Organic Reactions of Carbonylferrates(Dissertation_全文)

Mitsudo, Take-aki

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TAKE-AKI MITSUDO

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Preface

Organometal chemistry 1) has made a great progress for the last half a century. From the standpoint of the industrial chemistry, there are three main processes which closely concern organometal chemistry.

1) Polymerization of olefins by Ziegler-Natta type catalysts. 2)

2) Oxidation of olefins with Wacker process 3) by palladium complexes.

3) Oxo process 4) and Reppe's reactions (the synthesis of acrylic acid from acetylene by nickel carbonyl 5) and the hydroxymethylation of olefins by iron carbonyls. 6))

In order to elucidate the mechanism of these reactions, a number of studies have been made and the key compounds in these processes are found to have hydrogen- or carbon-transition metal bonds.

As for the oxo process, the cobalt or rhodium catalyst was found to react with olefins as hydridocarbonylmetal to give alkyl- and acylcarbonylmetal complexes as reaction intermediates. The reactions of hydrido-, alkyl- and acylcobalt complexes were investigated under an ambient condition and the results were compared with those under more drastic condition of oxo process. These results are recently reviewed by Orchin. 4b)

On the other hand, the reactivity of hydridocarbonylferrates which are considered to be the active species in the Reppe's hydroxymethylation of olefins has been briefly studied only by several workers. 6,7)

The intent of this thesis is to investigate the organic reactivity of the salts of dihydridocarbonylirons, acyl- and alkylcarbonyliron complexes under ambient conditions.

Carbonylirons, which have only carbonyl or hydride as ligands, are listed in Table 1. These complexes are isolated and characterized.[8)] The dihydride complexes are thermally unstable at room

Table 1

$Fe(CO)_5$	$H_2Fe(CO)_4$	$HFe(CO)_4$	$Fe(CO)_4^{2-}$
$Fe_2(CO)_9$	$H_2Fe_2(CO)_8$	$HFe_2(CO)_8$	$Fe_2(CO)_8^{2-}$
$Fe_3(CO)_{12}$	$H_2Fe_3(CO)_{11}$	$HFe_3(CO)_{11}$	$Fe_3(CO)_{11}^{2-}$
$Fe_4(CO)_{14}^{*}$	$H_2Fe_4(CO)_{13}$	$HFe_4(CO)_{13}^{-}$	$Fe_4(CO)_{13}^{2-}$

*Unknown

temperature as hydridotetracarbonylcobalt is. However, the salts of the dihyridocarbonyliron are fairly thermally stable. These salts are easily available by the base reaction of the neutral iron carbonyls with hydroxy ion or amines,[9)] and the oxidation of the uninuclear salt.[10)]

$$Fe(CO)_5 + 3\ OH^- \longrightarrow HFe(CO)_4 + CO_3^{2-} + H_2O$$

$$Fe(CO)_5 + 4\ OH^- \longrightarrow Fe(CO)_4^{2-} + CO_3^{2-} + 2\ H_2O$$

$$Fe_2(CO)_9 + 3\ OH^- \longrightarrow HFe_2(CO)_8 + CO_3^{2-} + H_2O$$

$$HFe(CO)_4 \xrightarrow{CH_3NO_2} Fe_2(CO)_8^{2-}$$

$$HFe(CO)_4^- \xrightarrow{I_2} Fe_3(CO)_{11}^{2-}$$

$$Fe(CO)_5 + Et_3N + H_2O \longrightarrow [Et_3NH]^+[HFe_3(CO)_{11}]^-$$

The salts of the dihydrides are very interesting compounds as the reagents because of the unusually low oxidation state of the irons in them (zero or minus two).

Sternberg et al. reported that the aquous solution of $KHFe(CO)_4$ reduces benzil, quinone, benzaldehyde and acetylene into benzoin, hydroquinone, benzyl alcohol and ethylene, respectively.[7] During our investigation, Sawa et al. reported that derivatives of these salts, lithium acylcarbonylferrates, react with acylhalides to give ketones and/or α-diketones.[11] It is worth while to investigate further organic reactions of these salts of the dihydridocarbonylirons. The results will also give some informations about the reactions which are carried out under drastic conditions.

This thesis is composed of seven chapters and the outline will be explained as follows.

The first chapter summarizes the reactions of olefin oxides with carbonylferrates, $KHFe(CO)_4$, $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$.[12]

The second chapter deals with the reduction of alkyl and aryl halides with the carbonylferrates into the corresponding hydrocarbons.[13]

The third chapter deals with the selective reduction of isoprene into monoolefins with the carbonylferrate, $HFe(CO)_4$.[14] The reduction of the monoolefins into isopentane did not occur. In the appendix, the selective reduction of cinnamaldehyde into 3-phenylpropionaldehyde was briefly mentioned.

The fourth chapter deals with the reduction of enamines to the saturated tertiary amines and the reductive alkylation of secondary amines [15] with the hydridocarbonylferrates, $HFe(CO)_4^-$, $HFe_2(CO)_8^-$ and $HFe_3(CO)_{11}$ in alcohol.

The fifth chapter deals with the reduction of pyrrolidine enamine of 2-methylcyclohexanone. The products were cis- and trans-1-methyl-2-pyrrolidinocyclohexane. The ratios of the cis to trans isomers will be characteristic of $HFe(CO)_4$, $HFe_2(CO)_8$ and

$HFe_3(CO)_{11}$. Indeed, they were 0.67, 1.2 and 2.1, respectively. These values are considered to represent the steric effects of the mononuclear and clustered hydride complexes. The effect of the reaction conditions on the ratio gives the information about the mechanism of the reduction and the reproduction of active hydride species.

The sixth chapter deals with the facile reduction of acyl halide into aldehyde with $Na_2Fe(CO)_4$.16)

The last chapter summarizes the reaction of diacyl halides with $Na_2Fe(CO)_4$ in aprotic solvents. Phthaloyl dichloride reacts with the salt to give biphthalidylidene.17) This reaction is reasonably considered to proceed via carbene carbonyl iron complex. The reactions of other aromatic and aliphatic polyacyl halides will be discussed.

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T. Mitsudo

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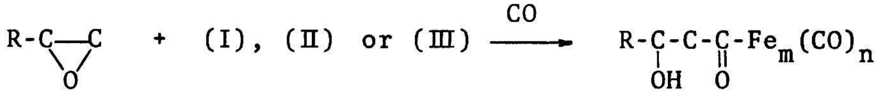
Capter 1. The Reaction of Olefin Oxides with Potassium Carbonylferrates

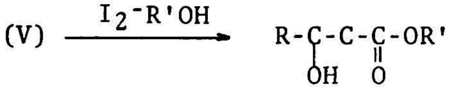
Introduction

Olefin oxides such as ethylene oxide and propylene oxide are known to react with potassium carbonyl metalate, $K_2Fe(CO)_4$ (I), $KHFe(CO)_4$ (II), $K_2Fe_2(CO)_8$ (III) and $KCo(CO)_4$ (IV) with absorption of carbon monoxide; the carbonylated products, β-hydroxy esters are obtained by the treatment of the reaction mixture with iodine in alcohol, indicating that the corresponding β-hydroxyacylcarbonyl metalates (V) or (VI) are formed.[1)]

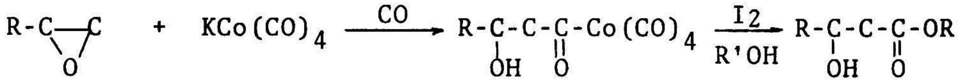


(1)

(V)



$$(V) \xrightarrow{I_2\text{-}R'OH} R\text{-}\underset{OH}{C}\text{-}C\text{-}\underset{O}{\overset{\|}{C}}\text{-}OR'$$



(2)

(VI)

However, in the reaction of (I), (II) or (III), the yield of the ester is very low. This suggests that some reaction other than the carbonylation occurs.

In the present chapter, the reaction of olefin oxides with (I), (II) and (III) were reinvestigated in detail.[2)]

Experimental

Infrared spectra were measured on a Shimadzu model 27 infrared spectrometer. Mass spectra were obtained with a JMS=OISJ mass spectrometer.

The Preparation of Potassium Carbonylferrates.

a) $KHFe(CO)_4$ and $K_2Fe(CO)_4$. These salts solution in ethanol were prepared by the method described by Kurmholz and Stettiner.[3)]

$KHFe(CO)_4$: A 100 ml four-necked flask, fitted with a 50 ml dropping funnel, a stirrer, and a rubber stopple, was connected with a gas buret and then flushed with carbon monoxide or nitrogen. Potassium hydroxide solution in ethyl alcohol (1 N, 33 ml) and 17 ml of ethanol and 1.5 ml (11mmol) of pentacarbonyliron were placed in the flask and then stirred vigorously for about two hours at 30°C to give a pale yellow solution with a white precipitate.

$$Fe(CO)_5 + 3KOH \longrightarrow KHFe(CO)_4 + K_2CO_3 + H_2O \quad (3)$$

$K_2Fe(CO)_4$: Pentacarbonyliron (1.5 ml, 11 mmol) was similarly treated with potassium hydroxide solution in ethyl alcohol (1 N 44 ml) and 6 ml of ethyl alcohol.

$$Fe(CO)_5 + 4KOH \longrightarrow K_2Fe(CO)_4 + K_2CO_3 + 2H_2O \quad (4)$$

When $KHFe(CO)_4$ or $K_2Fe(CO)_4$ is prepared, one or two equivalent mol of water are formed. Therefore, when a dry solution of these ferrates were required the solvent of the salts solutions were once distilled off under a vacuum (1 mmHg) at 30°C for 2 hr and then 50 ml of a new dry solvent was added.

b) $K_2Fe_2(CO)_8$. This salt solution in ethyl alcohol was prepared by the oxidation of $KHFe(CO)_4$ (11 mmol in 50 ml ethyl alcohol) solution with nitromethane (0.12 g) for 1 hr.[4)]

Materials. Ethylene oxide was obtained from ethylene chlorohydrin and alkali.[5)] Propylene oxide, butylene oxides, styrene oxide, cyclohexene oxide, trimethylene oxdie, pentacarbonyliron and the other compounds employed in this study were commercial products.

Tetrahydrofurane (THF) was dried over sodium dispersion for 48 hr, and distilled before use. Dry ethyl alcohol was obtained by the method described in a literature.6) Ethyl alcohol was refluxed over magnesium ethoxide for 24 hr and distilled before use.

<u>Reaction Procedures</u>. To the solution of potassium carbonylferrate described above, 3~5.5 mol[*1] of olefin oxide was added; the mixture was agitated vigorously at 30°C under an atmospheric pressure of carbon monoxide or nitrogen. The amount of carbon monoxide absorbed was determined volumetically. In the reaction of ethylene oxide, propylene oxide, epichlorohydrin or butylene oxide, after a certain reaction time, the reaction flask was connected to a trap immersed in liquid nitrogen, which was joined with a vacuum pump. The gases were collected in a trap at 80~30 mmHg for 5 minutes. The trap was then allowed to warm to room temperature and then heated to 80°C. The gas evolved was collected in a gas buret and submitted to g.c. analysis. The reaction solution was treated with excess iodine-ethanol and the excess iodine was decomposed with sodium thiosulfate. By this treatment, acylcarbonylirons are converted into the corresponding esters of carboxylic acids, as has been observed in the case of acyl cobalt carbonyls.7) The ethanol solution was filtered and the filtrate was submitted to g.c. analysis.

In the reaction of styrene oxide, the reaction mixture ~~was~~ poured into a separatory funnel, in which 100 ml of water has been placed, and extracted with two 100 ml portion of n-hexane and dried

[*1] "mol" means mol/g.atom.Fe, hereafter.

over sodium sulfate. The n-hexane solution was concentrated to about 10 ml and then submitted to g.c. analysis. In some cases, the reaction solution was treated with iodine-ethanol and analyzed by gas chromatography.

Analytical Procedures. The reaction products were identified by gas chromatography (Column: Dilaulyl Phthalate on cerite, 4 mm$^{\phi}$ x 3 m; SE-30 on chromosorb 3 mm$^{\phi}$x 3 m; Dimethylsulfolane on Neopak 3mm$^{\phi}$x 5 m) by the use of authentic samples, and the yields were determined using appropriate internal standards previously calibrated against the authentic samples.

Styrene was confirmed by being converted to ethyl benzene; after hydrogenation with Ranay nickel, the peak of styrene in the gas chromatogram vanished and a new peak of ethylbenzene appeared. Propylene was identified by means of mass spectrometry.

Results

The Reaction of $K_2Fe(CO)_4$ (I) with Styrene Oxide. 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 a nitrogen atmosphere.

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

Exp. No.	Reaction condition*1		CO absorbed	Products			
	Atmosphere	hr		Styrene	Ethylbenzene	Alcohols*2	Total
				mol/mol-$K_2Fe(CO)_4$			
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.

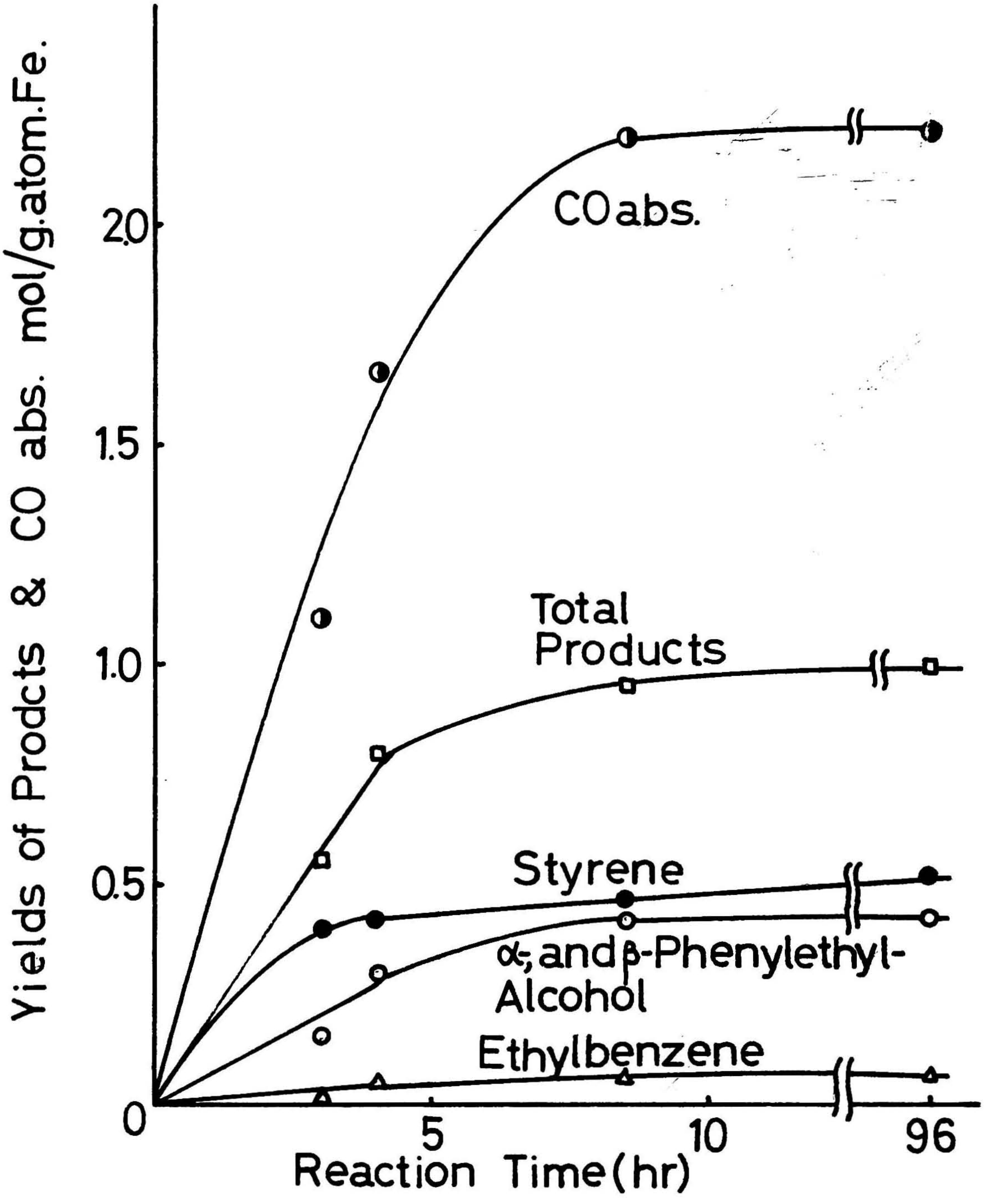


Fig. 1. The Reaction of Styrene Oxide with $K_2Fe(CO)_4$ in EtOH at 30°C

As Table 1 and Fig. 1 show, styrene oxide readily reacts with $K_2Fe(CO)_4$ and carbon monoxide, while the reaction solution turns from light brown to ruby red. As the reaction products, styrene, which is the major product, ethylbenzene α- and β-phenylethyl alcohols are obtained. In each case, the β-isomer predominates over the α-isomer: about two third of the alcohols was β. However, no carbonylated product such as β-hydroxy-β-phenylpropionate was detected by ir spectrum of the reaction mixture and by gas chromatography even when the reaction mixture was treated with iodine-alcohol.

The time plots of the yields of the products and the amount of absorbed carbon monoxide are illustrated in Fig. 1. The yield of styrene amounted to 0.4 mol in 3 hr and then it increased only slowly, almost independent of an absorption of carbon monoxide. On the other hand the yield of α- and β-phenylethyl alcohol increased with the absorption of carbon monoxide, which amounted to more than 2 mol and the total yield of the products was almost equivalent to the moles of $K_2Fe(CO)_4$ used. The yield of ethylbenzene was low and less than 0.06 mol. The reaction proceeded even under a nitrogen atmosphere, however, the yields of styrene and the alcohols were about three forth and one sixth of those in Exp. 2, respectively.

Effects of Solvents and Additives. The effects of solvents and additives on the reactions analogous to Exp. 2 were examined. The results are summarized in Table 2. In the reaction in dry ethyl alcohol at 30°C and at 50°C (Exp. 5 and 6), the yield of styrene is better and those of phenylethyl alcohols were worse than those in Exp. 2, in which some of the water formed during the preparation of the carbonylferrate is present in the solvent.[*2] 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 reaction products. When 10 mol of water is added, the yield of styrene decreased to about half of that in Exp.2, but the yields of the alcohols increased slightly. Addition of 10 mol of pyridine disturbed the formation of the alcohols completely. In dry THF solution, the reaction scarcely occurs (Exp. 7).

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 mol/mol-$Fe(CO)_4$	Alcohol*4	Total
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.

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 $K_2Fe_2(CO)_8$ in alcohol also readily react with styrene oxide and carbon monoxide to give styrene, phenylethylalcohols and ethylbenzene. As for the reaction of $KHFe(CO)_4$, the major product is not styrene, but phenylethyl alcohols (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 alcohols.

$K_2Fe_2(CO)_8$ is also more favorable for the production of the alcohols than for that of styrene. The selectivity of α-phenyl-

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*2 See, Eq. 4.

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 mol/g·atom·Fe[*2]	Alcohols	Total
10	$KHFe(CO)_4$	CO	1.6	0.16	0.04	0.52 [*3]	0.72
11	$KHFe(CO)_4$	N_2	—	0.14	0.06	0.13 [*3]	0.33
12	$K_2Fe_2(CO)_8$	CO	1.2	0.13	0.03	0.33 [*4]	0.49

[*1] At 30°C. Reaction time: 4 hr. Solvent: ethanol.

[*2] Fe exists as the carbonylferrates.

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

[*4] About 55% of the alcohols is β.

ethyl alcohol is better than those in Exps. 10 and 11.

The Reaction of $K_2Fe(CO)_4$ and $KHFe(CO)_4$ with Ethylene Oxide. The results of the reactions are summarized in Table 4. The reactions were carried out at 5°C for 5 hr. Ethylene oxide also reacts with $K_2Fe(CO)_4$ and carbon monoxide, while the reaction solution turns from light yellow to dark red brown. Ethylene obtained as the reaction product amounts to 0.50 mol (Exp. 13). 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 a nitrogen atmosphere, however, the yield of ethylene is low. $KHFe(CO)_4$ is less reactive than $K_2Fe(CO)_4$.

Table 4 The reaction of ethylene oxide with potassium iron carbonylates[*1]

Exp. No.	Iron carbonylate	Atmosphere	CO absorbed	Yield of ethylene
			mol/mol-$Fe(CO)_4^{2-}$	
13	$K_2Fe(CO)_4$	CO	1.2	0.50[*2]
14	$K_2Fe(CO)_4$	N_2	—	0.20
15	$KHFe(CO)_4$	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.

The Reaction of $K_2Fe(CO)_4$ and $KHFe(CO)_4$ with Propylene Oxide. The results of these reactions are summarized in Table 5. The reactions were carried out at 30°C for 4 hr. As Table 5 shows, propylene (0.65 mol) is obtained from the reaction of propylene oxide with $K_2Fe(CO)_4$ and 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.$^{1)}$ The reactions with $K_2Fe(CO)_4$ under a nitrogen atmosphere (Exp. 14) and with $KHFe(CO)_4$ (Exp. 18) have a tendency similar to those of the reactions of styrene oxide and ethylene oxide.

TABLE 5 THE REACTION OF PROPYLENE OXIDE WITH POTASSIUM IRON CARBONYLATES*1

Exp. No.	Iron carbonylate	Atmosphere	CO absorbed	Yield of propylene
			mol/mol-$Fe(CO)_4^{2-}$	
16	$K_2Fe(CO)_4$	CO	2.2	0.65*2
17	$K_2Fe(CO)_4$	N_2	—	0.32
18	$KHFe(CO)_4$	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 $K_2Fe(CO)_4$, $KHFe(CO)_4$ and $K_2Fe_2(CO)_8$ with 1,2-Butylene Oxide. The results are summarized in Table 6. In a moist ethanol, 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, however, the formation of butenes ceased in 1 hr and the yield of which is 0.5 mol at maximum. The major product is not the corresponding olefin, 1-butene, but 2-butenes which may be derived from 1-butene by isomerization.$^{8)}$ In Exp. 21, a carbonylated product (0.10 mol) and sec-butyl alcohol (0.13 mol) were also detected. However, n-butyl alcohol was not detected.

Two mol of carbon dioxide was evolved when the reaction mixture was acidified with concentrated hydrochloric acid (Exp. 21).

Although the reduction also proceeds under nitrogen, the yield

TABLE 6 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-$Fe(CO)_4^{2-}$			
19	$K_2Fe(CO)_4$	EtOH	CO	0.5	0.7	0.08	0.24	0.09	0.41
20	$K_2Fe(CO)_4$	EtOH	CO	1	1.1	0.12	0.28	0.10	0.50
21*2	$K_2Fe(CO)_4$	EtOH	CO	4	2.0	0.04	0.30	0.10	0.44
22	$K_2Fe(CO)_4$	EtOH	N_2	0.5	—	0.01	0.21	0.09	0.31
23	$KHFe(CO)_4$	EtOH	CO	2	1.2	0.05	0.07	0.02	0.14
24	$K_2Fe_2(CO)_8$	EtOH	CO	4	1.4		trace		
25	$K_2Fe(CO)_4$	dry EtOH	CO	2	1.2	0.31	0.18	0.05	0.54
26	$K_2Fe(CO)_4$	dry EtOH	CO	4	1.8	0.25	0.26	0.08	0.59
27	$K_2Fe(CO)_4$	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.

of butenes are low (Exp. 22) and $KHFe(CO)_4$ is less reactive for the deoxygenation of the olefin oxide than $K_2Fe(CO)_4$ (Exp. 23). $K_2Fe_2(CO)_8$ also reacts with 1,2-butylene oxide, absorbing carbon monoxide, but hardly any butenes could be detected (Exp. 24).

In a Dry Ethanol Solvent. When a dry ethanol solvent is used, the total yield of the olefins increases as in the reaction of styrene oxide. The major product is 1-butene, showing that the isomerization to 2-butenes are fairly well retarded (cf. Exp. 19 and 25). In an aprotic solvent such as acetone, 1,2-butylene oxide does not react with the carbonylferrate (Exp. 27).

The Reaction of $K_2Fe(CO)_4$ with Epichlorohydrin, Allyl Glycidyl Ether and Glycidol. The results are summarized in Table 7. These epoxy compounds also react with $K_2Fe(CO)_4$, absorbing a significant amount of carbon monoxide rapidly. Propylene, as the reaction product, is produced in all cases, but allyl chloride, diallyl ether and allyl alcohol, the corresponding reduction products, are not detected in the reaction mixtures.

The reactions of diallyl ether and allyl alcohol with $K_2Fe(CO)_4$ or $KHFe(CO)_4$ do not give propylene. On the other hand allyl chloride reacts with $K_2Fe(CO)_4$ or $KHFe(CO)_4$ to give propylene. This reaction will be investigated in the next chapter.

TABLE 7 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-$Fe(CO)_4^{2-}$	
28	Epichlorohydrin	CO	2	1.5	0.53
29	Epichlorohydrin	N_2	2	—	0.41
30	Allyl glycidyl ether	CO	3	2.4	0.54
31	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 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.

Trimethylene oxide does not react with $K_2Fe(CO)_4$ in ethanol at 30~50°C.

Discussion

The results obtained here show that ethylene oxide and its monoalkyl substituted derivatives generally react with $K_2Fe(CO)_4$ or $KHFe(CO)_4$ and carbon monoxide to give not only the carbonylated products and alcohols, but also the corresponding olefins, deoxygenated products. Aryl substituted ethylene oxide, styrene oxide, also gives the corresponding olefin and alcohols, styrene and α- and β-phenylethyl alcohol, however, any carbonylated products could not be detected.

Olefin oxides are known to be isomerized into ketone with $KCo(CO)_4$ or $HCo(CO)_4$.9) But ketones could not be detected in this reaction system.

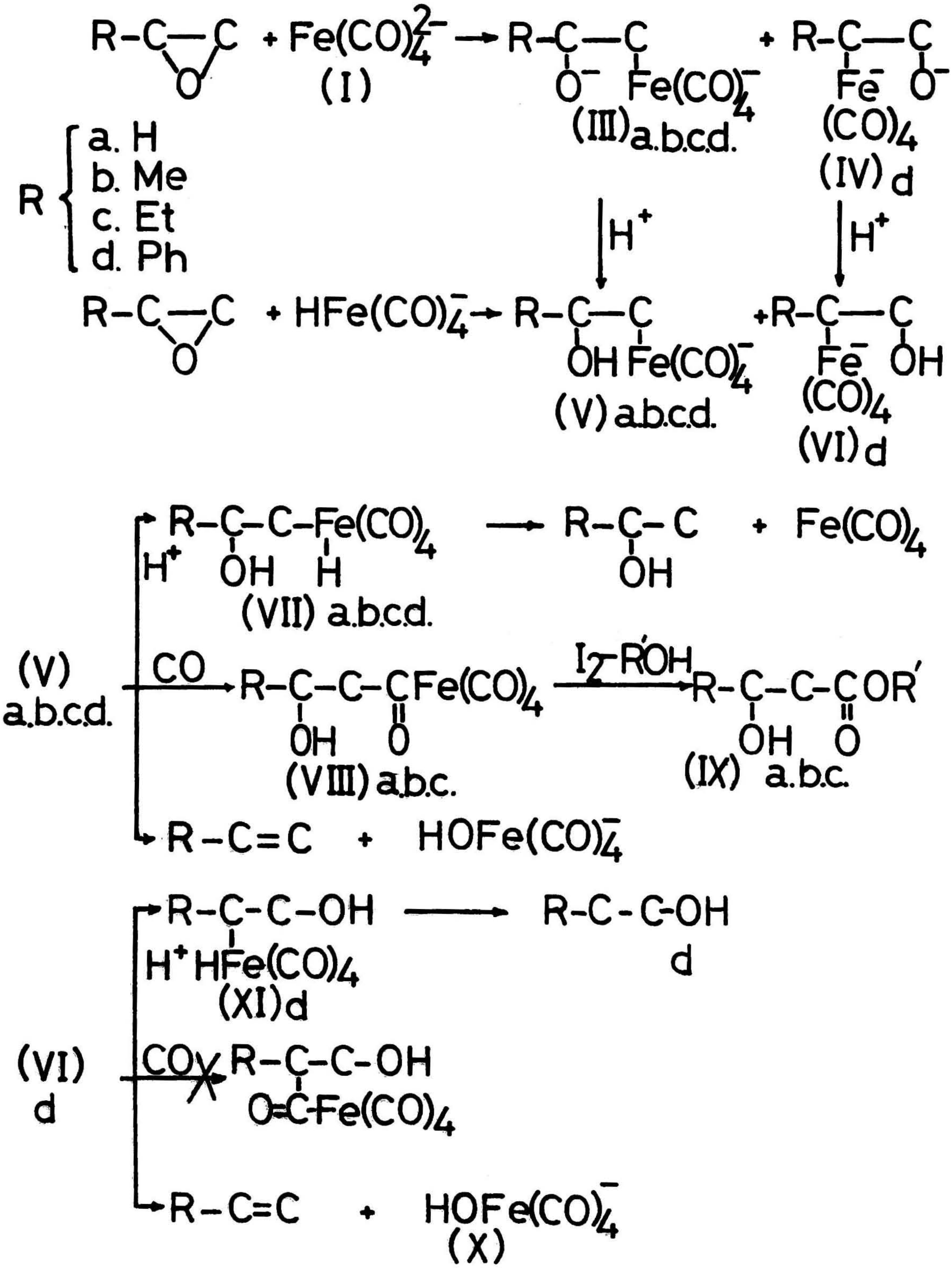
The mechanism of these reactions are not yet completely clear at the present time. But it can be concluded that $K_2Fe(CO)_4$ (KOH/$Fe(CO)_5$=4) and $KHFe(CO)_4$ (KOH/$Fe(CO)_5$=3) are the most active for the formation of olefins and alcohols, respectively. The first step of these reactions is surely the nucleophilic attack of these carbonylferrates on the olefin oxides. In general, the ring of olefin oxide is known to be opened by an S_N2 reaction of a nucleophile in a neutral or basic reaction solution.9) In the reaction of alkyl substituted ethylene oxide, the nucleophilic attack selectively occurs on the carbon which has no alkyl substituent.11) On the other hand, in the reaction of ethylene oxide which has a conjugative substituent such as styrene oxide, the nucleophilic attack occurs on the carbon which has the substituent if the bulkiness of the attacking nucleophile is neglisible,12) but the bulky nucleophile partly attacks on the nonsubstituted terminal carbon atom.13)

The reaction of olefin oxides with $K_2Fe(CO)_4$, $KHFe(CO)_4$ or $K_2Fe_2(CO)_8$ fully coincide with these observations in the literatures. The mechanism of these reactions are illustrated in Scheme 1.

In the reaction of $K_2Fe(CO)_4$ or $KHFe(CO)_4$ with propylene oxide or 1,2-butylene oxide, only the secondary alcohol or the carbonylated products (IX) derived from the complex (V), which is formed by the nucleophilic attack of the ferrates on the terminal carbon and the abstraction of a proton, are formed. The secondary alcohol may be produced by the reductive elimination *3 of the hydride complex (VII) which is formed from the complex (V) by the abstraction of a proton.

The carbonylated procuct (IX) is produced by the treatment of the acylcarbonylferrate (VIII) with iodine-ethanol. The complex

Scheme 1


R-C—C (O) + Fe(CO)₄²⁻ (I) → R-C—C (O⁻ Fe(CO)₄⁻) (III) a.b.c.d. + R-C—C (Fe⁻(CO)₄ O⁻) (IV) d
R a. H b. Me c. Et d. Ph
H⁺
H⁺
R-C—C (O) + HFe(CO)₄⁻ → R-C—C (OH Fe(CO)₄⁻) (V) a.b.c.d. + R-C—C (Fe⁻(CO)₄ OH) (VI) d
(V) a.b.c.d.
H⁺ R-C-C-Fe(CO)₄ (OH H) (VII) a.b.c.d. → R-C-C (OH) + Fe(CO)₄
CO R-C-C-CFe(CO)₄ (OH O) (VIII) a.b.c. I₂-R′OH R-C-C-COR′ (OH O) (IX) a.b.c.
R-C=C + HOFe(CO)₄⁻
(VI) d
H⁺ R-C-C-OH (HFe(CO)₄) (XI) d → R-C-C-OH d
CO R-C-C-OH (O=C-Fe(CO)₄)
R-C=C + HOFe(CO)₄⁻ (X)

(VIII) is formed by the insertion of carbon monoxide into the carbon-metal bond of the alkylcarbonylferrate (V).[*4]

In the reaction of styrene oxide with the carbonylferrates (I) or (II) , β-phenylethyl alcohol derived from the complex (IV), which is formed by the nucleophilic attack on the α-carbon of the styrene oxide, predominates over α-phenylethyl alcohol. In the reaction of mononuclear complex the ratio of β- to α-phenylethyl alcohol is about 2 : 1 and in the reaction of the dinuclear complex, the ratio is about 1 : 1. This is considered to be an effect of the bulkiness of the binuclear carbonylferrate.

The fact that the carbonylated product is not formed indicates that the carbonylation of the alkyl complex $(VI)_d$ does not occur. The reason is that the complex (VI) (R=phenyl) has a benzyl-iron bond. Recently, Cooke reported that the carbon monoxide insertion into the carbon-iron bond of benzyl-$Fe(CO)_4$ does not occur under the ambient condition.14) The rate of the insertion of carbon monoxide into alkyl-manganese bond is known to be in the order n-Propyl > Ethyl > Methyl ≫ Benzyl > CF_3.16)

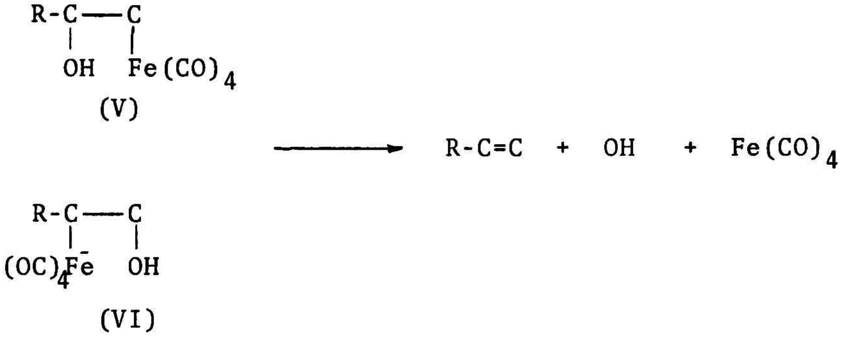
In the reaction of internal olefin oxides, the nucleophilic attack of $Fe(CO)_4^{2-}$ or $HFe(CO)_4$ may be retarded mainly by the

[*3] The example of a reductive elimination of an alkyl hydridocarbonyl iron is recently reported.14)

[*4] The insertion of carbon monoxide into iron-carbon bond of an alkylcarbonylferrate(0) is reported.1, 14,15)

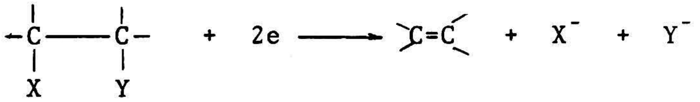
steric hyndrance of the substituents.

The mechanism of the formation of olefins is not clear. The possibility that the olefin is formed via the corresponding alcohols is rejected, because α- and β-phenylethyl alcohol did not react with $KHFe(CO)_4$ or $K_2Fe(CO)_4$. One of the possible mechanisms is the reductive elimination of β-hydroxyalkylcarbonylferrate(0) complex (V) or (VI).

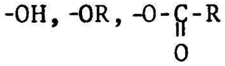


$$\begin{array}{c} \mathrm{R-\underset{OH}{C}-\underset{Fe(CO)_4}{C}} \\ \text{(V)} \\ \\ \mathrm{R-\underset{(OC)_4\bar{F}e}{C}-\underset{OH}{C}} \\ \text{(VI)} \end{array} \longrightarrow \mathrm{R-C{=}C} + \mathrm{OH} + \mathrm{Fe(CO)_4} \qquad (5)$$

In general β-substituted alkyl halides readily undergo a reductive elimination, which can be represented as follows.



$$-\overset{|}{\underset{\underset{X}{|}}{C}}-\overset{|}{\underset{\underset{Y}{|}}{C}}- + 2e \longrightarrow \rangle C{=}C\langle + X^- + Y^- \qquad (6)$$



X = halogen, Y = $-OH$, $-OR$, $-O-\underset{\underset{O}{\|}}{C}-R$

The best reducing agents for such systems are metals, e.g. sodium,17) zinc18) and magnesium.19) On the other hand, epoxides react with metal halides in the presence of magnesium amalgam to give olefins.*5) This reaction is considered to proceed by the magnesium

*5 The method of preparation of olefins from epoxides are reviewed.20) induced reductive elimination of the magnesium salt of a halohydrin.21)

In our reaction system, $Fe(CO)_4^-$ group is considered to be a pseudohalogen group and plays as the reducing agent simultaneously. This deoxygenation of olefin oxide favors the reaction conditions, 1) $K_2Fe(CO)_4$ ($KOH/Fe(CO)_5 = 4$) > $KHFe(CO)_4$ ($KOH/Fe(CO)_5 = 3$). 2) Dry ethanol solvent. 3) Protic solvents. 4) High temperature (50°C). The conditions 1) and 2) may disturb the protonation of the alkylcarbonylferrate (V) or (VI). Further protonation of (V) or (VI) will give the alcohols. In fact, the addition of water to the reaction mixture caused the yields of the olefins to decrease and that of alcohols to increase. The addition of pyridine caused the yields of the alcohols to decrease, since pyridine may abstract some proton or form a salt with $HFe(CO)_4^-$ to disturb the formation of alkylhydridocarbonylferrate (VII) . In aprotic solvents such as dry THF and acetone, the reduction does not occur, possibly because the protonation of the complex (III) or because of the low solubility of the carbonylferrates in these solvents.

Some iron carbonyl complex produced by the reductive elimination of the complex (V) or (VI) seems to regenerate the carbonylferrates $Fe(CO)_4^{2-}$, $HFe(CO)_4^-$ or $HFe_2(CO)_8^-$ with absorption of carbon monoxide, which then further react with the olefin oxides, because the yields of the olefins and the alcohols under carbon monoxide are larger than those under nitrogen.

However, the large amount of the carbon monoxide absorbed can not be explained and it suggests that some other side reaction occurs.

In the reaction of $KHFe(CO)_4$ with isoprene22) and enamine23), a large amount of carbon monoxide is absorbed, and the yields of the reduced products amount to more than 2 mol. In the reaction of $KHFe(CO)_4$ with enamines, the role of the carbon monoxide absorbed was examined in detail. It was found that the carbon monoxide was converted into carbon dioxide and pentacarbonyliron, and the formation of dinuclear hydride complex, $HFe_2(CO)_8$, with an absorption of carbon monoxide was strongly suggested (See, Chapter 4).

In the reaction of olefin oxides, the analogous reaction may possibly occur. Carbon dioxide and some $Fe(CO)_5$ was also formed in this reaction, and the reaction solution became ruby red with an absorption of carbon monoxide, indicating that some clustered complex is formed. The yield of the products was not over 1 mol, however. As the reaction is so complicated that systemetic quantitative analysis of $Fe(CO)_5$ and carbon dioxide were not carried out.

In the reaction of 1,2-butylene oxide with $K_2Fe(CO)_4$ (I), a dry and a moist ethanol solvents gave 1-butene and 2-butene, repectively, as major products. This fact can be explained by considering the equilibrium which exists between $K_2Fe(CO)_4$ and $KHFe(CO)_4$ and assuming that the reaction of the olefin oxide with $K_2Fe(CO)_4$ gives 1-butene,

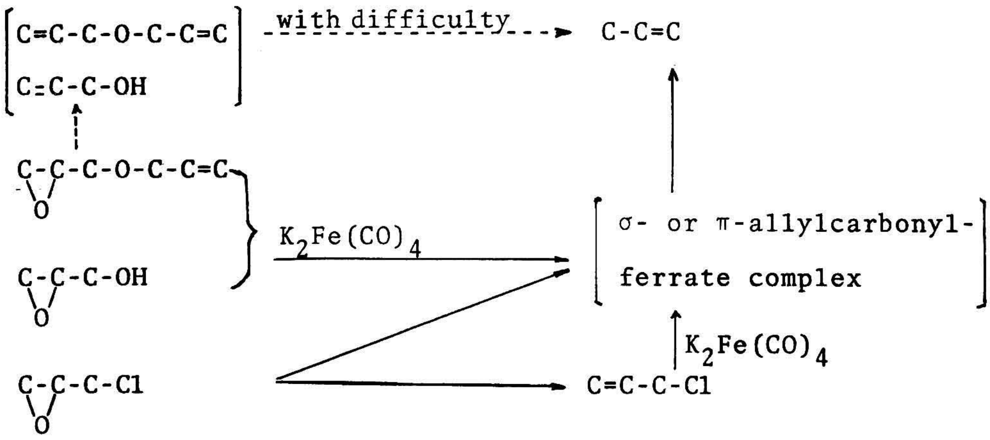
$$K_2Fe(CO)_4 + H_2O \rightleftharpoons KHFe(CO)_4 + KOH \qquad (7)$$

which is isomerized to 2-butenes by $KHFe(CO)_4$. Cramer and Lindsey showed that $KHFe(CO)_4$ is active for the isomerization of 1-butene to 2-butenes.8)

The mechanism of the formation of ethylbenzene in the reaction of styrene oxide is considered to be the hydrogenation of styrene with $KHFe(CO)_4$. Recently, styrene has been found to react with $KHFe(CO)_4$ to give ethylbenzene and a carbonylated product,15) the yield of which are very low in the reaction condition employed in that investigation.

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

On the other hand, allyl chloride and its derivatives reacts with $K_2Fe(CO)_4$ in ethanol very readily to give propylene and its derivatives.[24)] These reactions may proceed via σ- and π- allylcarbonylferrates and will be mentioned in detail later. The reaction of epichlorohydrin involves two possible routes; one is via allyl chloride, the other involves some other steps to the formation of a σ- or π-allylcarbonylferrates without the formation of allyl chloride.



Summary

The reaction between potassium carbonylferrates ($K_2Fe(CO)_4$ (I) $KHFe(CO)_4$ (II) and $K_2Fe_2(CO)_8$ (III)) and olefin oxides has been studied. Monoalkyl substituted ethylene oxides generally react with these ferrates in alcohol under ambient conditions with an absorption of carbon monoxide to give deoxygenated products, the corresponding olefins, as well as the secondary alcohols and carbonylated products, which are formed by the attack of the ferrates on the terminal carbon atom of the olefin oxides. Styrene oxide also reacts with the ferrates to give styrene as well as α- and β-phenylethyl alcohol. The latter predominates over α-isomer indicating the nucleophilic attack on the α-carbon of styrene oxide predominates.

Internal olefin oxides do not react with the ferrates.

The effects of the reaction conditions are studied and one of possible mechanisms including the elimination reaction of the β-hydroxyalkylcarbonylferrate(0) complex has been suggested.

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Chapter 2. The Reduction of Alkyl and Aryl Halides with Carbonylferrates

Introduction

In the previous chapter, potassium tetracarbonylterrates, $K_2Fe(CO)_4$ (I), $KHFe(CO)_4$ (II) , and $K_2Fe_2(CO)_8$ (III) were found to react with olefin oxides to give olefins as well as the alcohols and the carbonylated products.$^{1-3)}$ Several workers have also shown that (I) and (II) in aquous solution have a large activity in the reduction of organic compounds such as nitrobenzene, benzil, quinone,$^{4)}$ benzaldehyde,$^{5)}$ and acetylene$^{6)}$ into aniline, benzoine, hydroquinone, benzyl and ethylene, respectively.

In order to investigate the scope of the reduction ability of the carbonylferrates , the present chapter will deal with the reaction of the carbonylferrates, mainly $K_2Fe(CO)_4$, in alcohol with alkyl and aryl halides.

Alkyl and aryl iodides, and activated alkyl chlorides such as allyl chlorides$^{7)}$ and α-chloroacetone were readily reduced into the corresponding hydrocarbons, indicating carbon-iron bond is readily formed in the reaction of these halides with the carbonylferrates. In the reaction of allyl halide, it is suggested that olefin's are formed via σ- and π- ally carbonylferrates.

Experimental

The Preparation of Carbonylferrates. The potassium carbonylferrates, $K_2Fe(CO)_4$, $KHFe(CO)_4$ and $K_2Fe(CO)_8$ were prepared according to the method described in the previous chapter (P. 2)$^{8.9)}$. A 50 ml portion of a 0.22 M $K_2Fe(CO)_4$, $KHFe(CO)_4$ or 0.11 M $K_2Fe_2(CO)_8$ solution was used in each run. As mentioned in the previous chapter the ethanolic solution of $K_2Fe(CO)_4$ and $KHFe(CO)_4$ contains 2 or 1 mol[*1] of water respectively. Therefore, when a dry solution of these ferrates were required, the solvents of these ferrates were once distilled off under a vacuum and then 50 ml of a new solvent was added.

Materials. 1-Chloro-3-methyl-2-butene (a) and 3-chloro-3-methyl-1-butene (b) were prepared by bubbling hydrogen chloride into isoprene at $-10^{\circ}C$. These products were fractionated by vacuum distillation into two fractions.[*2] Alkyl halides and allyl halides, aryl halides, propargyl bromide, pentacarbonyliron and other compounds employed in this study were all commercial products which has been proved to be sufficiently pure by gas chromatography.

Reaction Procedures. To the solution of the potassium carbonylferrate a certain amount of alkyl, aryl and allyl halide or its derivatives were added, and then the mixture was agitated vigorously at $30^{\circ}C$ under an atmospheric pressure of nitrogen or carbon monoxide. After a certain reaction time, the reaction flask was connected with a cold trap immersed in liquid nitrogen and the gases in the reaction mixture were collected in the trap at 30 mmHg. The trap was allowed to warm to room temperature and then heated to $80^{\circ}C$, and the gas evolved was submitted to analysis. The liquid reaction mixture was

---

[*1] mol means mol/mol-$Fe(CO)_4^{2-}$ hereafter.

[*2] One, (a) 79%, (b) 21%; the other (a) 17%, (b) 83%.

analyzed at the same time.

Analytical Procedures. The reaction products were gas chromatographed. For the gaseous products, a column packed with dimethyl sulfolan (0.3 cmϕ, 5 m) was used. For the liquid products, a Golay R 45 column (0.25 mmϕ, 45 m) and a colum packed with SE-30 on Chromosolb (0.3 cmϕ, 3 m) were used.

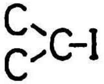
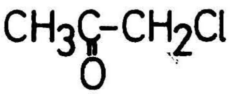
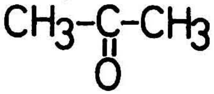
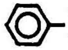
Results and Discussion

The Reaction of $K_2Fe(CO)_4$ with Alkyl and Aryl Halides. The results are summarized in Tables-1 and 2. n-Propyl iodide readily reacts with $K_2Fe(CO)_4$ in moist ethanol under a nitrogen atmosphere to give propane in a fairly good yield. The reactivity of n-propyl bromide is low and n-propyl chloride does not react with $K_2Fe(CO)_4$. The order of the reactivity, iodide > bromide > chlolide, coincides with that of the reactivity of the halide against S_N2 reaction.

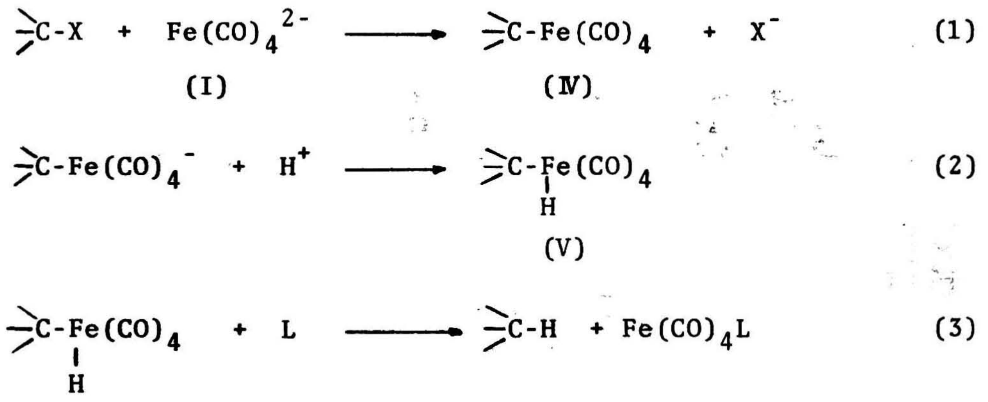
Polyhalogenated methane such as carbon tetrachloride, chloroform also react with $K_2Fe(CO)_4$ to give chloroform and and dichloromethane, respectively. Dichloromethane does not react with the ferrate. Activated alkyl halieds such as α-chloroacetone (Exp. 9) and allyl chlorides (Table-2,3 and 4) readily react with $K_2Fe(CO)_4$ to give acetone and olefins, respectively. The latter will be mentioned precisely later. Cooke reported that benzyl chloride reacts with $K_2Fe(CO)_4$ in tetrahydrofuran (THF) even at $-78^{\circ}C$ to give toluene in good yield after quenching with acetic acid.10)

Phenyl iodide also react with $K_2Fe(CO)_4$ to give benzene, however, aryl bromide and chloride does not react practically. The mechanism of these reactions can be illustrated as follows,

Table-1. The Reaction of Alkyl and Aryl Halide with $K_2Fe(CO)_4$*1

Exp. No.	Substrate	Solvent*2	Reaction Condition		Product	Yield*3
			Temp. °C	R.Time(hr)		
1	C-C-C-Cl	EtOH	30	3	C-C-C	~0
2	C-C-C-Br	EtOH	30	3	C-C-C	0.03
3	C-C-C-I	EtOH	30	3	C-C-C	0.54
4	 $\mathrm{C_2>C\text{-}I}$	EtOH	30	3	C-C-C	0.67
5	CCl_4	MeOH	30	1	$CHCl_3$	0.98
6	CCl_4	MeOH	30	8	$CHCl_3$	1.28
7	$CHCl_3$	MeOH	30	3	CH_2Cl_2	0.53
8	CH_2Cl_2	EtOH	40	10	CH_3Cl	0
9	 $CH_3\underset{\underset{O}{\Vert}}{C}-CH_2Cl$	EtOH	30	5	 $CH_3-\underset{\underset{O}{\Vert}}{C}-CH_3$	1.64
10*4	-CH_2Cl	THF	-78	3	-CH_3	>0.8
11	-Cl	EtOH	30	2.5		~0
12	-Br	EtOH	30	2.5		trace
13	-I	EtOH	30	2.5		1.05

*1 Under N_2.
*2 2.0mol of H_2O is contained except No.10.
*3 mol/mol-$Fe(CO)_4^{2-}$
*4 Quenched with AcOH after the reaction. Cooke, ref.10.



The first step may be the nucleophilic substitution reaction of the halide with the tetracarbonylferrate ion to give the complex (IV) which has alkyl or aryl-iron bond. The second step is the abstraction of a proton to form the hydridoalkyltetracarbonyliron (V),*3 which is very unstable and form alkane by the reductive elimination reaction which may be promoted by a base L such as hydroxy ion. Collman et al. recently isolated the complex (IV) from the THF solution as bis[triphenylphosphine]iminium salt and characterized.11) They found that alkane is produced only after the treatment of the complex (IV) with acetic acid. The complex (V) can not be isolated because of its unstability. L'eplattenier proved the existence of $OsMeH(CO)_4$ in THF by nmr spectra. Alkane is formed by the treatment of $OsMeH(CO)_4$ with a base such as triphenylphosphine.12) As the steps

*3 The complex (V) may be also formed from the reaction of RX with $HFe(CO)_4$ directly, which exists in equilibrium with $K_2Fe(CO)_4$. As the ratio of $KOH/Fe(CO)_5$ is 4, the main reactive species is considered to be $Fe(CO)_4^{2-}$.

(2) and (3) are considered to be very fast and the rate determining step is the step (1), the Table 1 shows the extent of the nucleophilic substitution of RX with $Fe(CO)_4^{2-}$ ion. The ability of the reduction of alkyl halide by this system is less than that of lithium aluminum hydride which reduces alkyl bromide more readily.

The Reaction of $K_2Fe(CO)_4$, $KHFe(CO)_4$ and $K_2Fe_2(CO)_8$ with Allyl Halides. Table 2 summarizes the results of the reactions, which were carried out under an atmosphere of carbon monoxide or nitrogen at 30°C. $K_2Fe(CO)_4$ reacts readily with allyl chloride, while the light brown reaction mixture immediately turns dark red, and then yellow brown. As the reaction products, propylene (the major product) and 1,5-hexadiene are obtained. The yield of propylene amounts to 1.9 mol in hydrous ethyl alcohol (Exp. 14). However, in dry ethyl alcohol, the yield of propylene decreases to 1 mol (Exp. 15). In both cases, the yield of 1,5-hexadiene is almost 0.2 mol. Under corbon

TABLE 2 THE REACTION OF $KHFe(CO)_4$, $K_2Fe(CO)_4$ AND $K_2Fe_2(CO)_8$ WITH ALLYL HALIDES AT 30°C

Exp. No.	Allyl halide	Reaction conditions*				Products**	
		Iron carbonylate	Solvent	H_2O Content	Atmosphere	Propylene	1,5-Hexadiene
14	Allyl chloride***	$K_2Fe(CO)_4$	EtOH	2	N_2	1.90	0.18
15	Allyl chloride****	$K_2Fe(CO)_4$	EtOH	0	N_2	1.00	0.15
16	Allyl chloride	$K_2Fe(CO)_4$	EtOH	2	CO	1.75	0.13
17	Allyl chloride	$KHFe(CO)_4$	EtOH	1	CO	1.31	0.18
18	Allyl chloride	$K_2Fe_2(CO)_8$	EtOH	1	CO	1.22*****	0.15*****
19	Allyl bromide	$K_2Fe(CO)_4$	EtOH	2	CO	0.75	0.16
20	Allyl iodide	$K_2Fe(CO)_4$	EtOH	2	CO	0.84	0.19
21	Allyl chloride	$K_2Fe(CO)_4$	THF	0	N_2	0.42	0
22	Allyl chloride	$K_2Fe(CO)_4$	Benzene	0	N_2	0.27	0.02

* 1 atm, 3—4 hr, allyl halide 3.0 mol/mol-$Fe(CO)_4^{2-}$

** mol/mol-$Fe(CO)_4^{2-}$

*** CO_2 (0.43 mol/mol-$Fe(CO)_4^{2-}$) and CO (0.81 mol/mol-$Fe(CO)_4^{2-}$) were evolved.

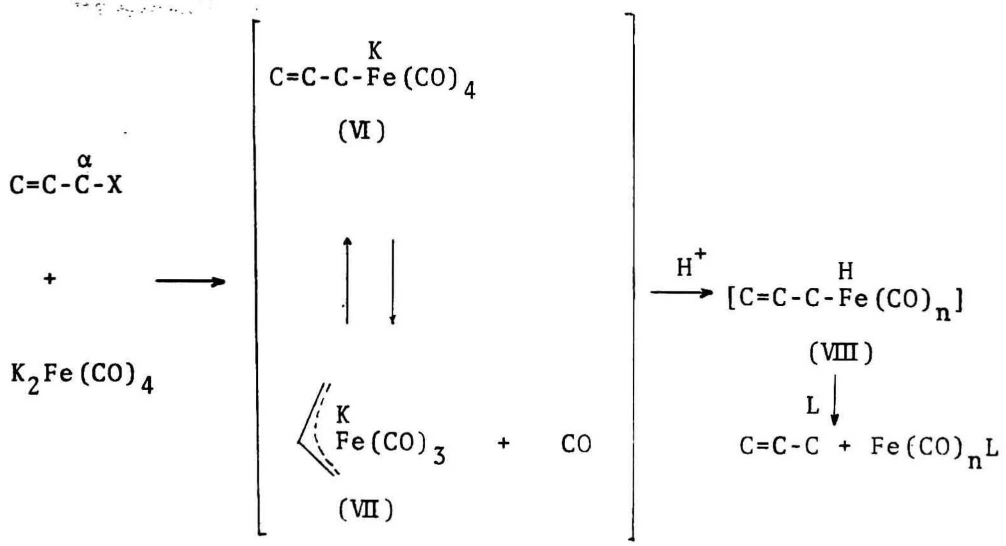
**** CO_2 (0.07 mol/mol-$Fe(CO)_4^{2-}$) and CO (0.67 mol/mol-$Fe(CO)_4^{2-}$) were evolved.

***** mol/g-atm Fe

monoxide, some carbonylation reaction occurs and the infrared spectrum of the reaction mixture treated with alcoholic solution of iodine and hydrogen chloride has a band at 1738 cm^{-1} characteristic of an ester, indicating that some acyl-iron carbonyl complex is formed. However, no further effort to identify the structure of the carbonylated product was made as the yield was very low. $KHFe(CO)_4$ and $K_2Fe_2(CO)_8$ also react with allyl chloride to give propylene and 1,5-nexadiene (Exps. 4 and 5), but the yields of propylene are less than that of the reaction of $K_2Fe(CO)_4$. The order of the iron carbonylates to the reduction seems to be; $K_2Fe(CO)_4 > KHFe(CO)_4 > K_2Fe_2(CO)_8$.

As Exps. 19 and 20 show, allyl bromide and iodide also react with $K_2Fe(CO)_4$. However, the yields of propylene are less than half that in the reaction of allyl chloride. The reason is not clear at the present time.

The reaction of $K_2Fe(CO)_4$ with allyl halide is considered to proceed via σ- and π-allyl iron carbonyl complexes and to follow the following reaction scheme.



In the first step, $Fe(CO)_4^{2-}$ makes nucleophilic attack on the α carbon of allyl halide to give the σ-allyl complex (VI), which seems ~~then~~ to be converted to the π-allyl complex (VII) with an evolution of carbon monoxide.*4 These complexes may be unstable in an moist alcoholic solution, thus abstracting a proton probably from water to give σ-allylhydridocarbonyliron complex (VIII) , which gives propylene in good yield by the reductive elimination promoted by a base such as hydroxy ion or solvents. The precise discussion about this step will be made in the reaction of trans-1-chloro-2-butene with $Fe(CO)_4^{2-}$. This reaction scheme is supported by the fact that, under a nitrogen, a considerable amount of carbon monoxide evolves (Exp. 14 and 15). 1,5-Hexadiene may be formed from a diallylcarbonyliron complex by the reductive elimination.*5

$$\mathrm{C{=}C{-}C{-}Cl} \quad + \quad \mathrm{Fe(CO)_4^{2-}} \longrightarrow [(\sigma\text{- or } \pi\text{-}\mathrm{C_3H_5})_2\mathrm{Fe(CO)}_n] \xrightarrow{L} \begin{array}{c}\text{1,5-Hexa-}\\ \text{diene}\\ + \\ \mathrm{Fe(CO)}_n\mathrm{L}\end{array}$$

The low yield of the 1,5-hexadiene in spite of the existence of excess allyl halide indicates that the rate of the protonation of the complex (VI) is very fast.

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*4 π-Cyclopentadienyldicarbonylferrate reacts with allyl chloride to give (π-allyl)(π-cyclopentadienyl)carbonyliron with an evolution of carbon monoxide.13)

$$\mathrm{C{=}C{-}C{-}Cl} \quad + \quad \mathrm{NaFe(CO)_2}(\pi\text{-}\mathrm{C_5H_5}) \longrightarrow \mathrm{C{=}C{-}C{-}Fe(CO)_2}(\pi\text{-}\mathrm{C_5H_5})$$

$$\xrightarrow{-\mathrm{CO}} (\pi\text{-allyl})\mathrm{Fe(CO)}(\pi\text{-}\mathrm{C_5H_5})$$

When 2 mol of water is present in the reaction system, a considerable amount of carbon dioxide is also evolved (Exp. 14). When the dry solvent system was used the yield of propylene is 1.0 mol and that of carbon dioxide is very low (Exp. 15). Judging from these facts, carbon dioxide is formed in the process of the reformation of a hydride species in the presence of water. The fact that 1.0 mol of propylene is formed even in the dry ethanol shows that the drying operation is not complete to eliminate water from the system. Probably, water remains as a water of crystallization of K_2CO_3.6) In dry THF and benzene the carbonylferrate is less reactive and the yield of propylene decreases to less than half of that in dry ethyl alcohol(Exps 8 and 9).

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*5 1,5-Hexadiene is formed from bis(π-allyl)nickel by the reductive elimination in the presence of a base such as carbon monoxide or triphenylphosphine.14)

*6 This incompleteness of the water elimination was observed in the reaction of $K_2Fe(CO)_4$ with acyl halide (see P 11). In the reaction of acyl halide with $K_2Fe(CO)_4$, which was prepared by the method described above, acyl halide is reduced to aldehyde without quenching with acetic acid. On the other hand $Na_2Fe(CO)_4$ which was prepared by the reduction of $Fe(CO)_5$ with sodium amalgam, reacts with acyl halide to give aldehyde after quenchig with acetic acid.10)

These solvents are unsuitable for this reaction, because the carbonylferrate attached to the wall of the reaction flask is insoluble and does not suspend in benzene and slightly soluble in THF. In these solvents, the formation of 1,5-hexadiene is also retarded.

The Reaction of trans-1-Chloro-2-butene and 3-Chloro-2-methyl-1-propene. The results of the reactions are summarized in Table-3. All of the reactions were carried out at $30^{\circ}C$ in ethyl alcohol. trans-1-Chloro-2-butene reacts with $K_2Fe(CO)_4$ to give trans-2-butene (the major produt), cis-2-butene, and 1-butene. The total yield of the olefins amounts to 1.1 mol. The distribution of these monoolefins is approximately independent of the atmophere, the amount of water and the reaction time (10-240 min). After 4 days (Exp. 27), however, the percentage of trans-2-butene increaces to 70% while those of 1-butene and cis-2-butene decreased to 15% and 15%, respectively, showing that under these conditions the isomerization among the butenes slowly occurs.$^{3,15)}$ The reaction can be explained by considering the scheme via σ- and π-allyl iron carbonyl complexes.

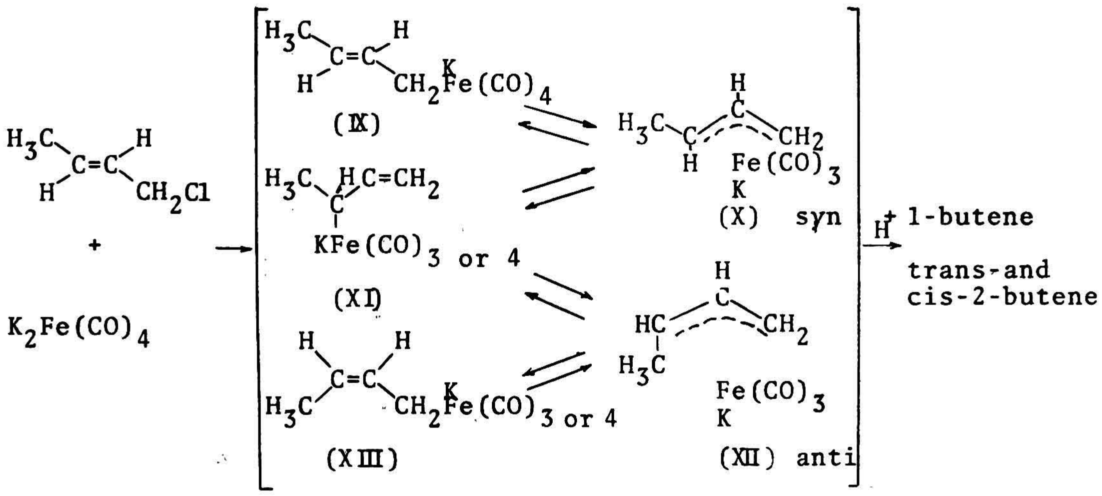


Table-3 The Reaction of $K_2Fe(CO)_4$ with the Derivatives of Allyl Halide*1

Exp. No.	Reagent*4	Reaction Condition			Products*2				
		H_2O Cont.*2	Atmos.	Time (min)	1-Butene	cis-2-Butene	trans-2-Butene	2-Methyl-Propene	Total Yield
23	trans-1-Chloro-2-butene	2	CO	10	0.16 (21)	0.14 (19)	0.44 (60)		0.74
24	trans-1-Chloro-2-butene	2	CO	60	0.15 (18)	0.15 (19)	0.51 (63)		0.81
25	trans-1-Chloro-2-butene	2	CO	240	0.20 (18)	0.20 (18)	0.72 (64)		1.12
26	trans-1-Chloro-2-butene	0	N_2	60	0.19 (19)	0.18 (19)	0.60 (62)		0.97
27	trans-1-Chloro-2-butene	0	N_2	4(d)*3	0.17 (15)	0.16 (15)	0.78 (70)		1.11
28	3-Chloro-2-methyl-1-propene	2	N_2	180				1.75	

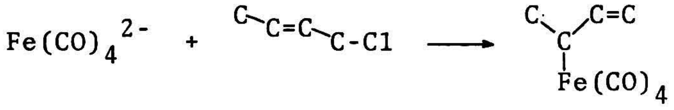
*1 In EtOH, at 30°C.

*2 mol/mol-$Fe(CO)_4^{2-}$, ( ): mol%, total yield=100%.

*3 d: day

*4 3.0 mol/mol-$Fe(CO)_4^{2-}$

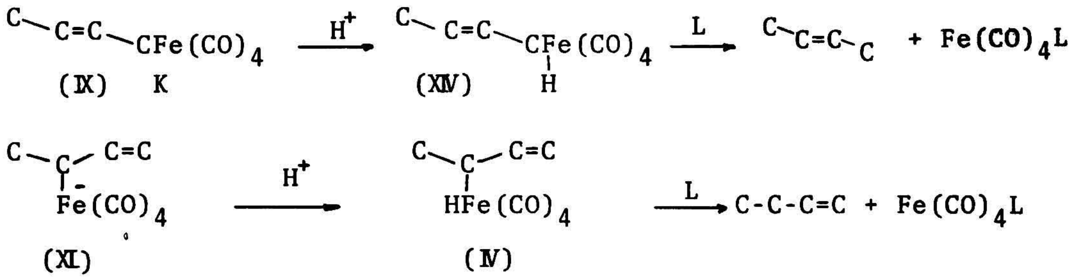
In the first step, $Fe(CO)_4^{2-}$ makes a nucleophilic attack on the α-carbon of trans-1-chloro-2-butene to form the σ-allylcarbonylferrate complex (IX), which may partly be converted to the secondary σ-allylferrate complex (XI) via syn-π-crotyltricarbonylferrate (X). The possibility that the complex (XI) is formed directly from trans-1-chloro-2-butene and $K_2Fe(CO)_4$ by S_N2' reaction is not neglected completely.

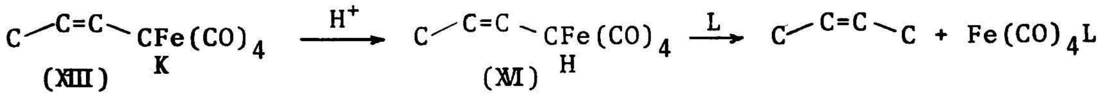


(XI)

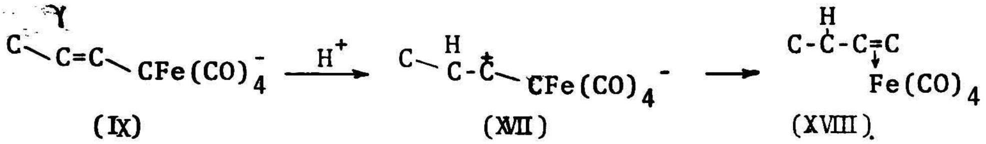
In both cases the concentration of (XI) is considered to be lower than that of (IX) because of the steric hindrance of the secondary alkyl-iron bond in the former. The formation of cis-2-butene strongly suggests the presence of cis-2-butenyliron complex (XIII), which may be formed from the complex (XI) via anti-π-crotyltricarbonylferrate (XIII).

There are several ways of the formation of butenes from these complexes. The first is the abstraction of protons from water or ethanol solvent to form σ-allylhydridocarbonyliron complexes to give butenes by the reductive elimination. Thus, (IX), (XI) and (XIII) give trans-2-butene, 1-butene and cis-2-butene, respectively.





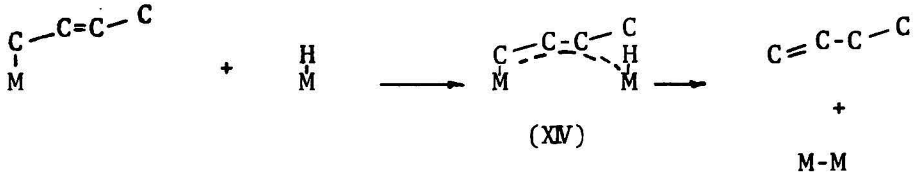
The second mechanism is the protonation of the γ-carbon atom of the σ-allyl complex to form the π-olefin iron complex (XVIII) via σ-alkyliron cation (XVII).

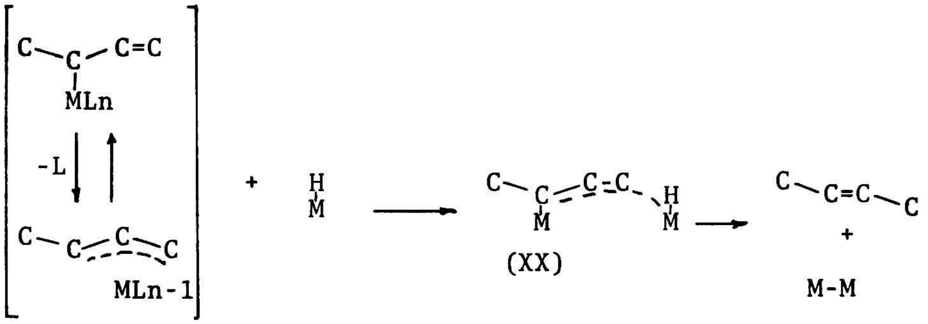


$$(XVIII) \xrightarrow{L} C\text{-}C\text{-}C{=}C + Fe(CO)_4L$$

This mechanism was proposed in the protonation of (π-cyclopentadienyl)(2-butenyl)iron.13) However, if the reaction proceeds by this mechanism the major product should be 1-butene, because the concentration of the complex (IX) is considered to be higher than that of the complexes (XI) or (XIII), and there may be no reason that the complex (XI) is much more reactive than the complex (IX). As the major product is actually trans-2-butene, and the isomerization of 1-butene to 2-butenes is slow,15) this mechanism should be rejected.

The third mechanism is the reduction of σ- or π-allyl complex with hydride species, which was proposed in the hydrogenation of crotyl halide with pentacyanocobaltate.16) In this case, the major product should be also 1-butene and the yield of olefins should be less than 0.5 mol, if the reproduction of the active species does not occur.





The direct fission of the iron carbon bond with a hydridocarbonylferrate should be rejected, because both complexes have minus charges on them.

Ultimately, the most probable mechanism is the first one. As the distribution of the productsis almost constant and it is far different from that of the mixture of butenes in thermal equilibrium,[*7] the equilibrium between the complexes (IX)∼(XIII) may exists in the reaction mixture.

3-Chloro-2-methyl-1-propene also reacts with $K_2Fe(CO)_4$ to give 2-methylpropene in a good yield (Exp. 28).

[*7] The distribution of butenes in thermal equilibrium at 25°C is 1-butene : trans-2-butene : cis-2-butene = 3 : 75 : 22.[19]

The Reaction of 1-Chloro-3-methyl-2-butene and 3-Chloro-3-methyl-1-butene. The results of the reactions are summarized in Table 4. All of the reactions were carried out in ethyl alcohol at $30^{\circ}C$. As Table 4 shows, 1-chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene react with $K_2Fe(CO)_4$ and $KHFe(CO)_4$ to give three monoolefins, 3-methyl-1-butene (A), 2-methyl-1-butene (B) and 2-methyl-2-butene (C). Under these conditions, the olefin (C) is predominant, amounting to 85~90% of the products. Exps. 29 and 33 show that the olefin (A) and (C) predominate in the initial stage of the reaction in the dry ethanol solvent and the yield of the olefin (B) is very low. As the distribution of these olefins in thermal equilibrium at $25^{\circ}C$ is A : B : C = 0.2 : 10.7 : 89.1,17) the distribution of (A) in this reaction system is abnormally high. It is also characteristic that the reaction of both 1-chloro-3-methyl-2-butene (a) and 3-chloro-3-methyl-1-butene (b) give almost the same distribution of the monoolefins. These observations are fully explained by the mechanism described in the previous reaction of trans-1-chloro-2-butene.

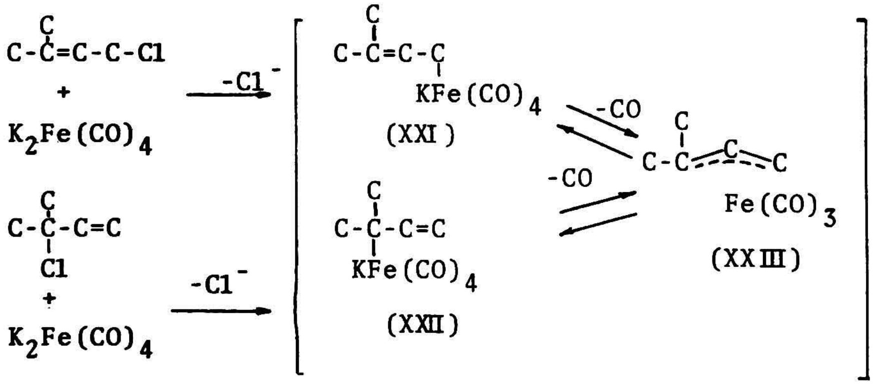


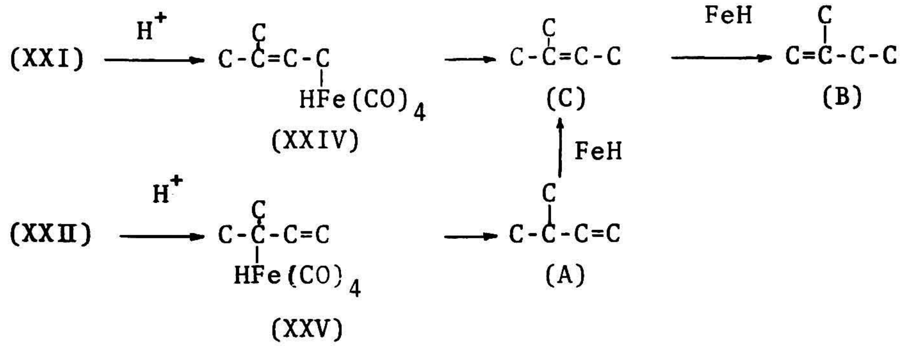
Table-4 The Reaction of $K_2Fe(CO)_4$ with 1-Chloro-3-methyl-1-butene and 3-Chloro-3-methyl-1-butene in EtOH at 30°C

Exp.	Reagent	Reaction mol ratio Reagent/ $Fe(CO)_4^{2-}$	Conditions			Distribution of Monoolefins %		
Exp. No.			H_2O content*1	Reaction*2 Time	Yield of monoolefins*1	$C{=}C{-}\overset{C}{\overset{\vert}{C}}{-}C$ (A)	$C{-}C{-}\overset{C}{\overset{\vert}{C}}{=}C$ (B)	$C{-}C{=}\overset{C}{\overset{\vert}{C}}{-}C$ (C)
29	1-Chloro-3-methyl-2-butene	1	0	1.5	0.64	20	1	79
30	1-Chloro-3-methyl-2-butene	1	0	2(d)	0.59	5	5	90
31	1-Chloro-3-methyl-2-butene	3	2	1.5	0.98	7	7	86
32	1-Chloro-3-methyl-2-butene*3	3	0	1.5	0.98	5	7	88
33	3-Chloro-3-methyl-1-butene	1	0	1.5	0.55	18	3	79
34	3-Chloro-3-methyl-1-butene	3	2	1.5	1.29	9	7	84
35	3-Chloro-3-methyl-1-butene	3	2	2(d)	1.23	9	6	85

*1 mol/mol-$Fe(CO)_4^{2-}$

*2 hr, (d):day

*3 $KHFe(CO)_4$



In the first step, 1-chloro-3-methyl-2-butene (a) and 3-chloro-3-methyl-1-butene (b) react with $K_2Fe(CO)_4$ to give σ-allyl complexes (XXI) and (XXII) ,respectively. There may be an equilibrium between these σ-allyl complexes via a π-allyl complex (XXIII). As the complex (XXII) is less stable because of the tertiary alkyl-iron bond than the complex (XXI), which has the primary alkyl-iron bond, the concentrarion of (XXI) is higher than that of (XXII). These σ-ally complexes abstract protons to form σ-allylhydridocarbonyliron complexes (XXIV) and (XXV), respectively, and the former gives 2-methyl-2-butene (C) and the latter gives 3-methyl-1-butene (A). 2-Methyl-1-butene (B) may be formed by the isomerization of (A) and (C). In this reaction system carbon monoxide was also detected as in the case of trans-1-chloro-2-butene, supporting the formation of π-allyl complex (XXIII).

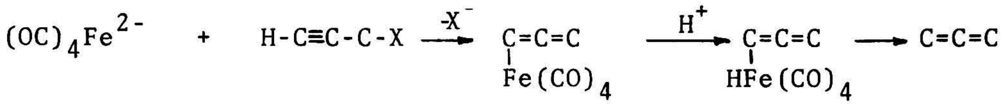
The Reaction of Propargyl Bromide with $K_2Fe(CO)_4$. Propargyl bromide also reacts with the ethanol solution of $K_2Fe(CO)_4$ at $30^\circ C$ under a nitrogen atmosphere. After 2 hr, methylacetylene (0.47 mol, 85%) and allene (0.08 mol, 15%) were obtained.

$$C\equiv C\text{-}C\text{-}Br \; + \; K_2Fe(CO)_4 \xrightarrow[H_2O(2\ mol)]{EtOH} C\equiv C\text{-}C \; + \; C=C=C$$

0.47 mol 0.08 mol

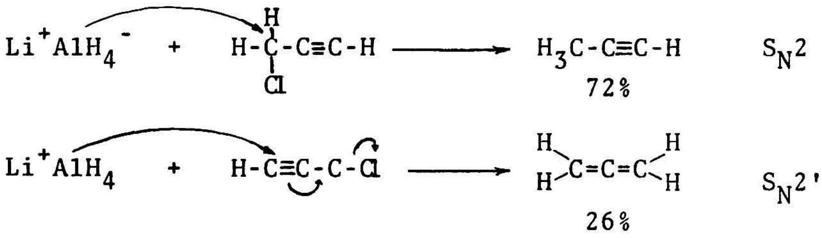
(85% 15%)

The former may be formed by the normal nucleophilic substitution followed by the protonation and the reductive elimination. The latter is considered to be formed by the S_N2' reaction of propargyl bromide with $K_2Fe(CO)_4$. The analogous reaction was observed in the reaction of lithium aluminum hydride with propargyl halide.[18)]



$$(OC)_4Fe^{2-} \; + \; H\text{-}C\equiv C\text{-}C\text{-}X \xrightarrow{-X^-} \underset{Fe(CO)_4}{C=C=C} \xrightarrow{H^+} \underset{HFe(CO)_4}{C=C=C} \longrightarrow C=C=C$$

In the reaction of lithium aluminum hydride with propargyl chloride, methylacetylene (72%) is formed by S_N2 reaction and allene (26%) is formed by S_N2' reaction.



$$Li^+AlH_4^- \; + \; H\text{-}\overset{H}{\underset{Cl}{C}}\text{-}C\equiv C\text{-}H \longrightarrow \underset{72\%}{H_3C\text{-}C\equiv C\text{-}H} \qquad S_N2$$

$$Li^+AlH_4 \; + \; H\text{-}C\equiv C\text{-}C\text{-}Cl \longrightarrow \underset{26\%}{H_2C=C=CH_2} \qquad S_N2'$$

Summary

The reactions of potassium carbonylferrates ($K_2Fe(CO)_4$ (I), $KHFe(CO)_4$ (II) and $K_2Fe_2(CO)_8$ (III)) in alcohol with alkyl, aryl and allyl halides have been studied. These halides react with (I), (II) or (III) to give the corresponding hydrocarbons via alkyl- aryl- and σ- or π-allylcarbonylferrates, respectively. The reactivity of alkyl and aryl halide decreases in the order RI > RBr > RCl .

Activated alkyl halides such as allyl halide, benzyl halide and α-haloacetone give the corresponding reduced products, propylene, toluene and acetone,respectively, even when the halides are chlorides. The derivatives of allyl halides such as trans-1-chloro-2-butene, 1-chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene are also reduced with (I) or (II) to give the corresponding olefins and their isomers. The mechanism of these reactions including σ- and π- allyl-iron comlexes has been discussed.

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Chapter 3. The Reaction of Potassium Carbonylferrates with Isoprene

Introduction

Potassium carbonylferrates ($K_2Fe(CO)_4$ (I), $KHFe(CO)_4$ (II) , and $K_2Fe_2(CO)_8$ (III)) in alcohol were found to have a characteristic reducing ability. The reaction of 1,2-olefin oxides with the ferrates gives the corresponding olefins as well as the alcohols and carbonylated products.1,2) Alkyl and aryl halides were reduced to the corresponding hydrocarbons.3) The scope of these rections has been described precisely in the previous chapters.

The present chapter will deal with the reaction of the carbonylferrates, mainly $KHFe(CO)_4$, with isoprene.4) The results obtained indicate that isoprene is selectively reduced to give three different monoolefins, and that the yields and distribution of the olefins are remarkably affected by the reaction conditions. The reduction of monoolefins into isopentane was not observed. As the yield of carbonylated product was very low, it could not be characterized.

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 according to the method described in a previous chapter (see P 2). An 80 ml portion of 0.14 M $KHFe(CO)_4$ or $K_2Fe(CO)_4$, and 0.07 M $K_2Fe_2(CO)_8$ was used in each run. When $KHFe(CO)_4$ is prepared, an equivalent mole of water is formed:

$$Fe(CO)_5 + 3\ KOH \longrightarrow KHFe(CO)_4 + K_2CO_3 + H_2O$$

Therefore when a dry solution of $KHFe(CO)_4$ was required, the solvent of $KHFe(CO)_4$ solution was once distilled off under vacuum, and then 80 ml of a new dry solvent was added.

Materials. The isoprene, pentacrbonyliron, ethanol, tetrahydrofuran(THF), propyl alcohols and other compounds employed in this study were all commercial products. THF was dried over sodium dispersion. Ethanol, propyl alcohols were dried over magnesium alkoxides.$^{6)}$

Reaction Procedures. Under Atmospheric Pressure. To the solution of the potassium carbonylferrates described above, 5 ml (50 mmol) of isoprene and 0.4 ml of cyclopentane, as internal standard for analysis, were added. The mixture was then agitated for a certain reaction time at 30°C under an atmosphere of carbon monoxide, nitrogen, or hydrogen. After a certain reaction time, a 0.5 ml sample of the solution was removed and then diluted with 1.5 ml of cyclohexane. This cyclohexane solution was immediately submitted to analysis.

Under Hydrogen Pressure. An autoclave (100 ml) equipped with a magnetic stirrer was used. One and a half ml of $Fe(CO)_5$, 33 ml of 1 N KOH solution in ethyl alcohol, and 5 ml of isoprene were placed into the autoclave at -80°C. After the air in the autoclave had been replaced with nitrogen, hydrogen were introduced at 60 kg/cm^2. The autoclave was then kept at a certain temperature for 5 hr.

Analysis of the Products. The reaction products (three different olefins were identified by gas chromatography (PEG=Goley column, 0.25 mm x 45 m) using the authentic samples. Further, the monoolefins produced were confirmed by being converted to isopentane: after hydrogenation with Raney nickel, the peaks of the monoolefins in a gas chromatogram vanished and a new peak of isopentane appeared.

Results

The Reaction of $KHFe(CO)_4$ and $K_2Fe(CO)_4$ with Isoprene in Ethyl Alcohol. The results of the reactions are summarized in Table 1 and in Figs. 1, 2 and 3. All of the reactions were carried out in ethyl alcohol at 30°C.

Isoprene slowly reacts with alcoholic solution of $KHFe(CO)_4$ with absorbtion of carbon monoxide, while the reaction solution turns from light brown to deep ruby red. As the reaction products, three monoolefins, 3-methyl-1-butene (A), 2-methyl-1-butene (B), and 2-methyl-2-butene (C) are obtained. The time prots of the carbon monoxide absorbed and the products are shown in Fig. 1. The reaction ceases after 12 days and carbon monoxide absorbed and yields of the olefins amount to 1.06 mol[*1] and 1.96 mol, respectively. Isopentane is not obtained, indicating that $KHFe(CO)_4$ is not active for the reduction of monolefins under the condition employed.

The infrared spectrum of the reaction mixture has strong bands at 2005, 1982 and 1971 cm^{-1} characteristic of νFeC≡O and a medium band at 1700 cm^{-1}. The band at 1700 cm^{-1} seems to be attributable to some carbonyl compounds, indicating that the carbonylation also occurs. However, no efforts for the identification has been made since the yield of the products was very low.

The Yield of the Monoolefins. The yield of the monoolefis is

[*1] 'mol' means mol/g.atom.Fe hereafter.

TABLE 1. THE REACTION OF $KHFe(CO)_4$ WITH ISOPRENE

Exp. No.	Reaction conditions*1			Yield of*2 monoolefins	Distribution of monoolefins (%)		
	Atmosphere	Time (hr)	H_2O*2 content		$\mathrm{C{-}\overset{C}{\overset{|}{C}}{-}C{=}C}$ (A)	$\mathrm{C{=}\overset{C}{\overset{|}{C}}{-}C{-}C}$ (B)	$\mathrm{C{-}\overset{C}{\overset{|}{C}}{=}C{-}C}$ (C)
1	N_2	2	0	0.15	20	13	67
		5	0	0.32	29	13	58
		7(d)	0	0.95	38	11	51
2	N_2	2	1	0.15	19	14	57
		5	1	0.30	26	13	61
		14(d)	1	1.40	32	16	52
3	N_2	4	10	0.21	12	20	68
		7(d)	10	1.32	18	16	66
4	CO	2	1	0.11	14	13	73
		7	1	0.29	13	13	74
		24	1	0.50	13	13	74
		12(d)	1	1.96	21	13	66
5	H_2	6	1	0.46	23	14	63
		18(d)	1	1.84	28	18	54
6*3	N_2	4	0	0.28	23	15	63
		3(d)	0	0.33	29	15	56
		7(d)	0	0.46	29	17	54

*1 In EtOH, at 30°C　　*2 mol/mol-$Fe(CO)_4^{2-}$　　*3 $K_2Fe(CO)_4$　　*4 (d): day

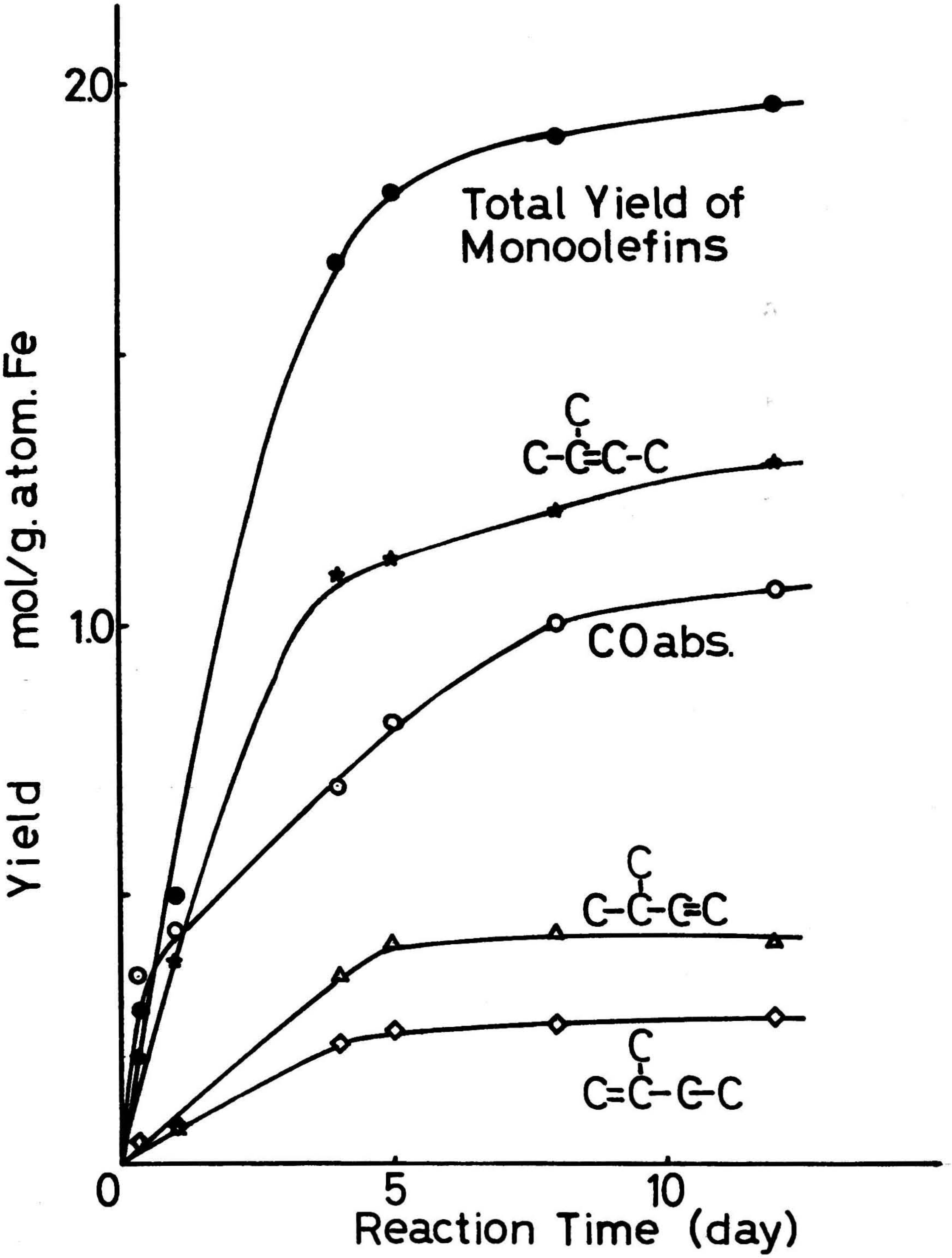


Fig.1. The Reaction of $KHFe(CO)_4$ with Isoprene

remarkably affected by the reaction conditions, atmosphere and the amount of water contained in the reaction system. These results are summarized in Fig. 2.

The reduction of isoprene also proceeds under a nitrogen atmosphere, but the yield of the olefins are 1.4 mol and lower than that under carbon monoxide (1.96 mol). In dry ethyl alcohol under nitrogen the yield of monoolefins is 0.95 mol at its maximum. When there is 1 or 10 mol of water, the yield increases to about 1.5 mol. The reduction of isoprene also proceeds under a hydrogen atmosphere, with a slow absorption of hydrogen, which amounts to 0.45 mol after 18 days and the yield of the olefins amounts to 1.84 mol. In dry ethyl alcohol, $K_2Fe(CO)_4$ also reduces isoprene, but more sowly, and the yield of the olefins is less than 0.5 mol.

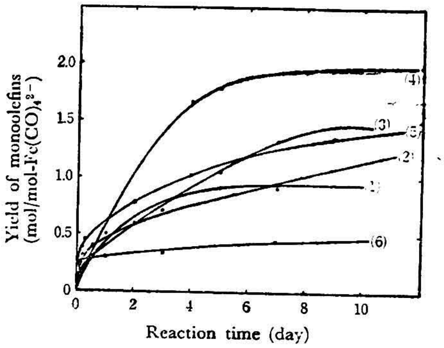


Fig. 2 Yield of monoolefins *vs.* time plots for the reaction of $KHFe(CO)_4$ with isoprene (in EtOH, at 30°C, 1 atm).
Number: (Exp. No. in Table 1)
(H_2O content mol/mol-$Fe(CO)_4^{2-}$, atmosphere)
(1) (0, N_2) (2) (1, N_2)
(3) (10, N_2) (4) (1, CO)
(5) (1, H_2) (6) $K_2Fe(CO)_4$ (0, N_2)

The Distribution of the Olefins. As Fig. 3 shows, the amount of water and the atmosphere have a great effect on the distribution of olefins (A) and (C). The percentage of the olefin (B), however, is almost constant (about 15 ± 5%) in all cases. In general, the percentage of (A) increases as the reaction prodeeds. In dry ethyl alcohol under nitrogen the percentage of (A) finally amounts to 38% (Exp. 1).

In the presence of 1 or 10 mol of water, the percentages of (A) decrease to about 32 or 18%, respectively (Exps. 2 and 3). Under carbon monoxide or hydrogen, the percentage of (A) also decreases to about 21 or 28%, respectively (Exps. 4 and 5). The periodical change of the distribution of the olefins is not attributed to the isomerization of the olefins, i.e. the olefin (A) is not formed by the reaction of the mixture of the olefins (B) and (C) (14 : 86) with $KHFe(CO)_4$.*2

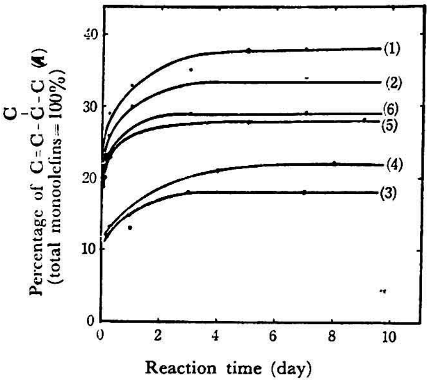


Fig. 3 Percentage of (A) *vs.* time plots for the reaction of $KHFe(CO)_4$ with isoprene (in EtOH, at 30°C 1 atm).
Number: (Exp. No. in Table 1)
(H_2O content mol/mol-$Fe(CO)_4^{2-}$, atmosphere)
(1) (0, N_2) (2) (1, N_2)
(3) (10, N_2) (4) (1, CO)
(5) (1, H_2) (6) $K_2Fe(CO)_4$ (0, N_2)

The Reaction of $KHFe(CO)_4$ with Isoprene in Other Solvents. The solvent effects on this reaction were examined; the results are summarized in Tables 2 and 3.

TABLE 2. THE REACTION OF $KHFe(CO)_4$ WITH ISOPRENE

Exp. No.	Reaction conditions*				Yield of** mono-olefins	Distribution of monoolefins (%)		
	Atmosphere	Solvent	Time (hr)	H_2O** content		$C-\overset{C}{C}-C=C$ (A)	$C=\overset{C}{C}-C-C$ (B)	$C-\overset{C}{C}=C-C$ (C)
7	N_2	*iso*-PrOH	4	0	0.14	~0	14	86
			4(d)***	0	0.51	11	18	71
			12(d)	0	0.62	13	17	70
8	N_2	*iso*-PrOH	5	1	0.38	2	14	84
			8(d)	1	1.05	6	17	77
9	CO	*iso*-PrOH	5	1	0.35	3	10	87
			10(d)	1	0.35	3	10	87
10	N_2	*n*-PrOH	5	1	0.34	22	17	61
			9(d)	1	1.18	23	18	59
11	N_2	*n*-PrOH	5	10	0.45	3	14	83
			9(d)	10	1.41	6	16	78
12	CO	*n*-PrOH	5	1	0.26	4	11	85
			5(d)	1	1.06	3	10	87

* at 30°C ** mol/mol-$Fe(CO)_4^{2-}$ *** (d): day

TABLE 3. THE REACTION OF $KHFe(CO)_4$ WITH ISOPRENE

Exp. No.	Reaction conditions*		Yield of** monoolefins	Distribution of monoolefins (%)		
	Solvent	Time (day)		$\overset{C}{\overset{\vert}{C-C}}-C=C$ (A)	$\overset{C}{\overset{\vert}{C=C}}-C-C$ (B)	$\overset{C}{\overset{\vert}{C-C}}=C-C$ (C)
13	Methyl ethyl ketone	4 (hr)	0.14	9	9	82
		18	0.50	11	12	77
14	Tetrahydrofuran	11	0.21	9	8	83
15	Isopropyl ether	8	0.16	14	24	72

* N_2: 1 atm, H_2O content 0, at 30°C. ** mol/mol-$Fe(CO)_4^{2-}$

In n- and isopropyl alcohol, the monoolefins are also produced (Table 2). The water added and atmosphere have effects on the yield and distribution of the olefins (A and C) similar to those in ethyl alcohol; the presence of a water and carbon monoxide atmosphere promotes the reduction, but is less favorable for the production of (A).

As Table 3 shows, in aprotic solvents such as tetrahydrofuran, methyl ethyl ketone and isopropyl ether, the reduction occurs much more slowly and the maximum yield of the olefins is less than 0.5 mol.

The Reaction of Isoprene under Hydrogen Pressure. The results are summarized in Table 4. Under 60 kg/cm^2 of hydrogen at 35^{o}C, the reduction occurs more rapidly to give 2.5 mol of the olefins (compare Exp. 16 with Exp. 5). Even at 100^{o}C, the yield of the olefins is 2.5 mol (Exp. 17), indicating that the carbonylferrate, $HFe(CO)_4^-$, does not catalyze the hydrogenation of isoprene under the conditions

*2 1-Butene is slowly isomerized into 2-butenes with $HFe(CO)_4^-$.7) used and that the ferrate acts as a reducing reagent in the reaction.

TABLE 4. THE REACTION OF $KHFe(CO)_4$ WITH ISOPRENE

Exp. No.	Reaction conditions*		Yield of monoolefins	Distribution of monoolefins (%)		
	Temperature °C	Time (hr)		$C-\overset{C}{\overset{\vert}{C}}-C=C$ (A)	$C=\overset{C}{\overset{\vert}{C}}-C-C$ (B)	$C-\overset{C}{\overset{\vert}{C}}=C-C$ (C)
16**	35	5	2.59	10	23	61
17**	100	5	2.51	15	24	61
18***	100	5	2.42	26	17	57

* In EtOH, H_2: 60 kg/cm², H_2O content 1 mol/mol-$Fe(CO)_4^{2-}$

** $KHFe(CO)_4$ (11 mmol): isoprene=1 : 4.5 (in mole ratio)

*** $KHFe(CO)_4$ (4 mmol): isoprene=1 : 13.5 (in mole ratio)

**** mol/mol-$Fe(CO)_4^{2-}$

The Reaction of $K_2Fe_2(CO)_8$ with Isoprene. The results are summarized in Table 5. All the reactions were carried out in ethyl alcohol. $K_2Fe_2(CO)_8$ also reacts with isoprene with absorbtion of 0.66 mol of carbon monoxide to give 1.37 mol of the monoolefins.

TABLE 5. THE REACTION OF $K_2Fe_2(CO)_8$ WITH ISOPRENE

Exp. No.	Reaction conditions*			Yield of** monoolefins	Distribution of monoolefins (%)		
	Atmosphere	H_2O** content	Time (day)		$C-\overset{C}{\overset{\vert}{C}}-C=C$ (A)	$C=\overset{C}{\overset{\vert}{C}}-C-C$ (B)	$C-\overset{C}{\overset{\vert}{C}}=C-C$ (C)
19	N_2	0	5	0.32	31	11	58
		0	14	0.53	31	14	55
20	N_2	1	5	0.86	3	17	80
		1	14	0.69	3	16	82
21	CO	1	5	1.06	4	13	83
		1	14	1.37	3	10	88

* EtOH solution, at 30°C

** mol/mol-g atm Fe, which exists as iron carbonylate.

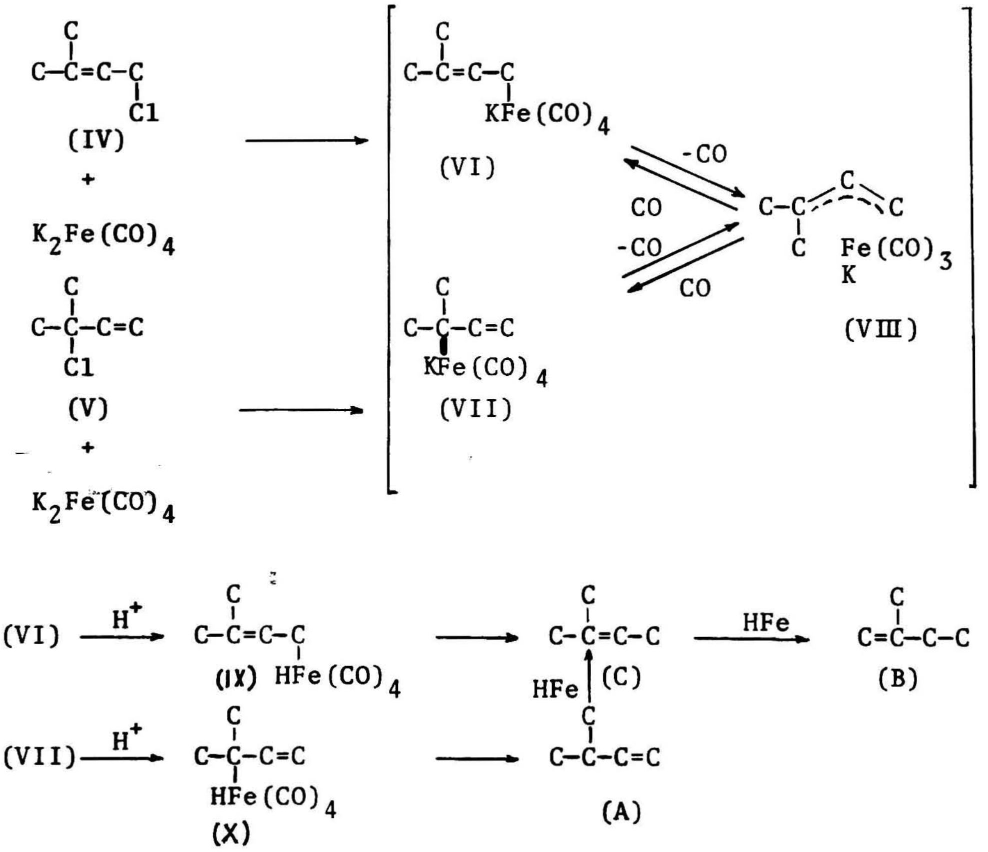
In dry ethyl alcohol under nitrogen, the reduction occurs slowly to give about 0.5 mol of the olefins, and the percentage of (A) amounts to 31% (Exp. 19). When 1 mol of water is present, the yield increases to about 0.9 mol, but the percentage of (A) decreaces to only 3% (Exp. 20).

Discussion

Isoprene is reduced with alcoholic $KHFe(CO)_4$ with absorption of carbon monoxide into three different monoolefins, but isopentane was not formed even under hydrogen pressure (60 kg/cm^2) and at 100°C. This is the limitation of the reducing ability of the hydrocarbonylferrate $KHFe(CO)_4$. The reduction does not proceed catalitically but the yield exceeds 1 mol when the reaction is carried out under a carbon monoxide atmosphere and/or some water is present in the reaction system. This fact shows that the mechanism of the reduction is not simple but the active hydride species are reproduced in these reation systems. The refomation of active hydride species with absorption of carbon monoxide in the presence of water is also observed in the reduction of olefin oxides[1,2], and enamines(see P 97).

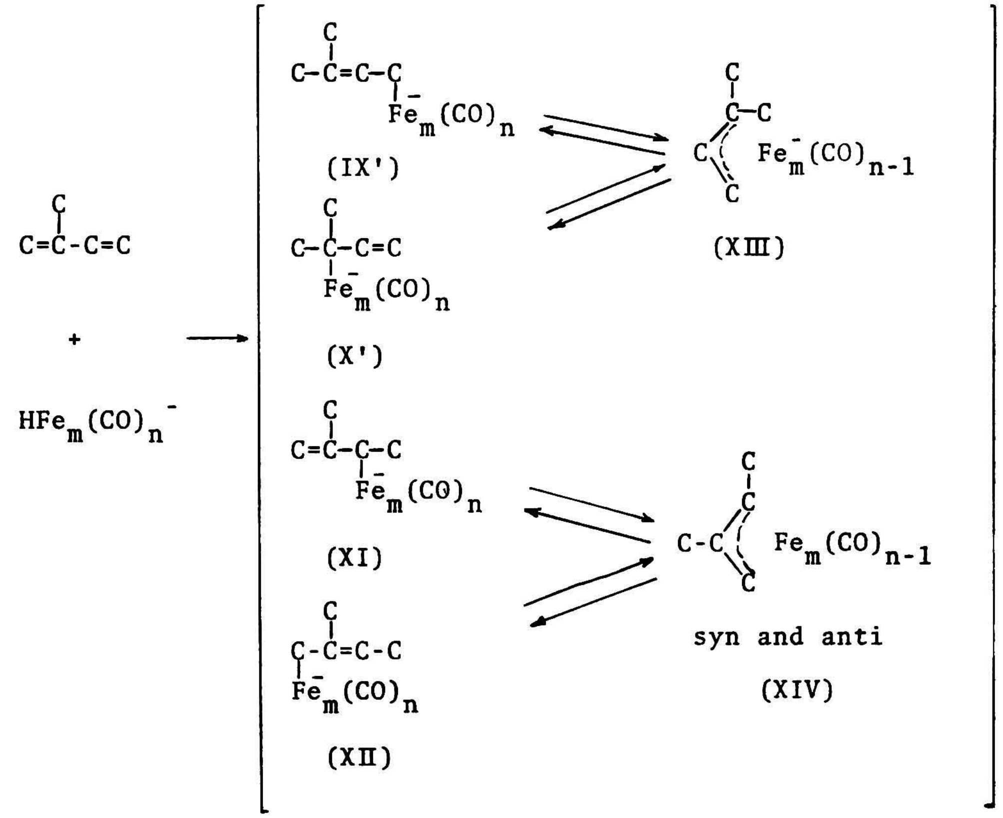
In Exp. 1, the ratio of the olefins (C)/(A) is 5.2 during the first one day. However, the ratio of the olefins newly formed during the last 11 days is 2.7. As the distribution of these olefins in the thermal equilibrium at 25°C is A : B : C = 0.2 : 10.7 : 89.1,[8] this observation is interesting. This fact suggests that the reduction proceeds at least in two ways. In the light of the reduction of olefin oxides[1,2] and enamines (see P 98), one may be the reduction with the mononuclear hydride, $HFe(CO)_4$, and the other may be the reduction with polynuclear hydrides such as $HFe_2(CO)_8$. Indeed, the reaction mixture turns from light brown to deep red, indicating the formation of clustered complexes. The promoting effect of water and carbon monoxide on the reduction may be attributed to the formation of the new hydrides, which reacts further with isoprene.

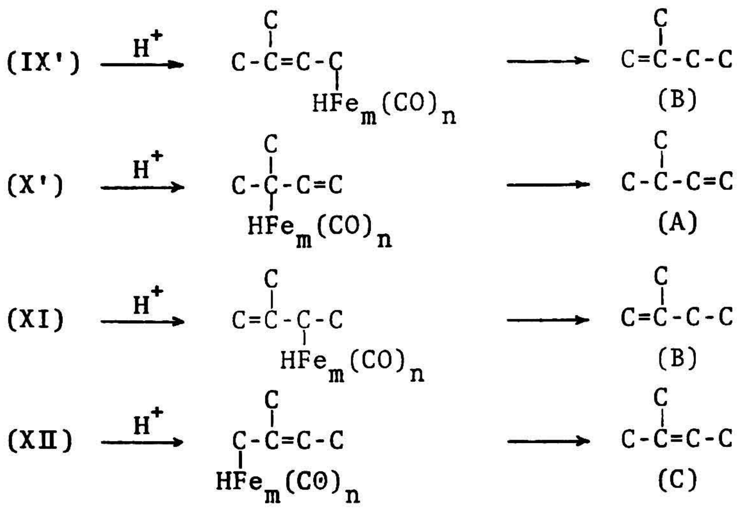
The mechanism of the reduction is not completely clear at the present time. There is, however, a reaction which is closely related to the reduction of isoprene. 1-Chloro-3-methyl-2-butene (IV) and 3-chloro-3-methyl-1-butene (V) were found to react with $K_2Fe(CO)_4$ in alcohol to give almost the same distribution of monoolefins.$^{3)}$ These reactions are reasonably considered to proceed by the following scheme.



At first, (IV)and (V) are nucleophilically attacked by $Fe(CO)_4^{2-}$ to give alkylcarbonylferrate complexes (VI) and (VII), which are in equiliblium via π-allyl comlex (VIII). The complexes(VI) and (VII) abstract protons to give alkylhydridocarbonylferrates (IX) and (X), which give the olefins (C) and (A) by the reductive elimination. Small amount of (B) may be formed by the isomerization of (C).

In the light of these discussions, the mechanism of the present reaction is considered to be partly represented by the following scheme. The hydride, $HFe(CO)_4$ and $HFe_2(CO)_8$ are represented as $HFe_m(CO)_n$.





$$(IX') \xrightarrow{H^+} C-\overset{C}{C}=C-\underset{HFe_m(CO)_n}{C} \longrightarrow \underset{(B)}{C=\overset{C}{C}-C-C}$$

$$(X') \xrightarrow{H^+} C-\overset{C}{\underset{HFe_m(CO)_n}{C}}-C=C \longrightarrow \underset{(A)}{C-\overset{C}{C}-C=C}$$

$$(XI) \xrightarrow{H^+} C=\overset{C}{C}-\underset{HFe_m(CO)_n}{C}-C \longrightarrow \underset{(B)}{C=\overset{C}{C}-C-C}$$

$$(XII) \xrightarrow{H^+} \underset{HFe_m(CO)_n}{C}-\overset{C}{C}=C-C \longrightarrow \underset{(C)}{C-\overset{C}{C}=C-C}$$

First, isoprene inserts between the hydrogen-iron bond of the hydridocarbonylferrate to form the alkylcarbonylferrates (XI), (XII), (X') and (IX'), which are in equilibrium via π-allylcarbonylferrates (XIII) and (XIV). Monoolefins are formed by the protonation of (XI), (XII) , (IX') and (X'), and the reductive elimination. As the Protonation and the reductive elimination proceed very fast,3) the rate determining step is the insertion of isoprene into the hydrogen-iron bond.

The distribution of the olefins, (A), (B) and (C), are determined by the following factors and it is so complicated that it is difficult to explain the effects of water, solvent and atmosphere.

1) The direction of the addition of the hydrides to isoprene.

2) The equilibrium between the alkylcarbonylferrates. 3) The rate of the protonation and the reductive elimination. 4) The isomerization between the monoolefins.

The hydrogen atmosphere and the hydrogen pressure promotes the reduction, and it is interesting that the yield of the olefins does not exceed 2.6 mol. However, the role of hydrogen is not clear at the present time.

Summary

The reaction between potassium carbonylferrates($KHFe(CO)_4$, $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$) and isoprene has been studied. Isoprene is selectively reduced at room temperature to give three olefins, 3-methyl-1-butene (A), 2-methyl-1-butene (B) and 2-methyl-2-butene (C). The reaction conditions (solvents, atmospheres, additives such as water) have a great effect on the yields and the distribution of the olefins. Under carbon monoxide in the presence of water, the reduction is highly promoted, giving 2 mol/mol-$Fe(CO)_4^{2-}$ of olefins. The percentage of (B) is almost constant (about 15%) in all cases, but the percentages of (A) and (C), very dependent on the reaction conditions, change in the 3∿40 and 50∿80% ranges respectively. The reaction is suggested to proceed via some kinds of σ- and π-allylcarbonyliron complexes.

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Appendix

The Selective Reduction of Cinnamaldehyde into 3-Phenylpropionaldehyde

Introduction

Conjugated compounds such as cinnamaldehyde, acrolein, metyl vinyl ketone, acetophenone, acrylonitrile, as well as diolefines such as isoprene[1] reacts with $KHFe(CO)_4$ in alcohol with an absorption of carbon monoxide. Any carbonylated products could not be detected, however. In the reaction of cinnamaldehyde, selectively reduced product, 3-phenylpropionaldehyde was formed. In other cases, products could not be detected by gas chromatography.

Experimental

$KHFe(CO)_4$ and $K_2Fe(CO)_4$ (11 mmol in 50 ml EtOH) was prepared as described in the previous chapter (see P 2). To this solution 3.7 mol* of α,β-unsaturated carbonyl compounds was added at 30°C and agitated for 4 hr. Then 100 ml of water was added and extracted with two portions of 100 ml of benzene-ether (10:1). The extracted solution was concentrated under vacuum to 20 ml and was analyzed by gas chromatography using an appropriate internal standard, (Columns: SE-30 on Chromosorb, 3 mm^{ϕ} x 3 m and DLP on celite, 4 mm^{ϕ} x 3 m).

Results and Discussion

Cinnamaldehyde is selectively reduced into 3-phenylpropionaldehyde with alcoholic $KHFe(CO)_4$. Other reduced products such as 3-phenylpropyl alcohol or cinnamyl alcohol were not detected. The results are summarized in Table 1.

* 'mol' means mol/mol-$Fe(CO)_4{}^{2-}$.

Table-1 The Reduction of Cinnamaldehyde into 3-Phenylpropionaldehyde

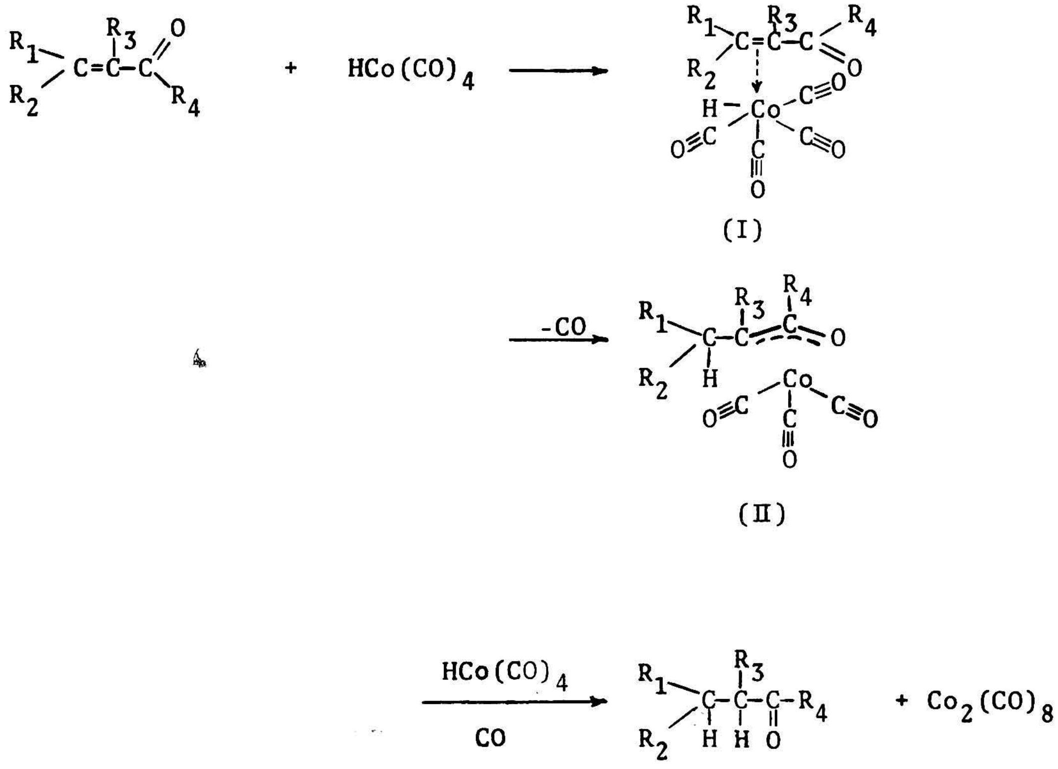
Exp. No.	Calbonyl-farrate	React. Atmos.	Cond.			
			Temp.	Time(hr)	CO_{abs}*	Yield*
1	$KHFe(CO)_4$	CO	30 °C	4	1.6	0·56
2	$KHFe(CO)_4$	N_2	30	4	-	0·53
3	$K_2Fe(CO)_4$	CO	30	4	1·4	0·15
4	$K_2Fe(CO)_4$**	CO	30	4	-	-

* mol/mol-$Fe(CO)_4^{2-}$

** Dry EtOH solvent was used.

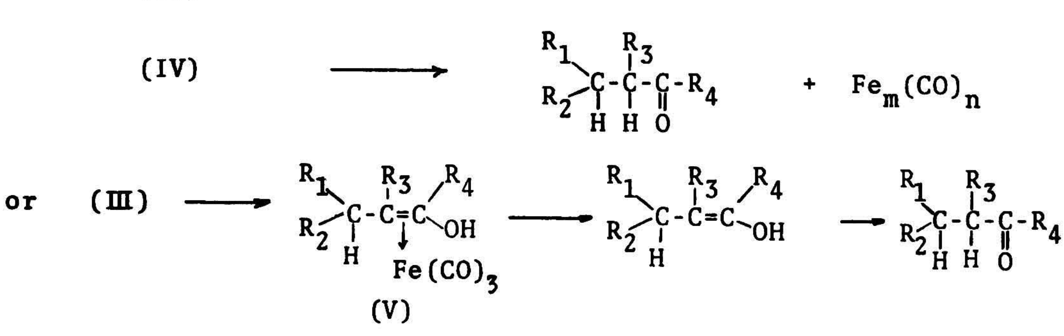
$KHFe(CO)_4$ is much more favorable for the reduction of cinnamaldehyde than $K_2Fe(CO)_4$. The yield does not exceed one mol in spite of the large amount of absorption of carbon monoxide, indicating some side reactions occur simultaneously.

On the other hand, Götz et al. reported the selective reduction of α,β-unsaturated carbonyl compounds with hydridotetracarbonylcobalt into saturated ones.2) They proposed the following reaction scheme (Scheme-1).



An α,β-unsaturated carbonyl compound coordinates to hydridocarbonyl cobalt to form the complex (I) , which then converts to a π-oxapropenyl complex (II) . This complex reacts with another hydridocarbonylcobalt to form a saturated carbonyl compound and octacarbonyldicobalt.

In the present reaction, the active hydride species is considered to be hydridotetracarbonylferrate, $HFe(CO)_4^-$, and would follow the analogous reaction scheme as in the reaction of hydridotetracarbonylcobalt. However, as the hydridotetracrbonylferrate and π-oxapropenyl complex (III) of iron have a minus charge on each complex, it is difficult to consider the attack of the hydridocarbonylferrate on the π-oxapropenyl complex (III). The last step may be the production of the π-oxapropenyl complex to form an alkylhydridocarbonyliron (IV), which gives the product by the reductive elimination, or the formation of π-vinyl alcohol complex (V), which decomposes to form the saturated carbonyl compound by isomerization.



Recently, Noyori et al. reported the selective reduction of α,β-unsaturated carbonyl compounds by the system closely analogous to ours, ($Fe(CO)_5$-NaOH (2:1) in moist methanol under a nitrogen atmosphere)$^{3)}$.

Addition of acrolein or methyl vinyl ketone into the solution of $KHFe(CO)_4$ caused the polymerization and the absorption of carbon monoxide, which amounted more than 1 mol. However, any products could not be detected by gas chromatography.

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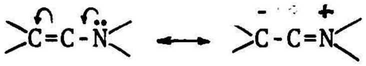
Chapter 4.

The Reduction of Enamines and the Reductive Alkylation of sec-Amines with Hydridocarbonylferrates

Introduction

Enamines are known to be very useful starting materials for the various organic syntheses, particularly for the formation of α-substituted carbonyl compounds and cyclic compounds.[1] This reactivity of enamine is due to the polarized carbon-carbon double bond as indicated below.



On the other hand, only a few reactions of enamines with transition metal complexes are known.[2]

This work will deal with the reaction of enamines with metal hydrides and their salts, especially with hydridocarbonyl ferrates.[3] In the course of this study, it was found that hydridocarbonylferrates are also effective for the reductive alkylation of secondary amines. As has been found in the reduction of isoprene[4] and olefin oxide[5] with carbonyl ferrates, the reproduction of active hydride species was observed in this reduction. The mechanism of these reactions will be discussed.

Experimental

Infrared spectra were measured on a Hitach model 21S grating infrared spectrometer. Pmr spectra were obtained on a JEOL model 3H60 NMR spectrometer. Mass spectra were obtained with a JMS=OISG mass spectrometer.

The Preparation of Carbonylferrates.

$KHFe(CO)_4$ and $K_2Fe(CO)_4$ were prepared according to the method described in a previous paper.6) Eleven mg.atom.Fe of each complex in 50 ml of solvent was used in each run.

When $KHFe(CO)_4$ is prepared, equivalent mole of water is formed;7)

$$Fe(CO)_5 + 3KOH \longrightarrow KHFe(CO)_4 + K_2CO_3 + H_2O \qquad (1)$$

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

$KHFe_2(CO)_8$ and $K_2Fe_2(CO)_8$ were prepared as follows.8,9) $Fe_2(CO)_9$ (2.0 g, 11 mg.atom.Fe) was treated with 16.5 mmol ($KOH/Fe_2(CO)_9=3$) or 22 mmol ($KOH/Fe_2(CO)_9=4$) of KOH in ethanol at 30°C for 2 hr.

$$\left.\begin{array}{l} Fe_2(CO)_9 + 3\ KOH \longrightarrow KHFe_2(CO)_8 + K_2CO_3 + H_2O \\ Fe_2(CO)_9 + 4\ KOH \longrightarrow K_2Fe_2(CO)_8 + K_2CO_3 + 2H_2O \end{array}\right. \qquad (2)$$

$[NEt_3H][HFe_3(CO)_{11}]$ was prepared according to the published method.10) 2.1g of $[NEt_3H][HFe_3(CO)_{11}]$ (11 mg.atom.Fe) in 50 ml of ethanol was used in each run.

Materials. 1-Morpholino-1-cyclohexene,11) 1-piperidino-1-isobutene,12) α-(1-morpholino)styrene,13) N-cyclohexylidenemorpholinium perchlorate14) were prepared according to the method described in literatures.

Pentacarbonyliron, morpholine, cyclohexanone and other compounds employed in this study were all commercial products and once purified by the distillation before use. Tetrahydrofuran was dried over lithium aluminum hydride.

Reaction Procedures.

To the solution of the carbonylferrate described above in a 300 ml of three necked flask connected to a gas buret, 33 mmol of enamine or the equimolar mixture of ketone and secondary amine and an internal standard for g.c. analysis were added. The mixture was then agitated under an atmosphere of carbon monoxide or nitrogen. After a certain reaction time 0.2 ml sample of the solution was removed and, after oxidized with air, submitted to g.c. analysis.

Analysis.

In some cases, the reaction product was isolated by distillation and identified.

Morpholinocyclohexane: b.p. 100°C/6 mmHg. Found: C,70.99; H,11.21 %, mol wt 169(mass). Calcd for $C_{10}H_{17}NO$, C,70.96; H,11.32 %, mol wt 169.26; PMR (acetone d-6) τ 3.3 (m , 4H), 2.3 (m , 4H), 1.6 (m, 6H) 1.1 (m , 5H) ppm.

α-Morpholinoethylbenzene: b.p. 80°C/0.3 mmHg Found: C, 75.28; H 8.89 % mol wt 191 (mass) Calcd for $C_{12}H_{17}NO$: C,75.35; H,8.96; N,7.32 ; O 8.37 % PMR ($CDCl_3$) τ 7.0 (m , 5H) 3.5 (m , 4H) 3.2 (q,1H, J=6Hz) 2.35 (m , 4H) 1.3 (d, 3H, J=6Hz) ppm.

α-Pyrrolidinoethylbenzene: b.p. 74°C/3 mmHg Found: C,82.11; H,9.75 %, mol wt 175 (mass). Calcd for $C_{12}H_{17}N$ C,82.23; H,9.78 % mol wt 175.27 PMR ($CDCl_3$) τ 7.2 (m, 5H), 3.15 (q,1H, J=6Hz) 2.4 (m, 4H), 1.7 (m, 4H), 1.35 (d, 3H,J=6Hz) ppm.

Tri(n-butyl)amine, N-isobutylpiperidine, and N-propylmorpholine were identified by g.c. analysis by the use of the authentic samples (Column: SE-30 on chromosorb, 3 mmø × 1.5 m; Diethylene Glycol Adipate Polyester on chromosorb, 3 mmø × 3 m).

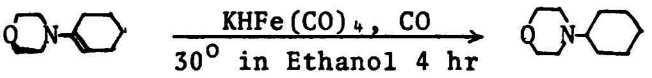
$Fe(CO)_5$ was analysed by TCD type gas chromatograph (Shimadzu model 3AH) using the latter column and benzene as internal standard.

The amount of $CO_3^{2\ominus}$ was analysed as follows. The gas evolved with acidification of the reaction solution was collected in a gas buret and after standing for 1hr, the gas was bubbled in aquons KOH. The volume of the absorbed gas was regarded as an amount of CO_2. This method was verified to be correct by g.c. analysis, (Column: active carbon 3 mmφ 3 m).

Results and Discussion

The Reaction of Enamines with KHFe(CO)$_4$.

When enamines, such as 1-morpholino-1-cyclohexene, are treated with alcoholic solution of potassium hydridotetracarbonylferrate,KHFe(CO)$_4$ (I), under a carbon monoxide atmosphere at 30°, a rapid absorption of carbon monoxide occurs. However, carbonylated products were not detected. But morpholinocyclohexane, the corresponding saturated tertiary amine, was produced. The results are summarized in Table-1. 1-Piperidino-1-isobutene and α-morpholinostyrene are also reduced to N-isobutylpiperidine and α-morphplinoethylbenzene , respectively.



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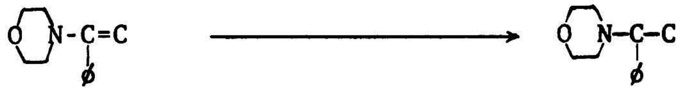
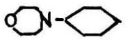
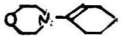
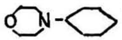
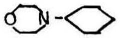
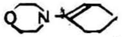
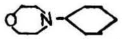
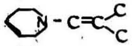
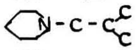
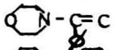
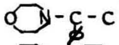
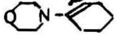
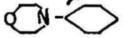
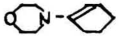
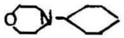
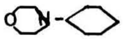
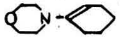
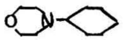
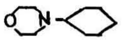
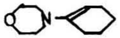
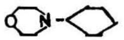


(5)

Table 1. The Reaction of Enamine with Carbonylferrates[*1]

Exp. No.	Enamine	Carbonyl-ferrate	Reaction Conditions			CO absd.		Product	Yield[*2]
			Time*4	Temp. °C	Atmos.	*2	Max.rate[*3]		
1		$KHFe(CO)_4$	4	30	CO	2.0	13		2.3
2		$KHFe(CO)_4$	96	30	CO	2.0	13	 *5	2.2
3		$KHFe(CO)_4$	1.5	30	N_2	—	—		0.9
4		$KHFe(CO)_4$	216	30	N_2	—	—		1.0
5		$KHFe(CO)_4$	48	30	CO	1.9	0.8		1.5
6		$KHFe(CO)_4$	48	30	CO	1.7	18		1.5
7		$K_2Fe(CO)_4$	5	30	CO	2.0	10		2.4
8		$KHFe(CO)_4$	24	50	CO	1.6	22		2.5
9		$KHFe(CO)_4$	24	10	CO	1.7	0.5		1.9
10		$KHFe(CO)_4$+5KOH	192	30	CO	4.9	1		1.3
11		$KHFe(CO)_4$+5H_2O	3	30	CO	1.3	6		1.0
12		$KHFe(CO)_4$+5H_2O	120	30	CO	1.3	6		0.9

*1 In ethanol solution.

*2 mol/mol.g.atom-Fe.

*3 cc/min

*4 hr

*5 0.43 mol of $Fe(CO)_5$ and 1.69 mol of CO_2 were also formed in the reaction solution.

The plots of the yield of the saturated amine and the carbon monoxide absorption vs. the reaction time in a typical reaction of 1-morpholino-1-cyclohexene are shown in Fig. 1. At first the rate of carbon monoxide absorption is slow, and after 1 hr a rapid absorption occurs and it amounts to 2 mol*1 in 4 hr.

The plot of the yield of the product vs. the reaction time is very characteristic. It has clearly two steps. At first the yield of the product increases rapidly with a slow absorption of carbon monoxide and the former amounts to 0.8~0.9 mol in 30 min. after the begining of the reaction. Then the rate of fomation of the product becomes very slow for about 30 min. and it becomes very fast again with an rapid absorption of carbon monoxide and the yield of the product amounts to more than 2.2 mol. When the reaction is carried out under a nitrogen atmosphere the yield of the product amounts to 1.0 mol (exp. 3, 4).

These results apparently show that there are at least two different ways for the reduction of the enamine; the first is the reduction with $KHFe(CO)_4$ itself and the second is that with newly produced active species with an absorption of carbon monoxide. However, this reaction cannot be regarded as a catalitic reaction, i.e., the yield of the product does not exceed 2.5 mol. As the reaction proceeds, the colour of the reaction solution changes from brown to dark red and $HFe_3(CO)_{12}^{\ominus}$*2 and $CO_3^{2\ominus}$ as well as $Fe(CO)_5$

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*1 'mol' means mol /g.atom.Fe. hereafter

*2 ~0.2 mol/g.atom.Fe of $HFe_3(CO)_{12}^{\ominus}$ was formed in the reaction mixture of Exp. 1.

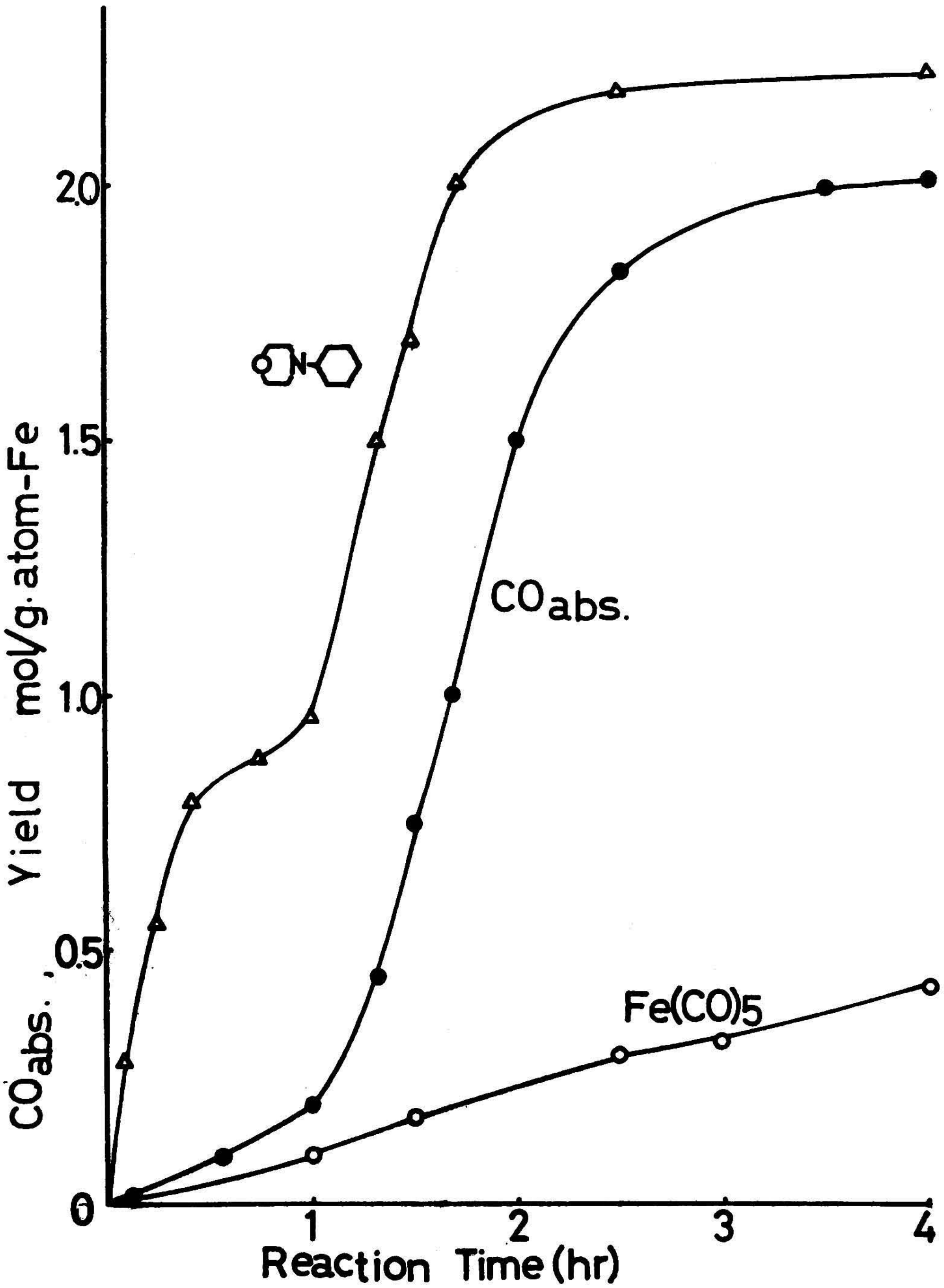
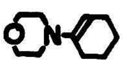


Fig.1. The Reaction of  with KHFe(CO)$_4$ at 30°C, in EtOH.

are found in the reaction mixture, indicating that clustered complexes are formed during the reaction. The amount of $Fe(CO)_5$ formed is also shown in Fig. 1.

The reaction of Enamines with $K_2Fe(CO)_4$ (II)

When an alcoholic solution of $K_2Fe(CO)_4$ is used, the rate of the carbon monoxide absorption is slower than in the case of $KHFe(CO)_4$, but the amount of the gas absorbed and the yield of the product were larger than those in the reaction of $KHFe(CO)_4$, (Exp. 7). In this reaction, $K_2Fe(CO)_4$ is thought to be hydrolyzed to $KHFe(CO)_4$ (eq. 6), which is active for the reduction of enamines and 1 mol of excess potassium hydroxide is considered to be effective for the reformation of the new hydride species.

$$K_2Fe(CO)_4 + H_2O \rightleftharpoons KHFe(CO)_4 + KOH \qquad (6)$$

However, large excess potassum hydroxide disturbed the reduction (Exp. 10). In this case, the concentration of the active hydride becomes low and the reaction is highly inhibited.

The Reaction of Enamines with $KHFe_2(CO)_8$ (III), $K_2Fe_2(CO)_8$ (IV) and $[NEt_3H]^+[Fe_3(CO)_{11}]^-$ (V).

1-morpholino-1-cyclohexene also reacts with an alcoholic solution of $KHFe_2(CO)_8$(III), $K_2Fe_2(CO)_8$(IV) and $[NEt_3H]^+[HFe_3(CO)_{11}]^-$ (V) with an absorption of carbon monoxide to give the saturated amine, morpholinocyclohexane. The results are summarized in Table 2.

The aspect of the reaction with $KHFe_2(CO)_8$(III) or $K_2Fe_2(CO)_8$(IV) is very different from that of $KHFe(CO)_4$. The induction period of the carbon monoxide absorption is not found and the rate of the

Table-2 The Reduction of Morpholinocyclohexene with Polynuclear Carbonylferrate *1

Exp. No.	Carbonyl-ferrate	React. Cond.			Max. Rate of $CO_{abs.}$ cc/min	Yield *3		
		Temp.°C	Time (hr)	$CO_{abs.}$ *3			$Fe(CO)_5$	CO_2
13	$KHFe_2(CO)_8$	3.0	24	1.72	12	1.60	0.78	0.87
14	$K_2Fe_2(CO)_8$	30	2	2.20	18	2.20	0.84	1.42
15	$K_2Fe_2(CO)_8$	20	48	2.26	7	2.27		
16	$K_2Fe_2(CO)_8$	45	24	2.14	32	1.92		
17	$K_2Fe_2(CO)_8$	0	4	Ar	-	1.00		
18	$[HFe_3(CO)_{11}]^-$	30	120	1.25	0.7	0.46	1.05	0.11
19	$[HFe_3(CO)_{11}]^{-}$ *2	30	24	1.73	3.8	1.20	0.41	1.31

*1. In EtOH

*2. 1.5 mol of KOH was added.

*3. mol/g·atom·Fe.

carbon monoxide absorption and that of reduction is very rapid in spite of the half concentration of the carbonylferrate complex as compared with the case of $KHFe(CO)_4$. The reaction of $K_2Fe_2(CO)_8$(IV) is illustrated in Fig. 2. The yield of the product increases smoothly without a step which was observed in the case of the reaction of $KHFe(CO)_4$ (Fig. 1), and it amounts to 2.2 mol, i.e. 4.4 mol/mol-$Fe_2(CO)_8^{2\ominus}$. In the reaction of $K_2Fe_2(CO)_8$, active species may be $KHFe_2(CO)_8$ which exists in the reaction system by the equilibrium (7).

$$K_2Fe_2(CO)_8 + H_2O \rightleftharpoons KHFe_2(CO)_8 + KOH \tag{7}$$

$HFe_3(CO)_{11}^-$ also reduces enamines but the rate of carbon monoxide absorption is slow and the yield of the product is low (Exp. 18). An addition of 1.5 mol of potassium hydroxide to this reaction system accerated the rate of carbon monoxide absorption and the yield of the product increased to 1.20 mol (Exp. 19).

In both cases, active hydride species are apparently reproduced. The mechanism of the reformation of the active species will be discussed later.

The Reaction of 1-Morpholino-1-cyclohexene with $KHFe(CO)_4$ in Dry THF and the Effect of Water.

In order to investigate the sourse of the hydrogen, 1-morpholino-1-cyclohexene was treated with $KHFe(CO)_4$ in dry THF. As shown in Fig. 3, no carbon monoxide absorption occurs and even after a prolonged reaction time only a small amount of the product is formed. When 1mol of water was added in the reaction solution, a rapid carbon

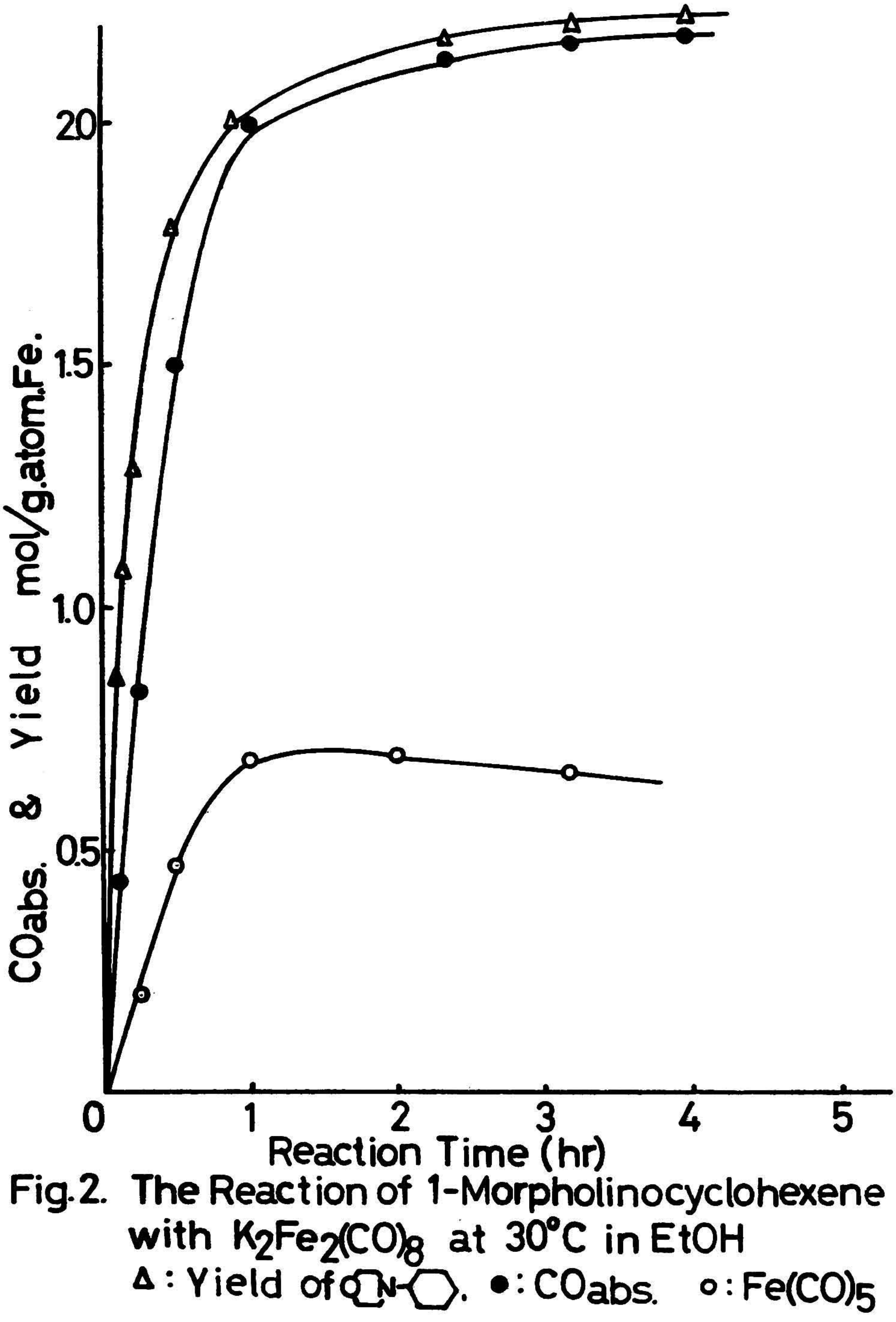


Fig.2. The Reaction of 1-Morpholinocyclohexene with $K_2Fe_2(CO)_8$ at 30°C in EtOH

Δ : Yield of . ● : CO abs. ○ : $Fe(CO)_5$

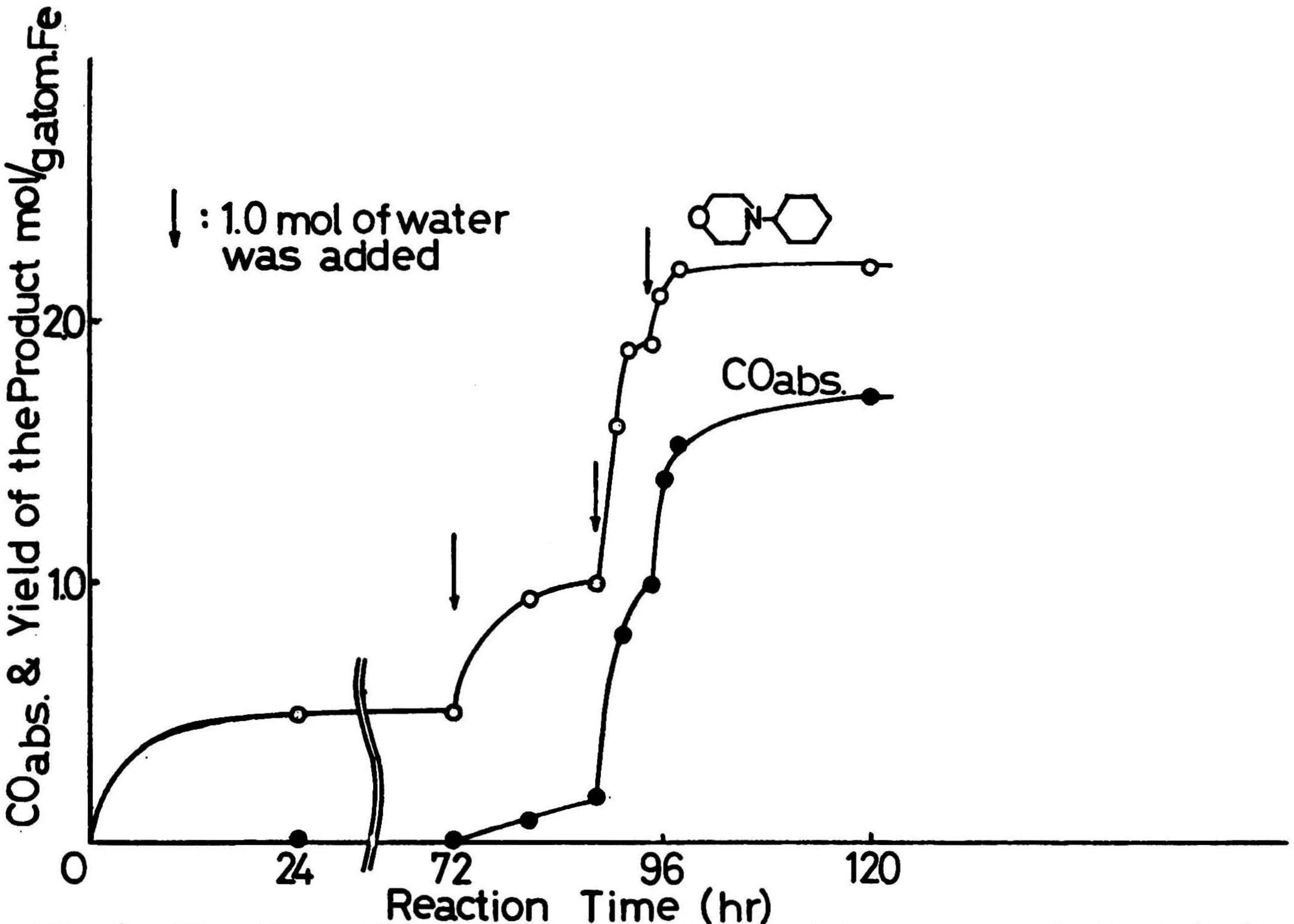


Fig. 3. The Reaction of 1-Morpholinocyclohexene with $KHFe(CO)_4$ in Dry THF and the Effect of the Addition of Water

monoxide uptake occured and the yield of the product increased rapidly. This result shows that the hydrogen source is water in this reduction. Water and carbon monoxide are indispensable for the reproduction of active species of the reduction. The product formed in dry $KHFe(CO)_4$ solution may be due to a trace of water remained in the system.

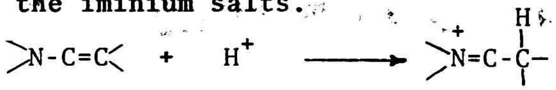
The Fate of Absorbed Carbon Monoxide

The fate of the carbon monoxide absorbed was investigated. In the reaction solution, pentacarbonyliron was formed and quantitalively analyzed by gas chromatography. In the gas which evolved when the reaction mixture was acidified by conc. HCl, was detected carbon dioxide, the amount of which was larger than that expected by the base reaction of iron carbonyls (eqs. 1, 2). The amounts of pentacarbonyliron and carbon dioxide formed during the reduction reaction are shown in Table 2. This results show that the carbon monoxide absorbed goes into pentacarbonyliron and carbon dioxide.

$$[\text{CO absorbed}] \fallingdotseq [Fe(CO)_5] + [CO_2] \qquad (8)$$

On the Mechanism of the Reduction of Enamines

The reduction of enamines with formic acid[15)] and sodiumborohydride[16)] has been studied. The first step of the reduction is shown to be the protonation of the β-carbon atom of the enamines to form the iminium salts.

 (9)

$$>N-C=C< \; + \; H^+ \longrightarrow \; >\overset{+}{N}=C-\overset{H}{\underset{|}{\overset{|}{C}}}- \qquad (9)$$

The mechanism of the hydrolysis of enamines was also investigated:

the first step of the reaction was also the formation of the iminium salts and this process is very fast.[17)] In our reaction system which contains some water,[*3] it is reasonable to consider that the first step of the reduction is also the formation of an iminium salt. In fact the infrared spectrum of the reaction solution did show the band characteristic for an iminium salt,[*4] and an enamine could not be detected by means of ir. spectra and by gas chromatography in the reaction solution even 10 min after the begining of the reaction. On the other hand, an enamine was detected in the reaction solution when the reaction was carried out in a dry solvent, and the reduction did not proceed.

The second step of the reduction is surely the nucleophilic attack of hydridocarbonylferrates on the iminium salts and the abstraction of a hydride ion.

$$>N^+{=}C{-}C + HFe_m^-(CO)_n \longrightarrow >\ddot{N}{-}\underset{H}{C}{-}C + Fe_m(CO)_n \qquad (10)$$

In the reduction of iminium salts with $LiAlH_4$[18)], $NaBH_4$[16)] and formic acid[1,15)], the similar abstraction of a hydride ion has been observed.

The fact that the iminium salt, N-cyclohexylidene-morpholinium perchlorate, reacts with $KHFe(CO)_4$ with an absorption of carbon monoxide to give morpholinocyclohexane (Table-3. Exp.28). also supports this mechanism.

[*3] See eq.1. The ethanol solvent contains about 0.2 % of water.

[*4] A new band appears at about 20 cm^{-1} above the parent enamine band.

On the Reproduction of Active Hydride Complexes.

As mentioned above, it is apparent that under a carbon monoxide atmosphere, active hydride species are formed repeatedly during the reaction. It has been shown that there are interconversions between mononuclear and polynuclear hydride species[19)] under certain conditions.

$$HFe^{\ominus}(CO)_4 \rightleftharpoons HFe_2^{\ominus}(CO)_8 \rightleftharpoons HFe_3^{\ominus}(CO)_{11} \qquad (11)$$

The results obtained in this study strongly support the following posturations.

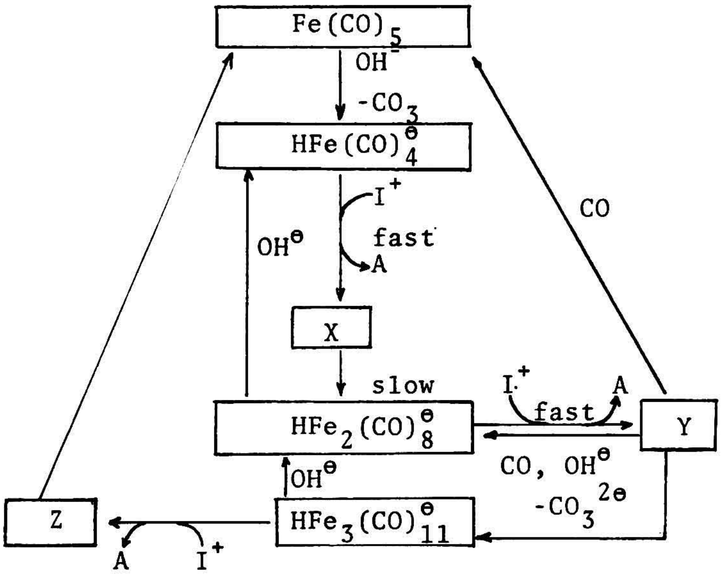
1. $HFe^{\ominus}(CO)_4$ reduces rapidly an iminium salt stoichiometrically without an absorption of carbon monoxide and then $HFe_2^{\ominus}(CO)_8$ is formed slowly.
2. Once $HFe_2^{\ominus}(CO)_8$ is formed, it reduces the iminium salt "catalytically[*5]" with an absorption of carbon monoxide in the presence of $OH^{\ominus}$ ion.
3. The cycle of the reduction is terminated by a lack of $OH^{\ominus}$ ion and the formation of some stable iron carbonyl complexes which can not reduce the iminium salt by itself.

The general aspect of the reaction including the formation of $Fe(CO)_5$ and $HFe_3(CO)_{11}^-$ is schematically summarized in Chart 1.

The mechanism of the reformation of the hydride species is not clear at the present time.

[*5] If the second step in Fig. 1 is attributed to $HFe_2^{\ominus}(CO)_8$, about 2 mol/mol-$HFe_2^{\ominus}(CO)_8$ of product is obtained by $HFe_2^{\ominus}(CO)_8^-$. A strong support for this posturation is obtained in the following chapter.

Chart I



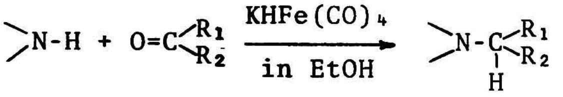
I$^+$: Iminium salt.

A : Tertiary amine.

X, Y, Z, : Unknown intermediates.

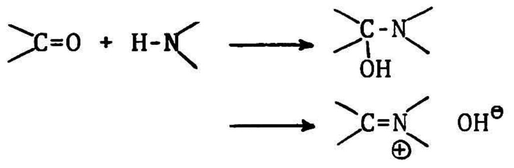
The Reductive Alkylation of sec-Amines with $KHFe(CO)_4$

It was found that the equimolar mixture of secondary amine and ketone or aldehyde reacts with $KHFe(CO)_4$ with an absorption of carbon monoxide to give the corresponding tertiary amine. The results are summarized in Table-3.



(12)

Morpholine and cyclohexanone give 1.4 mol of morpholinocyclohexane with an absorption of 1.7 mol of carbon monoxide. Acetophenone and pyrrolidine give α-pyrrolidinoethylbenzene. This reaction should be compared with the Leuckart-Wallach reaction[20)] i.e. the reductive alkylation of amines with formic acid and its derivatives. The mechanism of the Leuckart-Wallach reaction of a ketone and a secondary amine has been considered to be as follows.[1)] In the first step, a ketone and a secondary amine form a 1:1 adduct and then an iminium salt is formed, which abstracts a hydride ion from formic acid or its derivatives.

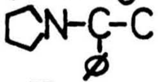
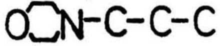


(13)

This mechanism of the formation of the iminium salt is also proposed as the first step of the preparation of enamines from ketones and secondary amines.[17)]

In the present reaction, neither ketones nor secondary amines separately react with $KHFe(CO)_4$, and the boundary of the

Table-3 Reductive Alkylation of sec-Amines with $HFe(CO)_4^-$[*1]

	Amine[*3]	Carbonyl[*3] Compounds	Temp.°C	Time (hr)	COabs.[*4]	Product	Yield[*4]
20	Morpholine	Cyclohexanone	30	48	1.7		1.4
21[*2]	Morpholine	Cyclohexanone	30	48	1.2		1.8
22	Dibutylamine	Butylaldehyde	30	24	1.4	$(t\text{-}Bu)_3N$	0.50
23	Pyrrolidine	Acetophenone	30	48	1.5		1.1
24	Morpholine	Propionaldehyde	30	24	1.4		0.41
25	Morpholine	Acetophenone	65	48	—	No Reaction	—
26	Diisopropyl amine	Acetone	30	24	—	No Reaction	—
27	Ethylene imine	Cyclohexanone	30	48	—	No Reaction	—
28	N-Cyclohexylidenemorpholium Perchlorate		30	24	1.0		1.0

*1 In EtOH, $HFe(CO)_4^-$: 11mol

*2 $K_2Fe(CO)_4$

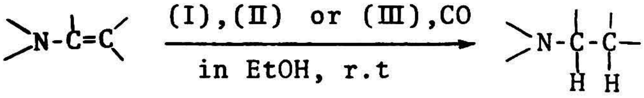
*3 33 mmol

*4 mol/mol·$Fe(CO)_4^{2-}$

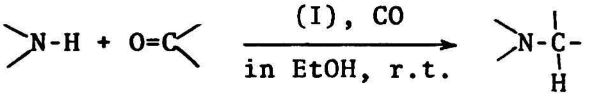
reaction is almost the same as that of Leuckart-Wallach reaction. These facts strongly suggest that in this reaction iminium salts is also formed by the equation (13), which abstracts a hydride ion from hydridocarbonylferrates, as in the reaction of enamines with the hydride complexes.

Summary

Enamines react with alcoholic solution of $KHFe(CO)_4$(I), $KHFe_2(CO)_8$(II), and $[NEt_3H][HFe_3(CO)_{11}]$(III) with absorption of carbon monoxide at room temperature to form the corresponding saturated tertiary amine.



However, the carbonylated product was not detected. The equimolar mixture of a ketone and a secondary amine was found to react with (I) with absorption of CO to form the corresponding tertiary amine



The yield of the product was much larger than that expected by the stoichiometic reaction of (I). The mechanism of the reactions including the reproduction of the active species has been discussed.

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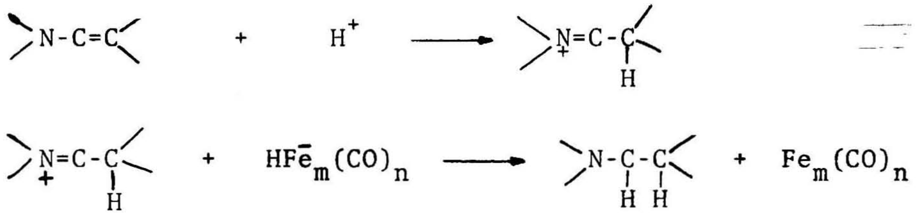
Chapter 5. The Stereochemical Course of the Reduction of Enamines with Mono- or Polynuclear Carbonylferrates

Introduction

In the previous chapter, enamines were found to react with $HFe(CO)_4$ (I), $HFe_2(CO)_8$ (II) and $HFe_3(CO)_{11}$ (III) in alcohol to give the corresponding saturated tertiary amines;



(I) : m=1, n=4; (II) : m=2, n=8; (III): m=3, n=11.

It was suggested that the first step of the reduction is the protonation of the enamines to form the iminium salts, and then the abstraction of hydrides from the hydridocarbonylferrates may give saturated tertiary amines.

In the reduction with the mononuclear hydride complex, $KHFe(CO)_4$ (I), under a carbon monoxide atmosphere, the aspect of the reaction is very characteristic; first, the yield of the tertiary amine increases rapidly with a slow absorption of carbon monoxide and then the yield becomes constant (about 0.9 mol)[*1]. After several tens minutes, it begins to increase again rapidly with a rapid absorption of carbon monoxide and amounts to more

[*1] "mol" means mol g.atom.Fe hereafter.

than 2.3 mol. In this reaction solution, clustered iron carbonyl complexes are found as well as pentacarbonyliron and carbonate (see Chapter 4,P 67).

On the other hand, in the reaction with $HFe_2(CO)_8$ (II) , the yield of the product increases smoothly with a rapid absorption of carbon monoxide and it amounts to more than 1.6 mol. A large amount of pentacarbonyliron is also formed in the reaction solution (P 70).

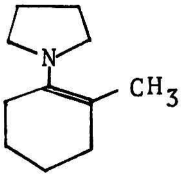
These facts show that there are interconversions between mono and clustered hydridocarbonylferrates during the reaction, and hydride complexes newly formed reduce the enamine repeatedly.

$$\underset{(I)}{HFe(CO)_4} \rightleftharpoons \underset{(II)}{HFe_2(CO)_8^-} \rightleftharpoons \underset{(III)}{HFe_3(CO)_{11}^-}$$

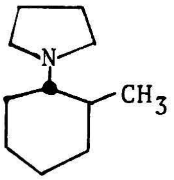
The aspect of the reaction with $HFe(CO)_4^-$(I) can be explained by the posturation that in the first step $HFe(CO)_4$ (I) reacts with the iminium salt stoichiometrically and then $HFe_2(CO)_8^-$ is formed in the presence of hydroxy ion. Then, $HFe_2(CO)_8^-$ reduces the iminium salt catalytically with an absorption of carbon monoxide. The catalytic reaction cycle may be terminated by the lack of the hydroxy ion and the formation of stable iron carbonyl complexes.

To verify this posturation, in this chapter, the reduction of a pyrrolidine enamine of 2-methylcyclohexane (1-methyl-2-pyrrolidinocyclohexene) (IV) with (I), (II) and (III) was attempted.

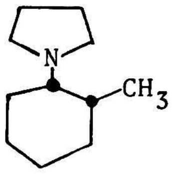
The products should be cis- and trans-1-methyl-2-pyrrolidinocyclohexane (V) and (VI).



(IV)



trans
(V)



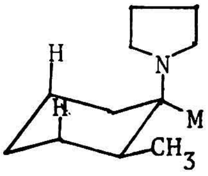
cis
(VI)

The hydride complexes (I), (II) or (III) are expected to have the ratio of the cis to trans isomers characteristic of each complex, at least at the beginning of the reaction.

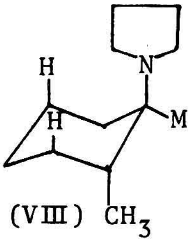
As mentioned above, the hydride species may be able to be converted to one another in the presence of hydroxy ion.1,2) Therefore, there is some possibility that several active species are acting during the reaction process. In this case, the ratio of the cis to trans isomers of the products will be affected by the conversion of active species.

Mitsui and his coworkers investigated the hydrogenation of 1-methyl-2-pyrrolidinocyclohexene (IV) with heterogeneous catalyst3) such as Raney nickel or palladium on carbon under a hydrogen atmosphere in ethanol at room temperature. In these reactions the less stable cis isomer predominates and the ratio of the cis to trans isomers is 2.7 in the case of Ranay nickel.

They explained this fact is due to the steric effect of intermediates (VII) and (VIII). The intermediate (VII) , in which the pyrrolidine group is axial, and the metal group is equatorial, is considered to be more stable than the intermediate (VIII) , in which the methyl group and the pyrrolidine ring are trans.



(VII)



(VIII)

On the other hand, a clustered metal complex is considered to be placed between a typical homogeneous complex, mononuclear complex, and a heterogeneous solid catalyst. The bulkiness is in the order mono- > bi- > trinuclear complex > heterogeneous solid catalyst.

Therefore, if the reduction of the enamine (IV) with the hydride complexes (I), (II) and (III) proceeds via analogous intermediates as (VII) or (VIII), and if the ratio of the cis to trans isomers is determined only by the bulkiness of the metal group, the ratio of the cis to trans isomers is expected to be in the order mono- > bi- > trinuclear complex > heterogeneous catalyst. The effect of the reaction conditions on the ratio of the cis to trans isomers will be examined in order to get informations on the mechanism of the reduction.

Experimental

Infrared spectra were measured on a Hitachi model 215 grating infrared spectrometer. Pmr spectra were obtained on a JEOL model 3H 60 NMR spectrometer. Mass spectra were obtained with a JMS=OISG mass spectrometer.

Materials. $KHFe(CO)_4$[4], $KHFe_2(CO)_8$, $K_2Fe_2(CO)_8$[5] and $[Et_3NH][HF_3(CO)_{11}]$[6] were prepared according to the method described in the previous chapter. 1-Methyl-2-pyrrolidinocyclohexene was prepared according to the published method.[7] To 153 g (1.37 mol) of 2-methylcyclohexanone, 128 g (1.80 mol) of pyrrolidine and 200 ml of benzene were added and refluxed for 63 hr, separating water by means of a Dien-Stark water separator. After the separation of water ceased, the product was separated by a distillation and purified by a carefull redistillation, b.p. 107∿110°C/10 mmHg, (Yield, 79% based on the ketone). It was stored in an ampoule under an argon atmosphere in a refrigerator.

Pentacarbonyliron, ethyl alcohol and other compounds employed in this study were all commercial products and the purity was checked to be satisfactory for the reaction.

Reaction Procedures. To the solution of the carbonylferrates $KHFe(CO)_4$, $KHFe_2(CO)_8$ or $[NEt_3H][HFe_3(CO)_{11}]$ (11 mg.atom. Fe in 50 ml ethanol) in a 300 ml of three necked flask conneted to a gas buret, 33 mmol of the enamine (IV) and 1.0 ml of tetraline as internal standard for g.c. analysis were added at 30∿-60°C, and then agitated magnetically. After a certain reaction time 0.2 ml of sample of the reaction mixture was taken off by a syringe, oxidized with air, and submitted to g.c. analysis.

When the reaction was carried out at -60°C, the sample was quenched with a dilute ethanol solution of iodine(0.11 M, 0.1ml) and a drop of ethylenediamine to terminate the reaction. The latter was added in order to disturb the formation of the salt of the product with hydrogen iodide and the formation of the complex of Fe^{2+} or Fe^{3+} and the products.

Analytical Procedures. Identification of the isomers of the products: To check the results of Mitsui and to identify the isomers of the products, 7.6 ml of the enamine (IV) was reduced catalytically with Ranay nickel (1.0 g) in dry ethyl alcohol at 30°C under 1 atm of hydrogen. After 2 hr , the reaction mixture was analyzed by gas chromatography. Two peaks, (A) and (B), were found and the ratio of (A) to (B) was 27 : 73 which was the same value as Mitsui has reported. Five gram of the mixture of (A) and (B) was separated by a distillation from the reaction mixture (b.p. 82∿85°C/9 mmHg, Yield, 63%, and tried to separate (A) and (B) by column chromatography (silica gel. 70∿325 mesh. Merck). Pure (A) or (B) could not be obtained, but the mixtures, 1) (A)/(B)=90/10 and 2) (A)/(B)=14/86, were obtained. The pmr spectra of these mixtures were taken and from the coupling constant of the methyl group it was concluded that (A) and (B) are the trans (V) and cis (VI) isomers respectively.[8] Found: C, 79.00; H, 12.65; N, 8.37%. M. wt. 167(mass). Calcd. for $C_{11}H_{21}N$: C, 78.82; H, 12.69; N, 8.24%. M. wt. 167.29. Mass: m/e, 167, 110, 97, 96, 84, 70. Pmr. (CCl_4). (A): τ, 9.06(d, J=6.0Hz, 3H), 8.5~8.9(m, 5H), 8.1~8.5(m, 8H), 8.0~7.6(m, 1H), 7.2~7.6(m, 4H) ppm. (B). τ9.11(d, J=6.8Hz, 3H), 8.6~8.8(m, 14H), 7.4~7.7(m, 4H) ppm.

Gas chromatographic analysis was carried out on a Shimazdu model GC-2C attached with a FID (Column: SE-30 on Chromosorb, 3 mm x 1.5 m; Column temperature, 120°C; Injection tempetrature, 250°C; Carrier Gas: N_2, 40 cc/min). Two peaks (A) and (B) were observed at the retention time of 8.3 and 9.9 min, respectively.

Results

1-Methyl-2-pyrrolidinocyclohexene (IV) is reduced with an alcoholic solution of $KHFe(CO)_4$, $KHFe_2(CO)_8$ or $[NEt_3H][HFe_3(CO)_{11}]$ to give trans- and cis-1-methyl-2-pyrrolidinocyclohexane. The results are summarized in Tables 1 and 2.

The Reaction of 1-Methyl-2-pyrrolidinocyclohexene (IV) with $KHFe(CO)_4$ (I). The plots of an amount of cabon monoxide absorbed, the yields of the products and the ratio of the cis to trans isomers vs. reaction time are shown in Fig. 1. The aspect of the reaction is similar as that was observed in the reaction of 1-morpholinocyclohexene with $HFe(CO)_4$ described in the previous chapter.

First, the reduction of the enamine proceeds rapidly without an absorption of carbon monoxide to give o.35 mol of 1-methyl-2-pyrrolidinocyclohexane. After 2 hr, a rapid uptake of carbon monoxide occurs with an increase of the yield of the

Table-1 The Reduction of 1-Methyl-2-pyrrolidinocyclohexene with Carbonylferrates[*1]

Exp.	Carbonyl		Enamine	React. Cond.			CO[*2]	Yield[*2]	cis/trans
No.	ferrate	m mol	m mol	Temp.°C	Time(min)	H_2O cont.[*2]	abs.		
1	$KHFe(CO)_4$	11	33	30	5	1	0	0.50	0.67
2	$KHFe(CO)_4$	11	33	30	300	1	1.1	1.94	0.88
3	$KHFe(CO)_4$	3.7	11	-60	3	1	0	0.27	0.61
4	$KHFe(CO)_4$	3.7	11	-60	30	1	0	0.16	0.65
5	$KHFe_2(CO)_8$	5.5	33	30	10	1	0.70	0.60	1.2
6	$KHFe_2(CO)_8$	5.5	33	30	300	1	1.3	1.70	1.0
7	$K_2Fe_2(CO)_8$	5.5	33	30	10	1	0.65	0.88	1.2
8	$K_2Fe_2(CO)_8$	5.5	33	30	300	1	1.45	1.88	0.94

[*1] Solvent: EtOH

[*2] mol/g.atom.Fe

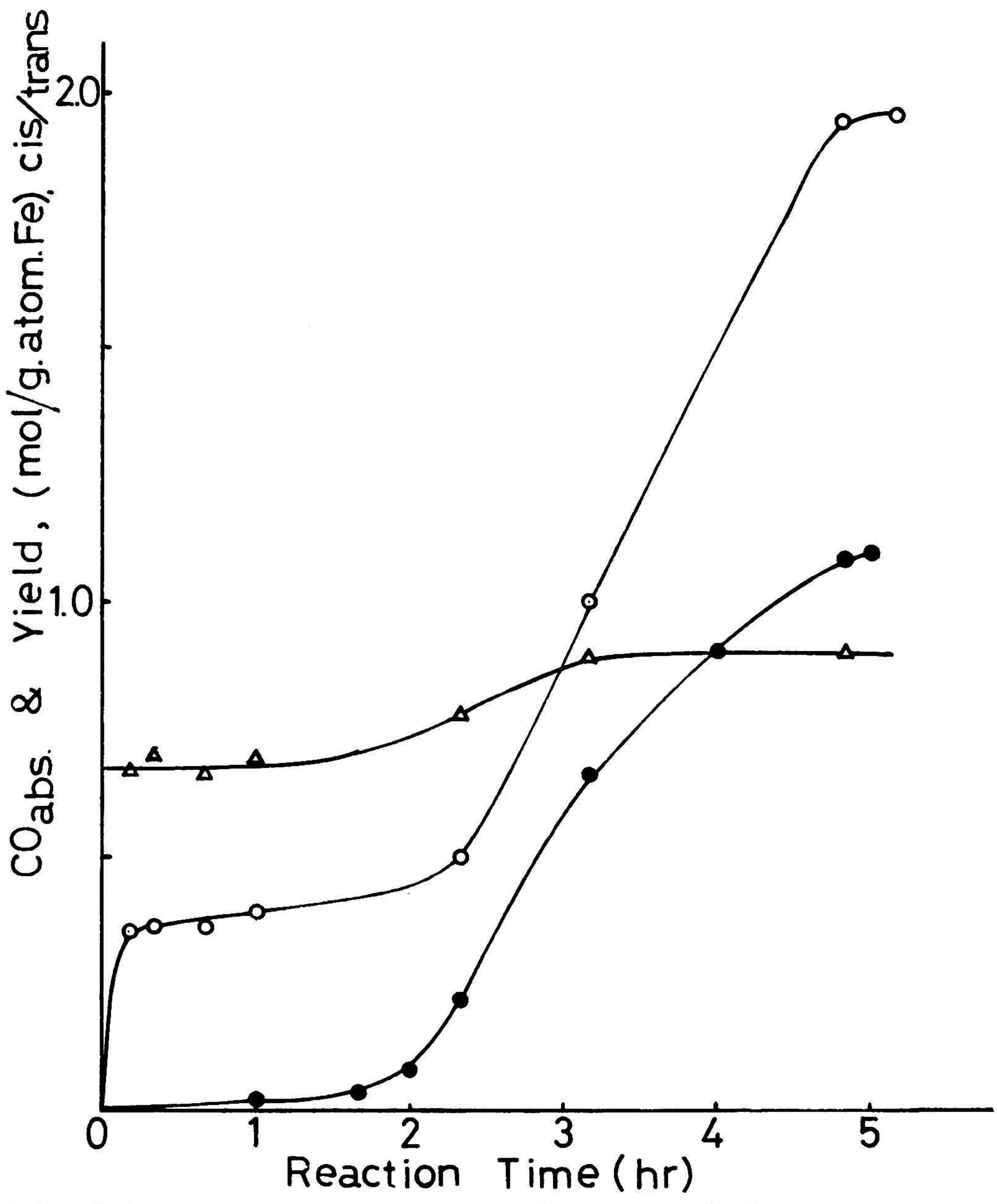


Fig. I. The Reaction of the Enamine(IV) with KHFe(CO)4

○ : Yield of 1-Methyl-2-pyrrolidinocyclohexane

● : CO absorbed

△ : cis/trans

product and the amount of carbon monoxide absorbed and the yield of 1-methyl-2-pyrrolidinocyclohexane reached to 1.1 and 1.9 mol, respectively.

The ratio of the cis to trans isomers was 0.67 at the beginning of the reaction and it stayed constant till the absorption of carbon monoxide took place, and it began to increase with the absorption of carbon monoxide and reached to 0.88 at the end of the reaction. The ratio of the cis to trans isomers which were newly formed with the absorption of carbon momoxide was 1.1, which was easily calculated from the data at 60 min. and 140 min.

The enamine (IV) reacts with the hydride even at -60°C (Exp. 3)to give 0.27 mol. of the product in 5 min without an absorption of carbon monoxide. The cis to trans ratio was only slightly affected by the reaction temperature.

The Reaction of the Enamine (IV) with $KHFe_2(CO)_8$ and $K_2Fe_2(CO)_8$. The periodical change of the yield of the product, the amount of absorbed carbon monoxide and the ratio of the cis to trans isomers in the reaction of $K_2Fe_2(CO)_8$ at 30°C were shown in Fig. 2. As has been found in the reaction of 1-morpholinocyclohexene the yield of the product increases rapidly with an absorption of carbon monoxide, The ratio of the cis to trans isomers is 1.2 at the beginning of the reaction. It stayed for about 1 hr and then it decreases gradually and finally reached to 0.95. $KHFe_2(CO)_8$ also reacts with the enamine and the ratio of the cis to trans isomers were also 1.2

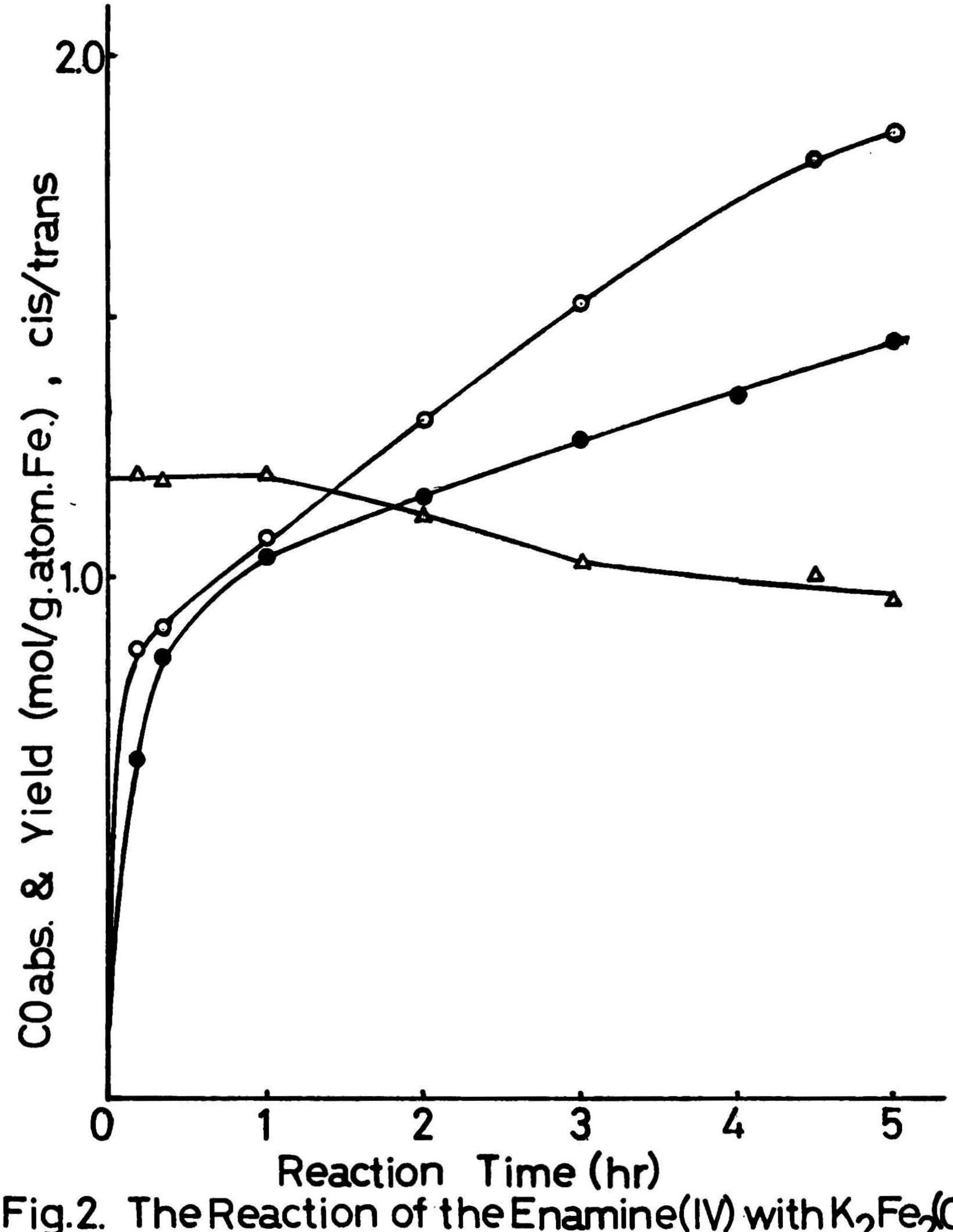


Fig.2. The Reaction of the Enamine(IV) with $K_2Fe_2(CO)_8$

○: Yield of 1-Methyl-2-pyrrolidinocyclohexane

●: CO absorbed

△: cis/trans

at the beginning of the reaction and it reached 1.0 at the end of the reaction.

The Reaction of the Enamine (IV) with $[NEt_3H][HFe_3(CO)_{11}]$. Hydridoundecacarbonyltriferrate also reduces the enamine (IV) to give the amines (V) and (VI) (Table 2). The aspect of the reduction was shown in Fig. 3. The reduction of the enamine proceeds rapidly and ceases in 10 min. The yield of the product is small (0.11 mol, i.e. 0.33 mol/mol-$HFe_3(CO)_{11}^-$) and the ratio of the cis to trans isomers is 2.1. Although slow absorption of carbon monoxide occurs, the yield of the products and the ratio of the cis to trans isomers stay constant for more than 4 hr. Addition of 11 ml of 1N ethanolic potassium hydroxide solution to this reaction solution caused the reaction aspect to change dramatically. The yield of the product increased rapidly with an absorption of carbon monoxide. The ratio of the cis to trans isomers decreases immediately to the value of 0.9. It is caluculated that the ratio of the cis to trans isomers newly formed is 0.9. The effect of the mole ratio of the trinuclear hydride to the enamine (IV) on the ratio of the cis to trans isomers was small (Exps. 9, 10).

The effects of the addition of water or the reaction temperature on the ratio were also small.

Table-2 The Reduction of 1-Methyl-2-pyrrolidinocyclohexene with $HFe_3(CO)_{11}^-$ *1

Exp. No.	$HFe_3(CO)_{11}^-$ mmol	Enamine mmol	React. Cond. Temp.°C	Time(min)	H_2O cont.*2	CO*2 abs.	Yield*2	cis/trans
9	3.7	33	30	30	0	0.10	0.11	2.1
10	3.7	33	30	60	0	0.14	0.11	2.1
11	3.7	33	30	210	0	0.40	0.11	2.1
12	11	33	30	300	0	0.57	0.17	1.9
13	11	33	30	300	1	0.61	0.08	1.8
14	3.7	33	-60	15	1	0	0.05	1.8
15	3.7	3.7	-60	5	1	0	0.01	1.6
16	3.7	11	-60	15	1	0	0.03	1.9

*1 Solvent: EtOH

*2 mol/g.atom. Fe

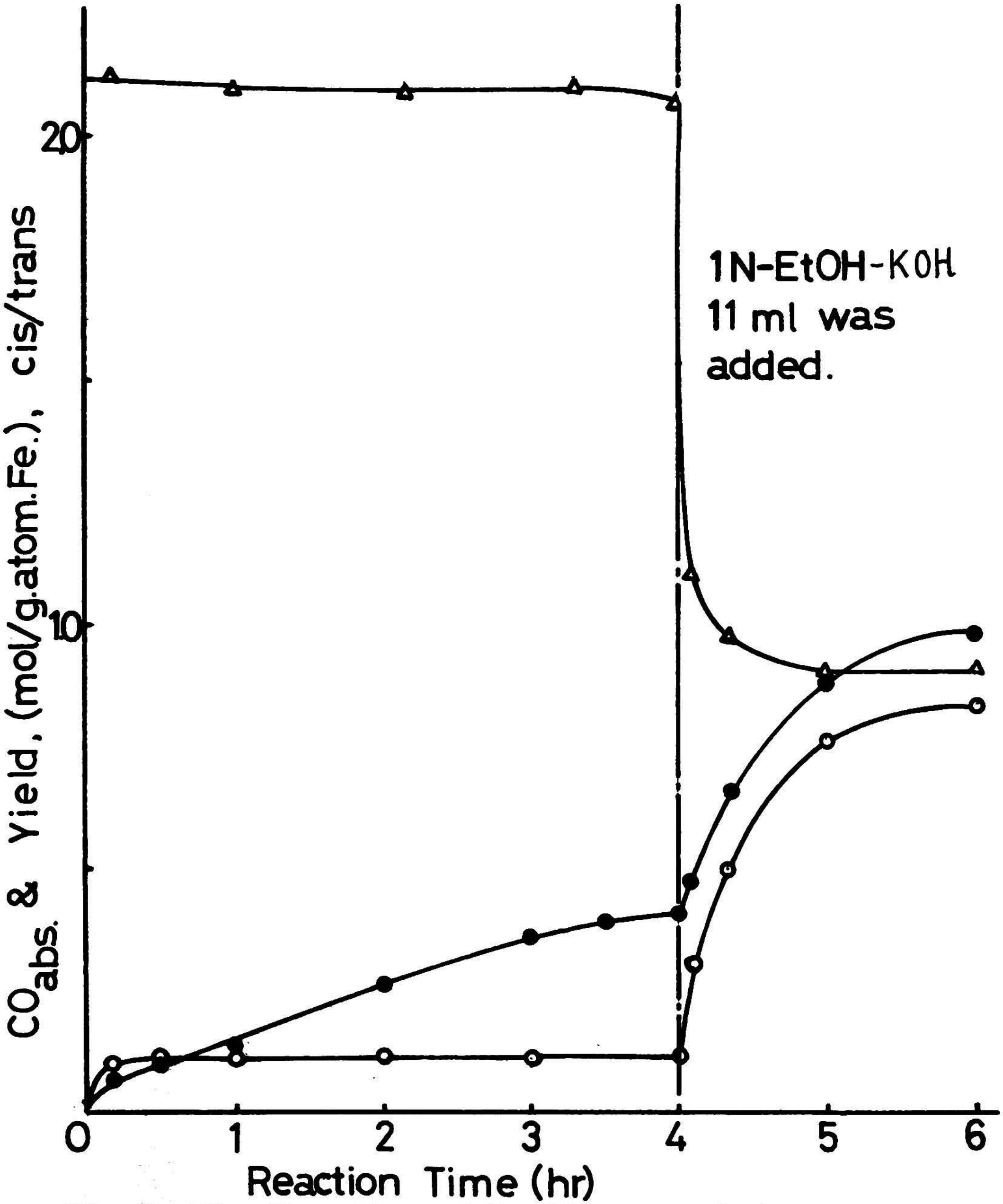


Fig. 3. The Reaction of the Enamine (IV) with $[Et_3NH]^+[HFe_3(CO)_{11}]^-$

○ : Yield of 1-Metyl-2-pyrrolidinocycloheane

● : CO$_{absorbed}$

△ : cis/trans

Discussion

The results show that $HFe(CO)_4^-$ (I), $HFe_2(CO)_8^-$ (II) and $HFe_3(CO)_{11}^-$ (III) have their own ability of the reduction of the enamine and have the characteristic values of the ratio of cis to trans isomers, 0.67, 1.2 and 2.1, respectively. From these values we are able to get much information on the mechanism of the reduction of enamines with the hydrides.

The fact that the ratio of the cis to trans isomers stays constant for more than one hour in each reaction systems shows that the isomerization between these isomers in these reaction system is negligible.

As has been mentioned in the introduction, it has been reasonably considered that in the reduction of the enamine, the first step is surely the formation of the iminium salt, which then abstracts a hydride from the hydridocarbonylferrates to give the corresponding saturated tertiary amine.

In the previous chapter, following posturations on the mechanism of the reduction were proposed.

1. $HFe(CO)_4^-$ rapidly reduces an iminium salt stoichiometrically without an absorption of carbon monoxide, and then binuclear hydride complex $HFe_2(CO)_8^-$ is formed slowly.
2. Once $HFe_2(CO)_8^-$ is formed, it reduces the iminium salt "catalytically" with an absorption of carbon monoxide in the presence of hydroxy ion.
3. The catalitic cycle of the reduction is terminated by the lack of hydroxy ion and the formation of some carbonyl-

iron complexes, inert for the reduction of the iminium salt.

The results in this chapter strongly support these posturations.

The reaction of $KHFe(CO)_4$ with the enamine (IV) appears to proceed at least in three steps. The first step is the reduction with $HFe(CO)_4^-$ and is characterized by 0.67 of the ratio of the cis to trans isomers. However, the yield is rather low in comparison with the reduction of 1-morpholinocyclohexene with $HFe(CO)_4^-$ and its reason is not clear.[*3] The second step is the reduction with a rapid absorption of carbon monoxide and is characterized by 1.1 of the ratio of the cis to trans isomers, characteristic value of the reduction with the binuclear hydride $HFe_2(CO)_8$. The third step, characterized by the low value of the ratio shows that the mononuclear hydride $HFe(CO)_4$ is formed again and the reduction with $HFe(CO)_4$ and $HFe_2(CO)_8^-$ proceeds simultaneously in this step.

The reaction of $HFe_2(CO)_8$ gives 1.2 mol (i.e. 2.4 mol/mol-$HFe_2(CO)_8^-$) of the product in 1.5 hr , having 1.2 of the ratio

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[*3] Probably, the reason may be the following. As the rate of the hydrolysis of the enamine (IV) into pyrrolidine and 2-methylcyclohexanone is much earlier than that of 1-morpholinocyclohexene, some pyrrolidine salt of the hydride (I) may be formed. This salt may be effective for the reductive alkylation of the ketone, however, the rate may be much slower than that of the reduction of the enamine.

of the cis to trans isomers. This fact apparently shows that $KHFe_2(CO)_8^-$ reduces the iminium salt 'catalytically'. After 1.5 hr, the ratio begins to decrease, showing the formation of the mononuclear hydride.

The reaction of $HFe_3(CO)_{11}$ stops after giving only 0.11 mol of the product. This shows that when a trinuclear hydride complex is formed in the reaction of $HFe(CO)_4$*4 and $HFe_2(CO)_8^-$, the reaction will soon stop in the absence of hydroxy ion.

The dramatic decrease of the ratio of the cis to trans isomers with an addition of alcoholic potassium hydroxide solution to the reaction solution may correspond to the reduction with the mixture of the mono- and binuclear hydride complexes in which the ratio of newly formed cis to trans isomers is 0.9. These results show that there is some interconversion among mono- and polynuclear hydride complexes as mentioned in the introduction.

In the reduction of iminium salt such as (IX) with lithium aluminum hydride, the ratio of the products (X)/(X') depends on the mole ratio of the iminium salt to the aluminum hydride.9) In the cases of the hydridocarbonylferrates (I), (II), and (III), such dependence of the mole ratio of the iminium salt to the hydrides was not observed.

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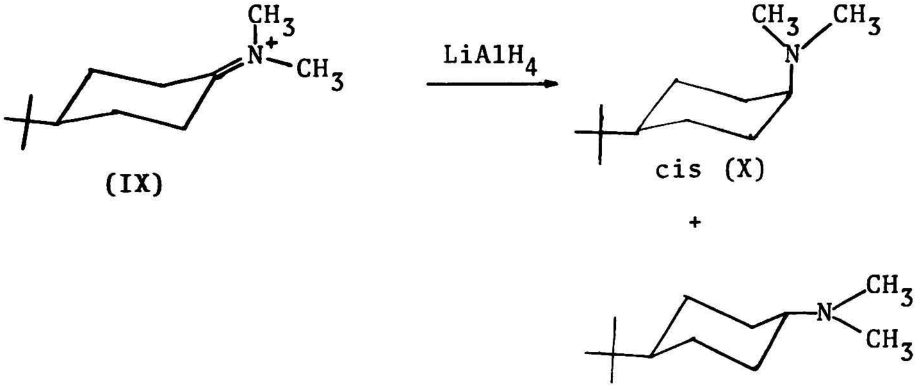
*4 In the reaction of 1-morpholinocyclohexene with (I), $HFe_3(CO)_{11}^-$ is detected in the reaction solution (see P 67).



(IX)

cis (X)

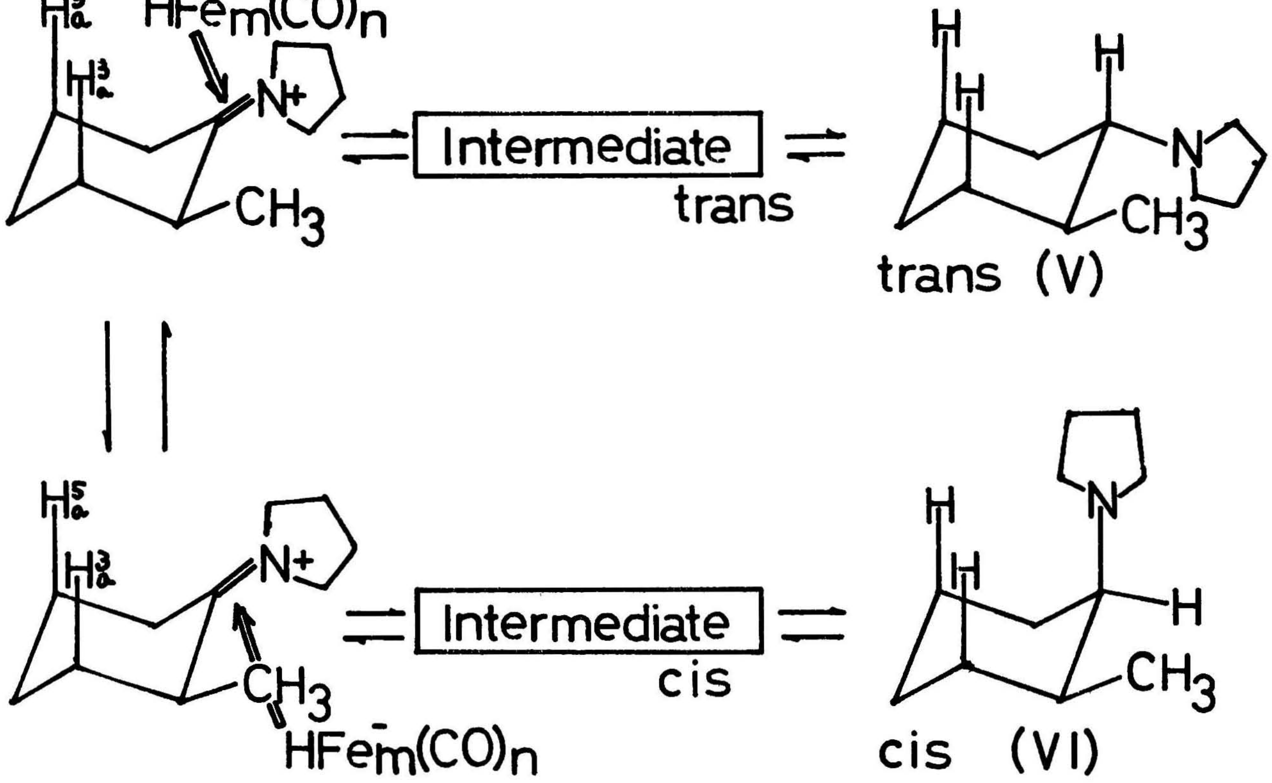
trans (X')

The Mechanism Which Determines the Ratio of the cis to trans Isomers. The following three factors which determine the ratio of the cis to trans isomers should be considered.

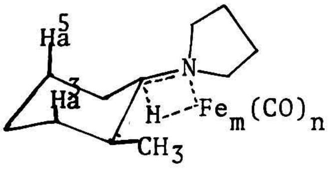
1) The first is the direction of the attack of the hydride complex to the iminium salt. The attack of the hydride complex from the side of H_a^3 and H_a^5 may give the trans isomers and the attack from the opposite side may give the cis isomer(Scheme 1). Usually, the attack of the hydride from the side of H_a^3 or H_a^5 is more retarded by the repulsion between the axial hydrogens H_a^3 and H_a^5 and the bulky hydride complex.

2) The second is the stability of intermediates. In the reaction of $HFe_m(CO)_n^-$, two kinds of intermediates sould be considered. One is the "multicentered" intermediates (XI) or (XI').

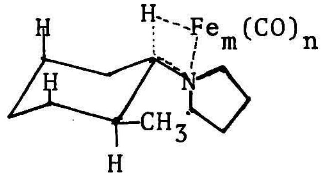
Scheme-1



H_a^5
H_a^3
$HFe_m^-(CO)_n$
N^+
CH_3
Intermediate
trans
H
N
CH_3
trans (V)
Intermediate
cis
cis (VI)



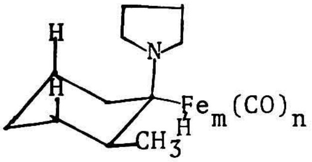
(XI)



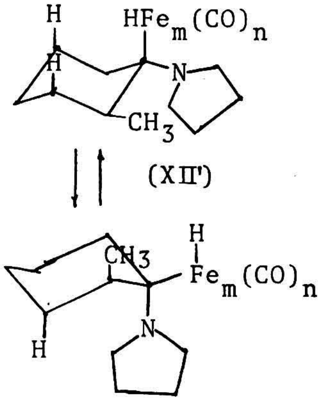
(XI')

In this case, (XI) and (XI') give the cis and the trans isomers, respectively. Considering the repulsion against the axial hydrogen at 3 or 5 position, (XI') may be more stable than (XI). Thus the trans isomer will predominate if the distribution of the products is determined with these intermediates.

The other is the intermediates having an iron-carbon bond such as (XII) or (XII').



(XII)



(XII')

In this case, (XII) and (XII') will give the cis and the trans isomers, respectively, with the reductive elimination. And the complex (XII) is resonably considered to be more stable than (XII') because $HFe_m(CO)_n$ group is more bulky than the pyrrolidine group. Thus, the cis isomer will predominate if the distribution of the products is determined with these intermediates.

3) The third is the stability of the products. As mentioned in the introduction, the trans isomer is more stable than the cis one. As described above, the results show that the isomerization between the cis and the trans isomers is actually negligible. Thus the distribution of the isomers is not determined by the stability of the isomers in this reaction system.

The results obtained in this study can be partly explained by two factors. The values of the ratio of the cis to trans isomers 2.1 and 1.2 for $HFe_3(CO)_{11}$ and $HFe_2(CO)_8$, respectively, can be explained by the direction of the attack. The values may be directly affected by the bulkiness of the hydride complexes. On the other hand, the small value of 0.67 of $HFe(CO)_4$, can not be explained by the direction of the attack of the hydride. It may be attributed to the stability of the intermediates. The repulsion between the hydrogens at 3 or 5 position and the attacking $HFe(CO)_4^-$ is smaller than that in the case of polynuclear hydride complexes. It is fully explained with the multicentered model (XI) or (XI').

In this case, the four centered model should be considered, which leads the ratio of the cis to trans isomers to less than

1.0. The intermediates having iron-carbon bond should be rejected since they would lead the ratio to more than 1.0.

There still remains some possibility that the high cis/trans ratio in the case of the polynuclear hydride complexes are due to the difference of the stability of the intermediates (XII) and (XII') , which have carbon iron bonds. However, it can not be explained why only the mononuclear hydride does not form these complexes.

Standing on these discussions, the series of the values of the cis/trans ratio, 0.67, 1.2 and 2.1 for (I), (II) and (III) respectively, represents the bulkiness of the complexes. However, these values can not be compared directly with that of the heterogeneous catalyst, because the mechanism of the reduction may be different.

To estimate the relative reactivities of the hydrides (I) (II) , and (III), the reaction of the enamine (IV) with these hydrides under an inert atmosphere was carried out. However, the reduction proceeds too repidly even at -60°C to be analyzed. This fact shows that the rate determining step of the reduction of enamine with an absorption of carbon monoxide is the reformation of hydride complexes in the reaction cycles.

Summary

The reduction of pyrrolidine enamine of 2-methylcyclohexanone with $HFe(CO)_4$ (I), $HFe_2(CO)_8$ (II) and $HFe_3(CO)_{11}^-$ (III) has been investigated. The products were cis- and trans-1-methyl-2-pyrrolidinocyclohexane. The ratio of the cis to trans isomers were characteristic of (I), (II) and (III), and they were 0.67, 1.2 and 2.1, respectively. These values are considered to represent the steric effect of the hydrides (I), (II) and (III). From the effect of the reaction conditions on the ratio, the mechanism of the reduction was discusses. The mechanism proposed in the previous chapter was strongly supported. The relative reactivity of (I), (II) and (III) could not be estimated, because tha rate of the reduction was very fast even at -60°C.

Refereces

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Appendix

In the reactions of the carbonylferrates (HFe(CO)$_4$, HFe$_2$(CO)$_4$ and HFe$_3$(CO)$_{11}^-$) with enamines, the reaction systems are so complicated that the precise mechanism of the reaction of the iminium salt and the reproduction of the active species with absorption of carbon monoxideis not clear at the present time. In this appendix, one of the possible mechanisms of these reactions will be proposed (Scheme-2).

The reaction of HFe(CO)$_4$: An iminium salt, I$^+$, which is formed by the protonation of an enamine, reacts with HFe(CO)$_4$ to give the amine complex A·Fe(CO)$_4$ 2. When a stronger base than the amine A, such as hydroxy ion exists, substitution reaction may occur to give the free amine and hydroxycarbonylferrate 3. As the complex 3 is also a base, it reacts with the complex 2 to give a dinuclear hydroxycarbonylferrate 4. Fig. 1 in Chapter 4 strongly suggests that this step is slow. During these steps 1 mol of the product is formed without an absorption of carbon monoxide. The complex 4 may react with carbon monoxide to give a hydroxy complex 5. The complex 5 is considered to be the same complex which is produced by the reaction of Fe$_2$(CO)$_9$ with hydroxy ion, and it decomposes to the dimeric hydride and carbon dioxide. The newly produced dinuclear hydride 6 further reduces the iminium salt (eq. 7). Since the binuclear hydroxy complex 4 is reproduced in the presence of hydroxy ion (eq. 8), the reaction proceeds catalytically. In these steps the amount of the product should be equal to that of carbon dioxide. The consumption of hydroxy ion may cause the termination of the catalitic cycle and there

Scheme 2.

$$\text{Enamine} + H^{+} \longrightarrow I^{+} \qquad (1)$$

$$I^{+} + \underset{\underline{1}}{HFe(CO)_4^{-}} \longrightarrow \underset{\underline{2}}{AFe(CO)_4} \qquad (2)$$

$$\underset{\underline{2}}{AFe(CO)_4} + OH^{-} \longrightarrow A + \underset{\underline{3}}{Fe(CO)_4OH^{-}} \qquad (3)$$

$$\underset{\underline{2}}{AFe(CO)_4} + \underset{\underline{3}}{Fe(CO)_4OH^{-}} \longrightarrow A + \underset{\underline{4}}{Fe_2(CO)_8OH^{-}} \qquad (4)$$

$$\underset{\underline{4}}{Fe_2(CO)_8OH^{-}} + CO \longrightarrow \underset{\underline{5}}{Fe_2(CO)_9OH^{-}} \qquad (5)$$

$$\underset{\underline{5}}{Fe_2(CO)_9OH^{-}} \longrightarrow \underset{\underline{6}}{HFe_2(CO)_8} + CO_2 \qquad (6)$$

$$\underset{\underline{6}}{HFe_2(CO)_8^{-}} + I^{+} \longrightarrow \underset{\underline{7}}{AFe_2(CO)_8} \qquad (7)$$

$$\underset{\underline{7}}{AFe_2(CO)_8} + OH^{-} \longrightarrow A + \underset{\underline{4}}{Fe_2(CO)_8OH^{-}} \qquad (8)$$

$$\underset{\underline{7}}{AFe_2(CO)_8} + 2\ CO \longrightarrow A + 2\ Fe(CO)_5 \qquad (9)$$

$$\underset{\underline{7}}{AFe_2(CO)_8} + \underset{\underline{3}}{Fe(CO)_4OH^{-}} \longrightarrow A + \underset{\underline{8}}{Fe_3(CO)_{12}OH^{-}} \qquad (10)$$

$$\underset{\underline{8}}{Fe_3(CO)_{12}OH^{-}} + \longrightarrow \underset{\underline{9}}{HFe_3(CO)_{11}} + CO_2 \qquad (11)$$

$$Fe(CO)_5 + 3\ OH^{-} \longrightarrow \underset{\underline{1}}{HFe(CO)_4^{-}} + CO_3^{2-} + H_2O \qquad (12)$$

I^{+} : Iminium salt

A : Saturated Amine

may be some ways in which the complex 7 is decomposed to the amine and pentacarbonyliron with an absorption of carbon monoxide. And the nononuclear hydride 1 is reformed by eq. 12. in the presence of hydroxy ion, then the reduction proceeds further.

If these assumptions are correct, the following equations should be satisfied. The results obtained in Chapter 4 show that these equations are approximately satisfied.

$$[CO_{absorbed}] = Fe(CO)_5 + [CO_{2\ formed}] \qquad (13)$$

$$[Product] = 1\ mol + [CO_{2\ formed}] \qquad (14)$$

The reaction of $HFe_2(CO)_8$: The first step is eq. 7. and the catalitic reduction by the cycle eqs. 7.→8.→5.→6. with absoption of carbon monoxide proceeds. Soon, the reduction with the mononuclear hydride complex 1 proceeds as descrived above.

The trinuclear hydride complex 9 detected in the reaction mixture of Exp.1(P 67)is considered to be formed by the reaction of the complex 7 with 3 (eqs.10. 11).

Chapter 6. The Reduction of Acyl Halide into Aldehyde via Acyltetracarbonylferrate(0)

Introduction

Previously, it has been reported that alkyl halides such as n-propyl iodide[1)] and ethyl α- or β-bromopropionate[2)] react with an ethanolic solution of tetracarbonylferrate, $Fe(CO)_4^{2-}$, with the absorption of carbon monoxide, to give a mixture of the corresponding carbonylated products, ethyl n-butyrate and n-butyraldehyde, and diethyl succinate and diethyl methylmalonate, respectively.

Recently, Cooke carried out an analogous reaction in tetrahydrofuran(THF) in the presence of triphenylphosphine; quenching with acetic acid, he found that alkyl bromides are carbonylated to the corresponding aldehydes in high yields.[3)] In these reactions, it can reasonably considered that acylcarbonylferrate complexes are formed as the reaction intermediates.[1-3)]

In this chapter, the reduction of acyl halide into aldehyde, which proceeds via acyltetracarbonylferrates is described.[4)]

Expeimental

Inrared spectra were measured on a Hitachi model 215 grating infrared spectrometer.

The reactions were carried out in two ways.

Method A. A 300 ml three necked flask was evacuated and flushed with nitrogen. One normal KOH-ethanol solution (44 ml) [5)] was added into the flask through a dropping funnel and 1.5 ml of $Fe(CO)_5$ (11 mmol) was added by use of a syringe. The mixture was agitated magnetically for 1 hr. The homogeneous yellow reaction mixture turned to pale yellow solution with a large amount of white precipitate, (K_2CO_3). The solvent was distilled off at 30°C under a vacuum of 1 mmHg and dried for 2 hr. Then 50 ml of dry aprotic solvent which had been dried over sodium dispersion, was added and the mixture was agitated to suspend the ferrate in the solvent. Acyl halide (11 mmol) was then added and agitated vigorously for a certain reaction time. Then the reaction mixture was submitted to g.c. analysis.

Method B. The reduction of benzoyl chloride to benzaldehyde illustrates a typical procedure. A $Na_2Fe(CO)_4$[3,6] solution in THF (7.3 mmol) was prepared by adding, drop by drop,[*1] 1.0 ml of $Fe(CO)_5$ in 25 ml of THF to 4 ml of a 1% sodium amalgam in 25 ml of THF under argon at room temperature with vigorous agitation. Almost equivalent mole of carbon monoxide is evolved during 1 hr. After the evolution of the gas stopped, the amalgam was removed through a side arm, and then to this solution was added 0.85 ml (7.3 mmol) of benzoyl chloride at 30°C. The mixture was stirred for 1 hr and then treated with 1.2 ml of glacial acetic acid. The mixture was stirred for an additional 5 min, then poured into 50 ml of water, and extracted with 20ml of pentane and then 20 ml of ethyl ether. The organic extracts were submitted to g.c. analysis.

Analytical Procedures. The products are identified by gas chromatography using the authentic samples (Column: SE-30 on Chromosorb, 3 mm x 1.5 m; Diethylene Glycol Adipate Polyester on Chromosorb, 3 mm x 3 m). Yields are determined using an appropriate internal standard previously calibrated against an authentic sample of pure aldehyde.

[*1] The THF solution of $Fe(CO)_5$ should be added drop by drop, or the reaction solution becomesorange red indicating the formation of clustered carbonylferrates.

Results

Acyl halides react with the ether solution of $K_2Fe(CO)_4$ prepared by the base reaction (method A) at room temperature to give the corresponding aldehydes.[4')] The results are summarized in Table 1. Aliphatic acyl halides as well as aromatic ones are reduced into the corresponding aldehydes, but the yields are not sufficient. The yields are not sufficient. The yield did not increase by the quenching with acetic acid. The decarbonylated products are also produced, but the yield of them are very low. α,β-Unsaturated acyl halides, acrylyl and crotyl chloride, react with $K_2Fe(CO)_4$, but acrolein and crotonaldehyde were not detected in the reaction solution. It is reasonably considered that α,β-unsaturated aldehydes are once produced and they further reacted. These α,β-unsaturated aldehydes have been found to react with carbonylferrates, however, no products were detected (See P 57). In the reaction of acrylyl chlolide, a trace of ethylene was dected.

Disodium tetracarbonylferrate(-II) in THF, which is prepared by the reduction of $Fe(CO)_5$ with sodium amalgam (method B), is more preferable for the reduction of acyl halides into aldehydes. The aldehydes are formed only after the quenching in contrast to the case of the method A. The results of the reactions are summarized in Table 2. Benzoyl chloride gives benzaldehyde almost quantitatively. Chloro-substituted benzoyl chloride should be treated at rather low temperature (Exps. 14 and 15). The yields of aliphatic aldehydes are more than 70%. Crotonyl chloride also react with $Na_2Fe(CO)_4$, however, crotonaldehyde was not detected. Diacyl halide such as phthaloyl dichloride was treated with 2 equivalent moles of $Fe(CO)_4^{2-}$ and quenched with acetic acid. The expected product, phthalaldehyde

Table-1 The Reduction of Acyl Halide into Aldehyde with $K_2Fe(CO)_4$ (Method A)

Exp. No.	Acyl Halide R-COX	Carbonyl-ferrate	Reaction Conditions Temp.°C	Time	Atmos.	Solvent	Yield R-CHO	mol/mol-$Fe(CO)_4^{2-}$ R-H
1	Benzoyl Chloride	$K_2Fe(CO)_4$	40	2 (hr)	N_2	THF	0.57	0.06
2	Butyryl Chloride	$K_2Fe(CO)_4$	30	3	N_2	THF	0.60	0.06
3	Isobutyryl Chloride	$K_2Fe(CO)_4$	40	2	N_2	THF	0.56	0.01
4	Isobutyryl Chloride	$K_2Fe(CO)_4$	30	2	CO	THF	0.39	~0
5	Isovaleryl Chloride	$K_2Fe(CO)_4$	30	2	N_2	THF	0.38	0.01
6	Isovaleryl Chloride	$K_2Fe(CO)_4$	35	3	N_2	Ethyl ther	0.32	0.01
7	Acrylyl Chloride	$K_2Fe(CO)_4$	30	3	N_2	THF	0	0.03
8	Crotonyl Chloride	$K_2Fe(CO)_4$	30	4	N_2	Dioxane	0	0

Table-2 The Reduction of Acyl Halide into Aldehyde with $Fe(CO)_4^{2-}$ (Method B)

Exp.	Acyl Halide	Reaction	Conditions*	Yield mol/mol-$Fe(CO)_4^{2-}$
No.	R-COCl	Temp.°C	Time(hr)	RCHO
9	Benzoyl Chloride	30	3·5	0·93
10	Benzoyl Chloride	30	1	0·95
11	Butyryl Chloride	30	1	0·75
12	Isobutyryl Chloride	30	1	0·71
13	Isobutyryl Chloride	60	1	0·71
14	p-Chlorobenzoyl Chloride	30	1	0·46
15	p-Chlorobenzoyl Chloride	0	1	0·74
16	o-Chlorobenzoyl Chloride	0	1	0·65
17	Crotonyl Chloride	30	1	0

* N_2 atmosphere, Solvent : THF

could not be detected but only phthalide was formed in low yield (7%).

Discussion

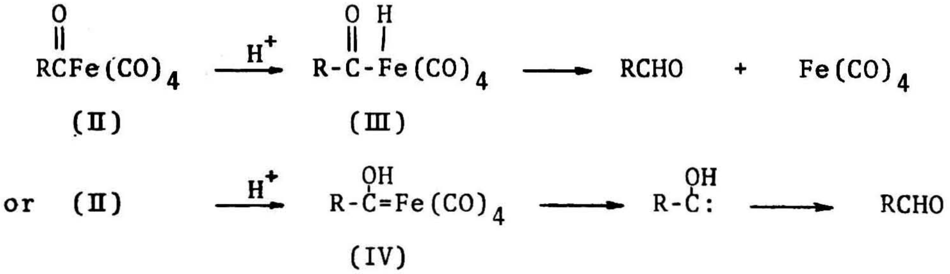
The mechanism of the reaction is reasonably considered to be as follows. In both methods A and B, acyl halide is attacked nucleophilically by tetracarbonylferrates(-II) to give acyltetracarbonylferrate(0) (II). In the method A, a proton may be abstracted from a trace of water, which remains in the reaction system, (See P 30) to give the corresponding aldehyde. In method B, as no proton source exists, the acylcarbonylferrate(0) (II) is stable in the reaction solution. Quenching the reaction solution with acetic acid causes the protanation of the acylcarbonylferrate and the aldehyde is formed.

$$\mathrm{RCOCl} \quad + \quad \underset{(\mathrm{I})}{\mathrm{Fe(CO)_4^{2-}}} \longrightarrow \underset{(\mathrm{II})}{\mathrm{RCOFe(CO)_4}} \xrightarrow{\mathrm{H^+}} \mathrm{RCHO}$$

In the case of method B, these reaction can ben followed by the infrared spectra. The band due to the stretching vibration of terminal carbonyl of the dianion $\mathrm{Fe(CO)_4^{2-}}$, 1780 $\mathrm{cm^{-1}}$, disappears with the addition of acyl halide and new bands at 1890 and 1590~1620 $\mathrm{cm^{-1}}$ appeared. The former is attributed to the terminal carbonyl of the acyltetracarbonylferrates (II) and the latter to the acyl group of the ferrates.$^{8)}$

Recently, Siegel et al. isolated the acylcarbonylferrates from the same reaction system as ours as bistriphenylphosphineiminium salts and characterized them.$^{8)}$ The lithium and tetraalkyl ammonium salts of the acylcarbonylferrates are also prepared by the reaction of alkyl lithium and pentacarbonyliron.$^{9)}$

The most different point of the acylcarbonylferrate in comparison with the acyltetracarbonylcobalt is that the former has a minus charge on it. As the low wave number of the stretching band of acyl and terminal carbonyls shows[*2] that the electron is back-donated to the acyl and terminal carbonyl group. This effect may be the main reason that the acylcarbonylferrate is much more thermally stable than acylcarbonylcobalt. Indeed, isobutyrylcarbonylferrate is stable even at 60°C, (Exp. 13). On the other hand, branched acylcarbonylcobalt is isomerized into a straight acylcarbonylcobalt at room temperature.11) As for the mechanism of the last step of the reduction, Cooke3) proposed a scheme in which the protonation of the acylcarbonylferrate occurs on the iron and acylhydridocarbonyliron(III) is formed, and then aldehyde is formed by the reductive elimination. There remains, however, the possibility that the protonation occurs on the oxygen atom of the acyl group, and unstable alkylhydroxycarbene complex (IV) is formed. Then the carbene ligand is liberated and isomerizes to aldehyde. However, it can not be concluded which scheme is correct in this study.



$$\underset{\text{(II)}}{\mathrm{R\overset{O}{\overset{\|}{C}}Fe(CO)_4}} \xrightarrow{H^+} \underset{\text{(III)}}{\mathrm{R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{/}{Fe}}(CO)_4}} \longrightarrow \mathrm{RCHO} + \mathrm{Fe(CO)_4}$$

$$\text{or}\quad \text{(II)} \xrightarrow{H^+} \underset{\text{(IV)}}{\mathrm{R-\overset{OH}{\overset{|}{C}}=Fe(CO)_4}} \longrightarrow \mathrm{R-\overset{OH}{\overset{|}{C}}:} \longrightarrow \mathrm{RCHO}$$

[*2] Ir spectra of neutral acylcarbonylcobalt complexes shows the bands at ~2000 and ~1700 $\mathrm{cm^{-1}}$.10)

The high yield and selectivity, the resistance against the skeletal rearrangement, and the facility of the reaction procedures enable us to utilize this reaction instead of the Rosenmund reduction[12) and the reduction with $LiAlH(OR)_3$.[13)

The acyltetracarbonylferrate can be attacked by another electrophile, indicating that it can be utilized as a starting materials for further organic syntheses. Recently, Collman et al. synthesized unsynmetrical ketones by the reaction of the acylcarbonylferrates and alkyl halides.[14)

In the next chapter, the intramolecular nucleophilic attack of the acyl group of the acylferrates will be discussed.

Summary

Acyl halides are easily reduced to aldehydes with $Fe(CO)_4{}^{2-}$ which was prepared in two ways. One is the base reaction of $Fe(CO)_5$ with KOH, (method A). The other is the reduction of $Fe(CO)_5$ with sodium amalgam, (method B). The yield of the aldehyde was not satisfactory in metod A. On the other hand, aldehyde is obtained in good yield by method B. In both cases, the reaction proceeds via acylcarbonylferrate, and the skeletal rearrangement has not been observed in contrast to acylcarbonylcobalt. The high yield of the aldehydes and the facility of the reaction procedures enables us to utilize this reaction instead of the Rosenmund reduction and the reduction with $LiAlH(OR)_3$.

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Chapter 7. The Reaction of Polyacyl Halides with Tetracarbonylferrate(-II)

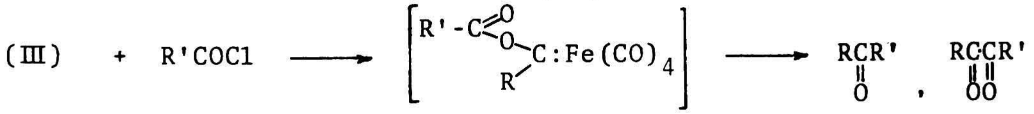
Introduction

In the previous chapter, it has been described that acyl halides react with disodium tetracarbonylferrate(-II) (I) to give the acyltetracarbonylferrates (II), which are then decomposed with acid to the corresponding aldehydes in good yields.[1]

$$\underset{\text{(I)}}{Na_2Fe(CO)_4} + RCOCl \longrightarrow \underset{\text{(II)}}{Na[RCOFe(CO)_4]} \xrightarrow{H^+} RCHO$$

On the other hand, Sawa and his coworkers reported that lithium acyltetracarbonylferrates (III), which are prepared from $Fe(CO)_5$ and organolithium compounds, react with acyl halides to give ketones and/or α-diketones. It is strongly suggested that the reaction proceeds via the aryl- or alkylacyloxycarbeneiron complex (IV);[2]

$$RLi + Fe(CO)_5 \longrightarrow \underset{\text{(III)}}{Li[RCOFe(CO)_4]}$$



(IV)

However, the coupling compund of the carbene ligand was not formed and the structure of the carbene ligand is not kept in the product.

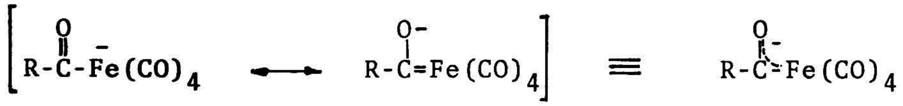
Recently, Collman et al. reported in a short communication that acyltetracarbonylferrates (II) react with alkyl halide to give ketones in good yields.[3] They proposed that the reaction proceeds by the following scheme.

$$Na[RCOFe(CO)_4] + R'Cl \longrightarrow \overset{RCO}{R'}{>}Fe(CO)_4 \longrightarrow R\underset{\underset{O}{\|}}{C}R'$$

(II) (V)

The nucleophilic attack of the acyltetracarbonylferrate on the alkyl halide forms alkylacylcarbonyliron(II) (V), which produces ketone by the reductive elimination.

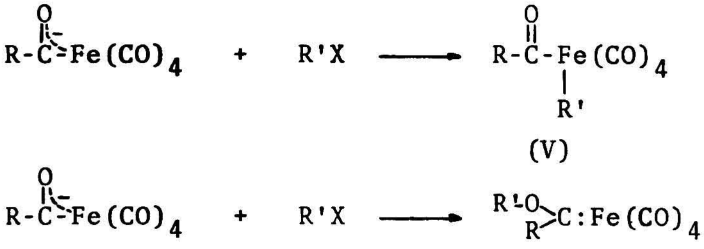
In these reactions, it is interesting to discuss about the electronic structure of acyltetracarbonylferrates (II) and the direction of the electrophilic attack on it. As mentioned in the previous chapter (see P 116) acyltetracarbonylferrate has a minus charge on it and the charge is delocalised on the molecule, especially on the acyl group, and should be represented as (VI).



$$\left[R-\overset{\overset{O}{\|}}{C}-\overset{-}{Fe}(CO)_4 \longleftrightarrow R-\overset{\overset{O^-}{|}}{C}=Fe(CO)_4\right] \equiv R-\overset{O^-}{C}\text{⋯}Fe(CO)_4$$

(VI)

Thus, an electrophilic attack on the acylcarbonylferrate should occur in two ways. One is the attack on the iron atom, and the other is on the oxygen atom of the acylgroup. When the electrophile is alkyl halide, the former attack will give an alkylacylcarbonyliron (V) and the latter attack will give an alkylalkoxycarbene complex (VII).



$$R-\overset{O^-}{C}\text{⋯}Fe(CO)_4 + R'X \longrightarrow R-\overset{\overset{O}{\|}}{C}-\underset{\underset{R'}{|}}{Fe}(CO)_4$$

(V)

$$R-\overset{O^-}{C}\text{⋯}Fe(CO)_4 + R'X \longrightarrow \overset{R'O}{R}{>}C:Fe(CO)_4$$

(VII)

In this chapter, the reaction of diacyl halides with disodium tetracarbonylferrate,in which the first step is considered to be the formation of acylcarbonylferrate complexes and the second step may be the intramolecular electrophilic attack, will be discussed.

Experimental

Infrared spectra were measures on a Hitachi model 215 grating infrared spectrometer. Mass spectra were obtained with a JMS-01SG mass spectrometer. UV spectra were taken with a Hitachi model EPS-3T spectrophotometer.

Materials. Pentacarbonyliron, hexacarbonylchrom, phthaloyl dichloride, succinoyl dichloride, tetrahydrofuran, N, N-dimethylformamide, methyl crotonate, cyclohexene were commercial products, and were distilled before use except metal carbonyls. Pyromellityl tetrachloride$^{5)}$ (benzene-1,2,4,5-tetracarbonyl tetrachloride) and 1,8-naphthalenedicarbonyl dichloride$^{6)}$ were prepared by the method described in literatures.

Pyromellityl tetrachloride: m.p. 68.5~70.0°C. Found: C, 36.82; H, 0.62%. Calcd. for $C_{10}H_2O_4Cl_4$: C, 36.63; H, 0.62%.

1,8-Naphthalene dicarbonyl dichloride: m.p. 86~88°C. Found: C, 59.58; H, 2.23%. Calcd. for $C_{12}H_6O_2Cl_2$: C, 56.95; H, 2.39%.

The Preparation of Disodiumtetracarbonylferrate. Disodium tetracarbonylferrate was prepared as described in the previous chapter (see P 111).$^{1)}$

The Reaction of Phthaloyl Dichloride with $Na_2Fe(CO)_4$. Into $Na_2Fe(CO)_4$ (11mmol) in 50 ml THF, was added 1.6 ml (11 mmol) of phthaloyl dichloride with stirring at -40°C under argon. After 1 hr, the mixture was warmed to 40°C and stirred for 2 hr. Then the solvent was distilled off under a reduced pressure and the residue was washed with water, 6 N HCl, water again, and then ethyl ether. The orange yellow precipitate (0.81 g) thus obtained was treated with acetone solution of $CuCl_2.2H_2O$ at 60°C for 10 min to decompose a small amount of $[HgFe(CO)_4]_n$ which is formed by the side reaction. The yellow precipitate was filtered and washed with water, ether and dried, and recrystalized from chloroform.

Biphthalidylidene, (0.33 g) yield, 35%; Mp 340~341°C (339~341°C).4) Found: C, 72.25; H, 3.17% Mol. wt. (Mass) 264. Calcd. for $C_{16}H_{18}O_4$; C, 72.73; H, 3.05%, Mol. wt. 264.22. IR (KBr); 3085(ν_{CH}, w), 1785($\nu_{C=O}$, s), 1605(m), 1590(m), 1478(m)(benzene ring), 758(s), 678 (s)(ortho disubstituted benzene) cm^{-1}. UV: $\lambda_{max}^{CH_3CN}$ mμ(logε); 221(4.35), 226(4.38), 257(4.09), 293(4.02), 304(4.07), 3.56(4.39). These spectra are identical with those of trans-biphthadylidene reported previously.4) The reaction was carried out in THF-DMF(1:1) solvent to give the product in 29.3% yield. The reflux of the reaction solution caused the yield of the product to decrease to 7%.

The Reaction of Phthloyl Dichloride with $Na_2Fe(CO)_4$ in the Presece of Olefin. An equivalent mole of cyclohexene or methyl crotonate was added to $Na_2Fe(CO)_4$ in THF before the addition of phthaloyl dichloride. However, the derivatives of cyclopropane was not detected.*1 The yield of biphthlidylidene was only 3~5%.

The Reaction of Pyromellityl Tetrachloride with Disodium Tetracarbonylferrate. Pyromellityl tetrachloride(3.6 g, 11mmol) in 25 ml THF was added dropwise at -65°C into $Na_2Fe(CO)_4$ (22 mmol)

*1 Cyclopropane derivatives has been prepared by the reaction of carbene complex with methyl crotonate.7) in 150 ml of THF. Then the reaction solution was warmed to room temperature and was stirred for 2 hr. Then, 80 ml of 6 N HCl and 50 ml of ether was added. Dark red precipitate formed was separated by filteration and washed with water, ethanol and ether. As this precipitate contained a small amount of $[HgFe(CO)_4]_n$, it was treated with the acetone solution of $CuCl_2.2H_2O$ at 60°C for 1 hr. Dark red precipitate (A) was separated by filteration and washed with acetone and water, and dried under vacuum. This precipitate (A) (1.8 g) was insoluble in almost organic solvents except DMF. The precipitate was dissolved in DMF (35 ml) and reprecipitated by the addition of 300 ml of benzene. Dark red precipitate was collected and washed with benzene and n-hexane and dried. Yield, 0.58 g. M.p.; the color slightly darkens at 340∼350°C, however, does not melt under 360°C. IR(KBr), 3400~3000(br. s), 1790(vs), 1720(m), 1620(m), 1220(br. m), 1020(s), 780(m) cm^{-1}. VR: λ_{max}^{DMF}(mμ)(logε)[*2] 377(4.9) 450(sh 3.96). Found: C, 56.15; H, 2.72%. Calcd. for $C_{30}H_{10}O_{16}$; C, 57.52; H, 1.62%. Calcd. for$C_{20}H_8O_{12}$: C, 54.56; H, 1.83%. Molecular weight was measured by a Hitach-Perkinelmer Molecular Weight Apparatus model 115 using DMF solvent, since the sample dissolves in only DMF. However the solvent was not appropriate and only approximate data were obtained. Mol. wt: 500∼600. As the sample was nonvolatile at 350°C under 10^{-7} mmHg, mass spectrum could not be taken.

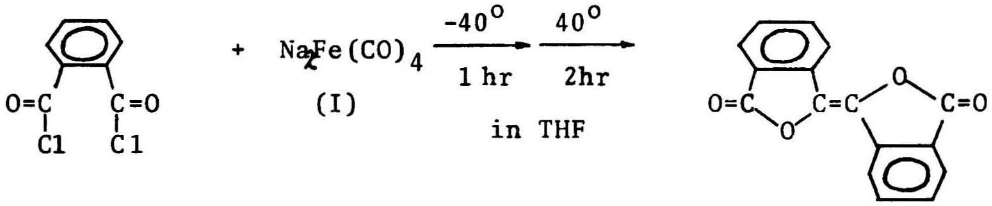
[*2] Calculated by the posturation that the molecular weight is 626.

The Reaction of 1,8-Naphthalene Dicarbonyl Dichloride. To a THF solution of $Na_2Fe(CO)_4$ (11 mmol in 75ml THF), was added 2.8 g (11 mmol) of 1,8-naphthalene dicarbonyl dichloride in 50 ml THF at -70°C. After 1 hr the mixture was warmed to 40°C and stirred for 4 hr. Then, 60 ml of 2 N HCl and 50 ml of ether was added and the precipitate formed was collected by filteration. As a trace of $[HgFe(CO)_4]_n$ was formed as a contaminant, it was decomposed by treating with $CuCl_2.2H_2O$ in acetone at 40°C for 10 min. The yellow orange precipitate was filtered off and washed with water and ether, and then dried. The precipitate was dissolved in chloroform and reprecipitated by the addition of n-hexane. Yield, 0.33 g. Mp 257°C decomp. IR(KBr): 3040(w), 1730(br. vs), 1590(m), 1465(m), 1350(m), 1240(m), 1180(m) 1100(m), 830(m), 775(s). UV: λ_{max}^{dioxan}(mμ)(logε) 328(4.09), 302(4.12). The nmr spectra could not be taken as the solubility was very low. Mass: m/e 364. Found: C, 75.64, 75.23; H, 3.62, 3.37%. Calcd. for $C_{24}H_{12}O_4$, C, 79.11; H, 3.32%. $C_{24}H_{14}O_5$, C, 75.39; H, 3.69%.

The Reaction of Succinoyl Dichloride. To $Na_2Fe(CO)_4$ in THF (44 mmol; THF, 325ml) was added 5.0 ml (44 mmol) of succinoyl dichloride at -60°C, and stirred for 2 hr and then warmed to room temperature and stirred for additional 1 hr at 40°C. The solvent was distilled off at 30°C under 80 mmHg and 12.2 g of residue was obtained. From the distillate 3.9 g (19.7 mmol) of $Fe(CO)_5$ was recovered. The residue was placed into a sublimation apparatus which has been connected to a trap immersed in a dry ice bath. Then the apparatus was heated to 140°C under 1 mmHg and 0.19 g of a pale yellow liquid was obtained. This liquid was a five membered lactone contaminated with $Fe(CO)_5$. IR(liquid film): 3020(w), 2000(s), 1940(m), 1780(vs), 1745(s), 1620(w), 1600(w), 1450(m), 1160(s), 1090(s), 1038(s), 880 (s), 810(s) cm^{-1}. This IR spectrum is almost identical with that of the authentic sample of the lactone of γ-hydroxycrotonic acid except the bands at 2000 and 1940 cm^{-1}.

Results and Discussion

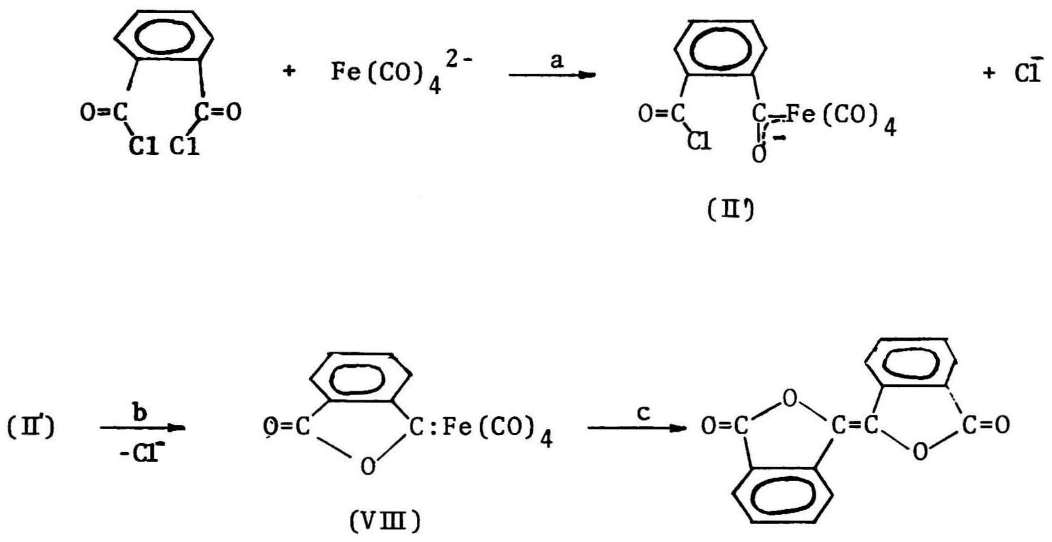
Phthaloyl dichloride reacts with an equivalent mole of $Na_2Fe(CO)_4$ (I) in THF at -40∿40°C to give biphthalidylidene.8) The yield was 35%.



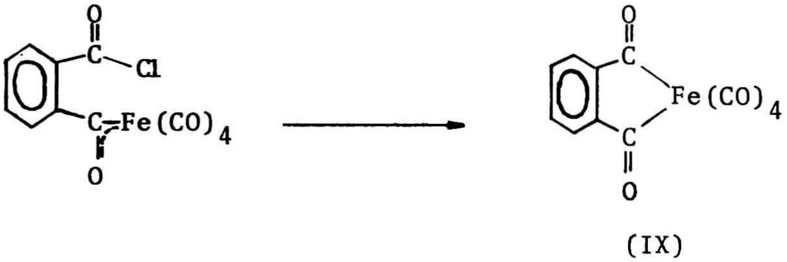
The reflux after the addition of phthaloyl dichloride at 70°C or the reaction in N,N-dimethylformamide gave the product in low yield.

The mechanism of the formation of biphthalidylidene is not completely clear at the present time, but a plausible reaction scheme may be presented(Scheme-1). First, $Fe(CO)_4^{2-}$ attacks one of the acyl halide group in phthaloyl dichloride to give an acylcarbonylferrate (II') (step a). Then the oxygen atom of the acyl group attached to iron attacks another acyl carbon atom nucleophilically to form a lactonic carbenecarbonyliron complex (III) (step b), which then decomposed thermally and the two phthalidylidene groups couple to form biphthalidylidene (step c).

Scheme 1



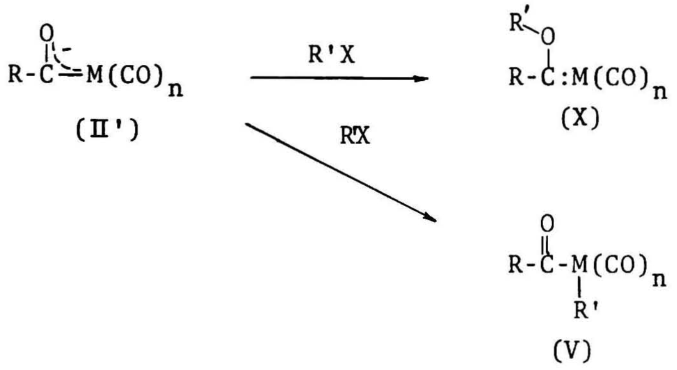
As for the first step a, this reaction is investigated in the previous chapter. The second step b is the key step for the formation of a phthalidyl ring. In this step, the oxygen atom of the acylcarbonylferrate attacks the other acyl carbon atom nucleophilically to form a lactonic carbene carbonyliron complex (VIII). If the iron atom attacks the acyl carbon atom, diacylcarbonyliron complex (IX) is formed.



(IX)

Indeed, the ir spectrum of the reaction solution shows a weak band at 1700 cm^{-1} of acyl carbonyl group. However, the complex (IX) could not be isolated.

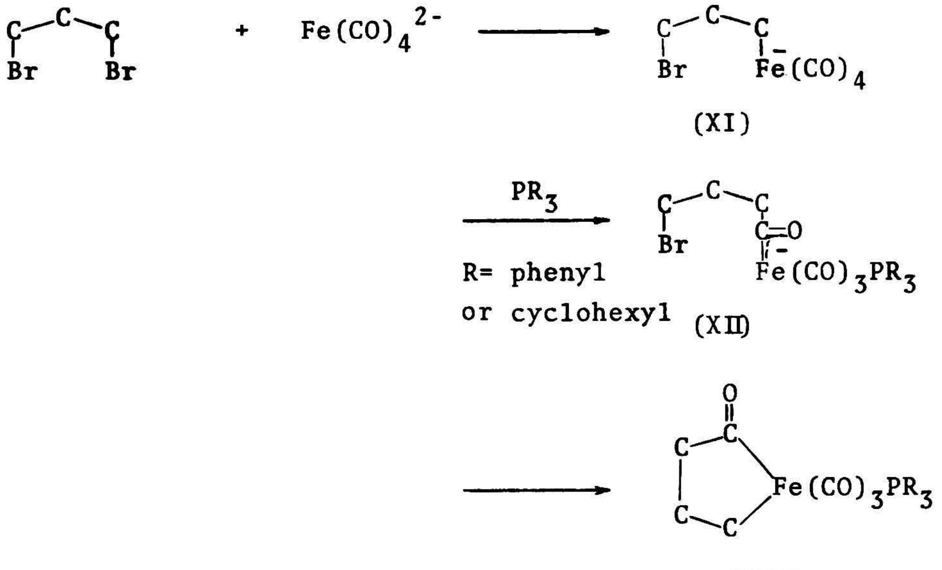
As described in the introduction, it is interesting that which atom of the acylcarbonylferrate complex, the oxygen or iron, makes a nucleophilic attack on another electrophile. The nucleophilic attack of the oxygen atom will produce a zerovalent carbene complex (X). The nucleophilic attack of the iron atom will give a divalent acylalkylcarbonyliron (V).



Fischer et al.$^{9)}$ and Connor et al.$^{10)}$ prepared alkylalkoxycarbene and alkylacetoxycarbene complexes of the VI group metal. Sawa et al.$^{2)}$ proposed that alkylacetoxycarbene complex is formed in situ in the reaction of lithium acylcarbonylferrate with acyl halide.

The nucleophilic attack of the iron atom is observed in the reaction of tetracarbonylferrate (I) with 1,3-dibromopropane in the presence of phosphines.$^{11)}$ In this reaction, 2-ferracyclopentanone complex (XIII) is isolated in about 10% yield.

Apparently, this reaction is reasonably considered to follow the Scheme-2. First, alkylcarbonylferrate (XI) is formed and then it is carbonylated to form the acyl complex (XII) ,in which iron, not oxygen, intramolecularly attacks the bromomethylene group nucleophilically to form a 2-ferracyclopentanone complex (XIII).



(XI)

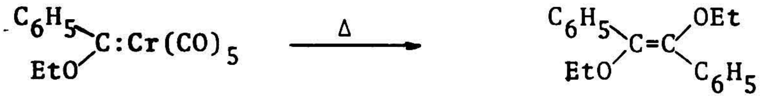
R= phenyl
or cyclohexyl

(XII)

(XIII)

The factors, which determine the direction of the nucleophilic attack of acylcarbonylferrate, are under studing.

As for the last step of the Scheme 1, Fischer reported that the pyrolysis of a phenylalkoxycarbenechromium complex (XIV) gives the dimer of the carbene ligand (XV).12)



(XIV)

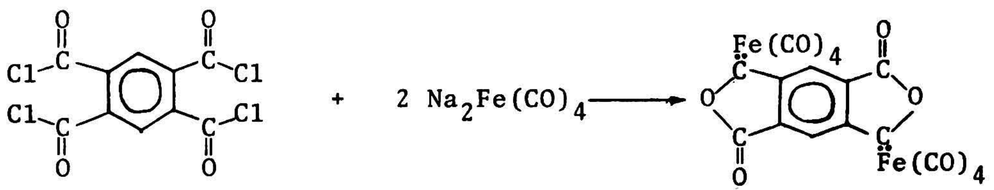
(XV) cis and trans

Since the steps b and c are fast, these steps could not be followed by means of infrared spectra even at -40°C. The band at 1780 cm^{-1} disappeared with an addition of acyl halide and the new bands at 2020, 1940, and 1790 cm^{-1} appeared.

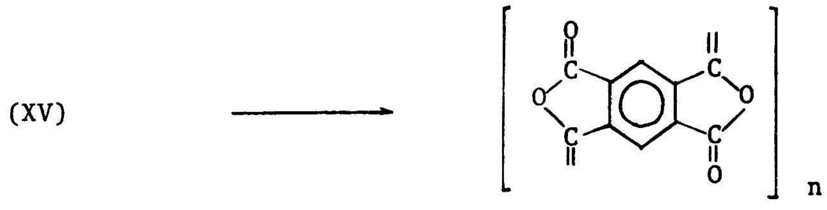
To confirm the formation of carbene carbonyliron complex, the reaction was carried out in the presence of olefins such as cyclohexene or methyl crotonate.[7)] However, the expected products, the derivatives of cyclopropane, were not detected. Since the yield of biphthalidylidene decreased less than 5%, some interactions of the olefins with the intermediate complexes are cosidered to occur.

The preparation of phthalidylidene complex of chromium pentacarbonyl by the reaction of phthaloyl dichloride with disodium pentacarbonylchromate has been attempted. However, the complex was not isolated probably because of the instability of the complex, and only a trace of biphthalidylidene was obtained.

The reaction of the pyromellityl tetrachloride with $Na_2Fe(CO)_4$ was carried out. If the reaction proceeds analogously in the case of phthaloyl dichloride, the polymer of the type (XVI) should be produced via bicarbenecarbonyliron complex (XV). This polymer is expected tobe heat-resisting and electrically conductive.



(XV) cis or trans



(XVI)

The product was shown to have a five membered lactonic ring and UV spectrum of the product shows that it is highly conjugated. But the molecular weight was not so large and the product is considered to be the mixture of oligomers in which n was less than 4. The major reason of the termination of the reaction may be the insolubility of the intermediates in the solvent.

The reaction of 1,8-naphthalene dicarbonyl dichloride with $Na_2Fe(CO)_4$ was carried out. Yellow powder (m.p. 257^oC decomp.) was obtained in fairly good yield but the product was the mixture of several compounds and the purification was unsuccessful. Mass spectra showed that one of the products has a molecular weight which corresponds to the dimer structure. The elemental analysis of the reprecipitated sample also supports the formation of the dimer, but it was just coincident with the monohydrated dimer, $C_{24}H_{12}O_4$. The nmr spectra could not be taken because of the low solubility of the product in any solvent, and the structure of the products could not be determined.

The reaction of succinoyl dichloride with $Na_2Fe(CO)_4$ was carried out. The coupling products of the lactonic carbene ligand could not be detected. However, a small amount of five membered unsaturated lactone was detected by ir spectra. The yield was less than 5%.

Summary

The reaction of polyacyl halides with $Na_2Fe(CO)_4$ (I) in THF at -40~40°C has been investigated. Phthaloyl dichloride reacts with (I) to give biphthalidylidene in 35% yield. The mechanism via carbene carbonyliron is proposed. Pyromellityl tetrachloride reacts with (I) to give a product which is considered to be an oligomer of the bicarbene ligand. 1,8-Naphthalene dicarbonyl dichloride also reacts with (I) to give a dimer, but the structure of which could not be determined. Succinoyl dichloride also reacts with (I), but the coupling product of the lactonic carbene ligands could not be detected. However, a small amount of unsaturated five membered lactone was detected by ir spectra.

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General Conclusions

The reactions of the carbonylferrates $Fe(CO)_4^{2-}$ (I), $HFe(CO)_4^-$ (II), $HFe_2(CO)_8^-$ (III), $Fe_2(CO)_8^{2-}$ (IV) and $HFe_3(CO)_{11}^-$ (V), with organic compounds have been investigated. Chapters 1∿5 dealt with the reactions of the alcoholic solution of the ferrates in wich hydrogen transfer readily occurs. Chapter 6 and 7 dealt with the reaction of (I) in aprotic solvent, which was prepared by the reduction of pentacarbonyliron with sodium amalgam. In this system, hydrogen transfer does not occur, and the electrophilic attack by a reagent other than a proton is possible.

In Chapter 1, the reactions of olefin oxides with the carbonylferrates $K_2Fe(CO)_4$ (I), $KHFe(CO)_4$ (II) and $K_2Fe_2(CO)_8$ (IV) were summarized. Aliphatic 1,2-olefin oxides are generally reduced with the carbonylferrate(I) into the corresponding olefins with an absorption of carbon monoxide with the by products such as carbonylated products and alcohols. In the reaction of styrene oxide, styrene is formed as wall as α- and β-phenylethyl alcohol. However, no carbonylated products were obtained. Internal olefin oxides did not react. As the mechanism of the deoxygenation of olefin oxides, the elimination reaction of β-hydroxyalkylcarbonylferrates has been proposed.

In Chapter 2, the reduction of alkyl, aryl and allyl halides with the carbonylferrates (I), (II) and (IV) in alcohol has been studied. These halides reacts with the ferrates to give the corresponding hydrocarbons. The reactivity of alkyl halide decreaces in the order RI > RBr > RCl. Activated alkyl halides such as allyl halide, benzyl halide and α-haloacetone give the corresponding reduced products, propylene, toluene and acetone, respectively, even when the halides are chlorides. The mechanism including alkyl-, aryl- and

σ- or π-allyl carbonylferrates is proposed.

In Chapter 3, the reaction of potassium hydridocarbonylferrate (II) with isoprene has been studied. Isoprene is selectively reduced at room temperature to give three monoolefins, 3-methyl-1-butene, 2-methyl-1-butene and 2-methyl-2-butene. The reduction of these monoolefins into isopentane did not occur. The reaction conditions (solvents, atmospheres and additives) have great effects on the yieldsand the distribution of the olefins. Under carbon monoxide and in the presence of water, the reduction is highly promoted giving 2 mol/mol-$Fe(CO)_4$ of olefins. The reaction is considered to proceed via σ- and π-allylcarbonyliron complexes. In the appendix, cinnamaldehyde is found to be selectively reduced into 3-phenylpropionaldehyde.

In Chapter 4, the reaction of enamines with alcoholic solution of $HFe(CO)_4^-$, $HFe_2(CO)_8^-$ and $HFe_3(CO)_{11}^-$ were investigated. The reaction proceeded with an absorption of carbon monoxide, however, no carbonylated product could be detected. Only a reduced product, saturated tertiary amine, was obtained in a good yield. In some cases, the yield of the product exceeds 2 mol/mol-$Fe(CO)_4^{2-}$, indicating that active species are reproduced during the reaction. The equimolar mixture of a ketone and a secondary amine was found to react with $HFe(CO)_4$ with absorption of carbon monoxide to form the corresponding tertiary amine.

In Chapter 5, the reduction of pyrrolidine enamine of 2-methylcyclohexanone with $HFe(CO)_4^-$, $HFe_2(CO)_8^-$ and $HFe_3(CO)_{11}^-$ was investigated. The products were cis- and trans-1-methyl-2-pyrrolidinocyclohexane. The ratios of the cis to trans isomers were characteristic of the mono-, di- and trinuclear hydrides and they were 0.67, 1.2 and

2.1 respectively. These values are considered to represent the steri effect of the mono and polynuclear complexes. From the effect of the reaction conditions on the ratio, much information about the mechanism of the reduction and the reproduction of the active hydride species were obtained. The following mechanisms have been strongly supported. In the reaction of $KHFe(CO)_4^-$, enamine is reduced with the mononuclear hydride in the first step and then the reduction with the dinuclear hydride proceeds with absorption of carbon monoxide. A small amount of the trinuclear hydride complex, $HFe_3(CO)_{11}$, is also detected in the reaction solution. In the reaction of $HFe_2(CO)_8$, at first, the enamines are reduced with the dinuclear hydride and then with the nononuclear hydride.

In Chapter 6, The reduction of acyl halides into aldehydes with $Fe(CO)_4^{2-}$ has been studied. The reaction is considered to proceed via acyltetracarbonylferrate. The isomerization of acyltetracarbonylferrate was not observed in contrast to the acylcarbonylcobalt. This reduction can be utilized instead of Rosenmund reduction and the reduction with $LiAlH(OR)_3$.

In the last chapter, the reaction of polyacyl halides with tetracarbonylferrate in THF has been investigated. The reaction of phthaloyl dichloride with the ferrate at -40∿40°C gave biphthalidylidene. This reaction is considered to proceed via a lactonic carbene carbonyliron complex.

The results obtained in this thesis show that the alcoholic solution of the carbonylferrates have strong reducing ability for various organic compounds. Though, the reducing ability of the carbonylferrates is not stronger than that of lithium aluminum hydride, the reducing ability of the ferrates is very characteristic. This ability of the reduction seems to indicate the degree of the nucleophilicity of the ferrates, because the first step of the reduction is the nucleophilic attack of the ferrates except the reduction of enamines and isoprene. In the reaction of $HFe(CO)_4$ with isoprene and enamine, more than 1 mol/mol-$Fe(CO)_4{}^{2-}$ of carbon monoxide is absorbed and the yield of the product amounts to more than that is expected by the stoichiometric reaction. These facts show that the active species are reproduced in the reaction system. The scheme including the interconversion of mono- and polynuclear hydrido complexes has been proposed in Chapter 5.

In a moist alcohol solution, the formed iron-carbon bonds are readily cleaved by the protonation of the complexes. If the protonation of the complexes are disturbed, the intermediate complexes which have alkyl or acyl-iron bonds are often stable in the reaction solution. These complexes can be utilized for further organic syntheses. The reactions in the last chapter show the examples of this method.

In each chapter, the mechanism of the reaction is proposed, however, the proof is not complete because of the complexity of the reaction. Further study is necessary for the full explanation of the mechanisms of these reactions.