*Studies of the Organic Reactions of Metal Carbonyl. III. The Hydroformylation of Olefin Oxides**

By Chikao YOKOKAWA, Yoshihisa WATANABE and Yoshinobu TAKEGAMI

(Received September 19, 1963)

Recent papers(1,2) have reported that an olefin oxide reacts with cobalt hydrocarbonyl and carbon monoxide to give acylcobalt carbonyl-type compounds, which are considered to be intermediates of the hydroformylation reactions.(3,4)

The reaction of ethylene oxide with water gas was carried out under the conditions of the ordinary Oxo-type reaction by Hamada, Baba and Hagihara,(5) who concluded that the hydroformylation of ethylene oxide did not take place. Lenel(6) concluded that olefin oxides, except ethylene oxide, undergoes the hydroformylation reaction, but he did not mention about the composition of the products. On the other hand, Seon and Leleu(7) obtained 2-hydroxyethyl hydracrylate from ethylene oxide by reaction with water and carbon monoxide in the presence of dicobalt octacarbonyl. Eisenmann, Yamartino and Howard(8) reported that the reaction product of propylene oxide with carbon monoxide and methanol in the presence of dicobalt octacarbonyl was methyl β-hydroxybutyrate.

Thus, the possibility of the hydroformylation of olefin oxide has been suggested, but no definite characteristics of this reaction are known. In this paper it will clearly be demonstrated that propylene oxide undergoes the hydroformylation reaction at a relatively low temperature (80°C) to give β-hydroxy-*n*-butyraldehyde as the major product.

Experimental

Reaction Procedures.—An autoclave of a 300 ml. capacity, made of 18—8 nickel-chrom-iron steel and equipped with a magnetic stirrer, was used. Ninety milliliters of toluene, 10 ml. of dicobalt octacarbonyl solution in toluene (containing 0.22 to 0.24 g. of cobalt by calculation from the content of the carbonyl), and 10 g. of olefin oxide were put into the autoclave. After replacing the air in the autoclave with hydrogen, hydrogen and carbon monoxide were introduced to 150 to 160 atm. using a compressor. The autoclave was kept at the desired temperature by electrical heating, but the heating was turned off when the gauge pressure ceased to decline.

Preparation and Standardization of the Dicobalt Octacarbonyl Solution in Toluene.—Ten grams of cobalt carbonate and 100 ml. of toluene were placed in the autoclave, and water gas was introduced to 160 atm. The autoclave was heated at about 150°C for 4 hr. The dicobalt octacarbonyl solution in toluene was then transferred into a flask by decantation and stored therein under a carbon monoxide atmosphere. An aliquot portion (10 ml.) of this solution was put into a gasometric apparatus by the use of a syringe, and the excess amount of iodine in toluene was added. The cobalt content of this solution was calculated from the amount of carbon monoxide evolved, with the assumption that all of the cobalt exsisted as dicobalt octacarbonyl or cobalt hydrocarbonyl.

Analysis of the Products.—In almost every case, an oily or resinous material which was insoluble in toluene was formed. After the separation of this material by the decantation of the toluene phase, the products in the toluene solution were identified and determined by gas chromatography. The products with boiling points lower than that of toluene were determined from the crude toluene solution, and other products, from the concentrated solution (the crude solution was concentrated under the reduced pressure of about 30 mmHg). The identification of the products was made by 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 50 to 80°C for the analysis of the low-boiling-point products and 130°C for the high-boiling-point products. The rate of flow of the carrier gas (hydrogen) was 60 ml. per min.

The infrared adsorption spectrum was obtained in the toluene solution by the use of a Shimadzu Model IR—27 spectrophotometer.

Materials Used.—Ethylene oxide, propylene oxide and toluene were commercial products which were proved to be sufficiently pure by gas chromatography. As authentic samples, the following commercial chemicals were used: acetaldehyde, acrolein,

---

* Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

1) R. F. Heck *J. Am. Chem. Soc.*, **85**, 1460 (1963).

2) Y. Takegami, C. Yokokawa, Y. Watanabe and H. Masada, This Bulletin, **37**, 672 (1964).

3) L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, **80**. 4428 (1958).

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

5) K. Hamada, K. Baba and N. Hagihara, *Memoirs Inst. Sci. Ind. Research, Osaka Univ.*, **14**, 207 (1957).

6) P. O. Lenel, *Proc. Chem. Soc.*, **1958**, 50.

7) M. Seon and J. Leleu, U. S. Pat. 2782226, Feb. 19 (1957).

8) J. L. Eisenmann, R. L. Yamartino and J. F. Howard Jr., *J. Org. Chem.*, **26**, 2102 (1961).

TABLE I. HYDROFORMYLATION OF PROPYLENE OXIDE

	No.	1	2*1	3	4	5	6*2	7*3
	Reaction temp., °C	115～120	105～110	90～95	85～90	80～85	110～115	110～115
	H_2/CO	1.0	1.4	1.0	1.0	1.0	2.0	2.0
	Reaction time, hr.	2.5	1.0	3.0	3.0	2.0	0.7	1.0
Yield of products (mol. per 100 mol. of propylene oxide used)	Acetone	51	21	6.4	15	4.6	24	6.4
	Isobutyraldehyde	5.1	4.9	1.2	0.5	trace	3.4	nil
	Metacrolein	trace	0.8	0.8	trace	trace	trace	2.1
	n-Butyraldehyde	16.4	8.5	1.4	0.7	0.6	9.3	trace
	Isobutyl alcohol	1.5	0.6	trace	nil	nil	0.2	nil
	Crotonaldehyde	trace	1.2	5.4	0.9	1.2	3.8	15
	n-Butyl alcohol	2.3	trace	trace	nil	nil	trace	nil
	β-hydroxy-isobutyraldehyde	trace	7.5	nil	trace	trace	nil	trace
	β-hydroxy-*n*-butyraldehyde	3.3	24	56	32	42	18	20
	Character of polymer	oily	oily	oily	oily	oily	resinous	resinous

*1 The compounds with the relative retention time of 313 and 450 were formed in 0.6 and 1.7 mol. per 100 mol. of propylene oxide, respectively.

*2 Two mol. of pyridine were added per mol. of dicobalt octacarbonyl.

*3 Four mol. of pyridine were added per mol. of dicobalt octacarbonyl. About 20 percent of propylene oxide were recovered unreacted.

metacrolein, acetone, isobutyraldehyde, *n*-butyraldehyde, isobutyl alcohol, *n*-butyl alcohol, crotonaldehyde and β-hydroxy-*n*-butyraldehyde (aldol).

Results

The Interpretation of a Typical Gas Chromatogram.—In order to facilitate further considerations, the gas chromatogram for the products obtained from propylene oxide by the reaction at 115 to 120°C (Exp. 1) will be discussed in detail. This chromatogram illustrates 20 peaks, 10 of which were identified by mixed chromatography with authentic samples. These compounds were propylene oxide (9.9), acetone (12.4), isobutyraldehyde (19.1), metacrolein (21.5), *n*-butyraldehyde (25.3), isobutyl alcohol (45.4), crotonaldehyde (53.0), *n*-butyl alcohol (72.6), toluene (100) and β-hydroxy-*n*-butyraldehyde* (194). (The numbers in ( ) denotes the relative retention time.) The peak with the relative retention time of 163 was believed to correspond with that for β-hydroxyisobutyraldehyde, though an authentic sample was not available, because metacrolein** and isobutyraldehyde, which are considered to have been derived from β-hydroxy-isobutyraldehyde, existed in the same sample and because the retention time of this product is a little smaller than that of β-hydroxy-*n*-butyraldehyde. There were 9 peaks of by-products, whose retention times were larger than that of β-hydroxy-*n*-butyraldehyde, in this gas chromatogram. They were not identified, but all of them diminished to negligible amounts when the reactions were carried out at temperatures below 100°C.

The Hydroformylation of Propylene Oxide.—The hydroformylation reaction of propylene oxide seems to take place at temperatures above 80°C; at any rate, the gauge pressure begins to decrease at this temperature.

The composition of the reaction products is listed in Table I, in which the yield of products is given in the number of mol. per 100 mol. of propylene oxide used. These values were obtained by calculations on the basis of the area of each peak in a gas chromatogram after the usual calibration using authentic samples. In the calculation of β-hydroxy-*n*-butyraldehyde, the amount of crotonaldehyde which is considered to be formed from the former in the course of the gas chromatographic analysis was accounted as before.

It is evident that the major product of the reaction at the temperature of the ordinary hydroformylation reaction of olefins, i. e., 110 to 120°C, is acetone, and so it has been concluded that the isomerization reaction predominates in this reaction condition. The hydroformylation reaction also takes place, giving β-hydroxybutyraldehydes, but these products are converted into isobutyraldehyde, metacrolein, *n*-butyraldehyde, isobutyl alcohol, crotonaldehyde and *n*-butyl alcohol by succeeding dehydration and hydrogenation reactions.

---

* β-Hydroxy-*n*-butyraldehyde is the major product of this reaction. This compound could be isolated by fractional distillation under reduced pressure in a sufficiently pure state. The infrared spectrum of this product showed strong absorptions at 1720 cm^{-1} and 3350 cm^{-1}. 2, 4-Dinitrophenyl hydrazone was formed, but this hydrazone seemed impure because it is known that β-hydroxy-*n*-butyraldehyde is easily dehydrated to form crotonaldehyde under the conditions of hydrazone formation. It was concluded that this product was β-hydroxy-*n*-butyraldehyde on the basis of the facts mentioned above and because this product showed a peak which corresponded to that of crotonaldehyde when gas chromatographed at 130°C.

** Metacrolein was identified in the crude solution. In the concentrated solution it was not observed but after the solution had been refluxed for 1hr. at the boiling point of toluene, it appeared clearly.

TABLE II. HYDROFORMYLATION OF ETHYLENE OXIDE

No.	Reaction temp. °C	H_2/CO	Reaction time hr.	Yield of products (mol. per 100 mol. of ethylene oxide used)		amount of gas absorbed (mol./mol. of ethylene oxide)
				Acetaldehyde	Acrolein	
8	90~100	1.0	0.8	16	2.8	1.3
9	85~ 86	1.0	1.3	28	1.0	1.2
10	80~ 82	1.5	3.0	26	0.9	0.8
11*	80~ 85	1.7	2.0	30	1.8	0.9
12**	85~ 90	4.0	2.0	8	0.9	—

* Two mol. of pyridine were added per mol. of cobalt.

** Four mol. of pyridine were added per mol. of cobalt.

Moreover, various kinds of high-boiling-point products are formed.

By lowering the reaction temperature for about 10°C (Exp. 2), the yields of the hydroformylation products, i. e., β-hydroxy-*n*-butyraldehyde and β-hydroxy-isobutyraldehyde, increased, and those of the by-products decreased, but still more than 20% of the propylene oxide charged were converted into acetone and various kinds of compounds were formed.

At the reaction temperature below 95°C, β-hydroxy-*n*-butyraldehyde is formed as the major product, as Exps. 3, 4 and 5 show, and so it has been concluded that the hydroformylation of propylene oxide proceeds relatively selectively under these controlled conditions.

The addition of pyridine has evident effects on the character of this reaction. As Exps. 6 and 7 show, the addition of this compound seems to prevent not only the isomerization but also the hydroformylation reaction; the amount of acetone decreases, and relatively large amounts of unreacted propylene oxide and resinous material are recovered.

The isomerization of propylene oxide to acetone in the presence of dicobalt octacarbonyl was studied by Eisenmann[9] in several kinds of solvents. He concluded that this isomerization takes place during a reversible exchange between the solvent molecule and propylene oxides serving as a coördinating molecule to cobalt, and that pyridine retards this isomerization reaction because of its strong coördinating effect. It is believed that the present object is to control the two competitive reactions, i. e., hydroformylation and isomerization, but it seems impossible to attain this purpose by the addition of pyridine.

The Hydroformylation of Ethylene Oxide.—The results of the reaction of ethylene oxide are summarized in Table II. Ethylene oxide produces acetaldehyde and a viscous, oily material as the major products, plus a small amount of acrolein. Thus, ethylene oxide seems to undergo isomerization and polymerization under the conditions which are effective for the hydroformylation of propylene oxide. On the other hand, an appreciable amount of gas is absorbed at temperatures above 80°C, as is indicated by the decrease in the gauge pressure, and acrolein is identified as a minor product. This evidence seems to indicate that the hydroformylation has taken to an appreciable extent. It is reasonably considered that the hydroformylation product of ethylene oxide, β-hydroxypropionaldehyde, would be formed, that this compound would be converted into acrolein by succesive dehydration reaction, and that the latter would polymerize to form the oily or resinous product.

Summary

The hydroformylation reactions of ethylene oxide and propylene oxide have been carried out; the character of this type of reaction may be summarized as follows:

1) Propylene oxide reacts with water gas, in the presence of dicobalt octacarbonyl serving as a catalyst, to give β-hydroxy-*n*-butyraldehyde as the major product, but it is important to keep the reaction temperature between 80 to 100°C in order to hold the high selectivity of this reaction.

2) At temperatures below 80°C, the reaction does not take place; on the other hand, at temperatures above 100°C, the isomerization of propylene oxide to acetone predominates, and the other side-reactions, such as the dehydration of the hydroformylation products, hydrogenation, condensation and polymerization, take place simultaneously.

3) Ethylene oxide seems to undergo hydroformylation under the same conditions as those used for the propylene oxide, but only a small amount of acrolein is obtained as the hydroformylation product. The expected product, i. e., β-hydroxypropionaldehyde, is formed, but this compound is easily converted into acrolein and the latter seems to polymerize to give a large amount of a resinous or oily material.

Department of Fuel Chemistry
Faculty of Engineering
Kyoto University
Sakyo-hu, Kyoto

---

[9] J. L. Eisenmann, *J. Org. Chem.*, 27, 2706 (1962).