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Studies of the Organic Reactions of Metal Carbonyls. XII.[*1] The Oxo Reaction of Ethyl Acrylate by Rhodium Carbonyl

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The oxo reaction of ethyl acrylate by rhodium carbonyl has been studied and compared with that by cobalt carbonyl. The reaction conditions (the temperatures, and the partial pressures of carbon monoxide and hydrogen) affect the distribution of the products (α- and β-carbethoxypropionaldehyde) more remarkably, but in a way similar to that in the reaction by cobalt carbonyl: the proportion of β-carbethoxypropionaldehyde increases greatly with an increase in the reaction temperature, but decreases with an increase in the partial pressure of carbon monoxide or hydrogen. Judging from this similarity, it is probable that rhodium carbonyl reacts with ethyl acrylate as rhodium hydrocarbonyl to give alkyl- and acylrhodium carbonyls in the course of the reaction.

According to recent papers, the cobalt catalyst in the hydroformylation of olefins is considered to react with olefins as cobalt hydrocarbonyl to give alkyl- and acylcobalt carbonyls as the reaction intermediates.¹⁾ On the other hand, although rhodium is known to be a more active catalyst than cobalt for the hydroformylation of olefins²⁾, the role of the rhodium catalyst is not completely clear. It seems of considerable interest to study whether the rhodium catalyst acts as rhodium hydrocarbonyl, which reacts with olefins much as in the case of cobalt.

Previous experiments in this laboratory have demonstrated that cobalt hydrocarbonyl reacts with ethyl acrylate to give, selectively, α-carbethoxypropionylcobalt carbonyl, that this then isomerizes to β-carbethoxypropionylcobalt carbonyl, and that such an isomerization of the acylcobalt carbonyl occurs under the hydroformylation of ethyl acrylate, having a great effect on the distribution of the products.³,⁴⁾

In this connection, in the present investigation the hydroformylation of ethyl acrylate, using rhodium carbonyl as a catalyst, has been studied in detail by examining the effects of various reaction conditions on the reaction, particularly on the distribution of the products.

Experimental

Reaction Procedures. The reactions were carried out in the way described in a previous paper.⁴⁾ Eighty milliliters of toluene, 10 m*l* of a rhodium carbonyl solution in toluene (containing 1 to 40 mg of rhodium carbonyl), and 20 m*l* of ethyl acrylate were used in each run.

Analysis of the Products. The reaction products were identified by gas chromatography and by means of the infrared absorption spectrum. The details have been given in a previous paper.⁴⁾

Materials. Rhodium carbonyl was prepared according to the method described by Lagally.⁵⁾ The ethyl acrylate, toluene, and the other materials were commercial products, which were proved to be sufficiently pure by gas chromatography.

Results and Discussion

The effects of the reaction conditions (the temperatures, the partial pressures of hydrogen and carbon monoxide, and the concentration of rhodium carbonyl) on the reaction were examined; the results are summarized in Table 1. Under the conditions used, 70 to 80% of ethyl acrylate was converted to α- and β-carbethoxypropionaldehyde in a good yield. The relative reaction rate was calculated on the basis of the rate of pressure drops (atm/min).

The Effect of the Concentration of Rhodium Carbonyl. The relative reaction rate and the percentage of α-carbethoxypropionaldehyde plotted against the reaction temperature are shown in Fig. 1.

[*1] Part XI: Y. Takegami, Y. Watanabe, H. Masada and I. Kanaya, This Bulletin, **40**, 1456 (1967).

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TABLE 1. THE OXO REACTION OF ETHYL ACRYLATE BY RHODIUM CARBONYL

Exp. No.	Reaction condition*1					Relative rate*3	Conversion of ethyl acrylate %	Product*4	
	Temp. °C	Partial pressure*2 CO atm	Partial pressure*2 H_2 atm	Amount of $(Rh(CO)_3)_n$ mg	Time min			*n*-Aldehyde mol%	Iso-aldehyde mol%
1	95	80	80	1	120	—	70	40.2	59.8
2	110	80	80	1	110	2.5	73	65.2	34.8
3	90	80	80	1	240	1	73	23.2	76.8
4	90	80	80	3	240	1	73	22.4	77.6
5	110	80	80	3	120	2.7	72	62.0	38.0
6	100	80	80	3	120	1.5	82	46.5	53.5
7	120	80	80	3	60	3.6	76	68.6	31.4
8	100	80	40	3	300	0.7	69	59.3	40.7
9	110	80	40	6	240	1	80	68.4	31.6
10	110	80	80	6	120	3.2	85	59.0	41.0
11	110	120	80	6	120	3.3	89	52.3	47.7
12	110	40	80	6	180	1.1	84	75.5	24.5
13	110	160	80	6	120	3.5	87	47.0	53.0
14	110	80	160	6	120	3.5	85	39.5	60.5
15	120	80	40	6	120	1.7	83	79.6	20.4
16	120	40	80	6	120	1.5	84	84.5	15.5
17	120	160	80	6	60	4.3	87	56.2	43.8
18	120	80	160	6	60	4.2	82	59.0	41.0
19	110	80	80	40	120	3.5	76	53.3	46.7

*1 Eighty milliliters of toluene and 20 m*l* of ethyl acrylate were used.
*2 Initial pressure.
*3 Calculated from pressure drops (atm/min).
*4 *n*-Aldehyde: β-carbethoxypropionaldehyde. Iso-aldehyde: α-carbethoxypropionaldehyde.

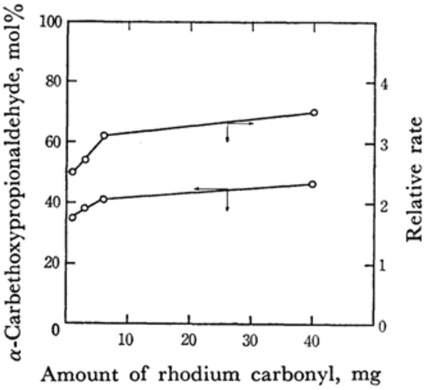

Fig. 1. The percentage of α-carbethoxypropionaldehyde and relative rate *vs.* amounts of rhodium carbonyl used plots for the oxo reaction of ethyl acrylate.
(Temp.: 110°C, Initial partial pressures of carbon monoxide and hydrogen: 80 atm, respectively.)

As Fig. 1 shows, when the other reaction conditions were fixed*2 the reaction rate increased with an increase in the concentration of rhodium carbonyl; when 1, 3, and 6 mg of rhodium carbonyl was used, the reaction rate increased almost proportionally with the amount of rhodium carbonyl to a maximum of 3.2 of the relative reaction rate, but even 40 mg of rhodium carbonyl made the reaction faster by only 0.3 to give 3.5 of the relative reaction rate. This fact shows that the amount of rhodium sufficient for this reaction is about 6 mg under the reaction conditions used. Figure 1 also shows that the percentage of α-carbethoxypropionaldehyde increased almost proportionally with an increase in the reaction rate under the conditions used. However, the effect on the distribution of the products was apparently rather small.

The Effect of the Reaction Temperature. The relative reaction rate and the percentage of α-carbethoxypropionaldehyde plotted against the reaction temperature are shown in Fig. 2.

As Fig. 2 shows, the percentage of the aldehyde with a branched-chain structure decreased with an increase in the reaction temperature when the other reaction conditions were fixed*3: at 90°C the aldehyde was obtained as the major product (78%), but at 110 and 120°C this aldehyde was a minor one (30 to 40%). A similar effect of the reaction temperature has been also observed in the

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*2 At 110°C under 80 atm of the partial pressure of hydrogen and carbon monoxide.

*3 Under 80 atm of the partial pressure of hydrogen and carbon monoxide.

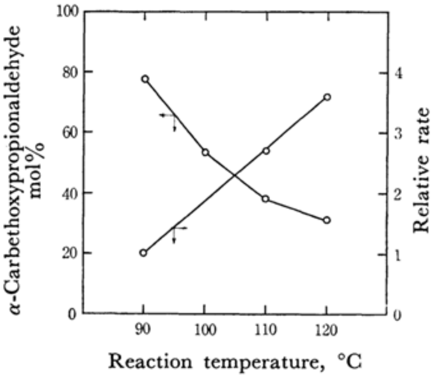


Fig. 2. The percentage of α-carbethoxypropionaldehyde and relative rate *vs.* the reaction temperature plots for the oxo reaction of ethyl acrylate.
(Initial partial pressures of carbon monoxide and hydrogen: 80 atm, respectively. Amounts of rhodium carbonyl: 3 mg.)

case of cobalt;4) in which the percentage of the aldehyde decreased from 20 to 5% with an increase in the reaction temperature (90—120°C). Thus, the effect of the reaction temperature on the distribution of the products is much greater in the case of rhodium than in the case of cobalt.

The reaction rate increased with an increase in the reaction temperature (see Fig. 2).

The Effect of the Partial Pressure of Carbon Monoxide. Figure 3 gives the plots of the percentage of α-carbethoxypropionaldehyde and the relative reaction rate *vs.* the initial partial pressure of carbon monoxide.

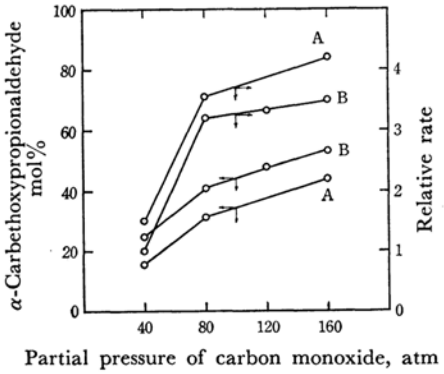


Fig. 3. The percentage of α-carbethoxypropionaldehyde and relative rate *vs.* the initial partial pressure of carbon monoxide plots for the oxo reaction of ethyl acrylate.
A; temp.: 120°C,
initial partial pressure of hydrogen: 80 atm,
amount of rhodium carbonyl: 6 mg
B; temp.: 110°C,
initial partial pressure of hydrogen: 80 atm,
amount of rhodium carbonyl: 6 mg

As Fig. 3 shows, when other reaction conditions were fixed,[*4] the percentage of the aldehyde increased with an increase in the partial pressure of carbon monoxide; the change of the pressure from 40 to 160 atm resulted in the change of the percentage of the aldehyde from 25 to 53%, indicating that the partial pressure of carbon monoxide also has a great effect on the distribution of the products. In the case of cobalt, the pressure of carbon monoxide has a similar effect,4) but it is much smaller than that in the case of rhodium.

As Fig. 3 shows, the reaction rate increased with an increase in the partial pressure of carbon monoxide. Particularly, the change in the partial pressure of carbon monoxide from 40 to 80 atm resulted in a greater increase in the relative reaction rate (see Exps. 12, 13, 16 and 17); the reaction rate at 80 atm seems to be three times as large as that at 40 atm. This shows that the partial pressure of carbon monoxide highly promotes the hydroformylation reaction in the case of rhodium. This observation is of interest in the light of the result obtained in the case of cobalt;4) the hydroformylation reaction is inhibited reversely by the higher partial pressures of carbon monoxide. It is, however, not completely clear how this difference has arisen in the present investigation. Further work is required to explain fully this interesting observation.

The Effect of the Partial Pressure of Hydrogen. Figure 4 shows the plot of the percentage of α-carbethoxypropionaldehyde *vs.* the partial pressure of hydrogen.

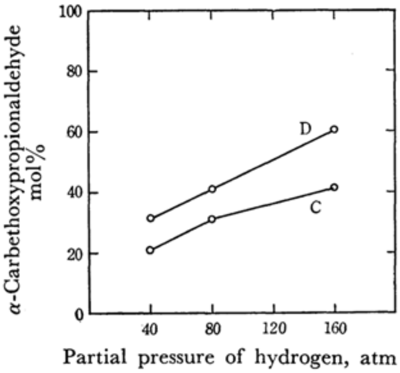


Fig. 4. The percentage of α-carbethoxypropionaldehyde *vs.* the initial partial pressure of hydrogen plots for the oxo reaction of ethyl acrylate.
C; temp.: 120°C,
initial partial pressure of CO 80 atm,
amount of rhodium catbonyl: 6 mg
D; temp.: 110°C,
initial partial pressure of CO: 80 atm,
amount of rhodium carbonyl: 6 mg

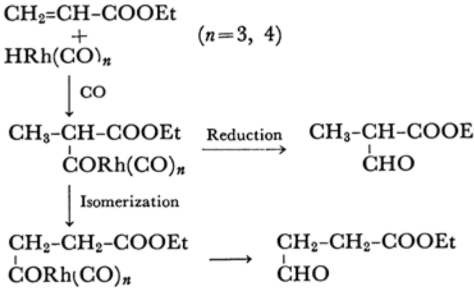
[*4] At 110 or 120°C under 80 atm of the partial pressure of hydrogen.

As Fig. 4 shows, the percentage of the aldehyde increased with an increase in the partial pressure of hydrogen when the other conditions were fixed; the increase in the partial pressure from 40 to 160 atm resulted in a great increase in the percentage of the aldehyde, from 31.6 to 60.5%. Thus, the partial pressure of hydrogen also has a great effect on the distribution of the products. In the case of cobalt, the pressure of hydrogen has been observed to have a similar but much smaller effect.[4)]

The reaction rate seems to increase with an increase in the partial pressure of hydrogen (see Exps. 9, 10, and 15).

Discussion on the Reaction Mechanism. As has been mentioned above, the effects of the reaction temperatures and the partial pressures of carbon monoxide and hydrogen on the distribution of the products are very similar in the two cases of rhodium and cobalt. In view of this similarity, it seems likely that, in these cases, the reaction follows a similar reaction scheme. Previous work in this laboratory has strongly suggested that the hydroformylation of ethyl acrylate follows a reaction scheme similar to that of the reaction of cobalt hydrocarbonyl;[3,4)] the distribution of α- and β-carbethoxypropionaldehyde is controlled by the two competitive reactions, the reduction and isomerization of α-carbethoxypropionylcobalt carbonyl, which is obtained by the reaction between ethyl acrylate and cobalt hydrocarbonyl, to β-carbethoxypropionylcobalt carbonyl. The effects of the various reaction conditions on the distribution of the products can be well attributed to the effects on these two reactions.[4)]

In the light of the results obtained here, the rhodium catalyst used is considered to act as rhodium hydrocarbonyl, which reacts with ethyl acrylate to give two isomeric acylrhodium carbonyls as the reaction intermediates; the reaction is assumed to proceed much as in the case of cobalt:



$$\begin{array}{lcl} \begin{array}{c} CH_2{=}CH{-}COOEt \\ + \\ HRh(CO)_n \end{array} \quad (n=3,\ 4) & & \\ \downarrow \text{CO} & & \\ CH_3{-}\underset{\displaystyle CORh(CO)_n}{\underset{|}{CH}}{-}COOEt & \xrightarrow{\text{Reduction}} & CH_3{-}\underset{\displaystyle CHO}{\underset{|}{CH}}{-}COOEt \\ \downarrow \text{Isomerization} & & \\ \underset{\displaystyle CORh(CO)_n}{\underset{|}{CH_2}}{-}CH_2{-}COOEt & \longrightarrow & \underset{\displaystyle CHO}{\underset{|}{CH_2}}{-}CH_2{-}COOEt \end{array}$$

Thus, in the course of the reaction, higher temperatures seem to favor the isomerization and to cause the percentage of α-carbethoxypropionaldehyde to decrease. On the contrary, higher pressures of hydrogen seem to be favorable to the reduction, and higher pressures of carbon monoxide seem to inhibit the isomerization, causing the percentage of the aldehyde to increase.