BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 202—205 (1969)

Studies of the Organic Reactions of Metal Carbonyls. XV.[*1] The Reaction of Potassium Iron Carbonylates with Various Kinds of Olefin Oxides

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(Received May 27, 1968)

The reaction between potassium iron carbonylates ($KHFe(CO)_4$, $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$) and different olefin oxides has been studied. 1,2-Olefin oxides generally react with these carbonylates and carbon monoxide under an atmospheric pressure and at 30°C. This reduction gives the corresponding terminal olefins and the internal olefins which are formed from the 1-olefins by isomerization. Internal olefin oxides do not react with the carbonylates under the reaction conditions employed. The reduction reaction seems to compete with the carbonylation reaction. A mechanism for the reduction reaction is suggested.

Ethylene oxide and propylene oxide react with potassium iron carbonylates ($KHFe(CO)_4$, $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$) and carbon monoxide;[1)] carbon monoxide is readily absorbed, and carbonylated products, β-hydroxy esters, are obtained by the treatment of the reaction mixture with an alcoholic solution of iodine. The yield of the esters, however, is very low. Previously it has been shown that styrene oxide also reacts with these iron carbonylates and carbon monoxide to give styrene, α- and β-phenylethyl alcohol, and carbon dioxide, but no carbonylated compound.[2)] These facts show that the structure of olefin oxides has a relatively large effect on this reaction. The present work will describe and interpret the reaction, mainly the reduction, o various olefin oxides with the iron carbonylates.

Experimental

The Preparation of Potassium Iron Carbonylates, $KHFe(CO)_4$, $K_2Fe(CO)_4$, and $K_2Fe_2(CO)_8$. The alcoholic solutions of these salts were prepared under a carbon monoxide atmosphere according to the method described in a previous paper:[1)] a 50-m*l* portion of a 0.22 M $KHFe(CO)_4$, $K_2Fe(CO)_4$, or 0.11 M $K_2Fe_2(CO)_8$ solution was used in each run.

When $K_2Fe(CO)_4$ is prepared, two equivalent moles of water are formed:[3)]

$$Fe(CO)_5 + 4KOH \xrightarrow{\text{in alcohol}} K_2Fe(CO)_4 + K_2CO_3 + 2H_2O \qquad (a)$$

Therefore, when a dry solution of $K_2Fe(CO)_4$ was required, the solvent of the $K_2Fe(CO)_4$ solution was distilled off once under a vacuum and then 50 m*l* of a new dry solvent was added.

Materials. The ethylene oxide was obtained from ethylene chlorohydrin and alkali. The propylene oxide,

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[*1] Presented at the 21st Annual Meeting of the Chemical Society, Osaka, April, 1968. Part XIV: Y. Takegami, Y. Watanabe, I. Kanaya, T. Mitsudo, T. Okajima, N. Morishita and H. Masada, This Bulletin, **41**, 2990 (1968).

[1)] Y. Takegami, Y. Watanabe, H. Masada and I. Kanaya, This Bulletin, **40**, 1456 (1967).

[2)] Y. Takegami, Y. Watanabe, T. Mitsudo, I. Kanaya and H. Masada, *ibid.*, **41**, 158 (1968).

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

the butylene oxides, the iron pentacarbonyl, and the other compounds employed in this study were commercial products.

Reaction Procedures. To the solution of potassium iron carbonylate described above, 2.6 g of propylene oxide was added; the mixture was then agitated vigorously at 30°C under an atmospheric pressure of carbon monoxide or nitrogen. The amount of carbon monoxide absorbed was determined volumetrically. After a certain reaction time, the reaction flask was connected to a cold trap immersed in liquid nitrogen, which was joined with a vaccum pump. The gases were collected in the trap at 30 mmHg for five minutes. The trap was allowed to warm to room temperature and then heated to 80°C, and the gas evolved was analyzed. The reaction mixture was analyzed at the same time. The reactions of other olefin oxides with $K_2Fe(CO)_4$ were carried out similarly.

Analytical Procedure. 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 infrared spectrometer.

Results

The Reaction of $K_2Fe(CO)_4$ and $KHFe(CO)_4$ with Ethylene Oxide. The results of the reaction are summarized in Table 1. The reactions were carried out at 5°C for 5 hr. Ethylene oxide readily reacts with $K_2Fe(CO)_4$ and carbon monoxide, while the reaction solution turns from light yellow to dark red brown. Ethylene is obtained as the reaction product in the amount of 0.5 mol[*2] (Exp. 1). As a previous paper has shown,[1)] 0.2 mol of a carbonylated product, β-hydroxypropionate, is obtained when the reaction mixture is treated with iodine and alcohol. The reaction also proceeds under nitrogen, but the yield of ethylene is low, 0.2 mol (Exp. 2). $KHFe(CO)_4$ is less reactive than $K_2Fe(CO)_4$ (Exp. 3).

TABLE 1. THE REACTION OF ETHYLENE OXIDE WITH POTASSIUM IRON CARBONYLATES[*1]

Exp. No.	Iron carbonylate	Atmosphere	CO absorbed	Yield of ethylene
			mol/mol-$Fe(CO)_4^{2-}$	
1	$K_2Fe(CO)_4$	CO	1.2	0.50[*2]
2	$K_2Fe(CO)_4$	N_2	—	0.20
3	$KHFe(CO)_4$	CO	1.1	0.33

[*1] At 5°C under atmospheric pressure. Reaction time: 5 hr. Solvent: EtOH. Ethylene Oxide/ $Fe(CO)_4^{2-}=5.5$.

[*2] β-Hydroxypropionate (0.2 mol/mol-$Fe(CO)_4^{2-}$) is obtained simultaneously.

TABLE 2. THE REACTION OF PROPYLENE OXIDE WITH POTASSIUM IRON CARBONYLATES[*1]

Exp. No.	Iron carbonylate	Atmosphere	CO absorbed	Yield of propylene
			mol/mol-$Fe(CO)_4^{2-}$	
4	$K_2Fe(CO)_4$	CO	2.2	0.65[*2]
5	$K_2Fe(CO)_4$	N_2	—	0.32
6	$KHFe(CO)_4$	CO	1.8	0.47

[*1] At 30°C under atmospheric pressure. Reaction time: 4 hr. Solvent: EtOH. Propylene Oxide/$Fe(CO)_4^{2-}=4.0$.

[*2] β-Hydroxybutyrate (0.4 mol/mol-Fe $(CO)_4^{2-}$) is obtained simultaneously.

The Reaction of $K_2Fe(CO)_4$ and $KHFe(CO)_4$ with Propylene Oxide. The results of these reactions are summarized in Table 2. The reactions were carried out at 30°C for 4 hr. As Table 2 shows, propylene (0.65 mol) is obtained from the reaction of propylene oxide with $K_2Fe(CO)_4$ and

TABLE 3. THE REACTION OF 1,2-BUTYLENE OXIDE WITH POTASSIUM IRON CARBONYLATES[*1]

Exp. No.	Iron carbonylate	Reaction conditions			CO absorbed	Yield			
		Solvent	Atmosphere	hr		1-Butene	*trans*-2-Butene	*cis*-2-Butene	Total
						mol/mol-$Fe(CO)_4^{2-}$			
7	$K_2Fe(CO)_4$	EtOH	CO	0.5	0.7	0.08	0.24	0.09	0.41
8	$K_2Fe(CO)_4$	EtOH	CO	1	1.1	0.12	0.28	0.10	0.50
9[*2]	$K_2Fe(CO)_4$	EtOH	CO	4	2.0	0.04	0.30	0.10	0.44
10	$K_2Fe(CO)_4$	EtOH	N_2	0.5	—	0.01	0.21	0.09	0.31
11	$KHFe(CO)_4$	EtOH	CO	2	1.2	0.05	0.07	0.02	0.14
12	$K_2Fe_2(CO)_8$	EtOH	CO	4	1.4		trace		
13	$K_2Fe(CO)_4$	dry EtOH	CO	2	1.2	0.31	0.18	0.05	0.54
14	$K_2Fe(CO)_4$	dry EtOH	CO	4	1.8	0.25	0.26	0.08	0.59
15	$K_2Fe(CO)_4$	Acetone	CO	2	0	0	0	0	0

[*1] 1,2-Butylene Oxide/$Fe(CO)_4^{2-}=3.2$

[*2] Carbonylated product (0.1 mol/mol-$Fe(CO)_4^{2-}$) and 0.13 mol/mol-Fe $(CO)_4^{2-}$ of *s*-butyl alcohol are obtained simultaneously.

[*2] "Mol" means mole per g atom of Fe, which is present as iron carbonylate.

carbon monoxide. The carbon monoxide absorbed amounts to more than 2 mol, and 0.4 mol of a carbonylated product, β-hydroxybutyrate, is formed simultaneously. The reactions with $K_2Fe(CO)_4$ under nitrogen (Exp. 5) and with $KHFe(CO)_4$, (Exp. 6) have a tendency similar to those of the reactions of ethylene oxide (Exps. 2, 3).

The Reaction of $K_2Fe(CO)_4$, $KHFe(CO)_4$, and $K_2Fe_2(CO)_8$ with 1,2-Butylene Oxide. *In an Ethanol Solvent (Including 2 mol of H_2O).*[*3] The results are summarized in Table 3. 1,2-Butylene oxide is also reduced with $K_2Fe(CO)_4$ and carbon monoxide to give butenes. More than 2 mol of carbon monoxide is absorbed in several hours, but the formation of butenes ceases after 1 hr and its yield is 0.5 mol at the maximum. The major product is not 1-butene, the corresponding olefin, but 2-butenes, which may be derived from 1-butene by isomerization. In Exp. 9, a carbonylated product (0.10 mol) and *s*-butyl alcohol (0.13 mol) were also detected, and 2.0 mol of carbon dioxide was evolved when the reaction mixture was acidified with concentrated hydrochloric acid.

The reduction reaction also proceeds under nitrogen, but the yields of butenes are low (Exp. 10), and $KHFe(CO)_4$ is less reactive than $K_2Fe(CO)_4$ (Exp. 11). $K_2Fe_2(CO)_8$ also reacts with 1,2-butylene oxide, absorbing carbon monoxide rapidly, but hardly any butenes are detected (Exp. 12).

In a Dry Ethanol Solvent. When a dry ethanol solvent is used, the total yield of the olefins increases and the major product is 1-butene, showing that the isomerization to 2-butenes is fairly well retarded (*cf.* Exp. 9 and Exp. 13).

In an aprotic solvent such as acetone, 1,2-butylene oxide does not react with the iron carbonylates (Exp. 15).

TABLE 4. THE REACTION OF OTHER EPOXIDE COMPOUNDS WITH $K_2Fe(CO)_4$

Exp. No.	Epoxide	Reaction conditions		CO absorbed	Yield of propylene
		Atmosphere	hr	mol/mol-$Fe(CO)_4^{2-}$	
16	Epichlorohydrin	CO	2	1.5	0.53
17	Epichlorohydrin	N_2	2	—	0.41
18	Allyl glycidyl ether	CO	3	2.4	0.54
19	Glycidol	CO	3	1.5	0.06

Solvent, EtOH at 30°C
Epichlorohydrin/$Fe(CO)_4^{2-}=5.8$
Allyl glycidyl ether/$Fe(CO)_4^{2-}=3.2$
Glycidol/$Fe(CO)_4^{2-}=4.5$

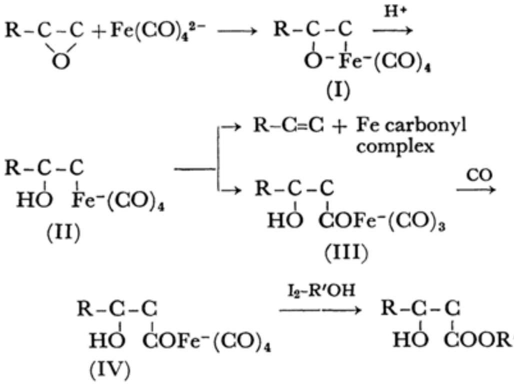
The Reaction of $K_2Fe(CO)_4$ with Epichlorohydrin, Allyl Glycidyl Ether, and Glycidol. The results are summarized in Table 4. These epoxide compounds also react with $K_2Fe(CO)_4$, absorbing a significant amount of carbon monoxide rapidly. Propylene, as the reaction product, is produced in any case, but allyl chloride, diallyl ether, and allyl alcohol, the corresponding reduction products, are not detected in the reaction mixture.

The Reaction of $K_2Fe(CO)_4$ with Internal Olefin Oxides. Internal olefin oxides, such as 2,3-butylene oxide and cyclohexene oxide, do not react with $K_2Fe(CO)_4$ under the conditions employed.

Discussion

The results obtained here show that 1,2-olefin oxides generally react with $K_2Fe(CO)_4$ and carbon monoxide to give not only the carbonylated products, but also the corresponding olefins. Further, the large amount of carbon monoxide absorbed suggests that some other reaction occurs. This complexity of the reaction was not observed in the reaction of $KCo(CO)_4$ with olefin oxides, which gives the carbonylated products selectively.[1)]

The mechanism of the formation of olefin is not yet clear. One probable scheme is suggested below. The facts that $K_2Fe(CO)_4$ is the most active in the formation of olefins and that only the 1,2-olefin oxides react under the reaction conditions employed seem to support the following reaction scheme: in the first step, $Fe(CO)_4^{2-}$ makes a nucleophilic attack on the terminal carbon atom of 1,2-olefin oxide to give complex (I). In the reaction of internal olefin oxides, the nucleophilic attack of $Fe(CO)_4^{2-}$ may be retarded, mainly by a steric hindrance.



The complex (I) abstracts a proton from water or a solvent to give the complex (II). Olefin seems to be derived by the decomposition of the complex (II). This interpretation is supported by the fact that even under nitrogen the olefin is formed. Some iron carbonyl complex produced by the decomposition seems to regenerate iron carbonylate (Fe-

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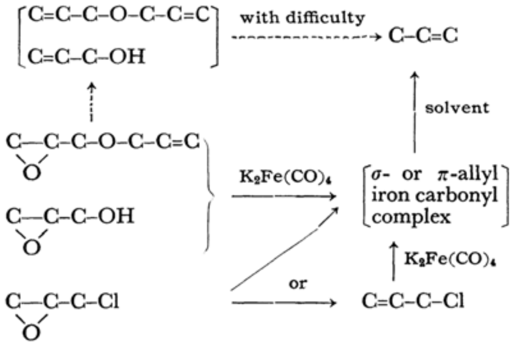
[*3] *Cf.* Eq. (a).

$(CO)_4^{2-}$), with the absorption of CO, which then further reacts with olefin oxide. This scheme is supported by the fact that the yield of olefin under carbon monoxide is larger than that under nitrogen. From the complex (II), β-hydroxyacyliron carbonylate (III and IV) may also be derived to give a β-hydroxy ester when treated with an alcoholic solution of iodine.

In the reaction of 1,2-butylene oxide with $K_2Fe(CO)_4$, a dry ethanol solvent is favorable to the formation of butenes. This effect can also be observed in the reaction of styrene oxide with $K_2Fe(CO)_4$.[2)] In a dry and moist ethanol solvents, the major products are 1-butene and 2-butene respectively. This fact can be explained by assuming that an equilibrium between $K_2Fe(CO)_4$ and $KHFe(CO)_4$ exists in the reaction solution; the reaction of $K_2Fe(CO)_4$ gives the corresponding olefin, and the reaction of $KHFe(CO)_4$ gives the isomerized olefin. Cramer and Lindsey showed that $KHFe(CO)_4$ is active in the isomerization of 1-butene to 2-butene.[4)]

$$K_2Fe(CO)_4 + H_2O \rightleftharpoons KHFe(CO)_4 + KOH$$

From allyl glycidyl ether, glycidol, and epichlorohydrin, the corresponding olefins, allyl ether, allyl alcohol, and allyl chloride, are not detected. However, propylene is formed in a relatively good yield. The fact that allyl ether and ally alcohol react with $K_2Fe(CO)_4$ with much difficulty indicates that these compounds are not the intermediates of the formation of propylene from allyl glycidyl ether and glycidol.



On the other hand, allyl chloride and its derivatives react with $K_2Fe(CO)_4$ very readily to give olefins such as propylene.[2,5)] These reactions may be considered to proceed *via* σ- and π-allyl iron carbonylate. In the light of this fact, the reaction of allyl glycidyl ether and glycidol with $K_2Fe(CO)_4$ seems to proceed *via* a kind of allyl iron carbonyl complex. The reaction of epichlorohydrin involves two possible routes; one is *via* allyl chloride, while the other involves some other step to the formation of a π- or σ-allyl iron carbonyl complex, as in the reaction of allyl glycidyl ether and glycidol.

This work was supported in part by The Kawakami Foundation, to which our thanks are due.

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4) R. Cramer and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **88**, 3534 (1966).

5) Y. Takegami, Y. Watanabe, I. Kanaya, T. Mitsudo, T. Okajima, N. Morishita and H. Masada, This Bulletin, in press.