

## Applications of Homogeneous Water-gas-shift Reaction. II. The Formation of Dipropyl Ketones as Primary Products from CO and H<sub>2</sub>O in the Presence of an Excess Amount of Propene. Cobalt-based Catalytic Hydrocarbonylation

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The hydrocarbonylation of propene with CO and H<sub>2</sub>O to give dipropyl ketones occurs predominantly over forming C<sub>4</sub>-aldehydes; the catalyst solutions employed are prepared *in situ* from Co<sub>2</sub>(CO)<sub>8</sub>, various phosphines as ligands, and H<sub>2</sub>O, a high molar ratio of propene to Co<sub>2</sub>(CO)<sub>8</sub> of 300/2 being required. Of the several phosphorus ligands examined, 1,2-bis(diphenylphosphino)ethane (diphos) and bis(diphenylphosphino)acetylene are relatively effective for the formation of the ketones (abbreviated as [ketones]). The effects of the reaction variables (CO pressure, temperature, and H<sub>2</sub>O concentration) on [ketones] are also examined using the Co<sub>2</sub>(CO)<sub>8</sub>-diphos system; [ketones] increases with the initial increase in CO pressure, but reaches a maximum at *ca.* 100 kg/cm<sup>2</sup> and decreases thereafter. Pronounced decreases of [ketones] are observed when pyridine as well as hydrogen is added to the catalyst solutions.

Hydrocarbonylation, by which dialkyl ketones are produced from olefins, can proceed under oxo conditions by means of a transition-metal catalyst.<sup>1)</sup> However, the selectivity of the reaction is significantly low when olefins other than ethene are used;<sup>2)</sup> generally, a mixture of ketones, aldehydes, and other oxygenated products is formed. Accordingly, the hydrocarbonylation reaction, despite its potential synthetic value, has scarcely been investigated at all.

We described in our previous papers that the presence of an excess amount of propene under the hydrocarbonylation conditions using CO-H<sub>2</sub>O leads to the formation of dipropyl ketones as primary products,<sup>3)</sup> and Co<sub>2</sub>(CO)<sub>8</sub>-phosphine system appeared to be much more effective for the ketone formation than other transition-metal catalysts, being especially active for the homogeneous water-gas-shift reaction (WGSR).<sup>4)</sup>

In the present paper, further studies of this cobalt catalyzed-hydrocarbonylation will be described, and the catalytic behavior will be compared with that in hydroformylation.

### Experimental

The experimental methods are roughly analogous to those described in the preceding paper.<sup>3)</sup> The few differences will be outlined below.

The phosphines and pyridine were obtained commercially.

The hydrocarbonylation reactions were performed in a 300 ml stainless-steel autoclave equipped with a vertical agitator. In all runs, the molar ratio of propene to Co<sub>2</sub>(CO)<sub>8</sub> was kept constant at 300 mmol/2 mmol.

A certain amount of hydrogen was added to a catalyst solution as soon as the solution had been brought to the reaction temperature (Fig. 5). A small amount of pyridine was mixed with the catalyst solutions (Co<sub>2</sub>(CO)<sub>8</sub>-diphos-dioxane-H<sub>2</sub>O) before the reactor was sealed (Fig. 6).

### Results and Discussion

All of the hydrocarbonylation experiments were carried out for a 5 h-reaction time<sup>5)</sup> with the propene/Co<sub>2</sub>(CO)<sub>8</sub> molar ratio being held constant at 300/2, since the maximum yield of dipropylketones was achieved at this ratio (see Fig. 3 in the preceding

paper<sup>3)</sup>). Co<sub>2</sub>(CO)<sub>8</sub> was also used as a catalyst precursor in the dioxane solvent. As is shown in Table 1, THF (Run 1) and the cobalt carbonyl cluster (CH<sub>3</sub>-CCo<sub>3</sub>(CO)<sub>9</sub>) (Run 2) lead to a reduction in the ketone formation.

*Effects of Several Phosphorus Ligand.* The results are summarized in Table 1 (Runs 3,4,9–15). The effectiveness of phosphorus ligands in increasing the formation of the ketones ([ketones]) decrease in this order: diphos > Ph<sub>2</sub>PC≡CPh<sub>2</sub> > PPh<sub>3</sub> > Ph<sub>2</sub>PCH<sub>2</sub>-PPh<sub>2</sub> > PBu<sub>3</sub> > Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> > (PhO)<sub>3</sub>P > Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>-PPh<sub>2</sub> = Ph<sub>2</sub>As(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>.

The effect of the diphos: Co<sub>2</sub>(CO)<sub>8</sub> ratio on the [ketones] was also examined (Runs 4–8); the most active catalyst appears to be formed with a *ca.* 0.75:1 ratio (Run 5). As we would expect, however, for the <1:1 ratios, the catalyst partially decomposes during the reaction.<sup>6)</sup> In the absence of diphos, 6.5 mmol of the ketones were obtained, with the Co<sub>2</sub>(CO)<sub>8</sub> being completely decomposed.<sup>6,7)</sup> (Run 8) Both the order of reactivity and the ratio effect reported here are quite similar to those observed for the hydroformylation using CO-H<sub>2</sub>O with a propene/Co<sub>2</sub>(CO)<sub>8</sub> molar ratio of 25/2.<sup>8)</sup> Hereafter, diphos is here used as a ligand.

*Effect of CO Pressure.* The [ketones] value is remarkably dependent on such reaction variables as CO pressure (*P*<sub>CO</sub>), H<sub>2</sub>O concentration, and the temperature. Figure 1 illustrates the *P*<sub>CO</sub> dependence. The [ketones] value increased with the initial increase in *P*<sub>CO</sub>, but nearly reached a maximum as the *P*<sub>CO</sub> increased to *ca.* 100 kg/cm<sup>2</sup> decreased thereafter. The C<sub>4</sub> aldehyde formation ([aldehydes]), on the other hand, smoothly decreased with the increase in *P*<sub>CO</sub>.

*Effect of Temperature.* The temperature dependence under 100 kg/cm<sup>2</sup> of *P*<sub>CO</sub> is shown in Fig. 2. The [ketones] value increased with an increase in the temperature from 135 °C to 165 °C, but rather decreased at 180 °C, whereas [aldehydes] successively increased; as a result, the selectivity to the ketones drastically decreased (---) at 180 °C.

*Effect of H<sub>2</sub>O Concentration.* Figure 3 displays a plot of the product formation as a function of the H<sub>2</sub>O added. The [ketones] value reached a maximum

TABLE 1. HYDROCARBONYLATION OF PROPENE USING CO-H<sub>2</sub>O CATALYZED BY Co<sub>2</sub>(CO)<sub>8</sub>  
 WITH SEVERAL PHOSPHORUS LIGANDS

 Co<sub>2</sub>(CO)<sub>8</sub>, 2 mmol; phosphine, 2 mmol; dioxane (solvent), 50 ml; propene, 300 mmol; H<sub>2</sub>O, 60 mmol;  
 CO 100 kg/cm<sup>2</sup> (const); time, 5 h; temp, 165 °C.

Run No.	Added phosphine	Products <sup>a)</sup>		
		[ketones] mmol	[aldehydes] mmol	[acids] mmol
1	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> <sup>b)</sup>	19.2	10.3	0.7
2	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> <sup>c)</sup>	14.1	8.1	0.6
3	Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub>	12.9	4.0	1.1
4	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	27.0	11.0	0.5
5	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> (1.5 mmol)	36.2	—	—
6	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> (1.0 mmol)	32.2	—	—
7	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> (0.5 mmol)	25.9	—	—
8	none	6.5	2.4	—
9	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub>	12.1	5.9	—
10	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>4</sub> PPh <sub>2</sub>	3.9	2.2	—
11	Ph <sub>2</sub> PC≡CPPh <sub>2</sub>	26.4	12.2	1.1
12	PPh <sub>3</sub>	21.6	7.0	0.5
13	PBu <sub>3</sub>	12.8	3.9	—
14	Ph <sub>2</sub> As(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	3.9	0.3	—
15	(PhO) <sub>3</sub> P	5.2	7.7	—

a) [ketones]: 4-heptanone + 2-methyl-3-hexanone + 2,4-dimethyl-3-pentanone, [aldehydes]: butyraldehyde + isobutyraldehyde, [acids]: butyric acid + isobutyric acid. b) Using THF (50 ml) as the solvent. c) Using CH<sub>3</sub>CCo<sub>2</sub>(CO)<sub>9</sub> as the precursor.

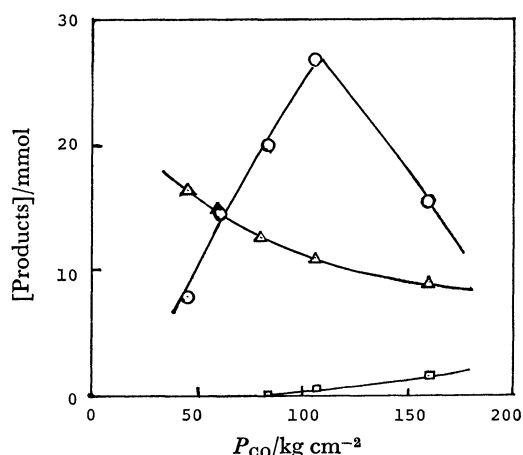


Fig. 1. Effect of CO pressure.

Co<sub>2</sub>(CO)<sub>8</sub> 2 mmol, diphos 2 mmol, dioxane 50 ml, H<sub>2</sub>O 60 mmol, 165 °C, propene 300 mmol, time 5 h.  
 —○—: Dipropyl ketones, —△—: C<sub>4</sub>-aldehydes,  
 —□—: C<sub>4</sub>-acids.

as the amount of H<sub>2</sub>O([H<sub>2</sub>O]) increased to ca. 120 mmol, and leveled off thereafter. In contrast, [aldehydes] linearly increased with the increase in [H<sub>2</sub>O]. Thus, the combined yield (---) increased with [H<sub>2</sub>O].

A plot of the product formation as a function of the Co<sub>2</sub>(CO)<sub>8</sub> concentration, where the diphos/Co<sub>2</sub>(CO)<sub>8</sub> ratio was kept constant at 1/1, gave results analogous to those shown in Fig. 3.

**Catalytic Intermediates.** It seems likely that catalytic intermediates (probably HCo(CO)<sub>m</sub>(diphos)<sub>n</sub>, (A)) which catalyze the hydroformylation of propene with CO and H<sub>2</sub>O, as has already been described

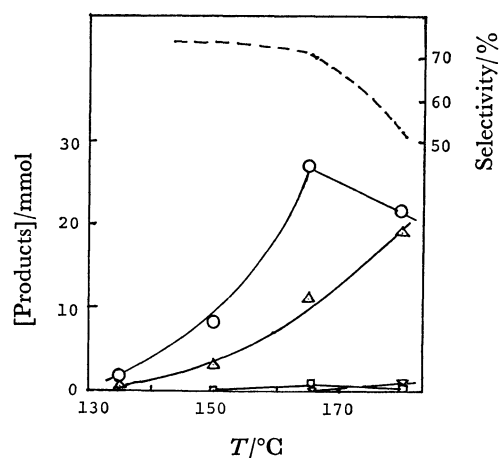
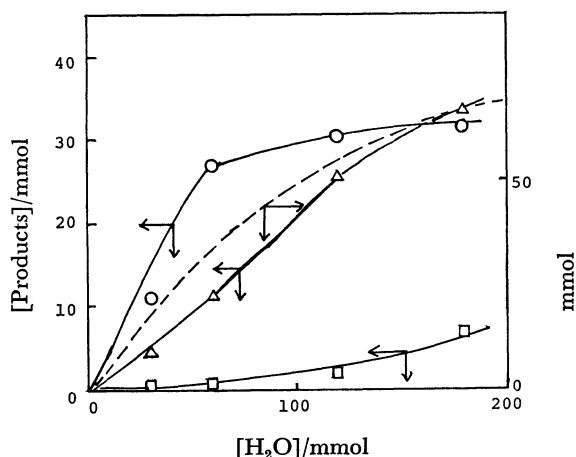


Fig. 2. Effect of temperature.

Co<sub>2</sub>(CO)<sub>8</sub> 2 mmol, diphos 2 mmol, dioxane 50 ml, H<sub>2</sub>O 60 mmol, P<sub>CO</sub> 100 kg/cm<sup>2</sup>, propene 300 mmol, time 5 h.  
 —△—: C<sub>4</sub>-alcohols, ----: the selectivity; [ketones]/([ketones] + [aldehydes] + [alcohols] + [acids]), other marks: see footnote of Fig. 1.

in the preceding paper,<sup>3)</sup> also participate in this hydrocarbonylation. In fact, C<sub>4</sub> aldehydes can be formed even during the reaction (Table 1, Figs. 1—3). The influence of phosphorus ligands on the [ketones] value (propene/Co<sub>2</sub>(CO)<sub>8</sub>=300/2, Table 1) is fairly analogous to that on the hydroformylation activity (the ratio=25/2).<sup>8)</sup> A smooth increase in the combined yield results when [H<sub>2</sub>O] is increased, since the concentration of (A) also increases (Fig. 3). The catalyst solutions active in the hydrocarbonylation have the

Fig. 3. Effect of H<sub>2</sub>O concentration.

Co<sub>2</sub>(CO)<sub>8</sub> 2 mmol, diphos 2 mmol, dioxane 50 ml, P<sub>CO</sub> 100 kg/cm<sup>2</sup>, propene 300 mmol, temp 165 °C, time 5 h.

----: A combined yield ([ketones] + [aldehydes]), other marks: see footnote of Fig. 1.

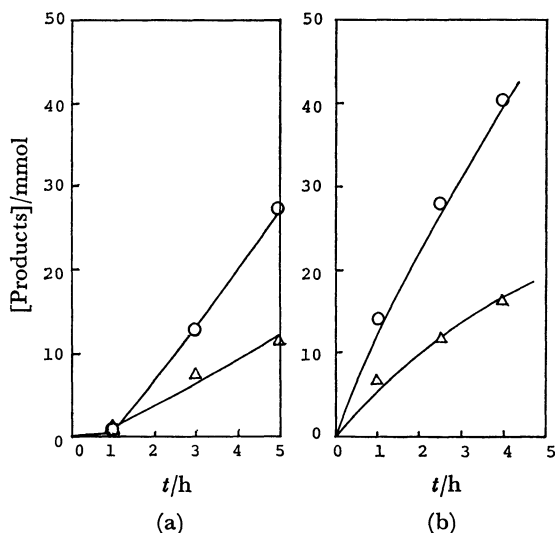


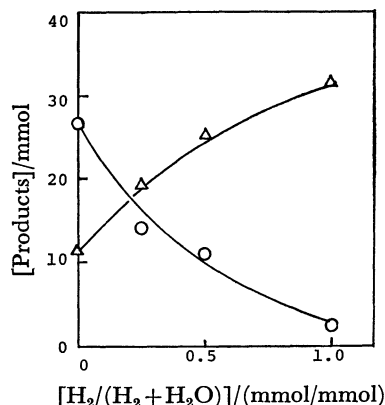
Fig. 4. Cobalt-catalyzed hydrocarbonylation as a function of time.

Co<sub>2</sub>(CO)<sub>8</sub> 2 mmol, diphos 2 mmol, dioxane 50 ml, P<sub>CO</sub> 100 kg/cm<sup>2</sup>, H<sub>2</sub>O 60 mmol, propene 300 mmol, temp 165 °C.

(a) A standard reaction, (b) a reaction after the pretreatment with both CO (100 kg/cm<sup>2</sup>) and H<sub>2</sub>O (60 mmol) at 165 °C for 1 h, marks (○, △): see footnote of Fig. 1. Other products omitted.

same IR absorptions in the metal-carbonyl region as in hydroformylation. Also, there is an induction period for the ketone formation as well as in the case of aldehydes (Fig. 4a); the period disappears on the pretreatment of the solution (Co<sub>2</sub>(CO)<sub>8</sub>-diphos-dioxane) with both CO (100 kg/cm<sup>2</sup>) and H<sub>2</sub>O (60 mmol) at 165 °C for 1 h in the absence of propene (Fig. 4b).

Thus, if (A) is present, we can postulate the following reaction, which produces acyl complexes (B) as other key intermediates for the hydrocarbonylation as well as hydroformylation. This is analogous to a scheme proposed by Jonassen<sup>9)</sup> and Heck<sup>10)</sup> with regard

Fig. 5. Effect of added H<sub>2</sub>.

Co<sub>2</sub>(CO)<sub>8</sub> 2 mmol, diphos 2 mmol, dioxane 50 ml, P<sub>CO</sub> 100 kg/cm<sup>2</sup>, propene 300 mmol, temp 165 °C, time 5 h.

Marks (○, △): See footnote of Fig. 1. Other products omitted.

Total amounts of H<sub>2</sub>O and H<sub>2</sub>: 60 mmol.

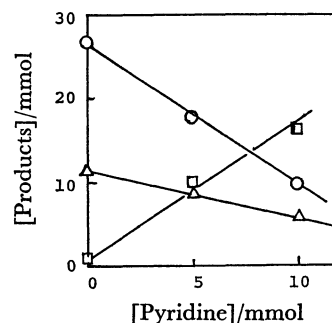
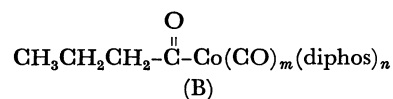
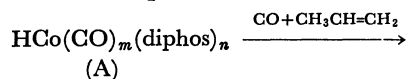


Fig. 6. Effect of added pyridine.

Conditions are the same as in Fig. 5.

Marks (○, △, □): See footnote of Fig. 1.

to these two reactions using a normal Co<sub>2</sub>(CO)<sub>8</sub> catalyst with CO-H<sub>2</sub>.



If (B) is rapidly consumed for the formation of C<sub>4</sub> aldehydes (or acids) before the interaction with propene, then the [ketones] value will be diminished. For example, when hydrogen is added to a catalyst solution, a pronounced increase in [aldehydes] results, as is illustrated in Fig. 5, where the total amount of hydrogen donors (H<sub>2</sub>O or H<sub>2</sub>) was kept constant at 60 mmol, whereas the [ketones] value decreases with an increase in the hydrogen concentration, even at a constant high molar ratio of propene/Co<sub>2</sub>(CO)<sub>8</sub> (=300/2). A further example was obtained from experiments featuring the addition of a small amount of pyridine; the results are shown in Fig. 6. The rapid reaction of (B) with H<sub>2</sub>O takes place, producing C<sub>4</sub> acids (□); as a result, both [ketones] (○) and [aldehydes] (△) decrease. The accelerating effects of pyridine have already been observed on the normal Co<sub>2</sub>(CO)<sub>8</sub>-catalyzed hydrocarboxylation of olefin.<sup>11)</sup>

Considering the data described above, it is probable that the intermediates (A) are present. However, because of the possible existence of cobalt carbonyl species different from (B), as is demonstrated by the variations in [ketones] and [aldehydes] with the CO pressure (Fig. 1), the above-mentioned acyl complexes, (B), can be considered only as possible models of the reaction intermediates.

## References

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- 2) G. Natta, P. Pino, and R. Ercoli, *J. Am. Chem. Soc.*, **74**, 4496 (1952).
- 3) K. Murata and A. Matsuda, *Bull. Chem. Soc. Jpn.*, **54**, 245 (1981).
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- 5) The time is the same as in the hydroformylation.<sup>3)</sup>
- 6) The dissolved cobalt in a 5-h-reaction solution was determined by means of EDTA-titration.

diphos/Co <sub>2</sub> (CO) <sub>8</sub> (mmol/mmol)	Dissolved Co (mg-atom)
2/2	3.9
1.5/2	2.4
0/2	0

- 7) Under the conditions employed, no hydrocarbonylation occurs with the resulting metallic cobalt.
- 8) K. Murata, A. Matsuda, K. Bando, and Y. Sugi, *J. Chem. Soc., Chem. Commun.*, **1979**, 785.
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- 11) In order to explain these accelerating effects, the following schemes have been proposed:
 
$$\begin{aligned} \text{RCOCo(CO)}_4 + \text{Py} &\longrightarrow [\text{RCO}\cdot\text{Py}]^+[\text{Co(CO)}_4]^- \\ &\longrightarrow \text{RCOOH} + [\text{HPy}]^+[\text{Co(CO)}_4]^- \\ &\longrightarrow \text{HCo(CO)}_4 + \text{Py} \end{aligned}$$

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