The Effect of the Partial Pressure of Carbon Monoxide and Hydrogen on the Rate of Oxo Reaction

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It was found by Natta[1] and Martin[2] that the rate of oxo reaction increases with the increasing pressure of hydrogen, but decreases with the increasing pressure of carbon monoxide. These kinetic results led them to propose a mechanism for the oxo reaction which involves the displacement of a mole of carbon monoxide by the olefin from the dicobalt octacarbonyl[1,2] or from the cobalt hydrocarbonyl[3]. Recently Breslow et al.[4] have proposed a mechanism modifying the mechanism postulated by Kirch and Orchin[5]. In Breslow's mechanism the acylcobalt tricarbonyl, $RCH_2CH_2COCo(CO)_3$, produced from cobalt hydrocarbonyl and olefin reacts with hydrogen to give the oxo product and hydrotricarbonyl, $HCo(CO)_3$, or with carbon monoxide to give the unreactive acylcobalt tetracarbonyl, $RCH_2CH_2COCo(CO)_4$, and cobalt hydrotetracarbonyl is regenerated from hydrotricarbonyl.

$$RCH{=}CH_2+HCo(CO)_4 \rightarrow RCH_2CH_2Co(CO)_4$$

$$RCH_2CH_2Co(CO)_4 \rightarrow RCH_2CH_2COCo(CO)_3$$

$$RCH_2CH_2COCo(CO)_3+CO \rightarrow RCH_2CH_2COCo(CO)_4$$

$$RCH_2CH_2COCo(CO)_3+H_2 \rightarrow HCo(CO)_3+RCH_2CH_2CHO$$

$$HCo(CO)_3+CO \rightarrow HCo(CO)_4$$

The above mechanisms were all based upon the consideration that the cardon monoxide might affect the formation of an intermediate complex of the oxo reaction.

The author established in a preceding paper[6] that the rate of formation of cobalt hydrocarbonyl is increased with the increasing partial pressure of hydrogen but decreased with the increasing partial pressure of carbon monoxide.

To clarify the relationship between this effect of the partial pressure on the rate of formation of cobalt hydrocarbonyl and the effect of the partial pressure on the rate of oxo reaction, the author has studied the initial rate of the oxo reaction of methylacrylate under various partial pressures of carbon monoxide and hydrogen. In this study the reaction was made under the same conditions as have been described in the preceding paper[6], in order that the initial rate of the oxo reaction might be compared directly with that of the formation of cobalt hydrocarbonyl.

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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 (1955).

[4] D. S. Breslow and R. F. Heck, *Chem. & Ind.*, **1960**, 467.

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

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

Methylacrylate was chosen for this study because it yielded only one kind of aldehyde, methyl-β-formylbutyrate⁷⁾, and reacted rapidly even at about 100°C. If the oxo reaction is carried out at a temperature higher than 100°C, cobalt carbonyl often decomposes under the partial pressure of carbon monoxide less than 10 kg./cm^2.

Experimental

The methylacrylate and toluene to be used were obtained from commercial sources; they were distilled in a nitrogen atmosphere and were kept in nitrogen before use in order to prevent the decomposition of the dicobalt octacarbonyl added as catalyst. The dicobalt octacarbonyl was also freshly recrystallized from ethyl ether before use. The method described in the preceding paper⁶⁾ was followed in general.

Determination of the Initial Rate of the Oxo Reaction of Methylacrylate.—One hundred milliliters of the solution containing 20.3 g. (232 mmol.) of methylacrylate and 0.86 g. (25 mmol.) of dicobalt octacarbonyl in toluene were put into a 300 ml. stainless steel rocking autoclave. After the autoclave had been heated to 100°C and the pressure of carbon monoxide had been adjusted to the pressure to be tested, hydrogen was added for a few seconds to bring it up to the pressure to be tested, and immediately the rocking was started. The temperature was controlled within ±1°C. The initial pressure and the initial ratio of carbon monoxide to hydrogen were maintained by a continuous addition of 1 : 1 synthesis gas throughout the time of the reaction, because about equal amounts of carbon monoxide and hydrogen were absorbed in the oxo reaction of methylacrylate. The initial rate of the oxo reaction was obtained as follows:

Several aliquots of about 2 ml. of the reaction mixture were withdrawn from the autoclave at intervals of 2.5 or 5 min. during the reaction through a high-pressure coil of a stainless tube cooled at −20°C; the amount of aldehyde in an aliquot was determined according to the procedure of Adkins⁷⁾. The aldehyde yield per minute at the initial period of reaction time indicates the initial rate of the oxo reaction.

Results and Discussion

The initial rate of the oxo reaction of methylacrylate in toluene at 100°C under various partial pressures of carbon monoxide and hydrogen are listed in Table I. It shows that under the constant pressure of carbon monoxide, the initial rate increases with the increasing pressure of hydrogen, and under

TABLE I. INITIAL RATE OF THE OXO REACTION OF METHYLACRYLATE UNDER VARIOUS PARTIAL PRESSURES OF CARBON MONOXIDE AND HYDROGEN

Methylacrylate, 232 mmol./dl.
$Co_2(CO)_8$, 2.5 mmol./dl. in toluene at 100°C

H_2 Pressure kg./cm^2	CO Pressure kg./cm^2	Observed initial rate (aldehyde per acrylate mol.%/min.)	Calculated initial rate (aldehyde per acrylate mol.%/min.)
25	3	1.2	
25	10	2.0	2.0
25	25	0.7	0.8
25	50	0.4	0.4
50	3	4.2	
50	5	5.1	
50	10	5.8	5.6
50	25	2.2	2.2
50	50	1.3	1.1
100	5	9.9	
100	10	15.3	16.0
100	25	5.6	6.4
100	50	3.1	3.2
100	100	1.5	1.6

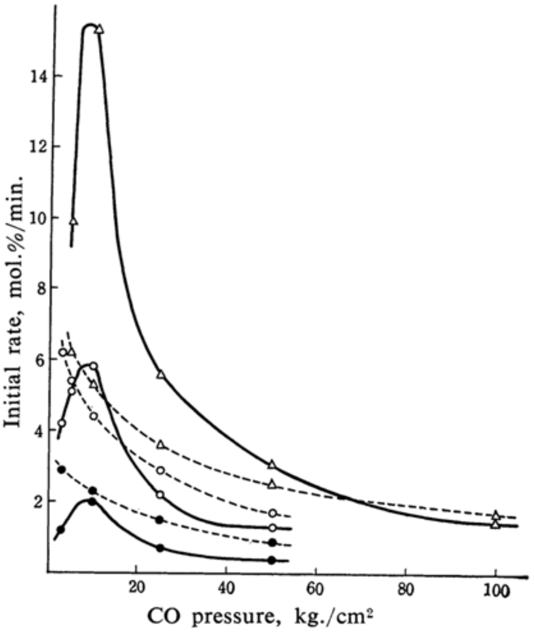

Fig. 1. Initial rate of the oxo reaction of methylacrylate and initial rate of the formation of $HCo(CO)_4$.

—— Initial rate of the reaction
······ Initial rate of the formation of $HCo(CO)_4$
● H_2 25 kg./cm^2
○ H_2 50 kg./cm^2
△ H_2 100 kg./cm^2

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7) H. Adkins and G. Krsek reported that ethyl-β-formylbutyrate was obtained by the oxo reaction of ethylacrylate in 74% of the theoretical yield. (*J. Am. Chem. Soc.*, 71, 3051 (1949).) We have also obtained an aldehyde in an 83% yield from methylacrylate, and the aldehyde was confirmed to be all methyl-β-formylbutyrate through its 2,4-dinitrophenylhydrazone and by infrared analysis in this laboratory.

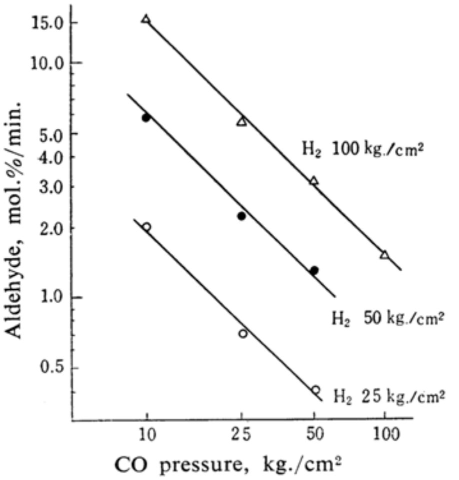

Fig. 2. Initial rate of the oxo reaction of methylacrylate in toluene at 100°C as a function of CO pressure.

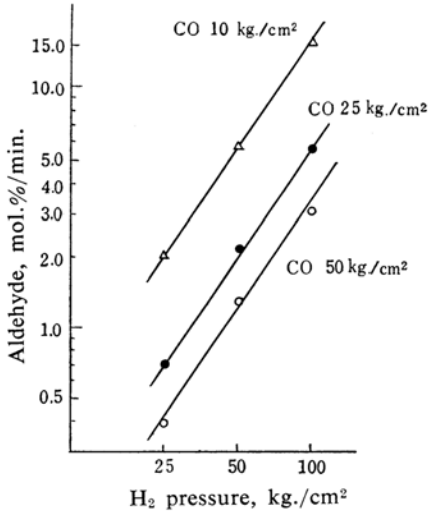

Fig. 3. Initial rate of the oxo reaction of methylacrylate in toluene at 100°C as a function of H_2 pressure.

the constant pressure of hydrogen the initial rate increases with the increasing pressure of carbon monoxide up to about 10 kg./cm², but decreases with the increasing pressure in the range of the high pressures of carbon monoxide (refer to Fig. 1). These results are in good agreement with the results obtained by Natta for the oxo reaction of cyclohexene in toluene[1,8]. In the range of the carbon monoxide pressures above 10 kg./cm², the plot of the rate against the pressure of carbon monoxide (Fig. 2) and the plot against the pressure of hydrogen (Fig. 3), both in logarithmic graphs, yielded straight lines. Therefore, the initial rate of the oxo reaction of methylacrylate can be represented by the equation:

$$\text{Initial rate} = 0.16\ (P_{H_2})^{1.5}/(P_{CO}) \qquad (1)$$

where P_{H_2} and P_{CO} are partial pressures in kg./cm² of hydrogen and carbon monoxide respectively. The data in the fourth column in Table I were calculated by the above equation, and they fit our observations quite well. Martin[2] proposed a rate equation for the case of the oxo reaction of diisobutene,

$$\text{Initial rate} = aP_{H_2}/(bP_{H_2}+cP_{CO})\cdot [Co_2(CO)_8]\,[C_8H_{16}] \qquad (2)$$

where a, b and c are constants. However, this equation did not fit our observations.

In Fig. 1 the initial rate of the reaction of methylacrylate, together with the initial rate of the formation of cobalt hydrocarbonyl obtained in the preceding paper[6] under identical conditions, are shown. The figure shows that under the pressure of carbon monoxide above 25 kg./cm², the former rate is parallel with the latter rate. However, comparing the magnitude of the initial rate of the formation of cobalt hydrocarbonyl from dicobalt octacarbonyl and that of aldehyde from acrylate, it will be seen that the former rate is much lower than the latter rate under identical conditions of partial pressure. For example, it is calculated from the curve in Fig. 1 that when the pressure of carbon monoxide is 25 kg./cm² and that of hydrogen is 50 kg./cm², the former rate is 0.046 mmol. per minute and the latter rate is 5.1 mmol. per minute. Therefore, assuming that, as Kirch and Orchin described[5], cobalt hydrocarbonyl is the true catalyst of the oxo reaction to combine with olefin, it is impossible to consider that the hydrocarbonyl is formed only from dicobalt octacarbonyl in the oxo reaction. If it is assumed that cobalt hydrocarbonyl is formed from a cobalt carbonyl different from dicobalt octacarbonyl in the oxo reaction and that its rate is very rapid and is affected by the partial pressure, as in the case from dicobalt octacarbonyl, the effect of the partial pressure of carbon monoxide and hydrogen on the rate of the oxo reaction may be attributed to the effect of the partial pressure on the rate of the formation of cobalt hydrocarbonyl from a cobalt carbonyl presumed to be formed in the oxo reaction.

The effect of carbon monoxide pressure on the rate of the oxo reaction under a partial pressure less than 10 kg./cm² was observed to be just the opposite to the effect on the rate of the formation of hydrocarbonyl. From this phenomenon, it seems that there may be a certain interaction between carbon monoxide

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8) G. Natta, *Brenstoff-Chemie*, **36**, 176 (1955).

and an intermediate complex and that this interaction may determine the rate of the oxo reaction. The author further observed that the color of the solution at an intermediate stage of the oxo reaction under 10 kg./cm^2 of carbon monoxide is light brown, and that at the end of the reaction it turns dark brown, while the color is dark brown throughout the reaction period under the carbon monoxide pressure above 10 kg./cm^2. In addition, analytical work has shown that the ratio of carbon monoxide liberated from the cobalt compound by the addition of iodine to cobalt in the solution is nearly 1.5 : 1 at an intermediate stage of the reaction under less than 10 kg./cm^2 of the carbon monoxide, but that at the end of the reaction the ratio is nearly 4 : 1. On the other hand , at under 10 kg./cm^2 of carbon monoxide, about 4 mol. of carbon monoxide are attached to a mole of cobalt even at the beginning of the reaction (Table II). Although the structure of the above cobalt compound with 1.5 mol. of carbon monoxide to a mole of cobalt could not be confirmed, it is clear that the carbon monoxide pressure significantly affects the structure of the cobalt compound under such a low pressure of carbon monoxide.

TABLE II. THE BEHAVIOR OF COBALT COMPOUND DURING THE OXO REACTION OF METHYLACRYLATE IN TOLUENE AT 100°C

Methylacrylate, 232 mmol./dl.
$Co_2(CO)_8$, 2.16 mmol./dl.

CO pressure	(kg./cm^2)	6	25
H_2 pressure	(kg./cm^2)	50	50
After 10 min. of reaction			
aldehyde formed	(mol.%)	35.0	17.8
acrylate unreacted	(mol.%)	47.7	65.7
Molar ratio of CO : Co		1.55	3.33
After complete reaction			
aldehyde formed	(mol.%)	63.9	
acrylate unreacted	(mol.%)	2.1	
Molar ratio of CO : Co		3.9	

Furthermore, we have observed that at the beginning of the oxo reaction of methylacrylate, cobalt hydrocarbonyl is scarcely found in the reaction solution when the partial pressure of carbon monoxide is higher than 10 kg./cm^2, but that a certain amount of it appears when the partial pressure is lower than 10 kg./cm^2 (Table III). This phenomenon may be accounted for by assuming that in the range of carbon monoxide pressures above 10 kg./cm^2 the velocity of the formation of an intermediate complex from cobalt hydrocarbonyl-olefin-carbon monoxide, the formation of which was proposed by Kirch and Orchin5), is so rapid that the hydrocarbonyl formed may immediately be consumed, while in the range of carbon monoxide pressures below 10 kg./cm^2 the velocity of the formation of cobalt hydrocarbonyl is so rapid, while the velocity of the formation of the complex is so slow, that some parts of the hydrocarbonyl may appear uncombined.

We have recently observed that in a toluene solution, cobalt hydrocarbonyl, which has been analyzed by the methylene blue method9), disappears rapidly on the addition of methylacrylate at −20°C in an atmospheric pressure of nitrogen, but disappears slowly on the addition of cyclohexene, and that the molar ratio of the cobalt hydrocarbonyl consumed to the methylacrylate consumed is about 2 : 1. The product of this reaction is now under study. This phenomenon suggests that the effect of olefin structure on the rate of the oxo reaction10) may be based upon the difference in rate of the combination of olefins with cobalt hydrocarbonyl and that, when the rate of combination is very rapid, as in the case of acrylate, the formation of cobalt hydrocarbonyl may be a rate-determining step in the oxo

TABLE III. $HCo(CO)_4$ PRESENT IN THE SOLUTION DURING THE OXO REACTION OF METHYLACRYLATE IN TOLUENE AT 100°C

I : Time, min.
II : Mol.% of aldehyde per acrylate added
III : Mol.% of $HCo(CO)_4$ per $Co_2(CO)_4$ added as Co

CO 25 kg./cm^2 H_2 50 kg./cm^2			CO 10 kg./cm^2 H_2 50 kg./cm^2			CO 5 kg./cm^2 H_2 50 kg./cm^2		
I	II	III	I	II	III	I	II	III
15	9.0	0.3	5	31.0	1.9	5	34.4	4.2
30	20.6	0.3	10	59.3	1.5	10	54.1	5.1
60	38.2	0.5	15	67.5	1.2	15	64.0	—
150	75.5	7.4	30	73.5	3.4	30	67.0	8.1
180	74.6	17.8	65	72.6	15.7	45	66.6	12.1

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9) R. Iwanaga, This Bulletin, 35, 247 (1962).

10) I. Wender, S. Metlin, S. Ergun, H. W. Sternberg and H. Greenfield, *J. Am. Chem. Soc.*, 78, 5401 (1956).

reaction. If the intermediate complexes of the oxo reaction could be isolated and the structures could be shown, the mechanism of the oxo reaction could undoubtedly be clarified.

Summary

The initial rates of the oxo reaction of methylacrylate in toluene at 100°C were measured under various partial pressures of carbon monoxide and hydrogen; they were then compared with the initial rate of the formation of cobalt hydrocarbonyl from dicobalt octacarbonyl measured under the same conditions in the preceding paper. The initial rate of the oxo reaction under the carbon monoxide pressure above 10 kg./cm^2 can be represented as follows:

$$\text{Initial rate (mol.\% of aldehyde/acrylate/min.)} = 0.16\ (P_{H_2})^{1.5}/(P_{CO})$$

However, the initial rate decreases with the decreasing partial pressure of carbon monoxide in the range below 10 kg./cm^2 of carbon monoxide. In addition, under the partial pressure of carbon monoxide below 10 kg./cm^2 some behaviors of cobalt carbonyl different from that under the pressure above 10 kg./cm^2 were observed. On the basis of these observations, a possible mechanism of the oxo reaction was discussed.

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