Studies of the Organic Reaction of Metal Carbonyl. V. The Reaction of Cobalt Hydrocarbonyl with Olefin—The Effects of the Reaction Conditions and of the Structure of Olefin

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In connection with the oxo reaction, several studies[1-4] of the reaction of cobalt hydrocarbonyl with olefin have been published. It have been established[3,4] that 1-olefin gives two isomeric acylcobalt carbonyls and aldehydes in this reaction. Heck and Breslow[3] have suggested that the direction of the addition of cobalt hydrocarbonyl to some olefins, such as methyl acrylate and isobutylene, at 0°C is essentially the reverse of that of hydroformylation reaction at 120°C. It has thus seemed of considerable interest to study the reaction in greater detail. Previous work[5] in this laboratory has shown that some alkyl- and acylcobalt carbonyls isomerize readily. It is, accordingly, considered that the distribution of two isomeric acylcobalt carbonyls is affected by the isomerization as well as by the direction of the addition.

In the present paper, this type of reaction has been investigated by examing the effect of the reaction conditions and the structure of olefin, mainly on the nature of the reaction and on the distribution of the products.

Experimental

The Reaction Procedures.—The reactions under one atmosphere of carbon monoxide or nitrogen were carried out in the way described in previous papers,[5,6] using 50 ml. of a 0.09 M cobalt hydrocarbonyl solution in toluene. The reactions under two atmospheres of carbon monoxide were carried out using a 200 ml. glass autoclave.

The Analytical Procedures.—The solution of crude products was treated with iodine and alcohol as described previously,[5,6] and the excess of iodine was reduced with crystalline sodium thiosulfate. After concentration, the analyses of the reaction products were carried out by gas chromatography and by means of the infrared spectra, which were measured on a Shimadzu model IR-27 spectrophotometer.

The Materials.—Ethyl acrylate, styrene, *n*-butyl vinyl ether and pentene-1 were commercial products, all of which had been proved to be sufficiently pure by gas chromatography.

Results and Discussion

The Reaction of Ethyl Acrylate.—The results of the reaction of ethyl acrylate, which were carried out under one atmosphere of carbon monoxide or nitrogen at various temperatures, are summarized in Table I and Fig. 1.

The gas absorption curves in Fig. 1 indicate that the amount of gas absorbed increased with a decrease in the reaction temperature, though the rate of the gas absorption decreased; for instance, at -15°C, 0.6 mol.[*1] of the gas was absorbed in 4 hr.; then the gas absorption ceased, but at 25°C about 0.4 mol. of the gas was absorbed in half an hour.

The reaction temperature had a significant effect on the distribution of the products; at

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[1] I. Wender, H. W. Sternberg and M. Orchin, *J. Am. Chem. Soc.*, **75**, 3041 (1953); P. Pino, R. Ercoli and F. Calderazzo, *Chim. e Ind.* (*Milan*), **37**, 783 (1955); L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, **80**, 4428 (1958); **81**, 3597 (1959).

[2] R. F. Heck and D. S. Breslow, *Chem. & Ind.*, **1961**, 467.

[3] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

[4] G. L. Karapinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).

[5] Y. Takegami, C. Yokokawa, Y. Watanabe and Y. Okuda, This Bulletin, **37**, 181 (1964).

[6] Y. Takegami, C. Yokokawa, Y. Watanabe and H. Masada, ibid., **37**, 662 (1964).

[*1] Mole of the gas absorbed per mole of cobalt hydrocarbonyl used.

TABLE I. THE REACTION OF ETHYL ACRYLATE WITH COBALT HYDROCARBONYL

Exp. No.	Reaction conditions[*1]			CO Absorbed (mol./mol. $HCo(CO)_4$)	Product	
	Atmosphere	Temp. °C	Time min.		Esters[*2] (mol./mol. $HCo(CO)_4$)	Distribution of esters $B/(B+S)^{*2}\times 10^2$
1	CO	25	120	0.39	0.31	3
2	CO	0	180	0.47	0.78	97
3	CO	0	180	0.51	0.72	97
4	CO	−10	210	0.55	0.72	97
5	CO	−15	250	0.59	0.57	97
6	CO	−20	240	0.32	0.28	97
7	N_2	0	120	—	0.21	30
8	N_2	−10	180	—	0.18	40
9	N_2-CO[*3]	0	20∼120	0.09	0.21	33

[*1] Other condition: 10 mol. of ethyl acrylate per mol. of cobalt hydrocarbonyl used. Under one atmosphere of carbon monoxide or nitrogen.

[*2] B: a ester with the branched structure, diethyl methylmalonate.
S: a ester with the straight structure, diethyl succinate.

[*3] At first under nitrogen atmosphere and then under carbon monoxide.

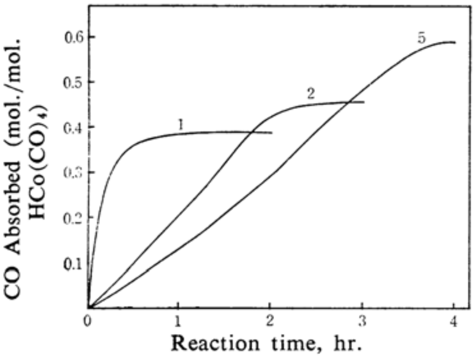
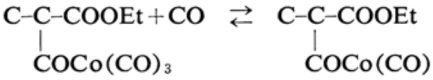


Fig. 1. CO Absorption vs. time plots for the reaction of ethyl acrylate at various temperatures.
Number corresponds with Exp. No. in Table I. Curve 1; at 25°C, curve 2; at 0°C and curve 5; at −15°C.

25°C, diethyl succinate[*2] was the major product, and only a trace of diethyl methylmalonate[*3] was also identified (Exp. 1). On the other hand, at 0∼−20°C, diethyl methylmalonate was the major product, and only a small amount of diethyl succinate was formed (Exp. 2—6). These facts, it would seem, can be interpreted by the following assumption; at a relatively low temperature, some effect of the ester group (–COOEt) on the adjacent carbon atom is more important, and then α-carbon atom is selectively carbonylated to form the acylcobalt carbonyl with the branched structure. However, at 25°C the steric effect is more important, and then a more stable acylcobalt carbonyl with a straight chain structure is formed.

At 0 and −10°C, the quantity of diethyl methylmalonate formed was more than that expected from the amount of the gas absorbed. It would seem that this fact can be explained by the following equilibrium:



$$\underset{\displaystyle COCo(CO)_3}{C\text{–}\underset{|}{C}\text{–}COOEt} + CO \rightleftarrows \underset{\displaystyle COCo(CO)_4}{C\text{–}\underset{|}{C}\text{–}COOEt}$$

At nitrogen atmosphere also had a significant effect on the distribution of the products, as was demonstrated by Exps. 7 and 8; even at 0 and −10°C, diethyl succinate was the major product, and a relatively large amount of diethyl methylmalonate was also formed, though the yield of the esters was not good. Under a nitrogen atmosphere, however, the color of the reaction solution changed much more readily than under carbon monoxide from yellow to brown; it took less than five minutes, even at −10°C. The reaction was carried out in two stages at 0°C, at first under a nitrogen atmosphere for 20 min. and then under a carbon monoxide. At the second stages, only 0.09 mol. of the gas was absorbed, and the yield of the esters was comparable to that under nitrogen (cf. Exps. 7 and 9). This fact seemed to indicate that under nitrogen, side reactions other than the formation of the acylcobalt carbonyl occurred rapidly to consume a large part of cobalt hydrocarbonyl used. Such a effect of a nitrogen atmosphere has been also observed in the reaction of olefin oxide with cobalt hydrocarbonyl.6)

Heck and Breslow3) have suggested that a nitrogen atmosphere promotes the carbonylation of olefin and that the inhibitory effect of a carbon monoxide atmosphere may be explained by the following equilibrium:

[*2,*3] Believed to have been derived from the corresponding acylcobalt carbonyls by cleavage with iodine and ethyl alcohol. Identified by gas chromatography and infrared spectrum using authentic samples.

TABLE II. THE REACTION OF ETHYL ACRYLATE—EFFECT OF CO PRESSURE

Exp. No.	Reaction conditions*1			CO Absorbed (mol./mol. $HCo(CO)_4$)	Product	
	Atmos-phere	Temp. °C	Time min.		Esters*2 (mol./mol. $HCo(CO)_4$)	Distribution of esters $B/(B+S)\times 10^2$
10	CO*3	0	240	0.71	0.73	97
11	CO*3	0	240	0.76	0.67	97
12	CO*3	25	240	0.76	0.32	12
13	CO*4	0	240	0.41	0.45	97

*1 10 mol. of ethyl acrylate per mol. of cobalt hydrocarbonyl used.
*2 Diethyl methylmalonate and diethyl succinate.
*3 Under two atmosphere of carbon monoxide.
*4 Under one atmosphere of carbon monoxide.

TABLE IIIa. THE REACTION OF PENTENE-1 WITH COBALT HYDROCARBONYL

Exp. No.	Reaction conditions*1			CO Absorbed (mol./mol. $HCo(CO)_4$)	Product	
	Atmos-phere	Temp. °C	Time min.		Esters*2 (mol./mol. $HCo(CO)_4$)	Distribution of esters $B/(B+S)$*2$\times 10^2$
14	CO	25	120	0.26	0.1	
15	CO	15	180	0.70	0.45	25
16	CO	0	420	0.54	0.35	25
17	CO	−10	960	0.44	0.33	30
18	N_2	0	5	—	0.03	—
19	N_2	0	30	—	0.03	—
20	N_2	0	180	—	0.03	—
21	N_2	0	780	—	0.03	—
22	N_2-CO*3	0	5∼300	0.07	0.06	—
23	N_2-CO	0	30∼180	∼0	0.05	—

TABLE IIIb. THE REACTION OF METHYL IODIDE WITH POTASSIUM COBALT CARBONYL

24	CO	0	200	1.00	—	—
25	N_2-CO	0	5∼200	1.00	—	—
26	N_2-CO	0	30∼200	0.96	—	—
27	N_2-CO	0	60∼280	0.70	—	—

*1 10 mol. of pentene-1 per mol. of cobalt hydrocarbonyl used.
5 mol. of methyl iodide per mol. of potassium cobalt carbonyl used.
*2 B: ethyl *α*-methyl-*n*-valerate.
S: ethyl *n*-caproate.
*3 At first under nitrogen and then under carbon monoxide.

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

that is, cobalt hydrotricarbonyl is more reactive.

In regard to this assumption, the reactions were carried out under two atmospheres of carbon monoxide to examine the effect of the pressure of carbon monoxide on the reaction. The resuluts are summarized in Table II. Under these conditions, the reaction seemed to occur relatively more smoothly because a larger amount of the gas was absorbed than under one atmosphere of carbon monoxide (cf. Exp. 11 and 13[*4]), suggesting that higher pressures of carbon monoxide are more advantageous fos this reaction, the formation of the acylcobalt carbonyls. This observation is not interpreted by Heck and Breslow's assumption. The reaction temperature, under these conditions, had almost the same effect on the distribution of the products as under one atmosphere of carbon monoxide.

In order to examine the effect of the atmosphere in greater detail, pentene-1 and methyl iodide were submitted to reactions with cobalt hydrocarbonyl and potassium cobalt tetracarbonyl respectively. The results are summarized in Table III.

Pentene-1 is evidently less reactive than ethyl acrylate (cf. Fig. 4). In this case, the reaction temperature (25∼10°C) had no effect on the distribution of the products; ethyl *n*-caproate was the major product, and ethyl *α*-methylvalerate was the minor (Exps. 14—17). Under a nitrogen atmosphere at 0°C, only 0.03 mol

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[*4] Carried out under one atmosphere of carbon monoxide using the same glass autoclave.

TABLE IV. THE REACTION OF ETHYL ACRYLATE—EFFECT OF THE CHANGE OF THE REACTION TEMPERATURE IN STAGES ON THE DISTRIBUTION OF PRODUCTS

Exp. No.	Reaction conditions*1			CO Absorbed (mol./mol. $HCo(CO)_4$)	Product	
	Atmosphere	Temp. °C	Time min.		Esters*2 (mol./mol. $HCo(CO)_4$)	Distribution of esters $B/(B+S) \times 10^2$
28*3	CO	25～10	120～150	0.34	0.29	3
29	CO	−10～25	220～60	0.58+0.42*4	0.65	3
30	CO	−10～25	120～60 ～120	0.43+0.43	0.29	5
31	CO	−10～25	180～60	0.48+0.52	0.58	3
32	CO	−10～15	190～160	0.53−0.16 +0.35	0.39	35
33*5	CO	0～25	180～120	0.55	0.70	40
34	CO	25	10	0.40	0.30	23
35	CO	0	300	0.50	0.57	90
36	CO	0	900	0.46	0.44	55
37	N_2	0	10	—	0.22	76
38	N_2	0	240	—	0.15	14

*1 10 mol. ethyl acrylate/mol. $HCo(CO)_4$.

*2 Diethyl methylmalonate and diethyl succinate.

*3 At first at 25°C for 120 min. and then at −10°C for 150 min.

*4 Absorbed at 25°C (at the second stage).

*5 Under two atmospheres of carbon monoxide.

of the ester, mainly ethyl α-methylvalerate, was identified independently of the reaction time from 5 min. to 13 hr. (Exps. 18—21); C_6-aldehyde seemed not to be formed its 2,4-dinitrophenylhydrazone was not obtained.

The reaction was carried out in two stages, as has been mentioned above: at the second stage under carbon monoxide, a small amount of the gas was absorbed (Exps. 22 and 23), and the amount of gas evolved by the treatment with an excess of iodine after the reaction was comparable to that calculated for the cobalt hydrocarbonyl used. However, the reaction of methyl iodide with potassium cobalt tetracarbonyl was not affected evidently by the pre-treatment with a nitrogen atmosphere (Exps. 25—27). Therefore, in the reaction of pentene-1 under nitrogen, a large part of the cobalt hydrocarbonyl used seemed to be consumed in less than 5 min. by side reaction other than the carbonylation. It may, accordingly, be concluded that a carbon monoxide atmosphere is advantageous for the carbonylation of olefin.

The Isomerization of Acylcobalt Carbonyl.—As has been described above, the reaction temperature and atmosphere have a significant effect on the distribution of the products from ethyl acrylate. In regard to this fact, several reactions were carried out in two or three stages by changing the reaction temperature (from 25°C to −10°C or from −10°C to 25°C, etc.) and by changing the reaction atmosphere in the course of an individual run.

By the change of the reaction temperature from 25°C to −10°C, the distribution of the products was not affected, as in Exps. 28 and 1. However, by the change from −10°C to 25°C or 15°C, the distribution was remarkably affected (cf. Exp. 4); at the first stage, at −10°C, about 0.6 mol. of the gas was absorbed in about 200 min. and the gas absorption ceased, but at the second stage, at 25°C, about 0.4 mol. more of the gas was absorbed in about 60 min. (curve 29 in Fig. 2) and then diethyl succinate was obtained as the major product (Exp. 29). This fact indicates that the acylcobalt carbonyl (or/and the alkyl-) with the branched structure isomerized to that with the

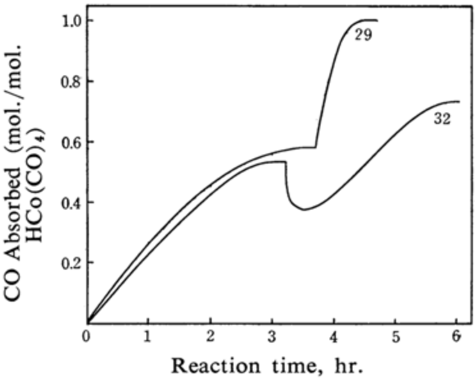
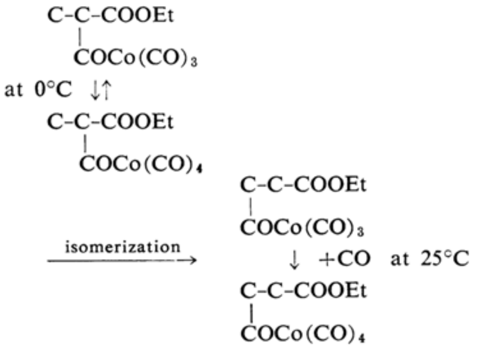


Fig. 2. CO Absorption vs. time plots for the reaction of ethyl acrylate——Effect of the change of the reaction temperature in stages.
Curve number: Exp. No.
Curve 29; at first at −10°C and then at 25°C.
Curve 32; at first at −10°C and then at 15°C.

straight one in this treatment; this may be represented as follows:

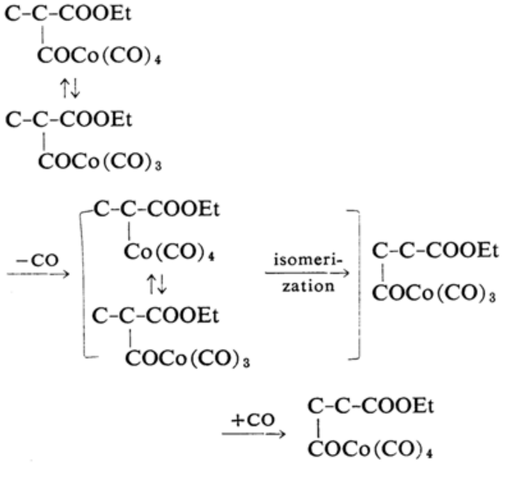


that is, the gas absorption at the second stage seemed to be due to the acylcobalt tricarbonyl with the straight-chain structure formed by the isomerization. The reverse isomerization, from the acylcobalt carbonyl with the straight-chain structure to that with the branched one, occurs only with difficulty, it seems.

When the reaction temperature at the second stage was set at 15°C, the gas evolution occurred first, followed by the gas absorption (curve 32 in Fig. 2). In this case diethyl succinate predominated in the product, but a relatively large amount of diethyl methylmalonate was also formed (Exp. 32); at 15°C, the isomerization also occurred, but more slowly than at 25°C. The gas evolution seemed to be due to the following change, as has been reported previously:⁵⁾

$$RCOCo(CO)_4 \underset{CO}{\overset{\Delta}{\rightleftarrows}} RCo(CO)_4 + CO$$

Thus, it seems that the overall reaction scheme may be represented as follows:



that is, the carbon monoxide-lacking state, such as in the alkylcobalt tetracarbonyl and the acylcobalt tricarbonyl, seemed to undergo isomerization.

Even at 25°C, when the reaction was carried out only for 10 min., the proportion of diethyl methylmalonate formed was larger than that formed in the reaction which was carried out for 2 hr. (Exps. 34 and 1), suggesting that, at 25°C, the acylcobalt carbonyl with the branched structure is formed at first and that it then isomerizes rapidly to that with the straight structure. Thus, at an elevated temperature this type of isomerization is considered to occur more easily. The distribution of the products obtained in the oxo condition seems to be considerably affected by the isomerization as well as by the direction of the addition of cobalt hydrocarbonyl to a C=C bond.

Under two atmospheres of carbon monoxide, the same isomerization occurred with the change in the reaction temperature from 0°C to 25°C, but more slowly than under one atmosphere of carbon monoxide (cf. Exps. 33 and 29). The fact that a relatively high pressure of carbon monoxide is unfavorable for the isomerization seemed to support the above mechanism.

Even at 0°C under one atmosphere of carbon monoxide, this isomerization occurred very slowly; after 15 hr. the amount of diethyl succinate was almost comparable to that of diethyl methylmalonate (Exp. 36). On the other hand, under nitrogen this isomerization occurred more rapidly than under carbon monoxide; at 0°C, when the reaction was carried out for only 10 min., mainly diethyl methylmalonate was formed (Exp. 37), but after 2 or 4 hr. diethyl succinate predominated (Exps. 38 and 7). Thus, a nitrogen atmosphere promotes the isomerization.

By the change of the reaction atmosphere in such stages, as from carbon monoxide to nitrogen, the distribution of the products was also affected (Table V). When the reaction was carried out in two stages at 0°C, at the second stage under nitrogen about 0.2 mol. of a gas was evolved in about 20 min., and then the gas absorption followed slowly, as is shown in Fig. 3 (curve 40). The amount of the isomerized product, diethyl succinate, increased with an increase in the reaction time under nitrogen (Exps. 39—41); a nitrogen atmosphere promoted the isomerization. This observation seemed to be interpreted well by the mechanism of the isomerization.

As has been described above (Exp. 9), pretreatment for 20 min. with a nitrogen atmosphere remarkably reduced the amound of the gas adsorbed at the second stage under carbon monoxide. However, when the reaction was carried out at first under carbon monoxide for

TABLE V. THE REACTION OF ETHYL ACRYLATE—EFFECT OF THE CHANGE OF REACTION ATMOSPHERE IN STAGES ON THE DISTRIBUTION OF PRODUCTS

Exp. No.	Reaction conditions[*1]		CO Absorbed (mol./mol. $HCo(CO)_4$)	Product	
	Atmosphere	Time min.		Esters[*2] (mol./mol. $HCo(CO)_4$)	Distribution of esters $B/(B+S)\times10^2$
39[*3]	$CO-N_2$	120~60	$0.44-0.20$	0.59	82
40	$CO-N_2$	120~180	$0.54-0.22+0.20$[*4]	0.31	52
41	$CO-N_2$	120~300	$0.45-0.20+0.20$	0.34	25
42[*5]	$CO-N_2-CO$	120~60~120	$0.47-0.25+0.30$	0.4	75
43	$CO-N_2-CO$	15~30~120	$0.14-0.07+0.36$	0.32	70
44	$CO-N_2-CO$	15~120~60	$0.14-0.05+0.18$	0.13	30
45	$CO-N_2-CO$	30~30~135	$0.26-0.07+0.34$	0.38	80
46	$CO-N_2-CO$	30~120~80	$0.26-0.07+0.23$	0.27	25

[*1] Other conditions: at 0°C 10 mol. of ethyl acrylate/mol. $HCo(CO)_4$.
[*2] Diethyl methylmalonate and diethyl succinate.
[*3] At first under carbon monoxide for 120 min. and then under nitrogen for 60 min. At the second stage 0.20 mol. of the gas was evolved.
[*4] Absorbed at the second stage.
[*5] Carried out in three stages: at the third stage 0.30 mol. of the gas was absorbed.

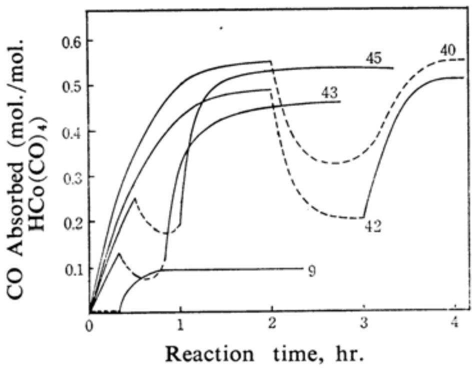


Fig. 3. CO Absorption vs. time plots for the reaction of ethyl acrylate——Effect of the change of the reaction atmosphere in stages.
Curve number: Exp. No.
(------) under a nitrogen atmosphere and
(——) under a carbon monoxide.

only 15 or 30 min.,[*5] a nitrogen atmosphere for 30 min.[*6] (or 120 min.) at the second stage did not prevent the gas absorption at the third stage under carbon monoxide (Exps. 43—46); in these runs the overall amount of gas absorbed was almost comparable to that absorbed when the reaction which was carried out under carbon monoxide (cf. Exp. 2). This fact seemed to support the consideration that, under nitrogen at the first stage, the cobalt hydrocarbonyl used is rapidly consumed by some side reaction other than the carbonylation. In these case the proportion of the isomerized product, diethyl succinate, also increased with an increase in the reaction time under nitrogen.

The Reaction of *n*-Butyl Vinyl Ether and Styrene.—With relation to ethyl acrylate, the effects of the reaction conditions on the reactions of *n*-butyl vinyl ether and styrene have been also investigated; the results are summarized in Tables VI and VII. These olefins are much more reactive than ethyl acrylate and pentene-1 (cf. Fig. 4);[*7] with *n*-butyl vinyl ether, even at −30°C, 0.96 mol. of the gas was absorbed in one hour. In these cases, the reaction temperature and the atmosphere had a similar effect on the distribution of the products and on the isomerization, as in the reaction of ethyl acrylate; under carbon mono-

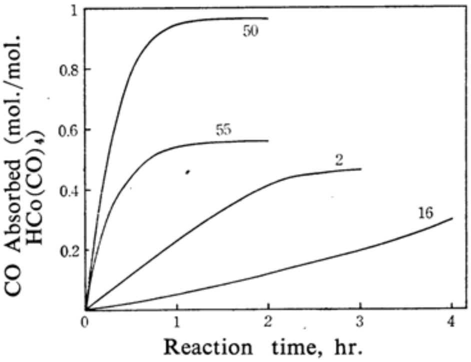


Fig. 4. CO Absorption vs. time plots for the reaction of several kinds of olefin.
Curve number: Exp. No.
Curve 50; *n*-butyl vinyl ether at −30°C, curve 55; styrene at 0°C, curve 2; ethyl acrylate at 0°C and curve 16; pentene-1 at 0°C.

[*5] The reaction was not finished; only 0.14 and 0.26 mol. of the gas were absorbed.

[*6] A relatively samll amount of the gas was evolved.

[*7] Styrene was relatively readily hydrogenated to give some ethyl benzene.

TABLE VI. THE REACTION OF *n*-BUTYL VINYL ETHER WITH COBALT HYDROCARBONYL

Exp. No.	Reaction conditions*1 Atmosphere	Temp. °C	Time min.	CO Absorbed (mol./mol. $HCo(CO)_4$)	Product Esters*2 (mol./mol. $HCo(CO)_4$)	Distribution of esters $B/(B+S)^{*2}\times 10^2$
47	CO	25	120	0.36	0.25	3
48	CO	0	120	0.70	0.36	75
49	CO	−20	120	1.00	0.60	97
50	CO	−30	120	0.96	0.63	97
51	N_2	0	120	—	0.28	13
52	CO	−20∼25	120∼120	0.99−0.32	0.29	20

*1 2 mol. *n*-butyl vinyl ether/mol. $HCo(CO)_4$.
*2 B: an ester with the branched structure, ethyl α-*n*-butoxypropionate.
S: an ester with the straight structure, ethyl β-*n*-butoxypropionate.

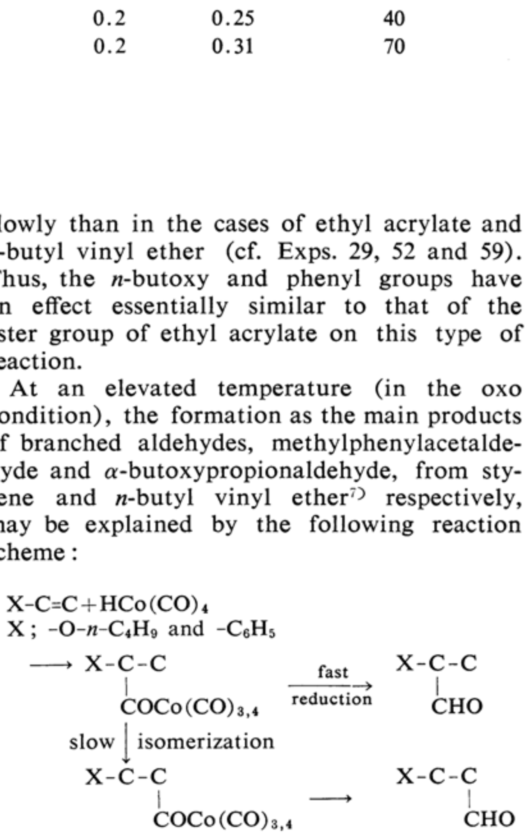
TABLE VII. THE REACTION OF STYRENE WITH COBALT HYDROCARBONYL

Exp. No.	Reaction conditions*1 Atmosphere	Temp. °C	Time min.	CO Absorbed (mol./mol. $HCo(CO)_4$)	Product Ethylbenzene (mol./mol.	Esters*2 $HCo(CO)_4$)	Distribution of esters $B/(B+S)^{*2}\times 10^2$
53	CO	25	120	0.43	0.2	0.25	30
54	CO	20	180	0.43	0.2	0.25	40
55	CO	0	120	0.56	0.2	0.38	96
56	CO	−10	300	0.51	0.2	0.38	97
57	CO	−20	340	0.52	0.2	0.35	97
58	N_2	0	120	—	0.2	0.25	55
59	CO	0∼25	120∼200	0.48	0.2	0.25	40
60	CO	−10∼20	240∼90	0.51	0.2	0.31	70

*1 10 mol. styrene/mol. $HCo(CO)_4$.
*2 B: ethyl α-phenylpropionate.
S: ethyl hydrocinnamate.

xide at a relatively low temperature (0∼−30°C), esters with a branched structure, ethyl α-*n*-butoxypropionate*8 and ethyl α-phenylpropionate,*9 predominated (Exps. 48—50 and 55—57), but at 25°C, esters with a straight-chain structure, ethyl β-*n*-butoxypropionate*10 and ethyl hydrocinnamate,*11 were mainly obtained (Exps. 47 and 53). Under nitrogen, even at 0°C, the esters with the straight-chain structure predominated (Exps. 51 and 58). Moreover, the isomerization of the acylcobalt carbonyls with the branched structure to those with the straight-chain structure occurred with the change in the reaction temperature from −20°C or 0°C to 25°C (Exps. 52 and 59). However, the isomerization of α-phenylpropionylcobat carbonyl seemed to occur more slowly than in the cases of ethyl acrylate and *n*-butyl vinyl ether (cf. Exps. 29, 52 and 59). Thus, the *n*-butoxy and phenyl groups have an effect essentially similar to that of the ester group of ethyl acrylate on this type of reaction.

At an elevated temperature (in the oxo condition), the formation as the main products of branched aldehydes, methylphenylacetaldehyde and α-butoxypropionaldehyde, from styrene and *n*-butyl vinyl ether[7] respectively, may be explained by the following reaction scheme:



$$X\text{-}C{=}C+HCo(CO)_4$$

X; $\text{-O-}n\text{-}C_4H_9$ and $\text{-}C_6H_5$

$$\longrightarrow \underset{\substack{|\\ COCo(CO)_{3,4}}}{X\text{-}C\text{-}C} \xrightarrow[\text{reduction}]{\text{fast}} \underset{\substack{|\\ CHO}}{X\text{-}C\text{-}C}$$

$$\text{slow}\ \Big\downarrow\ \text{isomerization}$$

$$\underset{\substack{\qquad |\\ \qquad COCo(CO)_{3,4}}}{X\text{-}C\text{-}C} \longrightarrow \underset{\substack{\qquad |\\ \qquad CHO}}{X\text{-}C\text{-}C}$$

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*8 Identified by gas chromatography and by means of its infrared spectrum, which had a band at 1760 cm^{-1} corresponding to a carbonyl grop with α-electronegative substituents.

*9 Infrared spectrum, 1720 cm^{-1}.

*10 Infrared spectrum, 1735 cm^{-1}. Further evidence; the retention time of the products (esters) increased as the molecular weight of the alcohol used for the cleavage reaction increased.

*11 Identified by using authentic ethyl hydrocinnamate.

[7] H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **70**, 383 (1948); **71**, 3051 (1949).

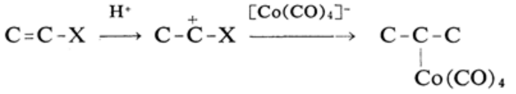
that is, the methylphenylacetyl and α-butoxypropionylcobalt carbonyls formed at the first step undergo reduction more rapidly than isomerization to give the corresponding aldehydes. On the other hand, in the case of ethyl acrylate, the isomerization of the branched acylcobalt carbonyl seems to occur more rapidly than the reduction; therefore, an aldehyde with a straight-chain structure, ethyl γ-oxobutyrate, is mainly formed.

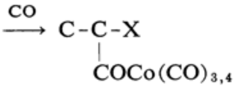
Summary

It has been observed that the reaction of 1-olefin with cobalt hydrocarbonyl is remarkably affected by the reaction conditions and by the structure of olefin.

Some functional groups, such as the ester, n-butoxy and phenyl groups, adjacent to a C=C bond increase the reactivity of the C=C bond; the order of the reactivity is n-butyl vinyl ether, $10^3 >$ styrene, $20 >$ ethyl acrylate, $5 >$ pentene-1. (The numbers indicate the relative reactivities, which have been roughly calculated from the gas absorption curve.)

At a relatively low temperature (below 0°C), the α-carbon atom of the C=C bond of all these olefins except pentene-1 is selectively carbonylated; the reaction scheme may be considered to be as follows; suggesting that cobalt hydrocarbonyl is acting as an acid:

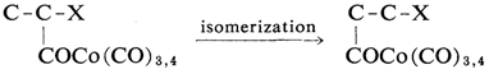




$$C{=}C{-}X \xrightarrow{H^+} C{-}\overset{+}{C}{-}X \xrightarrow{[Co(CO)_4]^-} C{-}\underset{\displaystyle Co(CO)_4}{\underset{|}{C}}{-}C \xrightarrow{CO} C{-}\underset{\displaystyle COCo(CO)_{3,4}}{\underset{|}{C}}{-}X$$

X: $-COOEt$, $-O-n-C_4H_9$ and $-C_6H_5$

However, these acylcobalt carbonyls with the branched structure isomerize to those with the straight one:



$$C{-}\underset{\displaystyle COCo(CO)_{3,4}}{\underset{|}{C}}{-}X \xrightarrow{\text{isomerization}} \underset{\displaystyle COCo(CO)_{3,4}}{\underset{|}{C}}{-}C{-}X$$

A relatively high temperature (25°C) and a nitrogen atmosphere promote this isomerization considerably. The reverse isomerization seems to occur only with difficulty. On the other hand, these olefins mainly give the β-carbon carbonylated product at 25°C, the formation of which seems to result from the two successive reactions, the carbonylation of the α-carbon atom and the isomerization of the corresponding acylcobalt carbonyl. However, the distribution of the products from pentene-1 is not affected by the reaction temperature.

A relatively high pressure of carbon monoxide is advantageous for this reaction. Under a nitrogen atmosphere, some reaction other than the carbonylation seems to occur very rapidly, consuming a large part of the cobalt hydrocarbonyl used; a nitrogen atmosphere has an inhibitory effect on the carbonylation.

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