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Studies of the Organic Reaction of Metal Carbonyl. X.* The Oxo Reaction of Ethyl Acrylate—The Effects of the Reaction Conditions on the Distribution of the Products

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The ratio between the α- and β-carbethoxypropionaldehyde formed in the oxo reaction of ethyl acrylate is affected by various reaction conditions; the proportion of β-carbethoxypropionaldehyde increases with an increase in the reaction temperature, but decreases with an increase in the partial pressure of carbon monoxide or hydrogen. These effects can be explained on the basis of the reaction mechanism between cobalt hydrocarbonyl and ethyl acrylate (Y. Takegami et al., This Bulletin, **37**, 1190 (1964)): in the first step of the reaction, ethyl acrylate reacts with cobalt hydrocarbonyl to give, selectively, α-carbethoxypropionylcobalt carbonyl (I), and then I isomerizes to β-carbethoxypropionylcobalt carbonyl (II). Accordingly, the rates of two competitive reactions, the isomerization of I to II and the reduction of I to the corresponding aldehyde, may be the factors determining the distribution of the oxo reaction products. Under the oxo reaction conditions, the isomerization of I to II seems to occur more easily at a relatively high temperature and to be prohibited by a high pressure of carbon monoxide. On the other hand, a relatively high pressure of hydrogen seems to be favorable to the reduction of I to the aldehyde.

Previous work[1] in this laboratory has demonstrated that the reaction of ethyl acrylate with cobalt hydrocarbonyl gives two isomeric acylcobalt carbonyls (α- and β-carbethoxypropionylcobalt carbonyl); that is, in the first step of the reaction, the α-carbon atom of the ethyl acrylate is selectively carbonylated to give α-carbethoxypropionylcobalt carbonyl, and then this isomerizies to the acylcobalt carbonyl with a straight chain structure. This fact strongly indicates that, in the reaction between cobalt hydrocarbonyl and olefin, the rates of the addition of cobalt hydrocarbonyl to an olefinic bond and the isomerization of acylcobalt carbonyls are the factors determining the distribution of the products. It is reasonable to consider that, under the oxo conditions, such an isomerization of acylcobalt carbonyls occurs, having a great effect on the distribution of the products. In the oxo reaction of 1-olefins, the effect of the reaction conditions on the distribution of the products has been studied in detail by several workers.[2] However, no attention has been paid to the effect of the isomerization of acylcobalt carbonyls.

The aim of the present investigation is to study whether the isomerization of alkyl and acylcobalt carbonyls does indeed occur in the oxo reaction of ethyl acrylate, by examining in detail the effects of various reaction conditions.

Experimental

Reaction Procedures.—An autoclave (300 ml.), made of 18-8 nickel-chrom-iron steel and equipped with a magnetic stirrer, was used. Eighty milliliters of toluene, 10 ml. of a dicobalt octacarbonyl solution in toluene (containing 0.22 to 0.24 g. of cobalt as calculated from the carbonyl content), and 20 ml. of ethyl acrylate were placed into the autoclave. After the air in the autoclave had been replaced with hydrogen, hydrogen and carbon monoxide were introduced at certain pressures. The autoclave was then kept at a certain temperature until the guage pressure ceased to decline.

Analysis of the Products.—The products were identified by mixed gas chromatography with authentic samples. A column (3 m. long and 3 mm. in diameter), filled with dilauryl phthalate on cerite, was used. The column temperature was 110 to 125°C, and the rate of flow of the carrier gas (hydrogen) was 50 to 100 ml. per min.

The infrared absorption spectrum of the toluene solution was recorded by the use of a Shimadzu Model IR-27 spectrophotometer.

Materials.—Dicobalt octacarbonyl solution in toluene was prepared according to the method described in a

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* Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965. Part IX: Y. Takegami, Y. Watanabe, H. Masada and C. Yokokawa, This Bulletin, **39**, 1499 (1966).

[1] Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, This Bulletin, **37**, 1190 (1964).

[2] V. L. Hughes and I. Kirshenbaun, *Ind.* & *Eng. Chem.*, **49**, 1999 (1957); *Petroleum Refiner*, **37**, 209 (1958); P. Pino, F. Piacenti and P. P. Neggiani, *Chem.* & *Ind.*, **1961**, 1400.

previous paper.[3] Ethyl acrylate, toluene and other materials were commercial products which had been proved by gas chromatography to be sufficiently pure. As authentic samples, the following commercial chemicals were used: α- and β-carbethoxypropionaldehyde and β-carbethoxypropyl alcohol.

Results and Discussion

The effects of the reaction conditions (the temperature, the partial pressures of hydrogen and carbon monoxide, and the solvents) on the ratio of the products were examined; the results are summarized in Tables I and II. Under the conditions used, 80 to 90% of ethyl acrylate was converted to α- and β-carbethoxypropionaldehyde. In Tables I and II, the values of the reaction times during which a pressure drop was observed, relative of that of Exp. 12, are shown as a measure of the relative reaction rate.

The Effect of the Reaction Temperature.— The relation between the reaction temperature and the percentage of α-carbethoxypropionaldehyde, and that between the reaction temperature and the relative rate, are illustrated in Figs. 1 and 2.

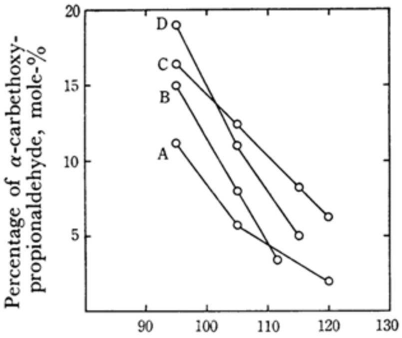


Fig. 1. The percentage of α-carbethoxypropionaldehyde vs. the reaction temperature.

A: H_2 80 atm., CO 40 atm.
B: H_2 80 atm., CO 80 atm.
C: H_2 80 atm., CO 120 atm.
D: H_2 120 atm., CO 80 atm.

As Fig. 1 shows, the percentage of the branched aldehyde decreased almost proportionally with an increase in the reaction temperature, when the initial pressures of hydrogen and carbon monoxide were fixed. With simple 1-olefins, the yield of branched aldehyde increases with an increase in the reaction temperature.[2] In this point, the behavior of ethyl acrylate is different from that of the simple 1-olefins in the oxo reaction. This contrast may be attributed to an ester group of ethyl acrylate. On the other hand, in the reaction of ethyl acrylate with cobalt hydrocarbonyl, a relatively high reaction tmperature is favorable to the formation of a product with a straight chain structure.[1] Therefore, the reaction temperature in the oxo reaction of ethyl acrylate has an effect on the distribution of the products similar to that in the reaction of cobalt hydrocarbonyl. This fact seems to support the consideration[4] that a cobalt catalyst in the oxo reaction acts as cobalt hydrocarbonyl. It may reasonably be considered that the oxo reaction of ethyl acrylate follows this reaction scheme, similar to that of the reaction of cobalt hydrocarbonyl[1]:

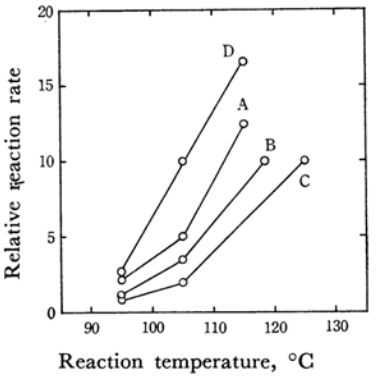
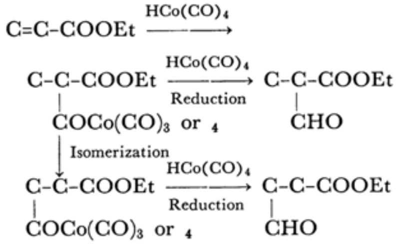


Fig. 2. The relative reaction rate vs. the reaction temperature.

A: H_2 80 atm., CO 40 atm.
B: H_2 80 atm., CO 80 atm.
C: H_2 80 atm., CO 120 atm.
D: H_2 120 atm., CO 80 atm.



$$\begin{array}{lcl} \text{C=C-COOEt} \xrightarrow{\text{HCo(CO)}_4} & & \\ \underset{\displaystyle\text{COCo(CO)}_3\text{ or }_4}{\text{C-C-COOEt}} & \xrightarrow[\text{Reduction}]{\text{HCo(CO)}_4} & \underset{\displaystyle\text{CHO}}{\text{C-C-COOEt}} \\ \downarrow\text{Isomerization} & & \\ \underset{\displaystyle\text{COCo(CO)}_3\text{ or }_4}{\text{C-C-COOEt}} & \xrightarrow[\text{Reduction}]{\text{HCo(CO)}_4} & \underset{\displaystyle\text{CHO}}{\text{C-C-COOEt}} \end{array}$$

In the light of the reaction scheme, the distribution of the two aldehydes seems to be controlled by the isomerization and reduction of α-carbethoxypropionylcobalt carbonyl, which is obtained by the reaction of ethyl acrylate with cobalt hydrocarbonyl. It has been shown[1] that the isomerization of this acylcobalt carbonyl occurs easily at a relatively low temperature (−10 to 25°C). In the oxo reaction, a higher temperature seems to be more favorable to this isomerization, from α-carbethoxypropionylcobalt carbonyl to β-carbethoxypropionylcobalt carbonyl, then causing the percentage of β-carbethoxy propionaldehyde to increase.

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[3] C. Yokokawa, Y. Watanabe and Y. Takegami, This Bulletin, **37**, 677 (1964).

[4] L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, **80**, 4428 (1958); **81**, 3597 (1959); R. F. Heck and D. S. Breslow, ibid., **83**, 4023 (1961).

TABLE I. THE OXO REACTION OF ETHYL ACRYLATE

Exp. No.	Reaction conditions: Temp. °C	Partial pressure,*1 atm.		Time*2 min.	Conversion of ethyl acrylate %	Relative reaction rate*4	Products,*3 mole-%: *n*-Aldehyde	*iso*-Aldehyde	*n*-Alcohol
		H_2	CO						
1	100—110	80	80	50	93	3.4	92	8.0	—
2	120—133	40	120	60	92	3.4	96	2.5	1.5
3	100—110	40	80	75	93	1.7	95.8	4.2	—
4	100—110	120	80	40	93	10	88.8	11.2	—
5	100—110	25	80	70	90	1.3	95.3	4.7	—
6	100—110	160	80	35	93	10	83.3	14.7	2.0
7	100—110	80	120	70	95	2	87.5	12.5	—
8	100—110	80	40	45	94	5	94.4	5.6	—
9	90—100	80	80	85	93	0.8	85	15	—
10	90—100	40	80	140	85	0.5	94	6.0	—
11	90—100	120	80	60	95	2.5	80	18.5	1.5
12	90—100	80	120	75	91	1	83.6	16.4	—
13	90—100	80	40	45	90	2.3	88.7	11.3	—
14	100—125	80	80	35	95	6	92.2	3.3	4.5
15	110—135	40	80	40	90	5	96	3.0	1.0
16	110—120	120	80	25	89	16	91.5	5.0	3.5
17	110—120	80	40	30	83	12	94.5	5.0	0.5
18	110—120	80	120	30	93	12	92	2.0	0
19	110—125	80	120	30	91	—	92	6.3	1.7
20	110—125	80	40	30	80	—	98	2.0	—
21	110—125	80	80	30	80	—	93.5	5.5	—

*1 Initial pressure.

*2 From the time when the reaction temperature reached to the certain one to that when pressure drop ceased.

*3 *n*-Aldehyde: β-carbethoxypropionaldehyde, *iso*-aldehyde: α-carbethoxypropionaldehyde, and *n*-alcohol: β-carbethoxy-*n*-propyl alcohol.

*4 The values of the reaction time, during which pressure drop was observed, relative to that of Exp. 12.

TABLE II. THE OXO REACTION OF ETHYL ACRYLATE—THE EFFECTS OF A MIXED SOLVENT

Exp. No.	Reaction conditions*1: Temp. °C	Partial pressure, atm.		Time min.	Relative reaction rate	Products,*2 mole-%: *n*-Aldehyde	*n*-Alcohol	Diethyl succinate	*iso*-Aldehyde	*iso*-Alcohol	*iso*-Aldehyde+*iso*-alcohol
		H_2	CO								
22	100—103	80	80	35	5	24.6	4.6	57.5	11.0	2.3	13.3
23	100—110	80	80	35	6	34.2	3.6	53.1	7.3	1.8	9.1
24	95—100	40	80	65	1.3	46.5	2.1	42.9	6.4	2.1	8.5

*1 Solvent: toluene - ethyl alcohol (60 : 25 in volume). In every case, about 95% of ethyl acrylate.

*2 Cf. Table I. *iso*-Alcohol: α-carbethoxy-*n*-propyl alcohol.

As Fig. 2 shows, the reaction rate increased with an increase in the reaction temperature.

The Effect of the Partial Pressure of Carbon Monoxide.—The relation between the initial pressures of carbon monoxide and the percentage of β-carbethoxypropionaldehyde is illustrated in Fig. 3.

The percentage of α-carbethoxypropionaldehyde increased with an increase in the initial pressure of carbon monoxide when the other reaction conditions were fixed (Fig. 3). Previous work[1,5] in this laboratory has demonstrated that the isomerization of the acylcobalt carbonyls (butyryl- and β-carbethoxypropionylcobalt carbonyl, etc.) generally occurs more rapidly under nitrogen than under carbon monoxide. Under oxo conditions, the isomerization of β-carbethoxypropionylcobalt carbonyl seems to be difficult at relatively high pressures of carbon monoxide; then the percentage of α-carbethoxypropionaldehyde increases with an increase in the carbon monoxide pressure. This fact supports the reaction scheme mentioned above.

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5) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, This Bulletin, **37**, 181 (1964); ibid., **38**, 787 (1965); ibid., **39**, 1495 (1966).

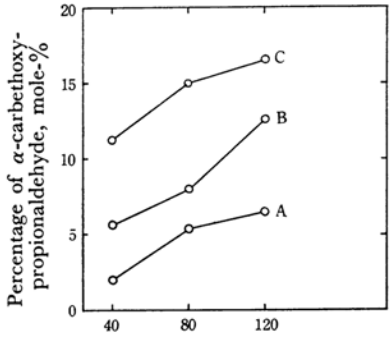

Fig. 3. The percentage of α-carbethoxypropionaldehyde vs. the initial pressure of carbon monoxide.

A: H_2 80 atm., Temp. 120°C
B: H_2 80 atm., Temp. 105°C
C: H_2 80 atm., Temp. 95°C

The relative reaction rate decreases with an increase in the initial pressure of carbon monoxide (cf. Exps. 1, 7 and 8).

The Effect of the Partial Pressure of Hydrogen.—The relation between the initial pressure of hydrogen and the percentage of α-carbethoxypropionaldehyde is shown in Fig. 4.

As Fig. 4 shows, the percentage of α-carbethoxypropionaldehyde increases almost proportionally with an increase in the partial pressure of hydrogen; when the initial pressure of carbon monoxide and the reaction temperature were fixed at 80 atm. and 100—110°C respectively, and when the initial pressures of hydrogen were 40, 80, 120 and 160 atm., the percentages of the aldehyde were 4.0, 8.0, 11.2 and 14.7 mole-% respectively.

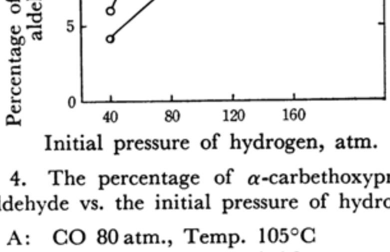

Fig. 4. The percentage of α-carbethoxypropionaldehyde vs. the initial pressure of hydrogen.

A: CO 80 atm., Temp. 105°C
B: CO 80 atm., Temp. 95°C

The relative reaction rate also increases with an increase in the partial pressure of hydrogen (cf. Exps. 1, 3, 4, and 5). The rate of the oxo reaction of simple 1-olefins may be represented as follows:⁽⁶⁾

$$\text{rate} = \frac{k_1 P_{H_2}}{k_2 P_{CO} + k_3 P_{H_2}} \qquad k\text{: constant} \quad P\text{: partical pressure}$$

This equation seems to be applicable to the case of ethyl acrylate.

From the standpoint of the reaction scheme, higher pressures of hydrogen are considered to be more favorable to the reduction of α-carbethoxypropionylcobalt carbonyl to the corresponding aldehyde rather than to its isomerization; hence, the formation of α-carbethoxypropionaldehyde seems to be relatively promoted. From this consideration, it may be suggested that the proportion of α-carbethoxypropionaldehyde increases with an increase in the reaction rate when the partial pressure of carbon monoxide and the reaction temperature are fixed. With simple 1-olefins, the oxo reaction rate is remarkably affected by the concentration of the catalyst and solvent.*,[2] Thus, with ethyl acrylate also the distribution of the products may be affected by solvents.

The Effect of the Solvent.—The effect of a mixed solvent, toluene - ethyl alcohol (60 : 25 in volume), on the reaction rate and the distribution of the products was also examined (Table II).

As the reaction products, the two aldehydes, two alcohols (α- and β-carbethoxy-*n*-propyl alcohol) and diethyl succinate were obtained. The diethyl succinate appeared to be formed by the reaction of β-carbethoxypropionylcobalt carbonyl with ethyl alcohol.

By comparing the results of Exps. 1 and 10 with those of Exps. 23 and 24 respectively, the reaction rate in the mixed solvent was found to be about two times as large as that in pure toluene when the other conditions were fixed; moreover, the percentage of the branched-chain products in the mixed solvent was evidently larger, supporting the assumption that the proportion of the branched-chain products increases with an increase in the reaction rate if the partial pressure of carbon monoxide and the reaction temperature are the same.

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* For example, the oxo reaction rate of acrylonitrile in ethyl alcohol is about five times as large as that in benzene.[7]

6) G. Natta, R. Ercoli, S. Castellano and F. H. Barbieri, *J. Am. Chem. Soc.*, **76**, 4049 (1954); R. A. Martin, *Chem. & Ind.*, **1954**, 1536; H. W. Sternberg, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **79**, 6116 (1957).

7) J. Kato, H. Wakamatsu, Y. Iwanaga and T. Yoshida, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kagyo Kagaku Zasshi)*, **64**, 2139 (1961).