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Studies of the Organic Reactions of Metal Carbonyls. XI.*1 The Reaction of Potassium Iron Carbonylates with Olefin Oxides

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The reaction between potassium iron carbonylates ($KHFe(CO)_4$, $K_2Fe(CO)_4$, $K_2Fe_2(CO)_8$, and $K_2Fe_3(CO)_{11}$) and olefin oxides has been studied. Propylene oxide reacts readily with these carbonylates and carbon monoxide at atmospheric pressure at room temperature. As the reaction product, β-hydroxy-*n*-butyrate is obtained by the treatment of the reaction mixture with an iodine and hydrogen chloride solution in alcohol, indicating that a complex with a type of β-hydroxy-*n*-butyryliron carbonyl is formed in the reaction. Ethylene oxide also reacts with the carbonylate to give β-hydroxypropionate.

The reaction between cobalt hydrocarbonyl and olefin oxides has been reported on several times in recent years,[1-3] as the reaction product β-hydroxyacylcobalt carbonyl is mainly formed.

It has previously been shown that iron carbonyls give several types of iron hydrocarbonyl, such as $H_2Fe(CO)_4$, $H_2Fe_2(CO)_8$, $H_2Fe_3(CO)_{11}$, and $H_2Fe_4(CO)_{13}$ and their salts.[4] The present paper will deal with the reaction between potassium salts of the iron hydrocarbonyls and olefin oxides.

Experimental

The Preparation of Potassium Iron Carbonylates. a) $KHFe(CO)_4$ and $K_2Fe(CO)_4$. These salts solutions in alcohol were prepared by the method described by Kurumholz and Stettiner.[5] A 100 m*l* four-necked flask, fitted with a 50 m*l* dropping funnel, a stirrer, and a rubber stopple, was connected with a gas buret and then flushed with carbon monoxide or nitrogen. By the use of a syringe, 1.5 m*l* of iron pentacarbonyl (11 mmol), 33 m*l* of a 1 N potassium hydroxide solution in alcohol, and 17 m*l* of alcohol (or 44 m*l* of a 1 N potassium hydroxide solution and 6 m*l* of alcohol) were placed in the flask and then stirred vigorously for about two hours at room temperature to give a brown solution with a white precipitation (potassium carbonate).

b) $K_2Fe_2(CO)_8$ and $K_2Fe_3(CO)_{11}$. These salts solutions in alcohol were prepared by the oxidation of

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[*1] Part X: Y. Takegami, C. Yokokawa and Y. Watanabe, This Bulletin, **39**, 2430 (1966). Presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

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. Roos, R. W. Goetz and M. Orchin, *J. Org. Chem.*, **30**, 3023 (1965).

4) *Cf.* M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

5) P. Krumholz and H. M. A. Stettiner, *J. Am. Chem. Soc.*, **71**, 3035 (1949).

a KHFe $(CO)_4$ solution in alcohol with nitromethane and iodine.[6]

c) $KCo(CO)_4$. This salt solution in alcohol and toluene was prepared according to the method described in a previous paper[7]. 50 m*l* of a 0.09 M $KCo(CO)_4$ solution was used in each run.

The Reaction Procedures. To the solution of potassium iron or cobalt carbonylate obtained as described above, 4 m*l* of an olefin oxide (propylene oxide or ethylene oxide) was added; the mixture was then agitated vigorously from for 1 to 30 hr at 0 to 25°C, under one atmosphere of carbon monoxide. After a certain reaction time, 9 to 11 m*l* of a 4 N hydrogen chloride solution in alcohol and 40 m*l* of a saturated solution of iodine in alcohol were stirred into the reaction mixture; the agitation was then continued until gas ceased to evolve. By this treatment, acyliron carbonyls seem to be converted into the corresponding esters of carboxylic acids, as has been observed in the case of acylcobalt carbonyls.[8] The solution was concentrated after the separation of a precipitated material, and then submitted to analysis.

The Analytical Procedures. The reaction products were analyzed by gas chromatography and by means of their infrared spectra, which had been taken on a Shimadzu model IR-27 infracord spectrophotometer. The details have been given in a previous paper.[2]

Materials. The ethylene oxide, the propylene oxide, the iron pentacarbonyl, and the other compounds employed in this study were all commercial products.

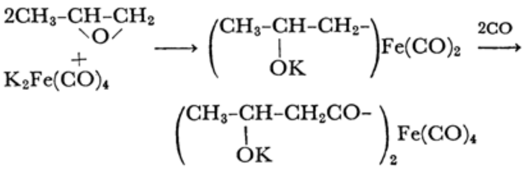
Results and Discussion

The Reaction of Potassium Iron and Cobalt Carbonylates with Propylene Oxide. The results of the reactions are summarized in Table 1. All of the reactions were carried out under one atmosphere of carbon monoxide.

As has been shown by Exps. 1 and 2, $KHFe(CO)_4$ readily reacts with propylene oxide and carbon monoxide; the gas absorption amounts to more than 2 mol,[*2] while the reaction solution turns from light brown to red brown. The treatment of the reaction mixture with an iodine and hydrogen chloride solution in alcohol gives β-hydroxy-*n*-butyrate as the reaction product, much as in the case of cobalt hydrocarbonyl.[2]

$K_2Fe(CO)_4$ also reacts with propylene oxide to give the same product as $KHFe(CO)_4$, though the yield of the ester is bad (Exps. 3—6). In this case, the gas absorption occurs more rapidly than in the case of $KHFe(CO)_4$.

As Exp. 13 shows, potassium cobalt carbonylate reacts with propylene oxide to give the ester in a good yield; this carbonylate seems to act like cobalt hydrocarbonyl to give the potassium alcoholate β-hydroxy-*n*-butyrylcobalt carbonyl. From these facts, the reaction of the iron carbonylates may be assumed to proceed as follows:



$$2CH_3\text{-}CH\text{-}CH_2(\text{-}O\text{-}) + K_2Fe(CO)_4 \longrightarrow \left(\begin{array}{c}CH_3\text{-}CH\text{-}CH_2\text{-}\\ |\\ OK\end{array}\right)Fe(CO)_2 \xrightarrow{2CO} \left(\begin{array}{c}CH_3\text{-}CH\text{-}CH_2CO\text{-}\\ |\\ OK\end{array}\right)_2 Fe(CO)_4$$

This reaction scheme, however, can not explain the fact that more than 2 moles of gas were absorbed (Exps. 1, 2, 5 and 6). The bad yield of the ester

TABLE 1. THE REACTION OF POTASSIUM IRON CARBONYLATES WITH PROPYLENE OXIDE

Exp. No.	Iron carbonylate	Reaction conditions[*1]		CO absorbed	Ester[*2]
		Temp., °C	Time, hr	(mol/g atom Fe[*3])	
1	$KHFe(CO)_4$	15	18	2.1	0.35
2	$KHFe(CO)_4$	15	18	2.2	0.30
3	$K_2Fe(CO)_4$	15	1	1.1	0.15
4	$K_2Fe(CO)_4$	15	7	2.0	0.38
5	$K_2Fe(CO)_4$	15	29	3.1	0.20
6	$K_2Fe(CO)_4$	15	29	3.1	0.20
7	$K_2Fe_2(CO)_8$	10	5	0.92	0.40
8	$K_2Fe_2(CO)_8$	10	4	0.83	0.38
9	$K_2Fe_2(CO)_8$	0	6	0.70	0.20
10	$K_2Fe_2(CO)_8$	25	4	1.0	0.15
11	$K_2Fe_3(CO)_{11}$	10	6	0.58	0.10
12	$K_2Fe_3(CO)_{11}$	25	5	1.1	0.20
13	$KCo(CO)_4$	10	8	1.0	0.85[*4]

[*1] Under one atmosphere of carbon monoxide.

[*2] Ethyl β-hydroxy-*n*-butyrate.

[*3] Fe exists as iron carbonylates.

[*4] Mole per mole of potassium cobalt carbonylate.

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6) J. R. Case and M. C. Whiting, *J. Chem. Soc.*, **1960**, 4632.

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

8) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **84**, 2499 (1962).

[*2] Mole means mole per g atom of Fe, which exists as iron carbonylate.

TABLE 2. THE REACTION OF POTASSIUM IRON CARBONYLATES WITH ETHYLENE OXIDE AND *n*-PROPYL IODIDE

Exp. No.	Substance	Reaction conditions*1		CO absorbed	Products	
		Temp. °C	Time hr	mol/mol $Fe(CO)_4$	Ester	Aldehyde
14	Ethylene oxide $KHFe(CO)_4$	0	10	0.9	0.30*2	
15	Ethylene oxide $KHFe(CO)_4$	0	18	1.7	0.15	—
16	*n*-Propyl iodide $KHFe(CO)_4$	30	6	0.85	0.18*3	0.50*4
17	*n*-Propyl iodide $K_2Fe(CO)_4$	20	8	1.6	0.53	0.22

*1 Under one atmosphere of carbon monoxide.
*2 Ethyl β-hydroxypropionate.
*3 Ethyl *n*-butyrate.
*4 *n*-Butyraldehyde.

seems to be partly due to the instability of alkyl- and acyliron carbonyls.

$K_2Fe_2(CO)_8$ reacts with propylene oxide (Exps. 7—10); when 1 mol of gas was absorbed, the gas absorption ceased. The yield of the ester is relatively good on the basis of the amount of the gas absorbed. This suggests that acyliron carbonyl with a dinuclear structure such as $(acyl)_2Fe_2(CO)_8$ is formed and is more stable than the mononuclear acyliron carbonyl.

$K_2Fe_3(CO)_{11}$ also reacts similarly with propylene oxide (Exps. 11 and 12).

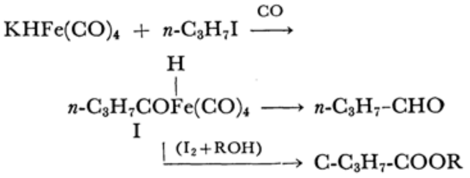
The gas absorption rate is the highest in $K_2Fe(CO)_4$, followed by $KHFe(CO)_4$, $K_2Fe_2(CO)_8$, and $K_2Fe_3(CO)_{11}$ in that order.

The Reaction of Potassium Iron Carbonylate with Ethylene Oxide or *n*-Propyl Iodide. The results are summarized in Table 2.

Ethylene oxide reacts with $KHFe(CO)_4$ to give β-hydroxypropionate, but the yield of the ester is bad, much as in the case of propylene oxide (Exps. 14 and 15).

In connection with the fact that a larger gas absorption, more than 2 mol of gas per mole of mononuclear iron carbonylates, was observed in the reaction of propylene oxide, the reaction between *n*-propyl iodide and the mononuclear iron carbonylates was carried out.

As has been shown by Exp. 16 *n*-propyl iodide also reacts with $KHFe(CO)_4$ and carbon monoxide; even at 30°C, though, less than 1 mol of the gas was absorbed, and then the gas absorption ceased. *n*-Butyraldehyde, as the major product, and *n*-butyrate, as the minor product, were obtained in good yields, indicating that the reaction proceeds as follows:



$$KHFe(CO)_4 + n\text{-}C_3H_7I \xrightarrow{CO} n\text{-}C_3H_7CO\overset{H}{\underset{I}{Fe}}(CO)_4 \longrightarrow n\text{-}C_3H_7\text{-}CHO$$
$$\xrightarrow{(I_2+ROH)} C\text{-}C_3H_7\text{-}COOR$$

That is, the *n*-butyryliron hydrocarbonyl (1), which is formed at the first step of the reaction, is reduced with iron hydrocarbonyls, such as $HFe(CO)_4^-$ and acyl $FeH(CO)_4$, to give the aldehyde.

As Exp. 17 shows, the iodide reacts readily with $K_2Fe(CO)_4$. The gas absorption amounted to less than 2 mol, and *n*-butyrate was obtained as the major product in a good yields, suggesting that di-(*n*-butyryl)iron carbonyl is formed in the course of the reaction and that then this carbonyl may be relatively well converted into the corresponding ester of acid by treatment with iodine and alcohol. In light of these facts, the larger gas absorption observed in the case of the olefin oxide may be attributed to some side reaction, not determined in the present investigation, other than the carbonylation mentioned above.