BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2966—2970 (1969)

# Synthetic Studies of Cobalt Carbonyl by Noble Metal Catalysts. II.*[1]
## The Investigation of Reaction Conditions

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(Received March 24, 1969)

The reaction conditions of cobalt carbonylation catalyzed by palladium have been investigated. Polar solvents have, with some exceptions, been shown to be superior to nonpolar solvents. The fact that the total pressure of synthesis gas and the partial pressure of hydrogen, especially the latter, have a great effect on the initiation temperature of reaction suggests that the presence of hydrogen is very important in the present reaction. The low reactivity and poor yield in the reactions of Raney cobalt indicate that a low-valency intermediate in the course of the cobalt-carbonylation reaction of cobaltous compounds may be somewhat different from the Raney-type Co(0). The initial step of the reaction seems to be affected only a little by various additives *e. g.*, water, triphenyl phosphine, lead naphthenate, and sodium hydroxide. The data previously available suggest that a palladium catalyst may primarily promote the reduction of Co(II) to Co(0) by activating hydrogen. The test of the lifetime of a palladium-on-carbon catalyst for a month indicates that there is no apparent decrease in the catalytic activity within this period.

Previous work[1] in our laboratory has shown that material containing palladium, platinum, gold, or silver, especially metals supported on active carbon, catalytically promotes the cobalt-carbonylation reaction.

In the present program, the effects of solvent, pressure, and additives on cobalt-carbonylation reactions catalyzed by palladium have been investigated.

Furthermore, in order to elucidate the behavior of palladium-on-carbon catalysts, the reaction of Raney cobalt has been studied. On the basis of these data, the role of the palladium catalyst will be briefly discussed.

### Experimental

**General Procedures.** The experiments and the analysis of the reaction products were carried out in the way described in a previous paper.[1] The initiation temperature of the reaction, which was defined in the previous paper,[1] was also used here as one of scales measuring the reactivities of cobalt compounds and of the materials added.

**Materials.** Cobalt compounds, solvents, and other chemicals which were proved to be sufficiently pure were commercially available materials and were used without further purification. Palladium-on-carbon (300 mesh up) containing 5 wt% of palladium metal was purchased from the Kawaken Fine Chemicals Co., Ltd.

**Raney Cobalt Feed.** Thirty grams of Al-Co (1 : 1) alloy were added, drop by drop, to a 10% excess of an aqueous sodium hydroxide solution in open air or in a nitrogen atmosphere. After the addition has been completed, the developed Raney cobalt was decanted, washed with distilled water, and exchanged by acetone and finally by 190 *ml* of *n*-butanol. The freshly prepared suspension was used for the carbonylation reaction. After the reaction, the insoluble materials, *i. e.*, unreacted Raney cobalt and the catalyst, were filtered out and the cobalt carbonyl in the filtrate was analyzed as usual. The yield of cobalt carbonyl was calculated on the basis of the filtered solution of the reaction mixture in order to avoid any overestimation of the yield caused by adsorption gas on the surface of the Raney cobalt and the Pd-on-carbon.

### Results and Discussion

**The Effects of Solvents.** The effects of solvents on the initiation temperature in the cobalt-carbonylation reaction promoted by palladium-on-carbon were studied, they are summarized in Table 1. The reaction was initiated at lower temperatures in such polar solvents as *n*-butanol, diethyl ether, isobutyraldehyde, and pyridine than in the nonpolar solvent, *n*-hexane. With isobutyraldehyde, however, the initiation temperature was somewhat higher compared to those of the polar solvents examined. Such a superior property of polar solvents has also been found in conventional cobalt-carbonylation reactions.[2,3] In any case, since the reaction catalyzed by palla-

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[*1] Presented in part at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[1] S. Usami, T. Kondo, K. Nishimura and Y. Koga, This Bulletin, **42**, 2961 (1969).

[2] J. Kato, H. Wakamatsu and R. Iwanaga, Japanese Pat. 265091 (1960).

[3] F. Calderazzo, R. Ercoli and G. Natta, "Organic Syntheses *via* Metal Carbonyls," Interscience Publishers, ed. by I. Wender and P. Pino, New York (1968), p. 20.

TABLE 1. EFFECTS OF SOLVENTS ON THE INITIATION TEMPERATURE OF THE REACTION

| Solvent used | Initiation temperature °C |
|---|---|
| Diethyl ether | 53 |
| Pyridine | 54.5 |
| *n*-butanol | 50—55 |
| Isobutyraldehyde | 61 |
| *n*-Hexane | 80 |

Reaction conditions: $Co(OH)_2$ 0.241 mol
Pd-C (5 wt% Pd; 300 mesh up): Pd/Fed Co 2.36 atom%
Solvent 190 m*l*, Synthesis gas ($H_2/CO$ 1.2) 150 kg/cm$^2$

dium proceeds smoothly at low temperatures in either solvent, it is possible to select a solvent according to whether the desired form of cobalt carbonyl is crystalline dicobalt octacarbonyl or another. However, care must be taken to use such solvents as pyridine or isobutyraldehyde, because the following reactions occur in these solvents to form the complex (I) or the trimer (II).

The isobutyraldehyde trimer (II) was identified by means of its molecular weight, elemental analysis, its melting point, and its IR spectra.

$$Co^{2+} + \text{Pyridine} \longrightarrow \underset{\text{(I)}}{Co(Py)_6[Co(CO)_4]_2}$$

$$3(CH_3)_2CHCHO \xrightarrow{HCo(CO)_4} \underset{\text{(II)}}{\text{2,4,6-triisopropyl-1,3,5-trioxane}}$$

For experimental convenience, *n*-butanol was used as the solvent in the subsequent experimental runs unless otherwise noted.

**The Effect of the Total Pressure.** The influence of the total pressure of the synthesis gas on the initiation temperature was examined at a fixed ratio (1 : 3) of hydrogen to carbon monoxide. As Table 2 shows, the initiation temperature becomes higher with a decrease in the total pressure.

TABLE 2. EFFECT OF TOTAL PRESSURE

| Total press (kg/cm$^2$) | Partial press (kg/cm$^2$) | | Equil. press $P_{CO}$* (kg/cm$^2$) | Initiation temp. (°C) |
|---|---|---|---|---|
| | $H_2$ | CO | | |
| 142 | 77.5 | 64.5 | 0.7 | 50—55 |
| 72 | 39.3 | 32.7 | 1.7 | 72 |
| 26 | 14.8 | 11.2 | 2.8 | 82 |

* Calculated from Rudkovskii's equation.

In these runs, the partial pressures of carbon monoxide were larger than the equilibrium pressures of carbon monoxide at each temperature, while dicobalt octacarbonyl began to decompose thermally. The equilibrium pressure was calculated from the following equation, proposed by Rudkovskii:[4)]

$$Co_2(CO)_8 \rightleftarrows 2Co + 8CO$$

$$\log P_{CO} = 7.94 - 2660/T$$

where $P_{CO}$ and $T$ are the partial pressure of CO (kg/cm$^2$) and the absolute temperature (°K) respectively. From this and other data to be presented in the next section, it seems more likely that the upward tendency of the initiation temperature with a decrease in the total pressure is to be attributed to the effective concentration of gases, particularly hydrogen, in the liquid phase rather than to the equilibrium pressure of carbon monoxide.

In order to ascertain the yield of cobalt carbonyl in the reaction under a low pressure, the experiments were carried out with 58 mmol of cobalt hydroxide and 2.45 atom% of a palladium catalyst on cobalt in 190 m*l* of *n*-butanol. The results are shown in Table 3.

The pressure was kept at 80 kg/cm$^2$ by adding carbon monoxide; two experimental runs were carried out, one at 80°C for 100 min and one at 100°C for 60 min. Under those sets of conditions cobalt carbonyl was obtained in 79 and 88% yields, respectively. However, these yields were considered to be minimum values because of the analytical difficulty caused by the precipitation of crystalline $Co_2(CO)_8$. For comparison, the results at 150 kg/cm$^2$ of synthesis gas are also shown in the table, within the range of experimental error, a quantitative yield of cobalt carbonyl was attained even at temperatures as low as 60°C.

TABLE 3. COBALT CARBONYL SYNTHESIS UNDER LOW PRESSURE

| Run No. | React. temp. (°C) | React. press. (kg/cm$^2$) | React. time (min) | Cobalt carbonyl yield (mole %) | Note |
|---|---|---|---|---|---|
| 1 | 80 | 80 | 100 | 79< | ppt of cryst. $Co_2(CO)_8$ |
| 2 | 100 | 80 | 60 | 88< | ppt of cryst. $Co_2(CO)_8$ |
| 3 | 60 | 150 | 60 | 97.0 | no ppt of cryst. $Co_2(CO)_8$ |

$Co(OH)_2$ 0.0580 mol, Pd/Co 2.45 atom%, $H_2/CO=1$, Solvent *n*-BuOH 190 m*l*
In No. 1 and No. 2 runs, a conspicuous gas absorption stopped after 15 and 27 min respectively.
In No. 3 run, mixed solvent of *n*-BuOH 90 m*l* and benzene 100 m*l* was used.

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4) a) D. P. Krinkin and D. M. Rudkovskii, *Zh. Prikl. Khim.* **38**(8), 1670 (1965). b) V. Yu. Gankin, D. P. Krinkin and D. M. Rudkovskii, *Zh. Fiz. Khim.* **40**(1), 215 (1966).

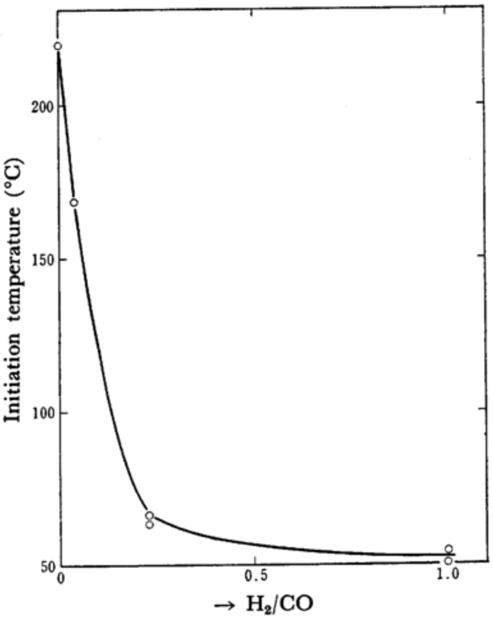

Fig. 1. Effect of $H_2/CO$ ratio.

$Co(OH)_2$ 0.241 mol, Pd/Co 2.36 atom% *n*-BuOH 190 m*l*, Synthesis Gas. 150 kg/cm$^2$

**The Effect of the Partial Pressure.** Reactions were conducted at a fixed total pressure of 150 kg/cm$^2$ but with various ratios of hydrogen to carbon monoxide. The results are shown in Fig. 1 as a plot of the ratio of hydrogen to carbon monoxide against the initiation temperature. In the absence of hydrogen, no decline in the gauge pressure was found until 220°C. However, after the reactor has been cooled, the gauge pressure became a little lower than the initial pressure, and about 10% of cobalt carbonyl was formed.

These facts suggest that the reaction rate under the above conditions is too slow for the pressure decline to be detected. It was interesting that, in the reaction under a carbon monoxide atmosphere, a dehydrogenation reaction of the solvent, *n*-butanol, occurred. Small amounts of *n*-butyraldehyde, 1,1-dibutoxy-*n*-butane, 2-ethylhex-2-en-1-al, and 2-ethylhexanol-1 were detected by gas chromatography. When *n*-butanol was treated with palladium-on-carbon under carbon monoxide pressure at 170°C for 7 hr, no dehydrogenation product was detected.

Therefore, hydrogen appears to be abstracted from *n*-butanol by cobalt. However, the above data are insufficient for us to conclude which is the immediate acceptor of hydrogen, cobalt or palladium, at 220°C, or how the hydrogen thus abstracted acts in the reaction. On the contrary, the cobalt-carbonylation reaction occurred at much lower temperatures when hydrogen was added. With a total pressure of 150 kg/cm$^2$ and otherwise identical conditions except that the partial pressures of hydrogen were 5.8, 28.0, and 81.8 kg/cm$^2$, the initiation temperatures were 170, 65, and 55°C respectively. These marked effects of added hydrogen on the initiation temperature are of great importance in considering the role of palladium catalysts.

**Cobalt Carbonylation of Raney Cobalt.** Experiments were carried out to see whether palladium catalysts participate on the step of the addition of carbon monoxide to a low-valent cobalt intermediate in the course of the cobalt-carbonylation reaction. Raney cobalt was selected on the assumption that the intermediate has zero valence and was very similar to Raney cobalt. The results are summarized in Table 4.

TABLE 4. COBALT CARBONYLATION OF RANEY COBALT

| Pd/Co (atom %) | $H_2/CO$ (V/V) | Atmosphere for develop. of Al-Co alloy | Reaction initiation temp. (°C) | Co carbonyl yield (mol%) |
|---|---|---|---|---|
| 0 | 0 | Air | 200< | 3.2 |
| 0 | 1 | Air | 185 | 1.2 |
| 2.22 | 0 | Air | 200< | 6.3 |
| 2.22 | 1 | Air | 163 | 2.2 |
| 0 | 0 | $N_2$ | 200< | 2.8 |
| 0 | 1 | $N_2$ | 183 | 1.4 |
| 2.22 | 0 | $N_2$ | 200< | 3.2 |
| 2.22 | 1 | $N_2$ | 178 | 1.7 |

Raney Co 15.0 g, *n*-BuOH 190 m*l*, Total press. 150 kg/cm$^2$ Pd-C (5 wt% Pd; 300 mesh up), Reaction time 60 min.

With 150 kg/cm$^2$ of carbon monoxide, no decline in the pressure was observed up to 200°C even in the presence of a palladium catalyst. On the other hand, a slow but apparent decline of the pressure was observed from 170 to 185°C in the reaction under 150 kg/cm$^2$ of synthesis gas, irrespective of the presence of a palladium catalyst. However, equally poor yields of cobalt carbonyl were obtained in both reactions under carbon monoxide and in the pressure of synthesis gas. A similar low yield in the conventional cobalt carbonylation with Raney cobalt has also been disclosed in the literature.[5]

According to a German patent,[6] cobalt carbonylation with reduced cobalt is strongly inhibited by a small amount of oxygen. In the present study, however, this factor may be excluded because the reactions of Raney cobalt developed in nitrogen and in an open atmosphere give very similar results. The results obtained here indicate that the reaction rate with Raney cobalt is much slower than that with cobalt hydroxide. In conclusion, it

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[5] Ref. 3, p. 19.

[6] I. G. Farben A. G., Brit. Pat. 307112 (1927); *Chem. Abstr.*, **23**, 5281 (1929).

seems reasonable to consider that the low-valent intermediate in the course of the cobalt carbonylation of a cobaltous compound, cobalt hydroxide, for example, is somewhat different from the Raney-type cobalt, Co(0), Therefore, the role of the palladium catalyst in this step is still obscure.

**The Effects of Additives.** In order to characterize the reaction in more detail, various materials, *i. e.*, dicobalt octacarbonyl, water, triphenyl phosphine, pyridine, dihexyl sulfide, lead naphthenate, and sodium hydroxide, were added to the reaction system. The results are listed in Table 5. The reaction where dicobalt octacarbonyl coexisted with a palladium catalyst gave essentially the same initiation temperature as the case without dicobalt octacarbonyl as an additive. Such organic ligands as triphenyl phosphine and pyridine also had little effect on the initiation temperature. These results may be understood from the consideration that the examined materials probably react with cobalt carbonyl once formed and do not participiate in the step of cobalt-carbonyl formation. The addition of sulfur compounds such as dihexyl sulfide and heavy metals such as lead naphthenate, which are regarded as strong poisons for a usual hydrogenation reaction, showed no significant retarding effect. Sodium hydroxide, which seems to be a retarder of autocatalysis by cobalt hydrocarbonyl, also exerted the same retardation as lead soap. It is noteworthy that the initial step of cobalt carbonylation catalyzed by palladium-on-carbon is affected only a little by various additives. This phenomenon is considered to be very closely related to the characteristic mode of cobalt carbonylation where cobalt is reduced by hydrogen, even in the presence of such a strong poison as carbon monoxide in the general hydrogenation reaction.

Table 5. Effect of various additives

| Additive | Additive/Pd (mol%) | $H_2O$/*n*BuOH (wt%) | Reaction initiation temp. (°C) |
|---|---|---|---|
| $Co_2(CO)_8$ | 26.0 | — | 51 |
| none | — | — | 50—55 |
| none | — | 7.9 | 58 |
| $Ph_3P$ | 10.8 | 7.9 | 58 |
| Pyridine | 38.2 | 7.9 | 64 |
| $(C_6H_{13})_2S$ | 10.8 | — | 55 |
| Pb-Naph. | 10.8 | — | 63 |
| NaOH | 10.8 | — | 61 |

**The Role of the Palladium-on-carbon Catalyst.** The reaction of cobalt carbonylation is schematically shown in Fig. 2. The first step (I) is the reduction of cobaltous cobalt to a low-valent intermediate; the second (II), is the coordination of carbon monoxide to the reduced cobalt intermediate, and the final step (III) is the reaction of the dicobalt octacarbonyl thus formed with hydrogen to produce cobalt hydrocarbonyl.

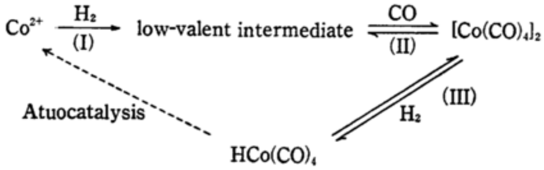

Fig. 2. Schematic reaction path of cobalt carbonylation.

Of these three steps, the contribution of hydrogen must be considered in I and III. If neither dicobalt octacarbonyl nor cobalt hydrocarbonyl is initially added as an autocatalyst, the contribution of hydrogen in III can be disregarded, at least at the beginning of the reaction. The following facts have been pointed out above:

1) The cobalt-carbonylation reaction is very slow under the pressure of only carbon monoxide, even in the presence of a palladium catalyst.

2) Even in the presence of hydrogen, when no palladium-on-carbon catalyst is used, a high initiation temperature is needed.

3) The reaction is promoted very much by the coexistence of hydrogen and a palladium catalyst.

In view of the above facts, the most reasonable conclusion to be drawn from the available data is that the role of a palladium-on-carbon catalyst consists in reducing Co(II) to a low-valent intermediate by activating hydrogen in I. From the observed difficulty in the cobalt carbonylation of Raney cobalt compared with that of cobalt hydroxide, a low-valent intermediate may be somewhat different from the Raney-type Co(0).

According to the equation presented by Rudkovskii,[4b] the equilibrium constant of Step III is calculated to be $3.37 \times 10^{-5}$ at 52.5°C.

On the other hand, Iwanaga[7] has reported that the rate of (III) at 100°C under 100 to 200 kg/cm$^2$ of synthesis gas ($H_2$/CO; 1) is 1.7 mol%min. Judging from these data, the contribution of an autocatalyst to the cobalt-carbonylation reaction with a palladium catalyst at a low temperature (55—55°C) is suspected to be very small.

**Test of Catalyst Life.** In order to ascertain the lifetime of a palladium-on-carbon catalyst, a flow test run was conducted for one month by using cobalt oleate at 120°C under a synthesis-gas ($H_2$/CO; 1.2) pressure of 200 kg/cm$^2$. No tendency of the catalytic activity to decrease could be observed within that period.

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[7] R. Iwanaga, This Bulletin, **35**, 774 (1962).

## Summary

Following the preceding experiment, the reaction conditions of cobalt carbonylation catalyzed by palladium-on-carbon have been investigated. The experimental results obtained here indicate the following:

1) Such polar solvents as *n*-butanol, diethyl ether, isobutyraldehyde, and pyridine show excellent properties compared with the nonpolar solvent, *n*-hexane. In an ether solvent, the reaction proceeds smoothly at lower temperatures. Isobutyraldehyde and pyridine are not suitable for simple cobalt-carbonyl synthesis, since they easily react under the present reaction conditions.

2) With a decrease in the total pressure below 100 kg/cm$^2$, the initiation temperature of the reaction becomes higher. On the other hand, a marked lowering of the initiation temperature upon the addition of a small volume of hydrogen to the carbon monoxide atmosphere was observed. These data indicate that the presence of hydrogen is very important for the reaction.

A high yield of cobalt carbonyl can be obtained even at low pressure by adding carbon monoxide.

3) It is difficult for Raney cobalt to give cobalt carbonyl under a synthesis gas even in the presence of a palladium catalyst. Therefore, the low-valency intermediate in the course of cobalt carbonylation from a cobaltous compound may be somewhat different from the Raney-type Co(0).

4) The initiation temperature of the reaction is not affected significantly by such additives as water, dicobalt octacarbonyl, triphenyl phosphine, pyridine, dihexyl sulfide, lead naphthenate, and NaOH. This fact indicates that at least the initial step of the reaction is affected only a little by the above additives.

5) The available data suggest that the role of a palladium catalyst consists in reducing Co(II) to Co(0) by activating hydrogen.

6) The test of lifetime of a palladium-on-carbon catalyst for a one-month period gives no proof of a decrease in catalytic activity.