The Rate of Formation of Cobalt Hydrocarbonyl under Various Conditions of Oxo Reaction

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It has been previously[1,2] reported that the rate of oxo reaction is inversely proportional to the partial pressure of carbon monoxide. In accordance with this kinetic requirement, several mechanisms have been proposed for this reaction which involve, as a rate-determining step, the displacement of a mole of carbon monoxide by the olefin from the dicobalt octacarbonyl[1,2] added as a catalyst, or from the cobalt hydrocarbonyl[3] presumed to be present in the system. Recently Kirch and Orchin[4] have proposed a mechanism for the

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[1] G. Natta, R. Ercoli, S. Castellano and P. H. Barbieri, *J. Am. Chem. Soc.*, **76**, 4049 (1954).

[2] A. R. Martin, *Chem. & Ind.*, **1954**, 1536.

[3] G. Natta, R. Ercoli and S. Castellano, *Chim. e. Ind.*, **37**, 6 (1953).

[4] L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, **81**, 3597 (1959).

oxo reaction which involves the formation and subsequent decomposition of a complex formed from cobalt hydrocarbonyl-olefin-carbon monoxide as follows:

$$2HCo(CO)_4 + RCH{=}CH_2 + CO \rightarrow \text{Complex} \qquad (1)$$

$$\text{Complex} \rightarrow Co_2(CO)_8 + RCH_2CH_2CHO \qquad (2)$$

This scheme is based upon the fact that cobalt hydrocarbonyl in hexane reacts with olefin and carbon monoxide to give aldehyde and dicobalt octacarbonyl. They considered that such a complex was formed at the first and rate-determining stage.

We have previously[5] found that the equilibrium concentration of cobalt hydrocarbonyl converted from dicobalt octacarbonyl in benzene is proportional to the rate of the oxo reaction of cyclohexene[1] under various partial pressures of carbon monoxide and hydrogen. From this result it has been considered that the formation of cobalt hydrocarbonyl from dicobalt octacarbonyl may determine the rate of the oxo reaction. However, in order to study the kinetics and mechanism of the oxo reaction it was necessary to determine the rate of formation of cobalt hydrocarbonyl in the system in the course of the oxo reaction.

In the present paper, the rate of formation of cobalt hydrocarbonyl from dicobalt octacarbonyl under various partial pressures of carbon monoxide and hydrogen is presented. In addition, some experimental results concerning the content of cobalt hydrocarbonyl in the system during the oxo reaction of methylacrylate and cyclohexene are presented and discussed.

Experimental

Determination of the Initial Rate of Formation of Cobalt Hydrocarbonyl from Dicobalt Octacarbonyl under Various Partial Pressures of Carbon Monoxide and Hydrogen. — A solution of 0.87 g. (2.55 mmol.) of $Co_2(CO)_8$ in 100 ml. of pure and oxygen-free toluene was placed in a 300 ml. stainless steel rocking autoclave. The autoclave was then sealed, placed in an electrically heated jacket, flushed and pressured with carbon monoxide so as to hold a pressure a little less than the partial pressure of the carbon monoxide to be tested. After the autoclave had been heated to 100°C and the pressure in the autoclave had been adjusted to the partial pressure of the carbon monoxide to be tested, hydrogen was added rapidly from high pressure hydrogen storage up to the mixed gas pressure to be tested, and the autoclave was then maintained at 100°C with rocking. After various periods of time after the addition of hydrogen, about 2 ml. aliquots of the solution were withdrawn directly into a nitrogen atmosphere from the autoclave through a valve and a coil of stainless steel tube of 1 m. in length and 1 mm. inner diameter which was immersed in a bath cooled at -20°C. The cobalt hydrocarbonyl in the aliquot was analyzed by the method described in the preceding paper[6].

Measurement of Cobalt Hydrocarbonyl in the Solution During the Oxo Reaction of Methylacrylate and Cyclohexene. — The apparatus and procedure were the same as has been described above. A solution of 100 ml. toluene containing 0.17 g. of $Co_2(CO)_8$ and 17.2 g. of methylacrylate (98.5% in purity) or 0.22 g. of $Co_2(CO)_8$ and 17.4 g. of cyclohexene (98% in purity) was introduced into a 300 ml. stainless steel rocking autoclave, and the autoclave was then filled with about 75 kg./cm^2 of carbon monoxide. After the autoclave had been heated to 120°C and the pressure had been adjusted to 102 kg./cm^2, hydrogen was added rapidly until the total pressure became 202 kg./cm^2, and the autoclave was then maintained at 120°C with rocking. During the reaction the pressure was maintained at the initial pressure of 202 kg./cm^2 by a continuous addition of the compressed gas mixture of carbon monoxide and hydrogen in a 1 : 1 ratio. The aldehyde in the sample was analyzed by the hydroxylamine hydrochloride method[7].

Results and Discussion

Figures 1 and 2 show plots of the initial rate of the formation of cobalt hydrocarbonyl against the partial pressure of carbon monoxide and hydrogen. From these results, it will be seen that under the constant pressure of carbon monoxide the initial rate increases with the increasing partial pressure of hydrogen, while under the constant pressure of hydrogen, the initial rate inversely decreases with the increasing pressure of carbon monoxide. These effects of partial pressures on the initial rate of formation of cobalt hydrocarbonyl are parallel with the effects of partial pressures on the rate of the oxo reaction reported by Natta[1].

The dotted line in Fig. 1 shows that the rate of formation of hydrocarbonyl is almost constant regardless of the total pressure when the gas mixture consists of equal moles of carbon monoxide and hydrogen. This fact is interesting in connection with Natta's statement[8] that the velocity of the oxo reaction is independent of the pressure of the gas phase of 1 : 1 ratio carbon monoxide and hydrogen.

Although the rate of the oxo reaction determined by Natta et al.[1] decreased with the decreasing pressure of carbon monoxide under

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[5] R. Iwanaga, T. Fujii and T. Yoshida, presented at the 9th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1956; R. Iwanaga, T. Fujii, H. Wakamatsu, T. Yoshida and J. Kato, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 960 (1960).

[6] R. Iwanaga, This Bulletin, 35, 247 (1962).

[7] H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **71**, 3051 (1949).

[8] G. Natta and R. Ercoli, *Chim. e. Ind.*, **34**, 503 (1952).

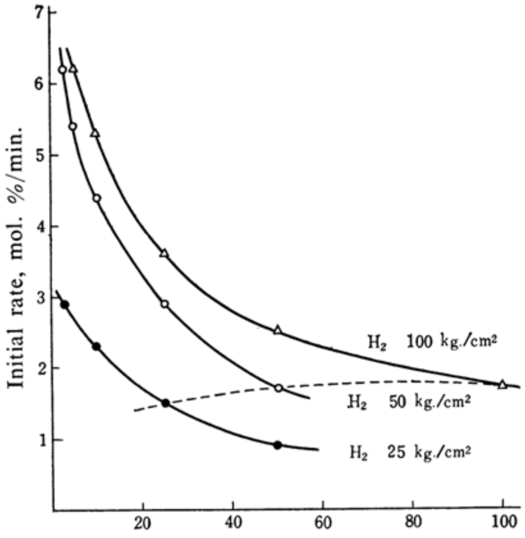

Fig. 1. Initial rate of formation of $HCo(CO)_4$ as a function of partial pressure of CO.

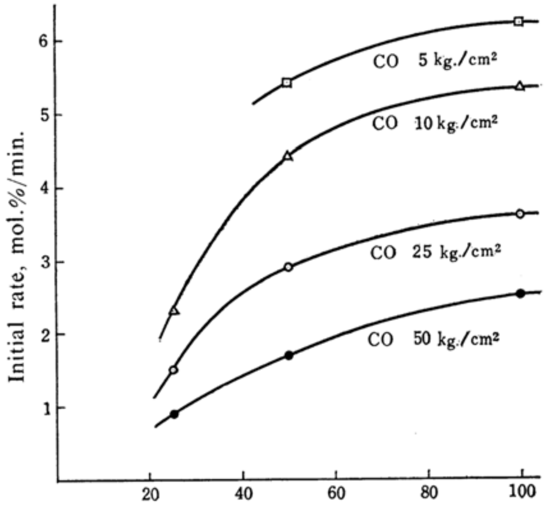

Fig. 2. Initial rate of formation of $HCo(CO)_4$ as a function of partial pressure of H_2.

pressure below about 10 atm., the rate of formation of hydrocarbonyl was observed to increase with the decreasing pressure of carbon monoxide in such a low pressure range. This phenomenon is very interesting for us in spite of the difficulty of explaining the rate of oxo reaction on the basis of the rate of formation of hydrocarbonyl. Under pressures less than 10 atm. of carbon monoxide, the rate of oxo reaction may presumably be influenced by certain other rate-determining stages, a study of which is in progress.

From Fig. 1 it was also induced that the rate is inversely proportional to the logarithm of the partial pressure of carbon monoxide under the constant pressure of hydrogen, but that the rate constant of the rate curve at 25 kg./cm² of carbon monoxide is different from that at 50 and 100 kg./cm². Therefore, no rate equation to fit the results throughout the whole range of the pressure of carbon monoxide and hydrogen could be obtained.

Since the formation of cobalt hydrocarbonyl from dicobalt octacarbonyl seems to take place according to the equation,

$$Co_2(CO)_8 + H_2 \rightarrow 2HCo(CO)_4 \tag{3}$$

it may be a matter of course that the rate increases with the increasing pressure of hydrogen. However, the inverse effect of carbon monoxide pressure on the rate can not be explained from the above equation. Metlin et al.[9] reported that 1 mol. of carbon monoxide is absorbed per mole of dicobalt octacarbonyl at about 400 atm. and 185°C, and that this is due to the formation of a dicobalt nonacarbonyl complex, $Co_2(CO)_9$.

$$Co_2(CO)_8 + CO \rightarrow Co_2(CO)_9 \tag{4}$$

If any of the dicobalt octacarbonyl would convert to nonacarbonyl under our experimental conditions, the inverse effect of carbon monoxide pressure might be attributed to the decrease of dicobalt octacarbonyl according to

TABLE I. INITIAL RATE OF FORMATION OF $HCo(CO)_4$, FROM $Co_2(CO)_8$ AT 100°C UNDER VARIOUS PARTIAL PRESSURES OF CARBON MONOXIDE AND HYDROGEN

H_2 Pressure kg./cm²	CO Pressure kg./cm²	Initial rate of formation of $HCo(CO)_4$* mol.%/min.
25	3	2.9
25	5	2.3
25	25	1.5
25	50	0.9
50	3	6.2
50	5	5.4
50	10	4.4
50	25	2.9
50	50	1.7
100	5	6.2
100	10	5.3
100	25	3.6
100	50	2.5
100	100	1.7

* Molar percentage of cobalt hydrocarbonyl formed in a minute against the total cobalt in dicobalt octacarbonyl added.

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[9] S. Metlin, I. Wender and H. W. Sternberg, *Nature*, **183**, 457 (1959).

TRBLE II. $HCo(CO)_4$ PRESENT IN THE SOLUTION DURING THE OXO REACTION OF METHYLACRYLATE IN TOLUENE AT 120°C AND 200 kg./cm² OF 1 : 1 CO AND H_2

Methylacrylate, 17.2 g./dl.
$Co_2(CO)_8$, 0.17 g./dl.

Reaction time min.	Aldehyde formed mol.%	$HCo(CO)_4$ per added $Co_2(CO)_8$ % as Co
0	0	0
10	17.4	0.4
30	48.2	0.7
50	71.9	3.6
70	81.6	19.8
90	82.4	59.4
110	83.0	70.0

TABLE III. $HCo(CO)_4$ PRESENT IN THE SOLUTION DURING THE OXO REACTION OF CYCLOHEXENE IN TOLUENE AT 120°C AND AT 200 kg./cm² OF 1 : 1 CO AND H_2

Cyclohexene, 17.4 g./dl.
$Co_2(CO)_8$, 0.22 g./dl.

Reaction time min.	Aldehyde formed mol.%	$HCo(CO)_4$ per added $Co_2(CO)_8$ % as Co
0	0	0
15	8.8	52.1
45	24.6	61.5
75	38.1	65.0
105	47.3	65.7
135	53.7	67.7
180	63.8	70.7
240	70.5	73.6

TABLE IV. FORMATION OF $HCo(CO)_4$ FROM $Co_2(CO)_8$ IN TOLUENE AT THE EQUILIBRIUM STATE AT 100°C

$Co_2(CO)_8$, 0.87 g./dl.

H_2 Pressure kg./cm²	CO Pressure kg./cm²	$HCo(CO)_4$ per added $Co_2(CO)_8$ % as Co	Time required until equilibrium state min.
26	10	23.7	40
27	48	24.8	50
25	96	26.8	70
49	9	33.6	45
47	47	33.9	55
48	94	36.6	65
98	10	41.9	20
95	43	41.8	45
97	97	43.3	45

Eq. 4. To examine the occurrence of this reaction, we have measured the amount of cobalt hydrocarbonyl in the equilibrium state by varying the partial pressures of carbon monoxide at a few fixed pressures of hydrogen. As illustrated in Table IV, the amount of cobalt hydrocarbonyl at the equilibrium state was independent of the partial pressure of carbon monoxide under the constant pressure of hydrogen. Thus, the carbon monoxide pressure affects only the rate of formation of cobalt hydrocarbonyl, not the equilibrium state of reaction 3. Therefore, it is clear that neither reaction 4 nor any other reaction to produce any compound other than cobalt hydrocarbonyl takes place under the experimental conditions employed. Furthermore, it can be noted that the inverse effect of carbon monoxide pressure on the rate is not due to a simple physical interference such as the effect of an inert dissolved gas, because it was observed that an added nitrogen pressure could affect neither the rate nor the equilibrium state of the formation of cobalt hydrocarbonyl under some carbon monoxide and hydrogen pressures. From the above observations it is not easy to explain why the carbon monoxide pressure causes a decrease only in the rate of formation of hydrocarbonyl. However, this phenomenon is an interesting fact for the study of the mechanism of the oxo reaction.

Tables II and III indicate the contents of cobalt hydrocarbonyl and aldehyde in the solutions during the oxo reaction of methylacrylate and cyclohexene in toluene at 120°C. In the former solution, in which the oxo reaction proceeds faster, only a trace of cobalt hydrocarbonyl appears when acrylate is present, while a large amount of it appears after the acrylate is consumed. This phenomenon agrees with the observations by Orchin et al.[10] However, in the latter solution, in which the oxo reaction proceeds more slowly, a large amount of hydrocarbonyl is present even at the beginning of the reaction.

From this result it seems likely that cobalt hydrocarbonyl will react rapidly with acrylate and slowly with cyclohexene. Although it could not be confirmed that cobalt hydrocarbonyl is consumed, whether in a main reaction to produce aldehyde or in some side reaction such as a hydrogenation reaction of double bond of olefin during the oxo reaction, it is significant for the study of the mechanism of the oxo reaction that cobalt hydrocarbonyl reacts rapidly with olefin whose oxo reaction is fast and slowly with that whose oxo reaction is slow.

Summary

By treating a solution of dicobalt octacarbonyl in toluene at 100°C under various partial pressures of carbon monoxide and hydrogen,

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[10] M. Orchin, L. Kirch and I. Goldfarb, *J. Am. Chem. Soc.*, **78**, 5450 (1956).

and by determining the initial rate of formation of cobalt hydrocarbonyl, we have found that the initial rate increases with the increasing pressure of hydrogen and decreases with the increasing pressure of carbon monoxide. These effects of partial pressures on the initial rate of formation of cobalt hydrocarbonyl are parallel with the effects of partial pressures on the rate of the oxo reaction reported by Natta.

In addition, the amount of cobalt hydrocarbonyl in the system during the oxo reaction of methylacrylate and cyclohexene in toluene at 120°C was determined; it was found that only a trace of cobalt hydrocarbonyl appears when acrylate is present, while a large amount of it is present even when cyclohexene is present in the system.

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