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Studies of the Organic Reactions of Metal Carbonyls. XVI.[*1] Solvent Effects on the Hydroformylation of Propylene and on the Reaction of Cobalt Hydrocarbonyl with 1-Pentene

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In the reaction of cobalt hydrocarbonyl with 1-pentene at 10°C, solvents have a great effect on the distribution of the products, caproylcobalt carbonyl (I) and α-methylvalerylcobalt carbonyl (II). The I-to-II ratio is 72 : 28 in toluene, in toluene-dioxane (1 : 1 in volume), and in toluene-ethyl acetate. The percentage of II increases to 40—66% in toluene-diethyl ether, -tetrahydrofuran, -acetone, -ethyl alcohol, and -acetonitrile. In the hydroformylation of propylene, the distribution of the products, *n*- and isobutyraldehyde, is also affected by the solvents. In toluene, the *n*-to-iso ratio is about 75 : 25, while in dioxane and in butyl acetate the percentage of the *n*-aldehyde increases to 79—83%. In methyl alcohol, dimethyl acetals of the aldehydes and *n*- and isobutyrate are formed. The *n*-to-iso ratio is the highest in the esters (3.2—8.5), followed by the acetals (0.7—1.6) and the aldehydes (0.4).

Several workers have reported on the influence of the reaction variables on the hydroformylation reaction of olefins, mainly on the composition of the products.[1] In the course of hydroformylation, a cobalt catalyst is considered to react with olefins as cobalt hydrocarbonyl to give alkyl- and acylcobalt carbonyls as the reaction intermediates.[2]

Previous studies of the hydroformylation of ethyl acrylate in this laboratory have shown that the isomerization of alkyl- and acylcobalt carbonyls has a remarkable effect on the isomeric distribution of the products.[3] Some of the present authors have also shown that the isomerization of *n*- and isobutyrylcobalt carbonyl is highly affected by the solvents; in dioxane only the iso isomer is isomerized; in ethyl acetate both isomer are isomerized, in a 7 : 3 *n*-to-iso ratio, and in toluene the isomerization is very slow.[4] On the basis of these results, the solvents can reasonably be considered to have a marked effect on the hydroformylation of olefins, particularly on the isomeric distribution of the products.

In the present study, the effects of different solvents on the hydroformylation of propylene and on the reaction of 1-pentene with cobalt hydrocarbonyl have been examined in detail.

Experimental

Reaction Procedures. Hydroformylation. An autoclave of a 300 m*l* capacity, made of 18-8 nickel-chrome steel and equipped with a magnetic stirrer, was used. Eighty milliliters of the solvent and 8 m*l* of a dicobalt octacarbonyl solution (containing 1.9 mmol of $Co_2(CO)_8$) were put into the autoclave. After the air in the autoclave had been replaced with hydrogen, 20 m*l* of liquid propylene was put into it, and then hydrogen and carbon monoxide were introduced at certain pressures using a compressor. The autoclave was kept at a certain temperature by electrical heating, but the heating was turned off when the gauge pressure ceased to decline.

Reaction with $HCo(CO)_4$. The reaction of 1-pentene with cobalt hydrocarbonyl was carried out

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[*1] Presented in part at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966. Part XV: This Bulletin, Y. Takegami, Y. Watanabe, T. Mitsudo and H. Masada, **42**, 202 (1969).

1) a) V. L. Hughes and I. Kirshenbaum, *Ind. Eng. Chem.*, **49**, 1999 (1957). b) S. Brewis, *J. Chem. Soc.*, **1964**, 5014. c) P. Pino, F. Piacenti and P. P. Neggiam, *Chem. & Ind.*, **1961**, 1400. d) P. Pino, S. Pucci and F. Piacenti, *ibid.*, **1963**, 294. e) M. Johnson, *ibid.*, **1963**, 684; *J. Chem. Soc.*, **1963**, 4859. f) F. Piacenti, P. Pino, R. Lazzaroni and M. Bianchi, *J. Chem. Soc., (C)*, **1966**, 488.

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

3) a) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, This Bulletin, **37**, 1190 (1964). b) Y. Takegami, C. Yokokawa and Y. Watanabe, *ibid.*, **39**, 2430 (1966).

4) a) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, *ibid.*, **38**, 787 (1965). b) Y. Takegami, Y. Watanabe, H. Masada, Y. Okuda, K. Kubo and C. Yokokawa, *ibid.*, **39**, 1495 (1966).

in the way described in a previous paper.[3a)]

Analysis of the Products. The products were identified by a mixed gas chromatography with authentic samples. A column three meters long and 3 mm in diameter, and filled with dilauryl phthalate on cerite, was used. The column temperature was 70 to 80°C, and the flow rate of the carrier gas (hydrogen) was 60 m*l*/min. The infrared absorption spectrum was taken on a Shimadzu Model IR-27 spectrophotometer.

Materials. The propylene, toluene, dioxane, butyl acetate, and other organic compounds were commercial products which had been proved to be sufficiently pure by gas chromatography. As authentic samples, the following commercial compounds were used: *n*- and isobutyraldehyde, *n*- and isobutyl alcohol, methyl caproate, and methyl α-methylvalerate. The dicobalt octacarbonyl solution was prepared according to the method given in a previous paper.[5)]

Results and Discussion

The Reaction of 1-Pentene with Cobalt Hydrocarbonyl. The results are summarized in Table 1. The reaction was carried out at 10°C for 4 hr in a mixed solvent (toluene: other solvent= 1 : 1 in volume). The 1-pentene reacts with cobalt hydrocarbonyl to give caproyl- and α-methylvalerylcobalt carbonyl, which then give the corresponding esters upon treatment with an iodine and alcohol.[2)]

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

Exp. No.	Mixed solvent toluene-other solvent (1:1 in volume)	CO absorbed (mol/mol-$HCo(CO)_4$)	Product** Yield (mol/mol-HCo-$(CO)_4$)	Product** α-Methyl valerate %
1	Toluene	0.53	0.5	28
2	Ethyl acetate	0.53	0.5	28
3	Dioxane	0.55	0.4	28
4	Tetrahydrofuran	0.51	0.5	39
5	Diethyl ether	0.53	0.5	50
6	Acetone	0.50	0.4	50
7	Ethyl alcohol	−0.1***	0.2	45
8	Acetonitrile	−1.2	0.2	66

* Under carbon monoxide at 10°C for 4 hr. 1-Pentene used: 10 mol/mol-$HCo(CO)_4$.

** Ethyl caproate and ethyl α-methylvalerate.

*** Gas was evolved.

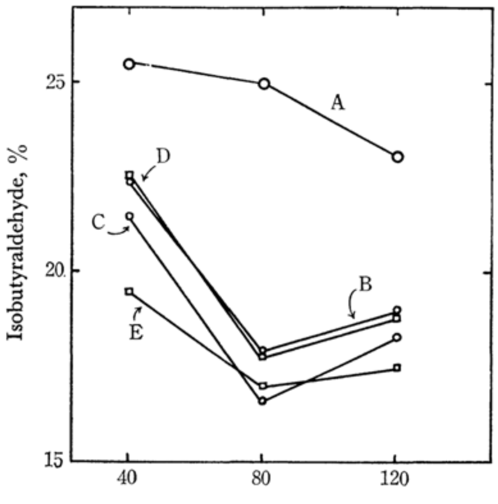

Fig. 1. The percentage of isobutyraldehyde *vs.* the initial partial pressure of carbon monoxide plots for the hydroformylation of propylene (P_{H_2}=80 atm).
A: in toluene at 100°C
B: in dioxane at 100°C
C: in dioxane at 90°C
D: in butyl acetate at 100°C
E: in butyl acetate at 90°C

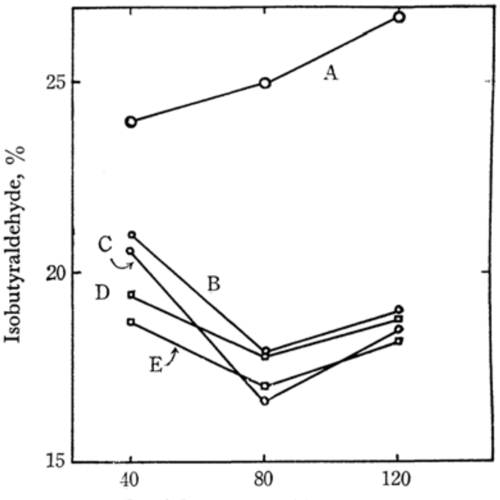

Fig. 2. The percentage of isobutyraldehyde *vs.* the initial partial pressure of hydrogen plots for the hydroformylation of propylene (P_{CO}=80 atm).
A: in toluene at 100°C
B: in dioxane at 100°C
C: in dioxane at 90°C
D: in butyl acetate at 100°C
E: in butyl acetate at 90°C

As Table 1 shows, the solvents have a great effect on the distribution of the two isomers. In toluene the isomer with a straight chain structure predominates (72%); this percentage is almost independent of the solvents in such mixtures as toluene-ethyl acetate and toluene-dioxane (Exps. 1—3). However, in toluene-acetonitrile, α-methylvalerate with a branched chain structure is

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5) Y. Takegami, C. Yokokawa and Y. Watanabe, *ibid.*, **37**, 677 (1964).

dominant. Tetrahydrofuran, acetone, diethyl ether, and ethyl alcohol are also a little more favorable to the formation of α-methylvalerate. In this reaction, the factors determining the distribution of the two isomers are the direction of the addition of cobalt hydrocarbonyl to the double bond of 1-pentene and the isomerization between the C_6-acylcobalt carbonyls. However, this iso-

Table 2. The hydroformylation of propylene in different solvents

2a. in Toiuene

Exp. No.	Reaction conditions				Gas absorption rate**	Distribution of products	
	Temp. (°C)	Partial pressure* H_2 (atm)	CO	Time (min)		Isobutyr-aldehyde (%)	*n*-Butyr-aldehyde
9	100	80	80	30	2.0	25.0	75.0
10	100	80	120	120	0.37	23.1	76.9
11	100	80	40	30	2.3	25.5	74.5
12	100	120	80	30	2.1	26.8	73.2
13	100	40	80	130	0.35	24.0	76.0
14	90	80	80	160	0.25	22.8	77.2
15	110	80	80	20	2.6	26.5	73.5

2b. in Dioxane

Exp. No.	Temp. (°C)	H_2 (atm)	CO	Time (min)	Gas absorption rate**	Isobutyr-aldehyde (%)	*n*-Butyr-aldehyde
16	110	80	80	60	0.75	19.6	80.4
17	100	80	80	100	0.52	17.9	82.1
18	100	40	80	160	0.23	21.0	79.0
19	100	120	80	50	0.87	19.0	81.0
20	100	80	120	180	0.33	19.0	81.0
21	100	80	40	30	0.87	22.4	77.6
22	90	80	80	180	0.22	16.6	83.4
23	90	80	120	250	0.15	18.3	81.7
24	90	40	80	220	0.11	20.6	79.4
25	90	120	80	160	0.27	18.5	81.5
26	90	80	40	140	0.34	21.5	78.5

* Initial pressure.

** Calculated from pressure drops (atm/min).

2c. in Butyl Acetate

Exp. No.	Reaction conditions				Gas absorption rate	Distribution of products	
	Temp. (C°)	Partial pressure H_2 (atm)	CO	Time (min)		Isobutyr-aldehyde (%)	*n*-Butyr-aldehyde
27	100	80	80	90	0.66	18.7	82.2
28	100	80	40	30	1.5	22.5	77.5
29	100	80	120	160	0.37	18.8	81.2
30	100	120	80	50	0.86	18.8	81.2
31	100	40	80	170	0.34	19.4	80.6
32	90	80	80	180	0.31	17.0	83.0
33	90	80	40	90	0.66	19.5	80.5
34	90	80	120	250	0.16	17.5	82.5
35	90	120	80	140	0.39	18.3	81.7
36	90	40	80	250	0.16	18.7	81.3

2d. in Acetone and Diethyl Ether

Exp. No.	Temp. (C°)	H_2 (atm)	CO	Time (min)	Gas absorption rate	Isobutyr-aldehyde (%)	*n*-Butyr-aldehyde
37*	100	80	80	30	2.0	34.3	65.7
38*	110	80	80	20	2.5	35.4	64.6
39**	100	80	80	15	5.0	40.0	60.0

* In acetone.

** In diethyl ether.

Table 3. The hydroformylation of propylene in methyl alcohol

Exp. No.	Reaction conditions				Distribution of products**						Percentage*** of iso-isomers
	Temp. (C°)	Partial pressure* (atm)		Time (min)	Aldehydes		Acetals		Esters		
		H_2	CO		%	n/iso	%	n/iso	%	n/iso	
40	100	80	80	220	5.3	0.36	80.4	1.6	13.3	7.5	36.2
41	110	80	40	150	7.7	0.40	73.5	1.2	18.8	6.6	41.4
42	110	80	80	130	8.0	0.36	79.3	1.2	12.7	6.5	42.8
43	120	80	20	100	3.3	0.44	67.9	1.0	28.8	5.9	40.5
44	120	80	10	110	0	—	43.8	0.72	56.2	5.0	34.9
45	130	80	10	50	0	—	42.7	0.94	57.3	5.2	31.3
46	130	40	10	40	0	—	66.2	0.86	33.8	3.2	43.5
47	130	120	10	45	0	—	43.4	0.94	56.6	5.4	31.0
48	130	80	5	90	0	—	30.0	1.0	70.0	5.6	26.5
49	150	80	10	30	0	—	46.6	0.94	53.4	5.1	32.5

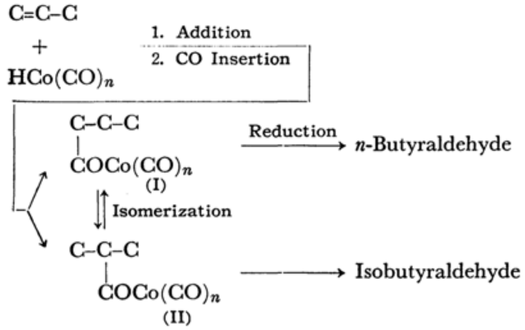
* Initial pressure.

** n- and isobutyraldehyde, n- and isobutyraldehyde - dimethyl acetal, and methyl n- and isobutyrate.

*** (iso-isomers/products) × 100.

merization occurs with much difficulty under the conditions employed.[4)] Thus, the results obtained here show that the direction of the addition of cobalt hydrocarbonyl to the olefin is highly affected by the solvents.

Hydroformylation of Propylene. The effects of variables, especially solvents, on the distribution of the products were also examined. The results are summarized in Tables 2 and 3 and in Figs. 1 and 2. Under the conditions employed, butyraldehydes were obtained in 93—97% yields, while butyl alcohols were also produced as minor products in 3—7% yields. The reaction is considered to proceed as follows:



In Toluene. The percentage of n-butyraldehyde changes over the 73—77% range at 100°C. In the light of the fact that n- and isobutyrylcobalt carbonyl isomerize with much difficulty in toluene,[4a)] the distribution of the two aldehydes may be determined mainly by the direction of the addition of cobalt hydrocarbonyl.

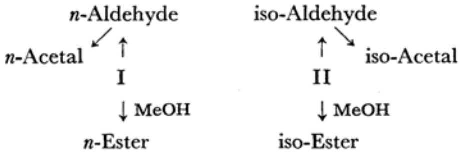
In Dioxane. Under any conditions, the percentage of n-butyraldehyde grows larger in dioxane (79—82% at 100°C) than in toluene (73—77% at 100°C). Dioxane has a great promoting effect on the isomerization of isobutyrylcobalt carbonyl to the n-isomer at room temperature.[4a)] Under hydroformylation conditions in dioxane, such an isomerization can reasonably be considered to occur, thus affecting the distribution of the products. This consideration seems to be supported by the fact that dioxane has no effect on the addition of cobalt hydrocarbonyl to 1-pentene, as has been described above.

In Butyl Acetate. As Table 2b shows, butyl acetate is also a more favorable solvent for the formation of n-butyraldehyde than toluene. Acetate also promotes the isomerization of the isobutyrylcobalt carbonyl[4a)] and has no effect on the addition of cobalt hydrocarbonyl to 1-pentene. Thus, it is possible to interpret the effect of butyl acetate by employing arguments similar to those presented for dioxane.

In Acetone and Diethyl Ether. The percentage of isobutyraldehyde increases to 35 and 40% in acetone and in diethyl ether respectively. This tendency is consistent with the fact that these are taken to be more favorable solvents for the formation of a compound with a branched chain structure in the reaction of cobalt hydrocarbonyl with 1-pentene. Under hydroformylation conditions in these solvents, isobutyrylcobalt carbonyl may be formed more readily by the addition of cobalt hydrocarbonyl to propylene.

Effects of Partial Pressures of Carbon Monoxide and Hydrogen. As Figs. 1 and 2 show, at 100°C in toluene the percentage of isobutyraldehyde decreases with an increase in the partial pressures of carbon monoxide, but increases with an increase in the partial pressures of hydrogen. In dioxane or butyl acetate, however, the percentage of the iso-aldehyde has a minimum at 80 atm of the initial partial pressures of both carbon monoxide and hydrogen. This phenomenon seems to be partly due to the tendency of butyrylcobalt carbonyls to isomerize in these polar solvents. The distribution of the products is considered to depend in part on two competitive reactions, the reduction and the isomerization of butyrylcobalt carbonyls. Larger partial pressures of carbon monoxide have an inhibitory effect on these reactions,[2,4] but larger partial pressures of hydrogen seem to promote the reduction. The reason why the minimum is observed is, however, not completely clear.

In Methyl Alcohol. As Table 3 shows, in methyl alcohol *n*- and isobutyraldehyde (0—8%), *n*- and isobutyraldehyde-dimethyl acetal (30—80%), and methyl *n*- and isobutyrate (13—70%) are obtained. Under any conditions employed, the aldehydes are readily converted to the corresponding acetals. At low pressures of hydrogen the esters predominate, but at high pressures of hydrogen the acetals predominate. These compounds may be formed according to the following reaction scheme:



The *n*-to-iso ratio is the highest in the esters (3.3—8.5), followed by the acetals (0.7—1.6) and the aldehyde (0.4). In the light of this fact, the esterification of *n*-butyrylcobalt carbonyl (I) to *n*-butyrate may be said to occur more readily than that of the iso-isomer (II), but the reduction rate of the *n*-isomer is alsmost comparable with that of the iso-isomer. In the stage of the addition of cobalt hydrocarbonyl, equimolar amounts of the *n*- and iso-isomer seem to be formed in methyl alcohol.[*2] Thus, under the conditions favorable for the formation of the esters, the fast esterification of I seems to promote the isomerization of II to I, and then the *n*-to-iso ratio of the products increases greatly (Exp. 48).

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[*2] 1-Pentene gives *n*- and iso-C_6-acylcobalt carbonyls in a 1-to-1 ratio in ethyl alcohol.