# Homogeneous Hydrogenation of $\alpha,\beta$-Unsaturated Ketones and Aldehydes Catalyzed by $Co_2(CO)_8$-Di(tertiary phosphine) Complexes

Kazuhisa MURATA* and Akio MATSUDA
*National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Tsukuba, Ibaraki 305*

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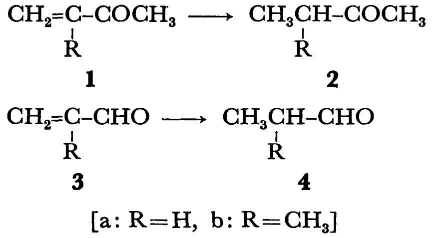
**Synopsis.** The cobalt complexes modified by some di(tertiary phosphine)s as ligands were found to be much more active catalysts than $Co_2(CO)_8$ for the hydrogenation of $\alpha,\beta$-unsaturated ketones and aldehydes under hydroformylation conditions.

When an $\alpha,\beta$-unsaturated ketone or aldehyde is treated with a cobalt catalyst under hydroformylation conditions, the olefinic linkage is hydrogenated rather than hydroformylated.[1] However, since the rate of hydrogenation is much slower than that of hydroformylation, little attention has been paid to the cobalt-catalyzed hydrogenation.

Recently, we reported that complexes prepared *in situ* from $Co_2(CO)_8$ and various di(tertiary phosphine)s are more active catalysts for the homogeneous hydroformylation of methyl acrylate than $Co_2(CO)_8$.[2] We find that these cobalt complexes can be successfully used as catalysts effective for the hydrogenation of $\alpha,\beta$-unsaturated ketones and aldehydes to give the corresponding saturated carbonyl compounds. We describe here the results of some of our studies on the hydrogenation under hydroformylation conditions.



$$\underset{\mathbf{1}}{CH_2{=}\underset{R}{C}{-}COCH_3} \longrightarrow \underset{\mathbf{2}}{CH_3\underset{R}{C}H{-}COCH_3}$$

$$\underset{\mathbf{3}}{CH_2{=}\underset{R}{C}{-}CHO} \longrightarrow \underset{\mathbf{4}}{CH_3\underset{R}{C}H{-}CHO}$$

[a: R=H, b: R=CH$_3$]

The results are listed in Table 1, where the initial rate of the reaction was taken as a measure of the catalytic activity. The hydrogenation of 2-butenone (**1a**) preferentially occurred under the experimental conditions to give 2-butanone (**2a**) in high yield; the catalytic activity of $Co_2(CO)_8$-1,2-bis(diphenylphosphino)ethane(diphos) complex was *ca.* 30 times or above that of $Co_2(CO)_8$[3] (Compare Runs 3 and 6). The reaction can proceed even at a temperature as low as 50 °C (Run 7). $Co_2(CO)_8$–diphos system was effective for the hydrogenation of **1b**, **3a**, and **3b** (Runs

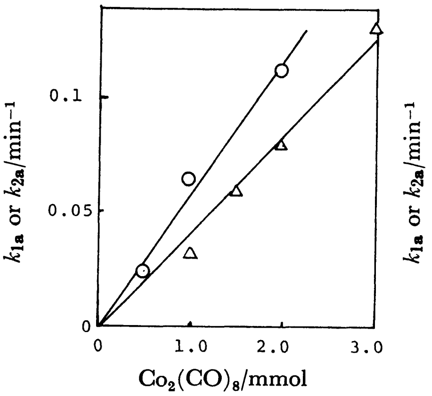


Fig. 1. Effect of catalyst concentration on $k_{1a}$ or $k_{2a}$. Diphos/$Co_2(CO)_8$=0.75 (const).
Toluene 50 ml, substrate 50 mmol, CO/$H_2$=1100 kg/cm$^2$ (const.), temp 110 °C.
—○—: **1a**, —△—: **2a**.

TABLE 1. HYDROGENATION OF $\alpha,\beta$-UNSATURATED KETONES AND ALDEHYDES UNDER HYDROFORMYLATION CONDITIONS

Toluene (solvent) 50 ml, substrate 50 mmol, CO/$H_2$=1,
total pressure 100 kg/cm$^2$ (const.), temp 120 °C.

| Run No. | Substrate | Diphos/$Co_2(CO)_8$ (mmol/mmol) | Time/min | Initial rate$^{a)}$/mmol min$^{-1}$ | $k^{b)}$/min$^{-1}$ | Products (yield/%)$^{c)}$ |
|---|---|---|---|---|---|---|
| 1 | **1a** | 1.5/1.0 | 180 | 0.02 | — | **2a**(1.1) |
| 2 | **1a** | 1.0/1.0 | 40 | 1.0 | — | **2a**(75) |
| 3 | **1a** | 0.75/1.0 | 15 | 2.4 | 0.09 | **2a**(80) |
| 4 | **1a** | 0.5/1.0 | 15 | 2.2 | — | **2a**(78) |
| 5 | **1a** | 0.25/1.0 | 30 | 0.85 | — | **2a**(65) |
| 6 | **1a** | 0/1.0 | 240 | 0.07 | — | **2a**(31) |
| 7$^{d)}$ | **1a** | 2.0/4.0 | 500 | — | — | **2a**(91) |
| 8$^{d)}$ | **1a** | 0/4.0 | 500 | — | — | **2a**(1.3) |
| 9 | **1b** | 0.5/1.0 | 30 | 1.2 | — | **2b**(80) |
| 10 | **1b** | 0/1.0 | 225 | 0.12 | — | **2b**(65) |
| 11 | **3a** | 1.0/2.0 | 20 | 2.5 | 0.095 | **4a**(74) |
| 12 | **3a** | 0/2.0 | 180 | 0.15 | — | **4a**(44) |
| 13 | **3b** | 1.0/2.0 | 20 | 2.4 | — | **4b**(82) |
| 14 | **3b** | 0/2.0 | 120 | 0.26 | — | **4b**(66) |

a) See text. b) The "$k$" denotes the first order rate constant. c) Based on substrate initially introduced.
d) The reaction was carried out at 50 °C.

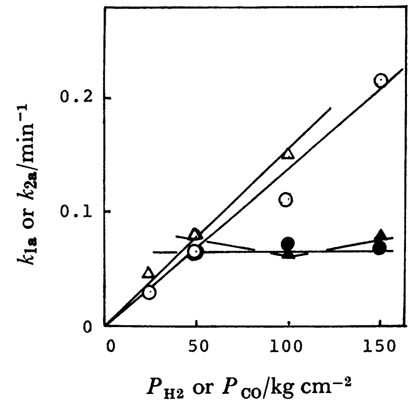


Fig. 2. Effect of partial pressure of hydrogen or CO. Toluene 50 ml, substrate 50 mmol, temp 110 °C, $Co_2(CO)_8$ 1 mmol (**1a**), 2 mmol (**2a**), diphos 0.75 mmol (**1a**), 1.5 mmol (**2a**).
—○—: **1a** ($P_{CO}$=50 kg/cm$^2$, const.), —△—: **2a** ($P_{CO}$=50 kg/cm$^2$, const.), —●—: **1a** ($P_{H_2}$=50 kg/cm$^2$, const.), —▲—: **2a** ($P_{H_2}$=50 kg/cm$^2$, const.).

9, 11, and 13).

In the hydroformylation of methyl acrylate, the maximum activity has been achieved when the molar ratio of diphos to $Co_2(CO)_8$ was *ca.* 0.5—0.75.[2] The results listed in Table 1 (Runs 1—6) are similar to this. The effect of phosphine structure on the activity was examined: the order of reactivity was in accordance with that of hydroformylation.[4]

Using **1a** and **2a**, kinetic behaviors were briefly examined. The rate of hydrogenation exhibits a first order dependence on the concentration of **1a** or **2a**, the rate constant $k_{1a}$ or $k_{2a}$ being calculated (See Table 1 (Runs 3 and 11)). Good Arrhenius plots of the constants provide the apparent activation energies of 12.3 kcal/mol with respect to $k_{1a}$ and 9.1 kcal/mol to $k_{2a}$ (temperature range: 90—120 °C).

As shown in Fig. 1, these constants increase with increase in $Co_2(CO)_8$ concentration. Also, plots of the constants *vs.* partial pressure of hydrogen reveal first order behaviors, while those *vs.* CO pressure give zero order (Fig. 2). These observations are identical with those described in the hydroformylation, with the exception of the CO pressure effect (Figs. 1, 2).

## Experimental

*Materials.* Phosphines and toluene were obtained commercially and used with no further purifications. All α,β-unsaturated carbonyls were distilled prior to use.

*Reaction Procedure.* A catalyst solution containing $Co_2(CO)_8$ (1—4 mmol), phosphine (0.25—2 mmol), and substrate (50 mmol) in toluene (50 cm$^3$) was placed in a stainless-steel autoclave (100 cm$^3$), which was subsequently charged with a mixture of $H_2$ and CO (*ca.* 1/1 ratio).[5] The reaction was carried out at 120 °C under 100 kg/cm$^2$ of total pressure (const.) and aliquot samples were withdrawn from the vessel at several reaction times and analyzed by GLC (determination of the initial rate, Table 1).

Kinetic measurements were performed as follows. The hydrogenation system described above was brought to the desired reaction temp and the total pressure was kept constant during the reaction by supplying hydrogen from a 100 ml pressure storage vessel through a pressure regulator. The amount of hydrogen consumed was calculated from the pressure drop in the storage (Figs. 1 and 2).

## References

1) R. W. Goetz and M. Orchin, *J. Org. Chem.*, **27**, 3698 (1962); R. W. Goetz and M. Orchin, *J. Am. Chem. Soc.*, **85**, 2782 (1963); H. Adkins and G. Krsek, *ibid.*, **71**, 3051 (1949).

2) K. Murata and A. Matsuda, *Bull. Chem. Soc. Jpn.*, **53**, 214 (1980).

3) It has been reported that in the absence of phosphine the hydrogenation is slow (See Table 1, Run 6), because a stable π-oxapropenyl complex (A) is formed.[1] Therefore, the phosphine ligand may play an important role in further hydrogenation of (A) to form the products, but there is no more evidence at the present time.

4) Diphos (2.2) > $Ph_2PC{\equiv}CPPh_2$ (1.5) > *cis*-$Ph_2PCH{=}CHPPh_2$(1.0) > $PhP(CH_2CH_2PPh_2)_2$(0.64) > $Ph_2P(CH_2)_3PPh_2$ (0.40) > $Ph_2PCH_2PPh_2$(0.16) > $Ph_2P(CH_2)_2AsPh_2$(0.14) > none (0.07) > $PPh_3$(0.04) (numerical values refer to the initial rate in Table 1).

5) In the absence of CO, a perfect decomposition of $Co_2(CO)_8$ occurred.