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Studies of the Organic Reactions of Metal Carbonyls. XIV.*[1] The Reaction of Potassium Iron Carbonylates with Isoprene

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The reaction between potassium iron carbonylates ($KHFe(CO)_4$, $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$) and isoprene has been studied. Isoprene is reduced at room temperature to give three olefins (3-methyl-1-butene (I), 2-methyl-1-butene (II), and 2-methyl-2-butene (III)). The reaction conditions (solvents, atmospheres, additives such as water) have a great effect on the yield and 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 the olefins. The percentage of II is almost constant (about 15%) in any case, but the percentages of I and III, very dependent on the conditions, change in the 3—40 and 50—80% ranges respectively. The reaction is suggested to proceed *via* some kinds of σ- and π-allyl iron carbonyl complexes. Under carbon monoxide the carbonylation of isoprene also occurs.

Previous work in this laboratory has shown that potassium iron carbonylates ($KHFe(CO)_4$, $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$) react with styrene oxide under carbon monoxide to give styrene and carbon dioxide.[1] Several workers have also shown that $H_2Fe(CO)_4$ and $KHFe(CO)_4$ have a large activity in the reduction of organic compounds, such as acetone, nitrobenzene, quinone, and acetylene.[2]

The present study will deal with the reaction of the iron carbonylate, mainly $KHFe(CO)_4$, with isoprene. The results obtained indicate that isoprene is reduced to give three different monoolefins, and that the yield and distribution of the olefins are remarkably affected by the reaction conditions.

Experimental

The Preparation of Potassium Iron Carbonylates, $KHFe(CO)_4$, $K_2Fe(CO)_4$. The alcoholic solutions of these salts were prepared according to the method described in a previous paper.[1] An 80 m*l* portion of 0.14 M $KHFe(CO)_4$ or $K_2Fe(CO)_4$ solution was used in each run.

When $KHFe(CO)_4$ is prepared, an equivalent mole of water is formed:[3]

$$Fe(CO)_5 + 3KOH \xrightarrow{\text{in alcohol}} KHFe(CO)_4 + K_2CO_3 + H_2O$$

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

Materials. The isoprene, iron pentacarbonyl, methyl ethyl ketone, tetrahydrofuran, isopropyl ether, and other compounds employed in this study were all commercial products.

Reaction Procedures. Under Atmospheric Pressure. To the solution of the potassium iron carbonylate described above, 5 m*l* (50 mmol) of isoprene and 0.4 m*l* of cyclopentane, as an 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 m*l* sample of the solution was removed and then diluted with 1.5 m*l* of cyclohexane. This cyclohexane solution was immediately submitted to analysis.

Under Hydrogen Pressure. An autoclave (100 m*l*) equipped with a magnetic stirrer was used. 1.5 m*l* of $Fe(CO)_5$, 33 m*l* of a 1 N KOH solution in ethyl alcohol, and 5 m*l* 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/cm². 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 using a PEG-Golay column. Further, the monoolefins produced were confirmed by being converted to isopentane; after hydrogenation with Raney

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*[1] Part XIII: This Bulletin, **41**, 158 (1968). Presented in part at the Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

1) Y. Takegami, Y. Watanabe, T. Mitsudo, I. Kanaya and H. Masada, This Bulletin, **41**, 158 (1968).

2) Ger. Patent 441, 179 (1925); H. W. Sternberg, R. A. Friedel, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **78**, 3621 (1956); H. W. Sternberg, R. Markby and I. Wender, *ibid.*, **78**, 5704 (1956); H. W. Sternberg, R. Marbky and I. Wender, *ibid.*, **79**, 6116 (1957).

3) P. Krumholz and H. M. A. Stettiner, *ibid.*, **71**, 3035 (1949).

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$_2$Fe(CO)$_4$ with Isoprene in Ethyl Alcohol. The results of the reactions are summarized in Table 1 and in Figs. 1 and 2. All of the reactions were carried out in ethyl alcohol at 30°C.

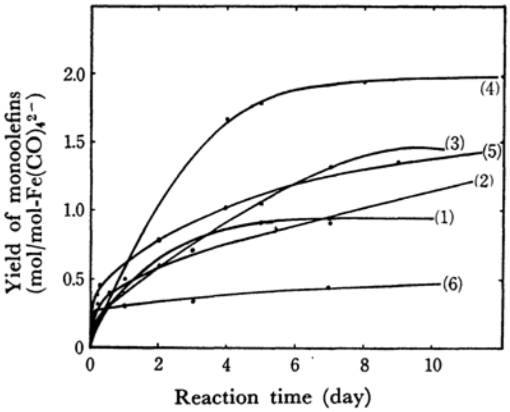


Fig. 1. Yield of monoolefins *vs.* time plots for the reaction of KHFe(CO)$_4$ with isoprene (in EtOH, at 30°C, 1 atm).
Number: (Exp. No. in Table 1)
(H$_2$O content mol/mol-Fe(CO)$_4^{2-}$, atmosphere)
(1) (0, N$_2$) (2) (1, N$_2$)
(3) (10, N$_2$) (4) (1, CO)
(5) (1, H$_2$) (6) K$_2$Fe(CO)$_4$ (0, N$_2$)

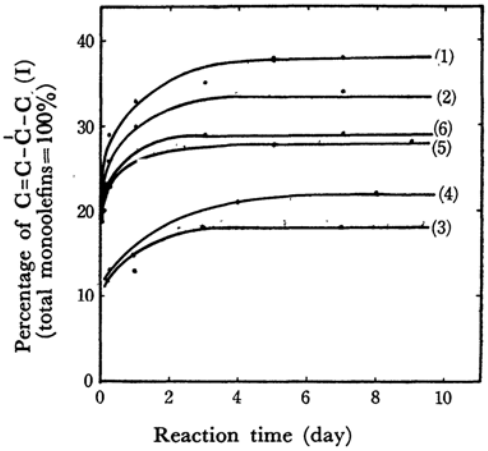


Fig. 2. Percentage of (I) *vs.* time plots for the reaction of KHFe(CO)$_4$ with isoprene (in EtOH, at 30°C 1 atm).
Number: (Exp. No. in Table 1)
(H$_2$O content mol/mol-Fe(CO)$_4^{2-}$, atmosphere)
(1) (0, N$_2$) (2) (1, N$_2$)
(3) (10, N$_2$) (4) (1, CO)
(5) (1, H$_2$) (6) K$_2$Fe(CO)$_4$ (0, N$_2$)

As Table 1 shows, isoprene reacts with KHFe(CO)$_4$ and K$_2$Fe(CO)$_4$, while the reaction solution gradually turns from light brown to deep ruby red. As the reaction products, 3-methyl-1-

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$_2$O*2 content		$\mathrm{C{-}\overset{C}{C}{-}C{=}C}$ (I)	$\mathrm{C{=}\overset{C}{C}{-}C{-}C}$ (II)	$\mathrm{C{-}\overset{C}{C}{=}C{-}C}$ (III)
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
		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$_2$Fe(CO)$_4$ *4 (d): day butene (I), 2-methyl-1-butene (II), and 2-methyl-2-butene (III) are obtained. Isopentane is not obtained, indicating that $KHFe(CO)_4$ is not active in the reduction of monoolefins under the conditions employed. As Figs. 1 and 2 show, the yield and distribution of the monoolefins obtained are remarkably affected by the reaction conditions.

The Yield of Monoolefins. In dry ethyl alcohol under nitrogen, the yield of the monoolefins is 1.0 mol/mol-$Fe(CO)_4{}^{2-}$ at its maximum (Exp. 1).

When there is 1 or 10 mol[*2] of water present in the system (Exps. 2 and 3), the yield increases to about 1.5 mol. Under carbon monoxide, the reduction is highly promoted and the maximum yield of the olefins amounts to 2.0 mol (Exp. 4). Under hydrogen the maximum yield is also 2 mol (Exp. 5). In dry ethyl alcohol, $K_2Fe(CO)_4$ also reduces isoprene, but more slowly, and the maximum yield of the olefins is less than 0.5 mol (Exp. 6).

The Distribution of the Olefins. As Fig. 2 shows, the amount of water and the atmosphere have a great effect on the distribution of the olefins (I and III). The percentage of the olefin II, however, is almost constant (about 15%) in any case. In dry ethyl alcohol under nitrogen, the percentage of I increases with an increase of the reaction time, finally amounting to 40% (Exp. 1). In the presence of 1 or 10 mol of water, the percentage of I decreases to about 32 or 18%, respectively (Exps. 2 and 3). Under carbon monoxide or hydrogen, the percentage of I also decreases to about 21 or 28%, respectively (compare Exps. 4 and 5 with Exp. 2). In the case of $K_2Fe(CO)_4$,

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		$C-\overset{C}{\overset{\mid}{C}}-C=C$ (I)	$C=\overset{C}{\overset{\mid}{C}}-C-C$ (II)	$C-\overset{C}{\overset{\mid}{C}}=C-C$ (III)
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)		$C-\overset{C}{\overset{\mid}{C}}-C=C$ (I)	$C=\overset{C}{\overset{\mid}{C}}-C-C$ (II)	$C-\overset{C}{\overset{\mid}{C}}=C-C$ (III)
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-$Fe(CO)_4{}^{2-}$

[*2] Mol means mole per mole of $Fe(CO)_4{}^{2-}$ in the further description.

even in dry ethyl alcohol under nitrogen, the percentage of I is less than 30% (Exp. 6).

Carbonylated Products. Under carbon monoxide, more than 1 mol of the gas is absorbed for about 20 hr (Exp. 4). The infrared spectrum of the reaction mixture has strong bands at 2005, 1982, and 1971 cm^{-1} characteristic of some iron carbonyls, and one at 1700 cm^{-1}. The band at 1700 cm^{-1} seems to be attributable to some acyliron carbonyl complex.

The reaction mixture treated with an iodine and hydrogen chloride solution in alcohol shows a band at 1735 characteristic of an ester and one at 1720 cm^{-1}.

On the basis of these facts, it may reasonably be concluded that isoprene is carbonylated to give some acyliron carbonyl complex, which seems to be converted to a corresponding ester by the treatment with iodine. The yield of the ester is about 0.1 mol. The structures of the complex and the ester, however, are not yet clear in this study.

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. 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 (I and III) 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 I. The distribution of the olefins (I and III) depends remarkably on the kind of alcohols. The percentage of I is greatest in ethyl alcohol, followed by *n*-propyl alcohol and isopropyl alcohol in that order; in isopropyl alcohol even in a dry system, the percentage of I is only 13% (Exp. 7 *cf.* Exp. 1). As Table 3 shows, in methyl ethyl ketone, tetrahydrofuran, 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°C, the reduction occurs more rapidly to give 2.5 mol of the olefins (compare Exp. 16 with Exp. 5). Even at 100°C, the yield of the olefins is 2.5 mol at most (Exp. 17), indicating that the iron carbonylate ($KHFe(CO)_4$) does not catalyze the hydrogenation of isoprene under the conditions used and that the carbonylate acts as a reducing reagent in the

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

Exp. No.	Reaction conditions*		Yield of monoolefins	Distribution of monoolefins (%)		
	Temperature °C	Time (hr)		$\text{C-}\overset{\text{C}}{\overset{\vert}{\text{C}}}\text{-C=C}$ (I)	$\text{C=}\overset{\text{C}}{\overset{\vert}{\text{C}}}\text{-C-C}$ (II)	$\text{C-}\overset{\text{C}}{\overset{\vert}{\text{C}}}\text{=C-C}$ (III)
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/cm^2, 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-$Fe(CO)_4^{2-}$

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)		$\text{C-}\overset{\text{C}}{\overset{\vert}{\text{C}}}\text{-C=C}$ (I)	$\text{C=}\overset{\text{C}}{\overset{\vert}{\text{C}}}\text{-C-C}$ (II)	$\text{C-}\overset{\text{C}}{\overset{\vert}{\text{C}}}\text{=C-C}$ (III)
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.

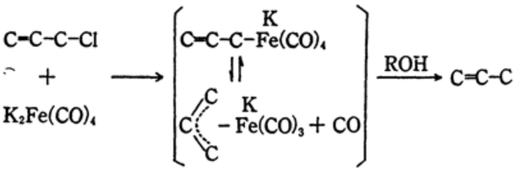
reaction. This explanation is consistent with the fact that the amount of olefins decreases proportionally with a decrease in the amount of the carbonylate used (Exp. 18).

The Reaction of $K_2Fe_2(CO)_8$ with Isoprene. The results are summarized in Table 5. All of the reactions were carried out in ethyl alcohol at 30°C.

As Table 5 shows, $K_2Fe_2(CO)_8$ also reacts with isoprene. In dry ethyl alcohol under nitrogen, the reduction occurs slowly to give about 0.5 mol of the olefins, and the percentage of I amounts to 31% (Exp. 19). When 1 mol of water is present, the yield increases to about 0.9 mol, but the percentage of I decreases to only 3% (Exp. 20). Under a carbon monoxide atmosphere the reduction is promoted to give more than 1 mol of the olefins (Exp. 21).

Discussion

Recently we have found that allyl halide reacts rapidly with $K_2Fe(CO)_4$ in ethyl alcohol, accompanied by an evolution of carbon monoxide and propylene.*3 This reaction is considered to proceed *via* the σ- and π-allyl iron carbonyl complexes.



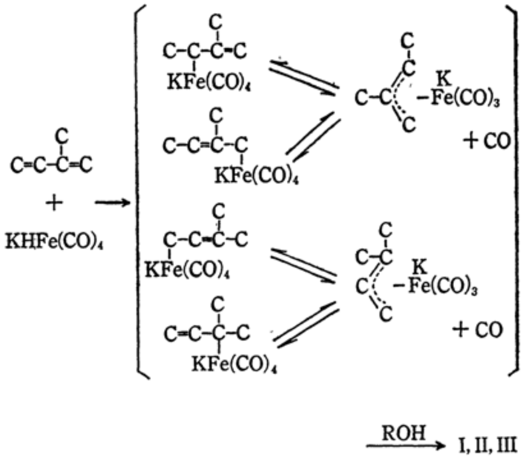
These complex may be unstable in an alcoholic solution, giving propylene in a good yield.

In the light of this reaction, the reaction of isoprene with $KHFe(CO)_4$ is considered to follow the following reaction scheme.

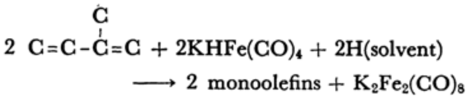
At first the four isomeric σ- allyl iron carbonylates are possible; then from these the two π- allyl iron carbonylates may be derived. In protic solvents these complexes decompose to give three different olefins and $K_2Fe_2(CO)_8$.

In aprotic solvents such as methyl ethyl ketone, $KHFe(CO)_4$ seems to give less than 0.5 mol of the olefins and $K_2Fe_2(CO)_8$. In these reactions $KHFe(CO)_4$ seems to be the only hydrogen source.

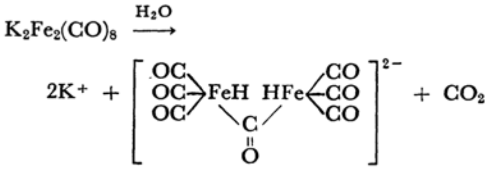
The formation of $K_2Fe_2(CO)_8$ may be supported by the fact that the reaction mixture turns from

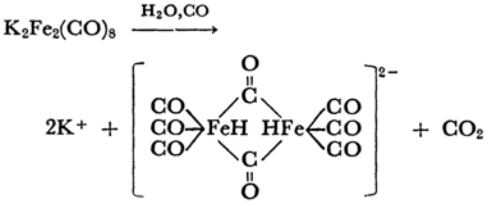


light brown to deep ruby red. In the presence of water and under carbon monoxide, the $K_2Fe_2(CO)_8$ thus formed has been proposed to give new iron hydride complexes:4)



$$2\ \mathrm{C{=}C{-}\overset{\displaystyle C}{C}{=}C} + 2KHFe(CO)_4 + 2H(\text{solvent}) \longrightarrow 2\ \text{monoolefins} + K_2Fe_2(CO)_8$$





Thus, the promoting effect of water and carbon monoxide on the reduction may be attributed to the formation of the new hydrides, which react further with isoprene.

A detailed mechanism, especially concerning the effect of water, solvents, and carbon monoxide on the distribution of the olefins, is not yet clear.

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

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*3 A more detailed study will be presented later.

4) H. W. Sternberg, and I. Wender, Advances in Catalysis IX p. 601 (1957).