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Studies of the Organic Reactions of Metal Carbonyls. XIII.[*1] The Reduction of Olefin Oxides with Potassium Iron Carbonylates

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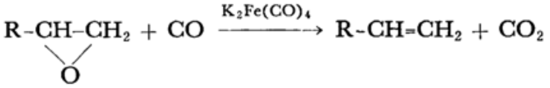
The reaction between potassium iron carbonylates ($KHFe(CO)_4$, $K_2Fe(CO)_4$, and $K_2Fe_2(CO)_8$) and olefin oxides has been studied. Styrene oxide reacts readily with these carbonylates and with carbon monoxide under an atmospheric pressure and at 30°C. As the reaction products, styrene, ethylbenzene, and α- and β-phenylethyl alcohol are obtained. The major product is styrene or β-phenylethyl alcohol for the reaction of $K_2Fe(CO)_4$ or $KHFe(CO)_4$ and $K_2Fe_2(CO)_8$ respectively. The effects of solvents and additives are examined. Further, propylene oxide and epichlorohydrin are found to react with $K_2Fe(CO)_4$ and carbon monoxide to give not only carbonylated products, but also propylene. The results indicate that olefin oxides are generally reduced with $K_2Fe(CO)_4$ and carbon monoxide to give the corresponding olefins and carbon dioxide.



$$\text{R-CH-CH}_2\text{(-O-)} + \text{CO} \xrightarrow{K_2Fe(CO)_4} \text{R-CH=CH}_2 + \text{CO}_2$$

Previous work in this laboratory has shown that propylene oxide and ethylene 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, as the carbonylated products, β-hydroxy esters[*2] are obtained by the treatment of the reaction mixture with iodine and alcohol, indicating that the corresponding β-hydroxyacyliron carbonyls are formed. However, the yield of the esters is very low. This suggests that some reaction other than the carbonylation also occurs.

In the present investigation, the reaction of styrene oxide and epichlorohydrin with the iron carbonylates has been mainly studied in detail in examining for a reaction other than the carbonylation.

Experimental

The Preparation of Potassium Iron Carbonylates, $KHFe(CO)_4$, $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$. These salt solutions in alcohols were prepared according to the method described in a previous paper[1]: A

[*1] Part XII: Y. Takegami, Y. Watanabe and H. Masada, This Bulletin, **40**, 1459 (1967).

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

[*2] β-hydroxybutyrate and β-hydroxypropionate.

50-m*l* portion of 0.22 M $KHFe(CO)_4$, $K_2Fe(CO)_4$, or a 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:[2)]

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

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

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

Reaction Procedures. *Styrene Oxide.* To the solution of the potassium iron carbonylate described above, 3.2 g of styrene oxide were added; the mixture was then agitated vigorously for 3 to 8.5 hr at 30 to 50°C, under an atmosphere of carbon monoxide or nitrogen. The amount of carbon monoxide absorbed was determined by following the change in the readings of a buret. After a certain reaction time, the reaction mixture was poured into a separatory funnel, in which 100-m*l* of water had been placed, and extracted with two 100-m*l* portions of *n*-hexane. The *n*-hexane solution was concentrated to about 10-m*l*, and then submitted to analysis.

Propylene Oxide or Epichlorohydrin. The reaction of $K_2Fe(CO)_4$ with propylene oxide or epichlorohydrin was similarly carried out, and the gas over the reaction mixture was analyzed.

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 infrared spectrophotometer. Further, styrene was confirmed by being converted to ethylbenzene; after hydrogenation with Raney nickel, the peak of styrene in the gas chromatogram vanished and a new peak of ethylbenzene appeared.

Results

The Reaction of $K_2Fe(CO)_4$ with Styrene Oxide. *The Relation between the Amount of Carbon Monoxide Absorbed and the Yield of the Products.* The results of the reactions are summarized in Table 1 and Fig. 1. All of the reactions were carried out at 30°C under an atmosphere of carbon monoxide, except for Exp. 4, which was carried out under nitrogen.

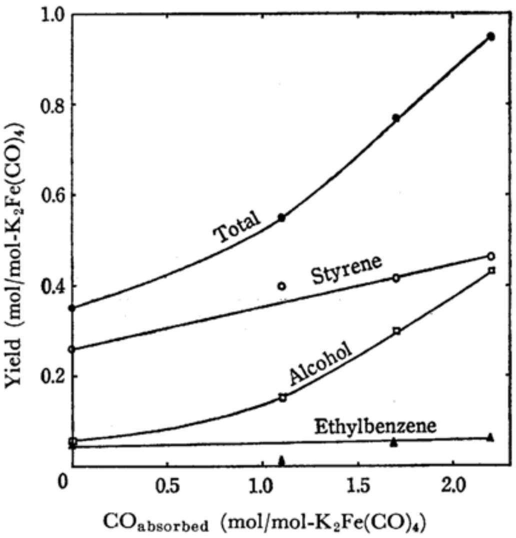


Fig. 1. The reaction of $K_2Fe(CO)_4$ with styrene oxide.

As Table 1 shows, styrene oxide readily reacts with $K_2Fe(CO)_4$ and carbon monoxide, while the reaction solution turns from light brown to dark red. As the reaction products, styrene, which is the major product, ethylbenzene, and α- and β-phenylethyl alcohol are obtained. However, no carbonylated product is obtained.[*3] The gas absorption amounts to more than two moles,[*4] therefore, the total yield of the products is almost equivalent to the $K_2Fe(CO)_4$ used (see Exp. 3). The plots of the yield of the products against the amount of carbon monoxide absorbed are illustrated in Fig. 1. As Fig. 1 shows, the yields of all products except ethylbenzene increase with the amount of carbon monoxide absorbed.

TABLE 1. THE REACTION OF $K_2Fe(CO)_4$ WITH STYRENE OXIDE

Exp. No.	Reaction condition[*1]		CO absorbed	Products			
	Atmosphere	hr		Styrene	Ethylbenzene mol/mol-$K_2Fe(CO)_4$	Alcohols[*2]	Total
1	CO	3	1.1	0.40	~0	0.15	0.55
2	CO	4	1.7	0.41	0.05	0.31	0.77
3	CO	8.5	2.7	0.46	0.06	0.43	0.95
4	N_2	4	—	0.26	0.05	0.05	0.36

[*1] At 30°C, under one atmosphere

[*2] α- and β-Phenylethyl alcohol. About 2/3 of the alcohols is β.

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

[*3] No carbonylated product, such as β-hydroxy-β-phenylpropionate, was detected by gas chromatography, even when the reaction mixture was treated with iodine and alcohol.

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

TABLE 2. THE REACTION OF $K_2Fe(CO)_4$ WITH STYRENE OXIDE
— Effects of solvents and additives —

Exp. No.	Reaction condition*1			CO absorbed	Product			
	Solvent	Additive*3	hr		Styrene	Ethylbenzene	Alcohol*4	Total
					mol/mol-$Fe(CO)_4$			
5	dry EtOH	—	4	1.6	0.59	~0	0.22	0.81
6*2	dry EtOH	—	4	2.2	0.65	0.05	0.33	1.03
7	dry tetrahydrofuran	—	4	0.06	0.11	~0	0.05	0.16
8	EtOH + H_2O	10	4	1.8	0.23	0.07	0.35	0.65
9	EtOH*5 + Pyridine	10	8	1.4	0.47	~0	~0	0.47

*1 At 30°C except Exp. 6. Under one atmosphere of carbon monoxide.
*2 At 50°C.
*3 mol/mol-$K_2Fe(CO)_4$.
*4 α- and β-Phenylethyl alcohol. About 2/3 of the alcohols is β.
*5 2 mol/mol-$K_2Fe(CO)_4$ of water is included.

TABLE 3. THE REACTION OF $KHFe(CO)_4$ OR $K_2Fe_2(CO)_8$ WITH STYRENE OXIDE

Exp. No.	Reaction condition*1		CO absorbed	Product			
	Iron carbonylate	Atmosphere		Styrene	Ethylbenzene	Alcohol*2	Total
				mol/g·atom·Fe*3			
10	$KHFe(CO)_4$	CO	1.6	0.16	0.04	0.52	0.72
11	$KHFe(CO)_4$	N_2	—	0.14	0.06	0.13	0.33
12	$K_2Fe_2(CO)_8$	CO	1.2	0.13	0.03	0.33	0.49

*1 At 30°C under one atmosphere. Reaction time: 4 hr. Solvent: EtOH.
*2 α- and β-Phenylethyl alcohol. About 2/3 of the alcohols is β.
*3 Fe exists as iron carbonylates.

Effects of Solvents and Additives. The effects of solvents and additives on reactions analogous to Exp. 2 were examined. The results are summarized in Table 2.

In the reaction in dry ethyl alcohol at 30 and 50°C (Exps. 5 and 6), the yield of styrene is better and that of phenylethyl alcohols is worse than those in Exp. 2, in which some of the water formed during the preparation of the iron carbonylate is present in the solvent. This fact indicates that a dry solvent is favorable to the production of styrene and that a relatively small amount of water has an effect on the distribution of the reduction products. In dry tetrahydrofuran solution, scarcely no reaction occurs (Exp. 7).

As additives, water and pyridine were used (Exps. 8 and 9). When 10 mol of water are added, the yield of styrene decreases to about half that in Exp. 2, but the yields of the alcohols increase slightly. When 10 mol of pyridine are added, scarcely no reduction product other than styrene is formed. These results show that the water added has an inhibitory effect on the formation of styrene, but that the pyridine added retards the production of phenylethyl alcohols completely.

The Reaction of $KHFe(CO)_4$ or $K_2Fe_2(CO)_8$ with Styrene Oxide. The results are summarized in Table 3. $KHFe(CO)_4$ and $K_2Fe_2(CO)_8$ also readily react with styrene oxide and carbon monoxide to give styrene and phenylethyl alcohols. As for the reaction of $KHFe(CO)_4$, the major product is not styrene, but β-phenylethyl alcohol (Exp. 10), the yield of which is about 1.7 times as much as that in the reaction of $K_2Fe(CO)_4$ (Exp. 2), indicating that $KHFe(CO)_4$ is very favorable for the production of the alcohol. As Exp. 12 shows, $K_2Fe_2(CO)_8$ is also more favorable for the production of the alcohol than for that of styrene.

The Reaction of $K_2Fe(CO)_4$ with Propylene Oxide or Epichlorohydrin. Propylene oxide and epichlorohydrin also readily react with $K_2Fe(CO)_4$ and carbon monoxide,*5 the reaction solution thus turning from light brown to red brown. Propylene was detected in the gas over both reaction mixtures, the amount being at least 0.2 mol in both cases.

Discussion

The results obtained here show that olefin oxides generally react with $K_2Fe(CO)_4$ and carbon monoxide to give the corresponding olefins. In the course of the reaction, carbon dioxide is definitely

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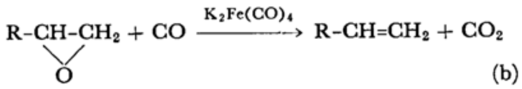
*5 At 20°C, about 2 mol of carbon monoxide were absorbed in both cases.

*6 Analyzed by gas chromatography and by means of a mass spectrum taken on a JMS=OISG mass spectrometer (Japan Electron Optics Laboratory Co.).

produced.*[7] Thus, the following reaction appears to occur:



$$R\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} + CO \xrightarrow{K_2Fe(CO)_4} R\text{-}CH{=}CH_2 + CO_2 \qquad \text{(b)}$$

This reaction is not considered to proceed *via* α- and β-phenylethyl alcohol, because they do not react with the iron carbonylate and carbon monoxide. The reaction mechanism, however, is not yet completely clear.

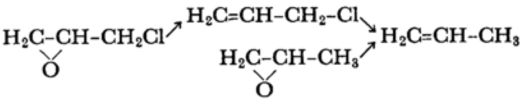
The yield of styrene is best when $K_2Fe(CO)_4$ and a dry ethanol solvent are used at 50°C. On the other hand, the reaction of $KHFe(CO)_4$ gives phenylethyl alcohols in the best yield. The addition of water to the $K_2Fe(CO)_4$ reaction system causes a significant decrease in the yield of styrene and a slight increase in the yield of the alcohols. This fact may 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 styrene, and that of $KHFe(CO)_4$ gives phenylethyl alcohols.

$$K_2Fe(CO)_4 + H_2O \rightleftarrows KHFe(CO)_4 + KOH \qquad \text{(c)}$$

The fact that pyridine used as an additive remarkably inhibits the formation of the alcohols suggests that the pyridine disturbs the reaction of $KHFe(CO)_4$ and styrene oxide by forming a kind of salt between $KHFe(CO)_4$ and the pyridine.

$K_2Fe_2(CO)_8$ shows a rather reduced reactivity in comparison with $K_2Fe(CO)_4$ and $KHFe(CO)_4$.

The reaction of epichlorohydrin with $K_2Fe(CO)_4$ involves another problem; in this reaction, allyl chloride, the corresponding olefin, was not detected by gas chromatography, but propylene was obtained. On the other hand, allyl chloride was found to react readily with $K_2Fe(CO)_4$ under the same conditions as in Exp. 2, with an evolution of propylene.*[8] This suggests that the active halogen atom of allyl chloride is readily replaced by a hydrogen atom under these conditions. Therefore, epichlorohydrin may be reduced to allyl chloride in the first step, and then the allyl chloride is converted to propylene as follows:



(d)

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*[7] Carbon dioxide was evolved when the reaction mixture was treated with concentrated hydrochloric acid. The amount of carbon dioxide evolved was almost equal to the sum of the carbon dioxide formed according to Eqs. (a) and (b).

*[8] The absorption of carbon monoxide did not occur.