BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 527—529 (1969)

Organic Syntheses by Means of Metal Complexes. II.[1] Oxo Reaction Catalyzed by Cyclopentadienyliron Dicarbonyl Dimer

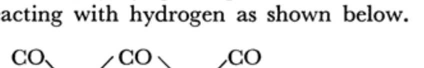
Jiro TSUJI and Yoichi MORI

Basic Research Laboratories, Toyo Rayon Co., Kamakura

(Received July 10, 1968)

It was found that cyclopentadienyliron dicarbonyl dimer is an active catalyst for oxo reaction and the characteristic features of the catalysis have been studied.

Carbonylation reactions of olefins are catalyzed by transition metal carbonyls, and iron, cobalt and nickel carbonyls are commonly used for the reactions. These metal carbonyls catalyze different types of the carbonylation reactions of olefins and acetylenes.[2,3] The relationship between the structure of the metal carbonyls and their catalytic activity seems to be an interesting problem. Metal carbonyls can be classified into mononuclear and polynuclear carbonyls as one way of the classification. Typical mononuclear carbonyls are nickel tetracarbonyl and iron pentacarbonyl. Dicobalt octacarbonyl (I) belongs to the latter and has a cobalt-cobalt bonding. The major difference of the catalytic activity of these two types of metal carbonyls can be explained in the following way from a mechanistic standpoint. It is known that the first step of the carbonylation reactions is the formation of a metal hydride bond in most cases. Dicobalt octacarbonyl forms cobalt tetracarbonyl hydride (II) by splitting the cobalt-cobalt bond by reacting with hydrogen as shown below.



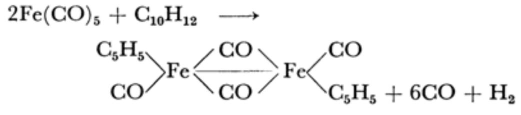
I II

On the other hand, the carbonylation reaction catalyzed by nickel tetracarbonyl proceeds in the presence of hydrogen halide and the first step of the carbonylation is the oxidative addition of hydrogen halide to nickel tetracarbonyl to form halonickeldicarbonyl hydride (III).[4)]

$$\mathrm{Ni(CO)_4 + HX \longrightarrow \underset{III}{HNi(CO)_2X} + 2CO}$$

Once these metal hydrides are formed, then follows the insertion of olefin into the metal hydride bond in both cases.

It is possible to convert mononuclear carbonyls into dinuclear carbonyls by the coordination of cyclopentadienyl anion. For example, nickel, iron and molybdenum carbonyls can be converted into the dinuclear ones by reacting with dicyclopentadiene ($C_{10}H_{12}$).



IV

On the other hand, dicobalt octacarbonyl can be converted into the mononuclear cyclopentadienyl cobalt dicarbonyl (V) by the reaction of cyclopentadiene as shown below.

$$\mathrm{\underset{I}{Co_2(CO)_8} + 2C_5H_6 \rightarrow \underset{V}{2C_5H_5Co(CO)_2} + 4CO + H_2}$$

Thus it seems interesting to investigate the catalytic activity of these mono- and dinuclear carbonyls coordinated with cyclopentadienyl anion. So far no studies have been reported on the catalytic activity of these metal carbonyls coordinated with

---

[1] Part 1. T. Susuki and J. Tsuji, *Tetrahedron Letters*, **1968**, 913.

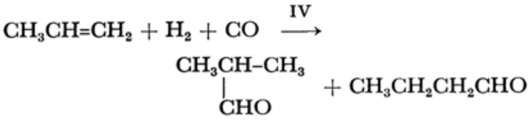
[2] C. E. Bird, *Chem. Revs.*, **62**, 283 (1962).

[3] H. Wakamatsu, *Yûki Gôsei Kagaku Kyokaishi* (*J. Soc. Org. Synth. Chem., Japan*), **25**, 999 (1967).

[4] R. F. Heck, *J. Am. Chem. Soc.*, **85**, 2013 (1963).

cyclopentadienyl anion. In other words, this study was undertaken to find whether there is any similarity in the catalytic activity between dicobalt octacarbonyl (I) and cyclopentadienyliron dicarbonyl dimer (IV). In this paper the catalytic activity of the complex (IV) in oxo reaction is described.

The oxo reaction, namely the formation of aldehydes from olefins, carbon monoxide and hydrogen, is carried out most satisfactorily by the catalytic action of typical dinuclear carbonyls such as cobalt and rhodium carbonyls. So far, there is no report that any iron carbonyls are active for the oxo reaction. Now it was found that the oxo reaction can be carried out with the complex IV as the catalyst under certain conditions. The reaction of propylene with carbon monoxide and hydrogen to form butyraldehydes was studied under several different conditions.



$$CH_3CH{=}CH_2 + H_2 + CO \xrightarrow{IV} \underset{\displaystyle CHO}{CH_3\overset{}{C}H{-}CH_3} + CH_3CH_2CH_2CHO$$

Table 1. Effect of pressure[a)]

Press. (atm)		Ratio of iso/*n*-aldehyde	Yield (%)[b)]	Higher aldehydes (g)
H_2	CO			
50	50	2.14	69.5	0.68
100	50	1.45	52.3	0.68
75	75	1.98	45.5	0.79

a) Reactions were carried out with the complex IV (0.7 g), propylene (10 m*l*), benzene (15 m*l*), and toluene (2 m*l*), at 150°C for 40 hr.

b) Total yield of C_4 aldehydes based on the charged propylene.

Table 2. Effect of reaction temperature and time[a)]

Reaction		Ratio of iso/*n*-aldehyde	Yield (%)	Higher aldehydes (g)
Temp. (°C)	Time (hr)			
175	40	2.52	10.5	0.3
150	40	2.14	69.5	0.68
150	15	2.06	9.1	trace
125	40	—	trace	—

a) Reactions were carried out with the complex IV (0.7 g), propylene (10 m*l*), benzene (15 m*l*), hydrogen (50 atm) and carbon monoxide (50 atm).

In Tables 1 and 2, the effects of the reaction temperature, time and pressure on the reaction are shown. From these results, several characteristic features of the catalytic activity of the complex IV are apparent. One of them is that a larger amount of isobutyraldehyde was formed than *n*-butyraldehyde, and higher hydrogen pressure relative to that of carbon monoxide tends to favor the formation of the normal aldehyde. In the usual oxo reaction catalyzed by dicobalt octacarbonyl, several by-products are formed. For example, the hydrogenation of aldehydes to alcohols is observed in a considerable extent by hydrogenating activity of dicobalt octacarbonyl. Also aldol condensation of the aldehydes to form higher unsaturated aldehydes is another side reaction. A strongly acidic cobalttetracarbonyl hydride catalyzes the aldol condensation. These side reactions were almost negligible in the oxo reaction catalyzed by the complex IV and the products of the reaction were almost free of the alcohols and aldol condensation products. Therefore, it can be said that the acidic property and hydrogenating activity of the complex IV are weaker than those of dicobalt octacarbonyl.

Table 3. Oxo reaction of butenes[a)]

Butene	Ratio of 2-methylbutyraldehyde/ *n*-valeraldehyde	Yield (%)[b)]	Higher aldehydes (g)
1-Butene	2.03	53.8	0.18
cis-2-Butene	2.59	25.4	0.62
trans-2-Butene	3.02	16.8	0.57

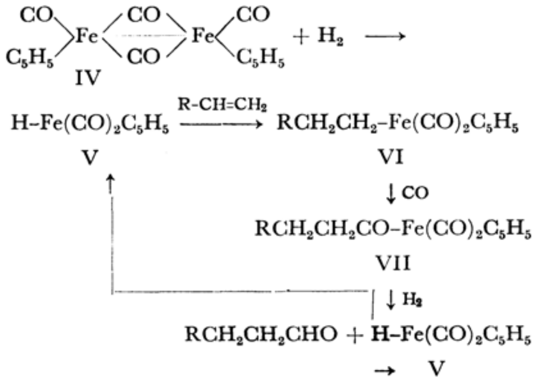
a) Reactions were carried out with the complex IV (0.7 g), butene (10 m*l*), benzene (15 m*l*), hydrogen (50 atm), and carbon monoxide (50 atm) at 150°C for 40 hr.

b) Total yield of C_5 aldehydes based on the charged butenes.

Several solvents were tested in the reaction and it was found that ethanol and benzene were most satisfactory. When the reaction was carried out in ethanol, the product was aldehydes and no ester was formed. Then the carbonylation of 1-butene, *cis*- and *trans*-2-butenes was carried out and the results are shown in Table 3. It was observed that 1-olefin is more reactive than 2-olefins, and cis olefin is more reactive than trans olefin as expected. It should be noticed that *n*-valeraldehyde was formed in a considerable amount from 2-butenes and it is apparent that the complex IV catalyzes the isomerization of the inner olefins to the terminal olefins.

It can be said that the catalytic activity of the complex IV is somewhat lower than that of dicobalt octacarbonyl and longer reaction time is necessary. The range of optimum reaction temperature seems to be narrow, and best result was obtained at 150°C. After the reaction, it is possible to recover the catalyst intact by handling the reaction mixture under mild conditions and the recovered catalyst can be used again.

Finally the mechanism of the reaction is proposed in the following way. The first step of the reaction is the splitting of the iron-iron bond with hydrogen to form cyclopentadienylirondicarbonyl hydride (V). The successive insertions of olefin and carbon monoxide are followed to form alkyl (VI) and acyl complex (VII). Finally, the acyl complex (VII) is converted into the aldehyde with the regeneration of the hydride complex (V).



Experimental

Material. Cyclopentadienyliron dicarbonyl dimer was prepared by a known method from iron pentacarbonyl and dicyclopentadiene (red purple crystals, mp 194°C (decomp.).[5]

Oxo Reaction of Propylene. Only typical reaction is described. The complex IV (0.7 g), benzene (15 m*l*) and toluene (2 m*l*) were mixed in a glass vessel equipped with a gas inlet capillary, and the vessel was placed in an autoclave (100 m*l*). Liquid propylene (10 m*l*) was measured in a measuring glass tube and then distilled into the autoclave with cooling in a dry ice bath. Carbon monoxide and hydrogen (50 kg/cm^2 each) were introduced at room temperature. The reaction was carried out at 150°C for 40 hr with shaking. Pressure drop of 80 kg/cm^2 was observed during the reaction. The amounts of the aldehydes formed were determined gas chromatographically (squalene at 100°C) and the formation of *n*-butyraldehyde (2.3 g) and isobutyraldehyde (4.93 g) was confirmed. By distillation, 0.68 g of a higher boiling aldehyde was obtained.

---

[5] R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York (1965), p. 114.