A New Catalyst for the Low Temperature Oxo Process with the Characteristic of Easy Separation[1)]

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(Received March 6, 1978)

A new type of catalyst, a cobalt carbonyl-complex has been found for homogeneous hydroformylation. The complex has been prepared from $Co_2(CO)_8$ and the ethylene glycol diester of 3-(2-pyridyl)propionic acid as a ligand. The catalyst is active even at the low temperature of 50 °C and very low carbon monoxide pressure range of less than 1 kg/cm². On subsequent cooling it separates from the reaction product. The ligand was prepared by the hydroesterification of 2-vinylpyridine with carbon monoxide and methanol (or ethanol), followed by the transesterification with ethylene glycol. The effect of the partial pressures of carbon monoxide and hydrogen on the product composition and on the recovery of the catalyst was examined. The catalytic activity of the new complex is considerably higher than that of $Co_2(CO)_8$ at a lower temperature. The selectivity to linear aldehyde in the presence of new complex is significantly higher than in the presence of $Co_2(CO)_8$ when the hydrogen to carbon monoxide ratio (H_2/CO) in gas phase is high, but this difference in selectivity is small when the above gas ratio is normal. The new complex can be applied as catalyst for removal of carbon monoxide in hydrogen by means of oxo process.

Catalyst recovery and recycling in the homogeneously catalyzed oxo process are very important from an industrial point of view, and many reports have been published concerning the separation of the catalyst from the reaction product. In the cobalt catalyzed process, for example, Moffat has developed a catalyst recovery and recycling system consisting of a tetracarbonylhydridocobalt-poly(2-vinylpyridine) complex.[2,3)] In the case of the rhodium catalyzed oxo process, even more efforts have been devoted to catalyst recovery. Haag *et al.* have attempted to insolubilize the rhodium-oxo catalyst by complex formation with phosphin- or amine-polymer ligands;[4)] Bayer *et al.* have prepared a homogeneous rhodium-oxo catalyst attached to a soluble phosphine-polymer,[5)] a catalyst which is easily separated from the reaction product by filtration, *etc.*

Previously, it has been reported that a cobalt carbonyl-pyridine complex catalyst for the homogeneous hydroesterification spontaneously separates from the reaction product.[6)] The separated catalyst phase consisted of an ionic complex: $H_2Co_3(CO)_9(py)_5$, where py represents pyridine. This complex proved to be of an ion-pair structure: $\{Co(H^+)_2(py)_5(CO)\}\{Co(CO)_4^-\}_2$; it is insoluble in hydrocarbons and ether, but soluble in alcohols, ketones, aldehydes and pyridine. Although the complex can also be used for hydroformylation, it does not separate from the hydroformylation product, since it is soluble in aldehydes.

The present paper deals with a new oxo catalyst which is derived from $Co_2(CO)_8$ and ethylene bis-(3-(2-pyridyl)propionate) (hereafter abbreviated as EBP), and soluble under the reaction conditions, but which spontaneously separates from the reaction product on cooling to room temperature. Also an interesting feature of the new catalyst is that it is active in the low temperature range of 50 to 70 °C. As a result, the hydroformylation can be carried out under a very low carbon monoxide partial pressure, so that, it can be used as a catalyst for the removal of carbon monoxide in hydrogen by means of the oxo process. For example, when hydrogen containing 4 to 6% of carbon monoxide was allowed to react with excess olefin in the presence of the catalyst in a suitable solvent at 50 to 60 °C, carbon monoxide was almost completely consumed by the hydroformylation, reasonably pure hydrogen containing less than 0.1% of carbon monoxide being left in the gas phase as a result.

Experimental

Preparation of Ligand. EBP was prepared by the transesterification of methyl (or ethyl) 3-(2-pyridyl)propionate with ethylene glycol.

Hydroesterification of 2-Vinylpyridine with Carbon Monoxide and Methanol(or Ethanol): Hydroesterification was carried out in a 300 ml stainless steel autoclave equipped with a vertical agitator. After charging with 2-vinylpyridine, an alcohol, solvent, and $Co_2(CO)_8$, the autoclave was flushed and pressurized with carbon monoxide, and heated to the reaction temperature. The pressure was kept constant during the reaction by supplying carbon monoxide from a pressure storage vessel through a pressure regulator, while the temperature was kept constant by a temperature controller. After the solvent and alcohol were distilled off under normal pressure, unchanged 2-vinylpyridine and methyl (or ethyl) 3-(2-pyridyl)propionate were distilled under reduced pressure.

Methyl 3-(2-pyridyl)propionate: bp 118 °C/10 mmHg, IR spectrum 1730 cm^{-1} (ester).

Ethyl 3-(2-pyridyl)propionate: bp 122 °C/10 mmHg, IR spectrum 1730 cm^{-1} (ester).

Some typical results of the hydroesterification experiments are listed in Table 1.

Transesterification with Ethylene Glycol: Transesterification was carried out with ethlene glycol (0.1 mol) in the presence of excess methyl(or ethyl) 3-(2-pyridyl)propionate (0.22—0.4 mol) at 200 °C, the liberated methanol (or ethanol) being continuously distilled off. The reaction time necessary to attain 64 to 87% yield of diester based on ethylene glycol was 20 to 40 h in the absence of a catalyst, but decreased to 2 to 5 h in the presence of sodium methoxide (0.2—0.4 mmol).

Hydroformylation of 1-Decene. Reactions were carried out in the same apparatus by essentially the same procedure as in the hydroesterification experiments except that reactions in a lower pressure range (10—50 kg/cm²) were carried out

Table 1. Hydroesterification of 2-vinylpyridine

Exp. No.	Temp (°C)	Press. (kg/cm²)	Time (h)	Alcohol (mol)	Conv.[a] (%)	Yield[b] (%)	Bottom[c] (%)
1	150	100	5	CH_3OH (0.25)	80.0	49.0	31
2	170	100	5	CH_3OH (0.25)	96.2	58.0	38
3	170	70	5	CH_3OH (0.25)	71.4	45.2	26
4	120	40	2	C_2H_5OH (1)	76.0	33.6	42
5	140	50	2	C_2H_5OH (1)	86.3	64.8	21
6	170	70	2	C_2H_5OH (1)	94.7	66.4	28
7[d]	170	70	2	C_2H_5OH (2.7)	95.4	70.4	25

2-Vinylpyridine 0.25 mol, $Co_2(CO)_8$ 1 g, benzene (solvent) 100 ml. a) Conversion of 2-vinylpyridine. b) Yield of methyl (or ethyl) 3-(2-pyridyl)propionate (mol %) from 2-vinylpyridine. c) Yield (wt %) of resinous distillation bottom based on the amount of 2-vinylpyridine used. d) Experiment No. 7 was carried out in the absence of benzene.

in a 400 ml autoclave fitted with windows for observation during the reaction.

Aldehydes were obtained by distilling the reaction product under reduced pressure. The crude aldehyde obtained was separated into four fractions by distillation with a rectifying column of a spining band type, and each fraction identified by IR and ^{13}C-NMR spectra.

Fraction 1 (undecanal): bp 62 °C/2 mmHg.

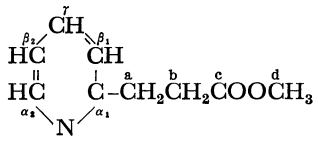
Fraction 2 (2-methyldecanal): bp 57.5 °C/2 mmHg.

Fraction 3 (2-ethylnonanal): bp 53.2—53.5 °C/2 mmHg.

Fraction 4 (mixture of 2-propyl octanal and 2-butyl heptanal): bp 52 °C/2 mmHg. IR spectra of these fractions showed an absorption attributable to formyl group at 1735 cm^{-1}.

Identification by Means of ^{13}C-NMR Spectra. Spectra were measured with Varian XL 100.

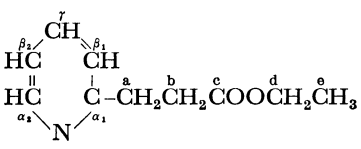
Methyl 3-(2-pyridyl)propionate



carbon	α_1	α_2	β_1	β_2	γ
ppm	160.5	149.6	123.3	121.7	136.7

a	b	c	d
33.0	33.0	173.5	51.5

Ethyl 3-(2-pyridyl)propinate



carbon	α_1	α_2	β_1	β_2	γ
ppm	160.8	149.8	123.3	121.7	136.5

a	b	c	d	e
33.5	33.5	173.0	60.4	14.5

Undecanal

$CH_3{}_{a}CH_2{}_{b}CH_2{}_{c}CH_2{}_{d}CH_2{}_{e}CH_2{}_{f}CH_2{}_{g}CH_2{}_{h}CH_2{}_{i}CH_2{}_{j}CHO{}_{k}$

carbon	a	b	c	d	e	f
ppm	14.5	23.4	32.7	30.3	30.3	30.3

g	h	i	j	k
30.3	30.3	22.8	44.3	200.6

2-Methyldecanal

$CH_3{}_{a}CH_2{}_{b}CH_2{}_{c}CH_2{}_{d}CH_2{}_{e}CH_2{}_{f}CH_2{}_{g}CH_2{}_{h}CH_2{}_{i}CH(CH_3){}_{j}CHO{}_{k}$

carbon	a	b	c	d	e	f
ppm	14.5	23.4	32.7	30.3	30.3	30.3

g	h	i	j	k
27.7	31.3	46.7	13.7	202.9

2-Ethylnonanal

$CH_3{}_{a}CH_2{}_{b}CH_2{}_{c}CH_2{}_{d}CH_2{}_{e}CH_2{}_{f}CH_2{}_{g}CH_2{}_{h}CH(CH_2CH_3){}_{i}{}_{j}CHO{}_{k}$

carbon	a	b	c	d	e	f
ppm	14.5	23.4	32.6	29.9	30.5	27.8

g	h	i	j	k
29.1	53.9	22.5	11.8	203.1

2-Propyloctanal

$CH_3{}_{a}CH_2{}_{b}CH_2{}_{c}CH_2{}_{d}CH_2{}_{e}CH_2{}_{f}CH_2{}_{g}CH(CH_2CH_2CH_3){}_{h}{}_{i}{}_{j}CHO{}_{k}$

carbon	a	b	c	d	e	f
ppm	14.4	23.5	32.7	30.0	27.7	29.6

g	h	i	j	k
52.4	31.8	21.0	14.4	203.1

2-Butylheptanal

$CH_3{}_{a}CH_2{}_{b}CH_2{}_{c}CH_2{}_{d}CH_2{}_{e}CH_2{}_{f}CH(CH_2CH_2CH_2CH_3){}_{g}{}_{h}{}_{i}{}_{j}CHO{}_{k}$

carbon	a	b	c	d	e	f
ppm	14.4	23.5	32.7	27.5	29.6	52.4

g	h	i	j	k
29.3	30.0	23.2	14.4	203.1

Isomerized decenes and decane formed by the isomerization and the hydrogenation of 1-decene were determined by gas chromatography (squalane, 0.25ϕ, 90 m, 90 °C). Dissolved cobalt in the reaction product was analyzed by heating an aliquot with 1.5M-sulfuric acid, followed by the chelate titration method.

Results

Effect of Recycling the Catalyst. Results of the hydroformylation of 1-decene carried out by recycling the initial catalyst are listed in Table 2.

TABLE 2. HYDROFORMYLATION OF 1-DECENE

Initial catalyst (run No. 1) was prepared *in situ* from 8 mmol of $Co_2(CO)_8$ and 20 mmol of EBP. $H_2/CO=1$, 1-decene 0.2 mol, liquid paraffin (solvent) 30 g.

Run No.		1	2	3	4
Temp (°C)		80	80	100	80
Press. (kg/cm²)		50	20	50	50
Time (h)		4	2	1	4
Conv. (%)		64.6	73.2	81.3	90.1
Select. (%)	A_1	65.8	47.9	54.9	64.1
	A_2	22.8	30.9	27.1	22.7
	A_3	5.2	9.7	8.0	6.2
	A_4	6.2	11.5	10.0	6.9
Dissolved Co (mg atom)		0.18	0.21	0.11	0.17
Co recovery (%)		98.9	98.7	99.4	98.9

Conv.; Conversion of 1-decene into aldehydes. Select.; Selectivity to each aldehyde determined by gas chromatography. A_1; undecanal. A_2; 2-methyl decanal. A_3; 2-ethylnonanal. A_4; 2-propyloctanal plus 2-butylheptanal. Dissolved Co; cobalt which remained dissolved in the reaction product. Co recovery; per cent of cobalt recovered and recycled.

It was observed through the windows of the reaction vessel that the catalyst complex was soluble during the reaction, but, on cooling to room temperature, separated as a dark red viscous liquid from the upper phase consisting of a solvent and reaction products. The remaining gas was discharged and the upper phase drained off; then 1-decene, the solvent, and the gas were charged again and the reaction repeated. The activity of the catalyst increased on repeated use as evident from a comparison of the results of the initial and the fourth runs.

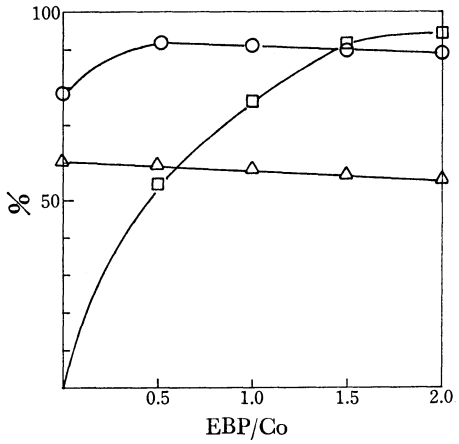


Fig. 1. Results plotted against the EBP/Co ratio.
1-Decene 0.2 mol, benzene 30 g, $Co_2(CO)_8$ 2 mmol, $H_2/CO=1$, 100 °C, 50 kg/cm², 1 h.
-○-: Conversion of decene (%), -△-: selectivity to linear aldehyde (%), -□-: Co recovery (%).

The Effect of the EBP to $Co_2(CO)_8$ Ratio. Results are plotted against the EBP/Co ratio in Fig. 1, where the amount of $Co_2(CO)_8$ was kept constant at 2 mmol.

The degree of conversion of decene increased by the addition of EBP, and reached a maximum when the ratio was 0.5, but slightly decreased as the ratio increased from 0.5 to 2.0. The selectivity to linear undecanal slightly decreased as the above ratio was increased. The catalyst did not separate at all from the reaction products in the absence of EBP, but began to separate as the ratio of EBP to $Co_2(CO)_8$ increased; Cobalt recovery reached near a maximum as the ratio increased to 1.5 and remained unchanged thereafter.

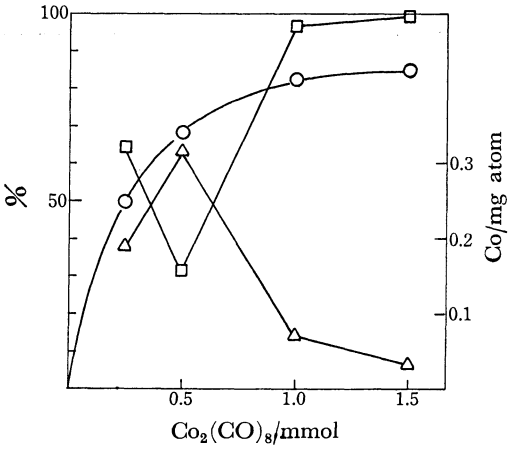


Fig. 2. Effect of catalyst concentration.
1-Decene 0.2 mol, liquid paraffin 30 g, $H_2/Co=1$, 100 °C, 50 kg/cm², 1 h, EBP: Co=4: 3.
-○-: Conversion of decene (%), -△-: dissolved Co (mg atom), -□-; Co recovery (%).

The Effect of Catalyst Concentration. In Fig. 2, the results are plotted against the amount of $Co_2(CO)_8$, where the EBP to $Co_2(CO)_8$ ratio was kept constant at 2.67, the ratio which corresponds to EBP 4: Co 3. The conversion of 1-decene after a definite reaction time increased as a natural result of increasing the amount of catalyst. Figure 2 shows, however, an unusual trend, *i.e.* a contrast between the amount of catalyst used and that of the cobalt remaining dissolved after the reaction. Thus, the larger the amount of catalyst employed, the better the separation of catalyst after the reaction.

The Effect of Pressure. The reactions were carried out under various partial pressures of hydrogen and carbon monoxide by recycling the initial catalyst, the results of which are summarized in Table 3.

The dissolved cobalt in the cooled reaction product decreased by increasing the ratio of hydrogen partial pressure(P_{H_2}) to that of carbon monoxide(P_{CO}); it decreased in the order: run No. 2 ($P_{H_2}/P_{CO}=0.25$)> No. 1($P_{H_2}/P_{CO}=1$)>No.4($P_{H_2}/P_{CO}=2$)>No.3($P_{H_2}/P_{CO}=4$)>No. 5($P_{H_2}/P_{CO}=9$). The selectivity to the linear aldehyde increased with the increase in partial pressure of hydrogen(No. 4<No. 3) and also increased with that of carbon monoxide(No. 7<No. 2). Nitrogen pressure did not affect the selectivity(No. 8). The rate constant

Table 3. Hydroformylation of 1-decene under various hydrogen and carbon monoxide pressure

Initial catalyst was prepared *in situ* from 8 mmol of $Co_2(CO)_8$ and 16 mmol of EBP. Synthesis gas($H_2/CO=1$) was supplied during the reaction. 1-Decene 0.2 mol, diethyl ether (solvent) 30 g.

Run No.		1	2	3	4	5	6	7	8
P_{H_2} (kg/cm²)		25	10	40	20	45	45	10	10
Pco (kg/cm²)		25	40	10	10	5	5	10	10
P (kg/cm²)		50	50	50	30	50	50	20	50
Temp (°C)		70	70	70	70	60	50	70	70
Time (h)		4	20	2	2	3	15	5	10
Conv. (%)		51.2	73.4	70.0	68.4	64.5	59.1	70.0	52.3
Select. (%)	A_1	73.0	68.8	69.8	63.4	66.0	73.1	54.1	54.1
	A_2	18.8	21.1	20.1	23.4	22.4	18.5	28.5	28.5
	A_3	4.3	5.1	4.7	6.3	5.5	4.4	8.0	8.1
	A_4	3.9	4.9	5.4	6.9	6.1	4.0	9.4	9.4
$k\times 10$ min^{-1}		0.30	0.11	1.0	0.96	0.58	0.10	0.40	0.12
Decane (%)		0.05	0	2.6	0.49	0.18	0.83	1.98	0
Isomer (%)		1.5	2.7	2.7	4.1	2.1	0.9	7.0	3.9
Dissolved Co (mg atom)		1.92	2.24	0.94	1.01	0.19	0.22	1.54	0.87
Co recovery (%)		88.0	84.1	92.0	90.7	98.1	97.7	83.8	89.0

P; Total pressure, which is equal to $P_{H_2}+P_{CO}$, except in run No. 8, where nitrogen pressure ($P_{N_2}=30$) is employed. Conv.; Conversion of decene. k; Rate constant: $k=1/t$ ln $(100/100-x)$, where x is conv. at time t. Decane; Yield (%) of decane. Isomer; Total yield (%) of internal decenes. Other abbreviations: See footnote of Table 2.

increased with increasing partial pressure of hydrogen-(No. 7<No. 4<No. 3), but significantly decreased with that of carbon monoxide(No. 7>No. 2). The extent of isomerization of 1-decene into internal decenes increased as the carbon monoxide partial pressure decreased. Hydrogenation of decene to decane was also favored by lower carbon monoxide pressure.

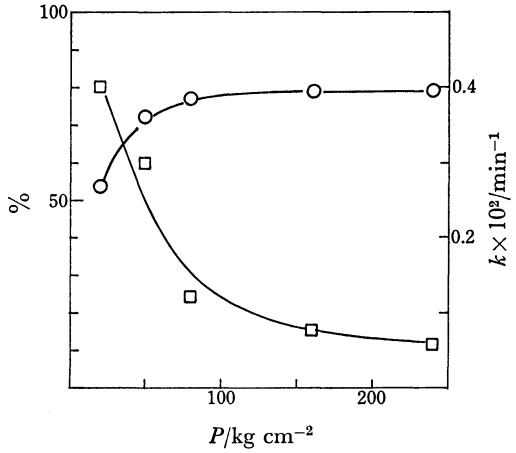


Fig. 3. Results plotted against total pressure.
1-Decene 0.2 mol, ether 30 g, $H_2/CO=ca.$ 1, 70 °C, EBP/Co=*ca.* 1.
-○-; Selectivity to linear aldehyde (%), -□-; rate constant k (min^{-1}).

Figure 3 illustrates the effect of the total pressure ($P_{H_2}+P_{CO}$) on the product composition and reaction rate. the selectivity to the linear aldehyde increased with increasing total pressure in the lower pressure range of 20 to 50 kg/cm², but leveled off thereafter. The rate constant decreased with increase in total pressure; this retarding effect of total pressure on the reaction rate was more pronounced in the lower pressure range.

Removal of Carbon Monoxide in Hydrogen by Means of the Oxo Process. Reactions were carried out by recycling the initial catalyst formed *in situ* from 4 mmol of $Co_2(CO)_8$ and 10.67 mmol of EBP. The autoclave was pressurized with hydrogen containing 4 to 6% of carbon monoxide to 100 kg/cm² (20 °C), then it was heated to 50 °C, and the reaction allowed to proceed, agitating at this temperature without supplying the synthesis gas. The results of consecutive experiments are listed in Table 4, the result of a control experiment carried out with 4 mmol of $Co_2(CO)_8$ but in the absence of EBP also being listed.

The activity of a catalyst formed *in situ* from $Co_2(CO)_8$ and EBP is initially very low, and the conversion of carbon monoxide into aldehyde is not complete even after 22 h reaction. The catalyst complex, however, gains in activity on recycling, attaining its highest activity when it has been recycled twice (after more than 40 h). Then, the carbon monoxide initially contained in the hydrogen is almost completely consumed by the hydroformylation in a few hours, and corresponding amount of aldehydes are formed in the liquid phase. The selectivity to the linear aldehyde in the presence of the recycled complex was 62%, which is significantly higher than that of the control experiment (53%) carried out with $Co_2(CO)_8$ in the absence of EBP. The separation of the catalyst after the reaction was in the range of 96 to 99%.

The conversion of carbon monoxide which was determined by analyzing the gas samples withdrawn at regular intervals in runs No. 4, No. 5, and No. 6 are

Table 4. Hydroformylation of 1-decene under pressure of hydrogen containing 4 to 6 per cent of carbon monoxide

Initial catalyst; $Co_2(CO)_8$ 4 mmol, EBP 10.67 mmol. Runs No. 1 to No. 5 were carried out recycling the initial catalyst. No. 6 is a controll experiment carried out with 4 mmol of $Co_2(CO)_8$ in the absence of EBP. 1-Decene 0.2 mol, ethyl acetate (solvent) 30 g, reaction temp 50 °C, initial pressure (20 °C) 100 kg/cm².

Run No.		1	2	3	4	5	6
CO content in hydrogen (%)	initial	4.2	5.5	5.2	5.3	4.8	4.8
	final	1.0	0.00	0.00	0.00	0.00	0.09
Time (h)		22	20	2	1.5	1.75	5
Conv. (%)		16.0	28.6	26.4	29.5	27.7	26.3
Select. (%)	A_1	58.4	61.6	62.4	62.6	62.4	53.6
	A_2	24.6	23.8	22.9	23.3	23.2	27.4
	A_3	7.7	6.5	6.7	6.4	6.8	8.9
	A_4	9.3	8.1	8.0	7.7	7.6	10.1
Decane (%)		0.45	2.0	1.2	3.9	4.5	3.0
Isomer (%)		0.63	34.2	50.8	49.0	60.9	57.8
Dissolved Co (mg atom)		0.25	0.31	0.21	0.059	0.095	—
Co recovery (%)		96.9	96.0	97.2	99.2	98.7	—

Abbreviations: See footnote of Table 3.

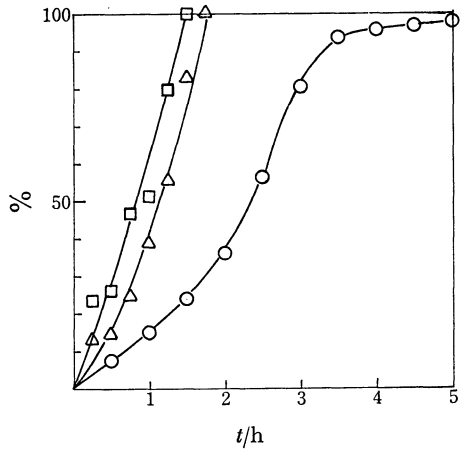


Fig. 4. Conversion of carbon monoxide *vs.* reaction time.
Mark Catalyst Run No. in Table 4
-○- $Co_2(CO)_8$ No. 6
-□- Recycled No. 4
-△- Recycled No. 5

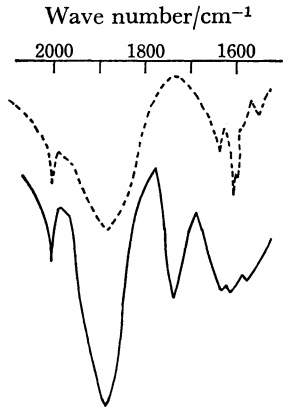


Fig. 5. Comparison of IR spectra.
Full line: New complex prepared from $Co_2(CO)_8$ and EBP in a molar ratio of 3: 8.
Dotted line; $H_2Co_3(CO)_9(Py)_5$.[6,7]

plotted against the reaction time in Fig. 4. Catalytic activities of the recycled complex in runs No. 4 and No. 5, according to Fig. 4, are markedly higher than that of $Co_2(CO)_8$ at the low temperature of 50 °C.

Infrared Spectrum of the New Complex. The complex, prepared from $Co_2(CO)_8$ (8 mmol) and EBP (21.3 mmol), and recycled several times as hydroformylation catalyst, was washed twice by agitating in petane (100 ml) at 100 °C, 40 kg/cm² ($H_2/CO=1$). A separated viscous phase was taken out of the autoclave after cooling and its IR spectrum together with that of a pyridine complex is shown in Fig. 5. The spectrum of the new complex shows the same absorptions at 2010 and 1890 cm^{-1} as that of the pyridine complex, indicating the structural analogy of the new complex to $H_2Co_3(CO)_9(py)_5$.

Discussion

The complex, $H_2Co_3(CO)_9(py)_5$, is selectively produced by the reaction of $Co_2(CO)_8$ and pyridine in the molar ratio of one to four at 100 °C, 50 kg/cm² ($H_2/CO=1$), followed by cooling to room temperature.[7] A complex of an analogous structure should also be formed under similar conditions from $Co_2(CO)_8$ and EBP which has two pyridyl groups in the molecule, shown by a comparison of the IR spectra (Fig. 5). The catalyst structure and the mechanism of the catalyst separation can be understood by the model illustrated in Fig. 6, where EBP is represented by a mark N–N (N stands for nitrogen of the pyridyl group).

The higher the concentration of the unit complex during the reaction, the higher the possibility that the unit complex can be linked by N–N bridges with neighboring complexes after being cooled to room temperature, thereby becoming insoluble. This explains the unusual experimental results shown in Fig. 2, that the catalyst separation after cooling is improved by employing larger amounts of $Co_2(CO)_8$ and EBP in a fixed ratio of 3/2: 4, a ratio which corresponds to the

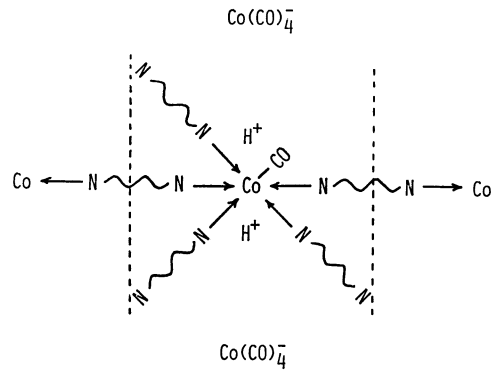


Fig. 6. Structural model of new complex, $H_2Co_3(CO)_9$-$(EBP)_n$, when n is 4.

formula: $H_2Co_3(CO)_9(EBP)_4$. When the temperature is raised, on the other hand, the linking between unit complexes by N–N bridge will dissociate, at least partially, and the solubility of the complex will increase as a result. This explains the change in solubility of the complex with temperature observed through the windows of the reaction vessel.

As the ionic complex, $H_2Co_3(CO)_9(py)_5$, has been found to be in equilibrium with such non-ionic species as $Co_2(CO)_8$ at elevated temperatures,[6] there should also be an equilibrium relation as Eq. 1, in the case of the new complex.

$$H_2Co_3(CO)_9(EBP)_n + 3CO = H_2 + 3/2Co_2(CO)_8 + nEBP \quad (1)$$

The number n in Eq. 1 can be 4 or 3, since the separation takes place satisfactorily when the EBP to Co ratio is 4: 3 (Fig. 2) or 3: 3 (Table 3). The separation occurs only partially when the EBP/Co ratio is less than 1 (Fig. 1).

This complex, $H_2Co_3(CO)_9(EBP)_n$, is probably an active catalyst for hydroformylation under mild conditions, since the analogous pyridine complex, H_2Co_3-$(CO)_9(py)_5$, has been found to react with an olefin even at room temperature.[7] The concentration of H_2Co_3-$(CO)_9(EBP)_n$, according to Eq. 1, should increase as the hydrogen partial pressure is increased, but decrease as the carbon monoxide partial pressure is increased. This explains the accelerating effect of hydrogen, and the retarding effect of carbon monoxide, on the reaction rate (Table 3). The reaction rate decreases with increasing total pressure (Fig. 3), probably because its decrease due to an increase in P_{CO} is larger than its increase due to an increase in P_{H_2}. The retarding effect of nitrogen pressure on the reaction rate, however, remains unexplained. The fact that the catalyst separation is improved by employing a mixed gas with a higher ratio of hydrogen to carbon monoxide can be explained, since such non-ionic species as $Co_2(CO)_8$ which remain dissolved in the cooled reaction product, will decrease with increasing hydrogen pressure and decreasing carbon monoxide pressure, according to Eq. 1.

The foregoing argument, however, does not exclude the presence of other active species such as $HCo(CO)_4$ and $HCo(CO)_3$ which can also be in equilibrium with $Co_2(CO)_8$ under these reaction conditions. In this connection, it should be noted that the selectivity to the linear aldehyde under extreme conditions of very high P_{H_2}/P_{CO} ratios was remarkably higher in the presence of $H_2Co_3(CO)_9(EBP)_n$ than in the presence of $Co_2(CO)_8$ (Table 4). This strongly suggests that the active catalyst, at least under the extreme conditions of high P_{H_2}/P_{CO} ratios, is different from $HCo(CO)_4$ or $HCo(CO)_3$, and that the active catalyst in this case must be the complex, $H_2Co_3(CO)_9(EBP)_n$, the formation of which is favored by the high P_{H_2}/P_{CO} ratio.

The selectivity to the linear aldehyde under the normal gas ratio ($P_{H_2}/P_{CO}=1$) was, on the contrary, a little lower in the presence of the new complex than in the presence of $Co_2(CO)_8$ (Fig. 1). Therefore, still unidentified catalyst species different from H_2Co_3-$(CO)_9(EBP)_n$, $HCo(CO)_4$, and $HCo(CO)_3$, must be taking part in this case.

The reasons for the selectivity to linear aldehyde increasing with increasing carbon monoxide pressure and increasing hydrogen pressure cannot be explained, because there are still unknown factors affecting the selectivity as discussed above. However, the effect of the total pressure on the selectivity to linear aldehyde is, evidently, a result of the co-effects of the respective partial pressures of carbon monoxide and hydrogen, since the increase in total pressure due to such inert gas as nitrogen does not affect the selectivity (Table 3).

The authors wish to express their thanks to Messrs. Toshiyuki Murakami and Ryuji Yamazaki for their assistance in the experimental work.

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