The photochemical reaction in the absence of phosphine is faster than that in the presence of phosphine, but the *n*/*i* value is low ($n/i \approx 2$). This value is similar to that in a typical $Co_2(CO)_8$ catalyzed hydroformylation. In the absence of phosphine, aldehydes are obtained mainly as dimethyl acetals. $HCo(CO)_4$, a well-known active species in a $Co_2(CO)_8$ catalyzed hydroformylation, dissociates to H^+ and $Co(CO)_4^-$ in methanol solvent, and high acidity of the solution promotes the acetal formation. On the other hand, $HCo(CO)_3L$ (L=phosphine) in a cobalt–phosphine catalyst system is a very weak acid (K_a=1×10^{-7} for L=PBu_3[11]), thus aldehydes cannot be converted into acetals. The thermal reaction without phosphine scarcely occurs under these conditions due to a long induction period as reported previously.[2] The thermal reaction in cobalt–phosphine catalyst system at 120 °C is still very slow, whereas the photochemical reaction proceeds with a similar rate to that at 30 °C. In the absence of phosphine the reaction proceeds thermally as well as photochemically, and the *n*/*i* ratios in both thermal and photochemical reactions are low.

Table 3. Influence of Phosphine on Hydroformylation[a)]

Temp	PBu_3	Product yield[b)]/%	
°C	mol dm^{-3}	Photochemical	Thermal
30	0.163	13.6 (10.5)[c)]	0
30	0	0	0
80	0.163	16.0 (10.6)	0
80	0	59.3[d)] (2.2)	0.75[d)] (2.0)
120	0.163	15.5 (8.0)	3.3 (7.8)
120	0	94.3[d)] (1.8)	97.6[d)] (1.8)

a) Conditions as in Table 1. b) Total yield of hydroformylated products (Aldehydes, alcohols, acetals, and ester). c) Values in parentheses indicate the *n*/*i* ratio in (aldehydes+acetals). d) Obtained mostly as dimethyl acetals.

Consequently, the characteristic of the photochemical hydroformylation is that the reaction proceeds at ambient temperature when phosphine-modified cobalt catalysts are employed.

Photochemical Process. Reductive carbonylation of $Co(ClO_4)_2\cdot6H_2O$ in the presence of phosphines affords $[Co(CO)_3L_2]^+$ (L=PBu_3) in alcoholic media under ambient conditions.[12] On the basis of UV and IR absorption spectra from the reaction of $Co(OAc)_2$ with PBu_3 under the elevated pressure of synthesis gas, Mirbach and co-workers ascertained the formation of $[Co(CO)_3(PBu_3)_2]^+$ at room temperature.[2]

$$Co^{2+} + 2PBu_3 \xrightarrow[20\,^\circ C,\ in\ MeOH]{H_2/CO,\ 80\ atm} [Co(CO)_3(PBu_3)_2]^+$$

As the cation $[Co(CO)_3(PBu_3)_2]^+$ has a large absorption coefficient in UV region (λ_{max}=245 nm, ε=80000), they believed that this cation is a sole photoactive species and is converted into a phosphine-coordinated hydridocarbonylcobalt under the photochemically hydroformylating conditions (Eq. 1). They assumed that the hydride initiates *thermally* the hydroformylation reaction in a similar manner proposed in a conventional hydroformylation reaction (Eqs. 2—4).

$$[Co(CO)_3(PBu_3)_2]^+ \xrightarrow[+H_2,\ -H^+,\ -PBu_3]{h\nu} HCo(CO)_3PBu_3 \quad (1)$$

$$HCo(CO)_3PBu_3 \rightleftarrows HCo(CO)_2PBu_3 + CO \quad (2)$$

$$HCo(CO)_2PBu_3 + olefin \xrightarrow{CO} RCOCo(CO)_2PBu_3 \quad (3)$$

$$RCOCo(CO)_2PBu_3 + H_2 \longrightarrow RCHO + HCo(CO)_2PBu_3 \quad (4)$$

We also observed immediate appearance of UV absorption maximum at 245 nm when a methanol solution of $Co(OAc)_2$ and PBu_3 was pressurized with 80 atm of synthesis gas. Upon irradiation to the solution the absorption at 370 nm, which can be assigned to $Co_2(CO)_6(PBu_3)_2$, appeared as a shoulder. It is probable that $HCo(CO)_3PBu_3$ was generated photochemically under the conditions employed. However, it is doubtful whether the phosphine-coordinated hydridocarbonylcobalt *thermally* initiates the hydroformylation reaction under Mirbach's conditions (85 °C) and especially under our conditions (30 °C). Because $HCo(CO)_3PBu_3$ is known to react with olefins only above 100—120 °C, in contrast to the behavior of $HCo(CO)_4$ which is active at room temperature.[5,13] Thermal reaction of $HCo(CO)_3PBu_3$ with 1-hexene was examined, and the

Table 4. Reaction of $\mathrm{HCo(CO)_3PBu_3}$ with 1-Hexene[a]

Temp	Time	Product yield[b]/%			
°C	h	*n*-Ald[c]	*i*-Ald[c]	*n*-Alc[c]	*i*-Alc[c]
30	4	0	0	0	0
80	4	0.8	0.1	0.2	0
80	15	1.0	0.1	0.4	0
100	4	24.7	2.3	5.0	0.6
100[d]	4	2.3	0.2	0.3	0
120	4	142.7	19.8	27.3	3.3

a) Conditions and procedure: See Experimental in the text. b) Based on $\mathrm{Co_2(CO)_6(PBu_3)_2}$. c) See footnotes in Table 1. d) Without pretreatment at 120 °C for 2 h.

results are shown in Table 4. The thermal hydroformylation of 1-hexene by $\mathrm{HCo(CO)_3PBu_3}$ catalyst occurs only above 100 °C, and scarcely below 80 °C. No increase in the yield with prolonged reaction time (15 h) at 80 °C implies that $\mathrm{HCo(CO)_3PBu_3}$ decomposes rather than reacts with olefin as reported earlier (Eq. 5).[5]

$$2\mathrm{HCo(CO)_3PBu_3} \longrightarrow \mathrm{Co_2(CO)_6(PBu_3)_2} + \mathrm{H_2} \tag{5}$$

In these experiments the formation of $\mathrm{HCo(CO)_3PBu_3}$ is confirmed by no reaction taking place at 100 °C without the pretreatment at 120 °C for 2 h (see experimental section). Thus, absorption of light by the hydride should be required for the initiation of the reaction below 80 °C, though its steady concentration will be low.

$$\mathrm{HCo(CO)_3PBu_3} \xrightarrow{h\nu} \mathrm{HCo(CO)_2PBu_3} + \mathrm{CO} \tag{6}$$

The photochemistry and UV spectral feature of the hydride have not been investigated. With respect to $\mathrm{HCo(CO)_4}$, its photolysis in a matrix isolation system has been studied, in which the major process was the liberation of CO,

$$\mathrm{HCo(CO)_4} \xrightarrow[\text{Ar matrix}]{h\nu(254\text{ nm})} \mathrm{HCo(CO)_3{+}CO}$$

and $\mathrm{HCo(CO)_4}$ had a absorption maximum at 227 nm with a large absorption coefficient (ε=ca. 55000).[14] A similar spectral feature may be expected for $\mathrm{HCo(CO)_3PBu_3}$.

Consequently, two photochemical processes must be included in the photochemical hydroformylation reaction below 80 °C: First, the formation of $\mathrm{HCo(CO)_3PBu_3}$ from the ionic species $\mathrm{[Co(CO)_3(PBu_3)_2]^+}$ (Eq. 1), and second, the formation of the coordinatively unsaturated cobalt hydride $\mathrm{HCo(CO)_2PBu_3}$ (Eq. 6).

Temperature Dependence. The reaction with $\mathrm{Co(OAc)_2/PBu_3}$ catalyst affords the hydroformylation products almost in the same yield at different temperatures of 30, 80, and 120 °C as seen in Table 1. It seems to be rather unusual that the reaction rate does not change with temperature. Detailed temperature dependence on the product yield (or the reaction rate) was examined in the range of 0 °C and 140 °C, and shown in Fig. 2. The reaction proceeds slowly even at 0 °C. The yield increases with temperature up to 60 °C, then decreases and again begins to increase at 100 °C. It can be seen that the yields at 30, 80, and 120 °C happened to lie on a similar value in the curve. Similar temperature dependence was found in the reactions of other substrates such as 1-pentene, 2- and 3-hexene, and 1-octene. The yield curve obtained in the thermal reaction is shown together in dotted line in Fig. 2. Thermal hydroformylation occurs above 120 °C, and at 140 °C no enhancement by irradiation is found. Thus, the reaction can be classified in two temperature regions of the photocatalytic reaction below 100 °C and the thermal reaction above 120 °C. In the photocatalytic region, the reaction is retarded above 60 °C. No detailed mechanistic consideration can be made here, but a most probable assumption is as follows: Photochemically generated $\mathrm{HCo(CO)_3PBu_3}$ mostly decomposes to $\mathrm{Co_2(CO)_6(PBu_3)_2}$ (Eq. 5), and regeneration of the hydride by the reverse reaction of Eq. 5 does not occur over the photocatalytic temperature range. If the photochemical generation of $\mathrm{HCo(CO)_3PBu_3}$ has little temperature effect, then the steady concentration of the hydride will be lower at higher temperature. Although $\mathrm{Co_2(CO)_6(PBu_3)_2}$ formed in Eq. 5 is consumed by the disproportionation in a polar solvent such as methanol,[15]

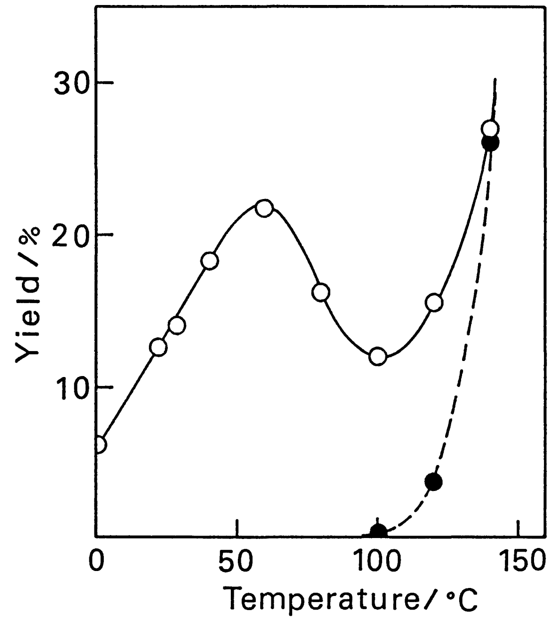


Fig. 2. Influence of reaction temperature on the hydroformylation of 1-hexene.
Reaction conditions as in Table 1, ○; photochemical, ●; thermal.

$$\mathrm{Co_2(CO)_6(PBu_3)_2} \xrightarrow{\mathrm{CO}} \mathrm{[Co(CO)_3(PBu_3)_2]^+[Co(CO)_4]^-} \tag{7}$$

small amounts of $\mathrm{Co_2(CO)_6(PBu_3)_2}$ prevent largely the photochemical hydroformylation reaction due to its large absorption coefficient (ε=21500 at 370 nm).[16] The disappearance of the dicobalt species by disproportionation is more facile at higher temperature, then the expected photochemical reactions become more favorable with increasing temperature.

Unsaturated hydride species $HCo(CO)_2PBu_3$, which is probably generated photochemically as described before (Eq. 6), reacts with olefins to lead to hydroformylation, or reacts with CO or phosphine to return to the saturated species.

$$HCo(CO)_2PBu_3 \xrightarrow{\text{olefin}} HCo(CO)_2(PBu_3)(\text{olefin}) \quad (8)$$

$$\xrightarrow{CO} HCo(CO)_3PBu_3 \quad (9)$$

$$\xrightarrow{PBu_3} HCo(CO)_2(PBu_3)_2 \quad (10)$$

These reactions may have different temperature dependence. Hydroformylation cycle (Eqs. 3 and 4) will have positive temperature effects, though the activation energies in each step may be low as the alkyl and acyl cobalt complexes readily react with CO and H_2, respectively, at room temperature.[5] Complex sequence of these reactions under applied conditions would result in the observed yield curve.

Thermal generation of $HCo(CO)_3PBu_3$ by the reverse reaction of Eq. 5 will become substantial above 120 °C, and thermal equilibrium (Eq. 2) has been assumed under the hydroformylating conditions. Then the irradiation becomes less effective, and at 140 °C the light has little effect on the hydroformylation reaction.

Effect of CO Partial Pressure. In conventional hydroformylation reactions, it is known that both the reaction rate and the *n*/*i* ratio in the products increase with lowering the CO partial pressure.[13,17] The former has been explained by the equilibria (Eqs. 2 and 11),

$$HCo(CO)_4 \rightleftarrows HCo(CO)_3 + CO \quad (11)$$

and the latter by the equilibrium between the phosphine substituted and unsubstituted hydride (Eq. 12), respectively.

$$HCo(CO)_3PBu_3 + CO \rightleftarrows HCo(CO)_4 + PBu_3 \quad (12)$$

In the photochemical hydroformylation of 1-hexene, similar dependence of CO partial pressure was observed as shown in Table 5. The yields of aldehydes and alcohols, and the selectivities toward normal products increased with lowering CO partial pressure. Here, following characteristic aspects are found: a) At 80 °C, the *n*/*i* ratio obtained under low CO pressure is only 1.5 times larger than that under high CO pressure. On the other hand, at 30 °C, it shows a extremely high value of 77, which corresponds to 98.7% of normal aldehyde and 1.3% of branched aldehydes. Such high selectivity has never been reported with cobalt catalysts except for the case of propene in the photochemical hydroformylation.[2] b) When high CO pressure is employed, lowering the temperature causes no increase in the *n*/*i* ratio (n/i=10 at 30 and 80 °C). c) Considerable hydrogenation of olefinic substrate is accompanied under low CO pressure, especially at 30 °C.

Thus, the high selectivity is achieved only at low pressure and low temperature. This can not be ascribed to only the above equilibrium (Eq. 12), since its equilibrium constant has been reported to have negative temperature dependence.[18] Existence of other catalytic species besides $HCo(CO)_3PBu_3$ can be expected under the conditions of low CO pressure and low temperature. Bis(phosphine) species $HCo(CO)_2(PBu_3)_2$ is most probable as the formation of about 1 : 1 mixture of $HCo(CO)_3PBu_3$ and $HCo(CO)_2(PBu_3)_2$ has been suggested in the photolysis of the cationic cobalt(I) complex $[Co(CO)_3(PBu_3)_2]^+$ under 50 atm of hydrogen.[19]

In order to ensure the contribution of $HCo(CO)_2(PBu_3)_2$ in the photochemical hydroformylation in the $Co(OAc)_2/PBu_3$ system, the hydroformylation of 1-hexene with $HCo(CO)_2(PBu_3)_2$ was carried out, and the results are summarized in Table 6. In the photochemical reaction, surprisingly high value of the *n*/*i* ratio was obtained at 30 °C and CO/H_2=1.5 atm/40 atm (n/i =215). However, when the temperature was raised to 80 °C, the *n*/*i* ratio largely decreased (n/i=25) to

Table 5. Effects of CO Partial Pressure on the Photochemical Hydroformylation of 1-Hexene[a)]

P_{CO}	Temp	Product yield[b)]/%						n/i[d)]	n/i[e)]
atm	°C	*n*-Ald[c)]	*i*-Ald[c)]	*n*-Alc[c)]	*i*-Alc[c)]	Hexane	2- and 3-Hexenes	(ald)	(alc)
1.5	30	21.6	0.28	2.02	0.05	11.7	2.8	77	41
2	30	19.2	0.37	1.46	0.05	5.9	1.4	52	30
4	30	14.3	0.52	0.67	0.04	1.9	0.3	23	15
8	30	11.1	0.76	0.26	0.03	1.5	0.3	15	9
16	30	9.5	0.75	0.16	0.03	1.3	0.2	13	7
40	30	9.3	0.95	0.11	0.01	1.1	0.1	10	8
1.5	80	12.8	0.85	5.01	0.21	5.8	12.2	15	24
2	80	14.1	0.96	3.95	0.17	4.8	8.2	15	23
4	80	14.6	1.06	2.81	0.13	3.9	7.6	14	21
8	80	13.0	1.14	1.30	0.07	2.4	4.9	11	18
16	80	10.2	0.93	0.74	0.05	2.2	3.4	11	16
40	80	10.1	1.04	0.45	0.03	1.4	2.4	10	13

a) Conditions: P_{H_2}, 40 atm; $Co(OAc)_2 \cdot 4H_2O$, 0.0170 mol dm^{-3}; PBu_3, 0.180 mol dm^{-3}; 1-hexene, 3.20 mol dm^{-3}; solvent, methanol; reaction time, 16 h. b) Based on starting 1-hexene. c) See footnotes in Table 1. d) The *n*/*i* ratio in aldehydes. e) The *n*/*i* ratio in alcohols.

Table 6. Hydroformylation of 1-Hexene with $HCo(CO)_2(PBu_3)_2$[a)]

P_{CO}/P_{H_2}	Temp	Photochem or dark	Product yield[b)]/%			
atm/atm	°C		*n*-Ald[c)]	*i*-Ald[c)]	Alc[d)]	Hexane
1.5/40	30	$h\nu$	30.2	0.14 (215)[e)]	3.0	14.0
1.5/40	80	$h\nu$	17.1	0.68 (25)	1.2	5.2
1.5/40	80	Dark	0	0	0	0
40/40	30	$h\nu$	23.3	1.65 (14)	0.5	1.3
40/40	80	Dark	<0.1	0	0	0

a) Conditions: $HCo(CO)_2(PBu_3)_2$, 0.022 mol dm^{-3}; PBu_3, 0.21 mol dm^{-3}; 1-hexene, 0.80 mol dm^{-3}; solvent, methanol; reaction time, 6 h. b) Based on 1-hexene. c) See footnotes in Table 1. d) 1-Heptanol (2-methyl-1-hexanol was not detected). e) Values in parentheses indicate the n/i ratio in produced aldehydes.

approach to the value obtained in the $Co(OAc)_2/PBu_3$ catalyst system (n/i=15 in Table 5). Similar situation is found at high CO pressure and low temperature. Hydrogenation of olefin is remarkable only at low CO pressure and low temperature. No reaction occurs without irradiation under the conditions employed.

Predominant photochemical reaction of $HCo(CO)_2(PBu_3)_2$ is perhaps ligand dissociation, mainly of CO.

$$HCo(CO)_2(PBu_3)_2 \xrightarrow{h\nu} HCo(CO)(PBu_3)_2 + CO$$

This coordinatively unsaturated hydride will afford exclusively normal aldehyde owing to its highly steric crowding. Decrease in the n/i ratio with increasing CO pressure is due to the known equilibrium (Eq. 13).[8)]

$$HCo(CO)_2(PBu_3)_2 + CO \rightleftarrows HCo(CO)_3PBu_3 + PBu_3 \qquad (13)$$

Low n/i value obtained at 80 °C under much low CO pressure suggests that the above equilibrium shifts to the right-hand side at higher temperature. Lower hydrogenation activity at higher temperature also suggests the conversion of $HCo(CO)_3(PBu_3)_2$ to $HCo(CO)_3PBu_3$ under these conditions, because the hydrogenation activity of phosphine-coordinated cobalt hydrides increases with increasing the number of phosphine coordinated to the hydride.[8)]

The results obtained in the reaction of $HCo(CO)_2(PBu_3)_2$ under various conditions are in accord with those in the reaction with $Co(OAc)_2/PBu_3$ catalyst. Thus, $HCo(CO)_2(PBu_3)_2$ will largely contribute to the high selectivity toward normal aldehyde as observed in the photochemical hydroformylation reaction with $Co(OAc)_2/PBu_3$ catalyst under low CO pressure and low temperature. $HCo(CO)_2(PBu_3)_2$ is known to be fairly stable up to 140 °C in various organic solvents,[8)] then it can not contribute to the thermal hydroformylation reaction because higher temperature must be required to initiate the reaction and under such conditions $HCo(CO)_2(PBu_3)_2$ will be readily converted into $HCo(CO)_3PBu_3$ even under much low CO pressure. Consequently, the highly selective hydroformylation can be achieved only by the photochemical reaction which is able to proceed readily at low temperature.

References

1) E. A. Koerner von Gustorf, L. H. G. Leenders, I. Fischler, and R. N. Perutz, *Adv. Inorg. Chem. Radiochem.*, **19**, 65 (1976); G. L. Geoffroy and M. S. Wrighton, "Organometallic Photochemistry," Academic Press, New York (1979); G. W. Parshall, "Homogeneous Catalysis," John Wiley & Sons, New York (1980), p. 229; R. G. Salomon, *Tetrahedron*, **39**, 485 (1983).

2) M. J. Mirbach, M. F. Mirbach, A. Saus, N. Topalsavoglou, and T. N. Phu, *J. Am. Chem. Soc.*, **103**, 7594 (1981).

3) A. Saus, T. N. Phu, M. J. Mirbach, and M. F. Mirbach, *J. Mol. Catal.*, **18**, 117 (1983).

4) E. M. Gordon and R. Eisenberg, *J. Organomet. Chem.*, **306**, C53 (1986).

5) F. Piacenti, M. Bianchi, and E. Benedetti, *Chim. Ind.* (*Milan*), **49**, 245 (1967).

6) G. F. Pregaglia, A. Andreetta, G. Gregorio, G. Montrasi, and G. F. Ferrari, *Chim. Ind.* (*Milan*), **54**, 405 (1972).

7) A. R. Manning, *J. Chem. Soc. A*, **1968**, 1135.

8) G. F. Pregaglia, A. Andreetta, and G. F. Ferrari, *J. Organomet. Chem.*, **30**, 387 (1971).

9) B. Fell, W. Rupilius, and F. Asinger, *Tetahedron Lett.*, **1968**, 3261.

10) M. J. Mirbach, N. Topalsavoglou, T. N. Phu, M. F. Mirbach, and A. Saus, *Chem. Ber.*, **116**, 1422 (1983).

11) J. Falbe, "New Syntheses with Carbon Monoxide," Springer-Verlag, Berlin (1980), p. 40.

12) P. Rigo, M. Bressan, and A. Morvillo, *J. Organomet. Chem.*, **105**, 263 (1976).

13) I. Wender and P. Pino, "Organic Syntheses via Metal Carbonyls," John Wiley & Sons, New York (1977), Vol. 2, p. 105.

14) R. L. Sweany, *Inorg. Chem.*, **19**, 3512 (1980).

15) A. Andreetta, G. Montrasi, G. F. Ferrari, G. F. Pregaglia, and R. Ugo, *Nouv. J. Chim.*, **2**, 463 (1978).

16) R. W. Wegman and T. L. Brown, *Inorg. Chem.*, **22**, 183 (1983).

17) F. Piacenti, M. Bianchi, E. Benedetti, and P. Frediani, *J. Organomet. Chem.*, **23**, 257 (1970).

18) M. van Boven, N. Alemdaroglu, and J. M. L. Penninger, *J. Organomet. Chem.*, **84**, 65 (1975).

19) M. F. Mirbach, M. J. Mirbach, and R. W. Wegman, *Organometallics*, **3**, 900 (1984).