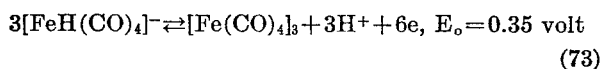
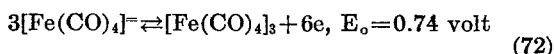


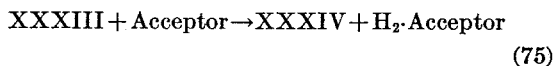
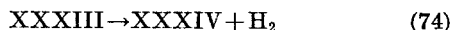
to equation (60), contained a high concentration of $[\text{HFe}(\text{CO})_4]^-$ and therefore decomposed rapidly.

The rate of dimer formation depends on the concentration of $[\text{HFe}(\text{CO})_4]^-$ ions: Two solutions were prepared, one by treating 1 mole of $\text{Fe}(\text{CO})_5$ with 3 moles of NaOH and the other by treating 1 mole of $\text{Fe}(\text{CO})_5$ with 6 moles of NaOH . Both were prepared and stored under helium. The first solution became deep red after 2 days, indicating dimer formation, and in the course of 2 weeks it gave off 0.05 mole of hydrogen and 0.01 mole of carbon monoxide per mole of $\text{Fe}(\text{CO})_5$ used. The second solution remained light colored and did not evolve gas in 2 weeks.

The evolution of hydrogen (115) from and the reducing properties (63) of solutions obtained by treating $\text{Fe}(\text{CO})_5$ with aqueous alkali were first attributed to the presence of $\text{H}_2\text{Fe}(\text{CO})_4$. After its absence had been established, the reducing properties were attributed to the oxidation-reduction potential (62)



However, there is no evidence that iron tetracarbonyl is formed in alkaline solutions from $[\text{Fe}(\text{CO})_4]^-$ or $[\text{HFe}(\text{CO})_4]^-$. The preparation of iron tetracarbonyl by the action of oxidizing agents on solutions containing $[\text{Fe}(\text{CO})_4]^-$ and $[\text{HFe}(\text{CO})_4]^-$ ions always leads to dark-red solutions which yield the tetracarbonyl only on acidification (70). The necessity for this acidification is not apparent from equations (72) and (73), but follows from equations (65) and (66). In the absence of a hydrogen acceptor, XXXIII splits off hydrogen (equation (74)), but in the presence of a hydrogen acceptor, it acts as a hydrogen donor:



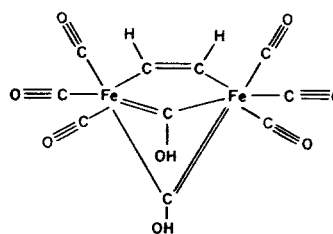
Equation (75) implies that a substrate is reduced by transfer of hydrogen from XXXIII and not by transfer of electrons (equation (72) or (73)) with the subsequent addition of protons. Hydrogen may be transferred in a manner similar to that involved in heterogeneous catalysis. The distance between the iron atoms in XXXIII is probably close to that found in $\text{Fe}_2(\text{CO})_9$; that is, 2.46 Å. (113). This is also the distance of closest spacing in a hydrogenation catalyst such as nickel (141).

The Iron Carbonyl-Acetylene Complex $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$

STRUCTURE

Reppe and Vetter isolated an iron carbonyl-acetylene complex ($\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$) from the reaction of acetylene with an aqueous solution of $\text{NaHFe}(\text{CO})_4$ (116). They recognized that this complex had acidic properties, but they offered no suggestion as to a possible structure.

The method of preparation, elementary composition, and molecular weight of $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ suggest that it consists of $\text{HFe}(\text{CO})_4$ and C_2H_2 . The following evidence led to the bridged structure XXXVIII for this complex:



XXXVIII

The iron complex contains two acidic hydrogen atoms, as shown by the two peaks in the titration curve (fig. 8).

A Beckman pH meter (model H2) was used in conjunction with a Beckman type 42 glass electrode which permitted measurements in the range of 0 to 14 pH. The samples were titrated in an atmosphere of helium. Reppe and Vetter reported that the complex contained one acidic hydrogen. However, their potentiometric titration gave an equivalent weight of 284 instead of that calculated for $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$, which is 363 for a monobasic acid or 182 for a dibasic acid. Their failure to observe two sharp breaks in their titration curve may have been due to the presence of oxygen.

To 0.4951 g. of anhydrous $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ was added 75 ml. of oxygen-free water. The mixture was stirred and titrated with 0.05 N KOH. The sample was completely dissolved after 2.50 ml. of titrant had been added. The data in figure 8 and table 16 yield a pK_{2a} (=pH at the second half-neutralization point) of 9.14

TABLE 16.—Potentiometric titration of 0.0181 molar $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ with 0.50 N KOH; initial volume, 75 ml.

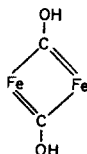
KOH, ml.	pH	KOH, ml.	pH	KOH, ml.	pH
2.5-----	7.28	3.5-----	8.78	5.4-----	10.44
2.6-----	7.48	4.0-----	9.12	5.5-----	10.62
2.7-----	7.75	4.5-----	9.42	5.6-----	10.77
2.8-----	8.05	4.9-----	9.74	5.7-----	10.89
2.9-----	8.21	5.0-----	9.83	5.8-----	11.01
3.0-----	8.35	5.1-----	9.93	6.0-----	11.19
3.1-----	8.50	5.2-----	10.06	6.6-----	11.48
3.2-----	8.58	5.3-----	10.20	7.0-----	11.59

The value for pK_{1a} could not be obtained because the sample was not completely dissolved at the first half-neutralization point; that is, after addition of 1.40 ml. of titrant. To determine pK_{1a} , 100 ml. of aqueous $Fe_2C_{10}H_4O_8$ was titrated. From the data listed in table 17 and plotted in figure 9, a value of 6.30 was obtained.

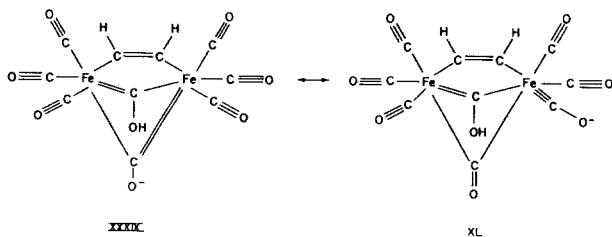
TABLE 17.—Potentiometric titration of 0.00145 molar $Fe_2C_{10}H_4O_8$ with 0.050 N KOH; initial volume, 100 ml.

KOH, ml.	pH	KOH, ml.	pH
1.2	6.20	2.9	7.63
1.4	6.28	3.0	7.90
1.6	6.38	3.1	8.05
1.8	6.48	3.2	8.21
2.0	6.58	3.4	8.45
2.2	6.72	3.6	8.58
2.4	6.87	4.0	8.78
2.6	7.04	4.5	8.95
2.8	7.39	5.0	9.08

The infrared spectrum of a solution of $Fe_2C_{10}H_4O_8$ in carbon disulfide (fig. 10) shows two strong bands and a somewhat weaker band in the —OH region at 3,565 cm^{-1} and 3,463 cm^{-1} , and three bands in the —C—O single bond region at 1,271, 1,174, and 1,093 cm^{-1} . The three sharp bands at 1,998, 2,033, and 2,073 cm^{-1} are similar to those in the spectrum of the cobalt acetylene complex (51) and in that of dicobalt octacarbonyl (46), where these bands have been attributed to C—O stretching vibrations in the six terminal carbonyl groups. The hydroxyl groups in XXXVIII are attached to carbon atoms that are part of the conjugated system



and are comparable to phenolic hydroxyl groups. This system is analogous to cyclobutadiene and is part of a resonating structure containing two $Fe(CO)_3$ groups. Since the ion XXXIX is highly stabilized by resonance (one of the contributing structures is shown in XL),



the pK_{1a} of the acid (XXXVIII) might be expected to be comparable with that of a phenol whose anion is highly stabilized by resonance. Indeed, the pK_{1a} of $Fe_2C_{10}H_4O_8$, as determined from the pH at the half-neutralization point, is 6.30 (compare with p-nitrophenol, $pK_a=7.16$). The second hydrogen in $Fe_2C_{10}H_4O_8$ ($pK_{2a}=9.14$) is comparable with that in phenol ($pK_a=9.89$). Further evidence for the presence of phenolic-type hydroxyl groups is the shift to longer wavelengths and the increase in intensity of the ultraviolet spectrum when excess alkali is added to an aqueous solution of XXXVIII. This change is similar to that accompanying the transformation of phenol to phenolate ion.

Although several metal carbonyls containing hydrogen, such as cobalt and iron hydrocarbonyl, have been synthesized and studied, the position of the hydrogen in these compounds has not been established (42). The data just given indicate that in the present complex the hydrogen is attached to oxygen. To obtain direct chemical evidence for the presence of hydroxyl groups, the dibenzoate and dimethyl ether of $Fe_2C_{10}H_4O_8$ were prepared as follows:

To a solution of 1.53 g. of anhydrous $Fe_2C_{10}H_4O_8$ in 100 ml. of dry pyridine was added 4 ml. of freshly distilled benzoylchloride; the mixture stood overnight at room temperature under nitrogen and was then poured into about 700 ml. of water. The mixture was stored in a refrigerator for a few hours, filtered, and dried in a vacuum desiccator over P_2O_5 . The residue (2.77 g.) was dissolved in 400 ml. of absolute ethanol at room temperature; 30 ml. of water was added; and the benzoate was crystallized at $-20^\circ C$. The precipitate was filtered and dried in the vacuum desiccator over $CaCl_2$ and finally over P_2O_5 . The yellow microscopic crystals melted at 155° to $160^\circ C$. with decomposition.

Calculated for $Fe_2C_{24}H_{12}O_{10}$: C, 50.39; H, 2.11; Fe, 19.53.

Found: C, 50.34; H, 2.13; Fe, 19.33.

To 50 ml. of an aqueous solution containing 2.16 g. (54 millimoles) of NaOH and 10.3 g. (27 millimoles) of $Fe_2C_{10}H_4O_8 \cdot H_2O$ was added 7 ml. (74 millimoles) of dimethyl sulfate in 1-ml. portions. The solution was vigorously shaken between additions. During the addition, which was carried out under nitrogen, a bright-yellow precipitate (the dimethyl ether) formed. The reaction mixture was made alkaline. The alkaline solution and the yellow precipitate were transferred to a separatory funnel and extracted with about 1 liter of ether. The ether extract was extracted several times with dilute NaOH, dilute H_2SO_4 , and finally water. After drying with Drierite¹¹ (anhydrous $CaSO_4$), the ether solution was filtered, concentrated to about 400 ml. in a current of nitrogen, and allowed to stand at $-20^\circ C$. overnight. The dimethyl ether crystallized in bright-orange crystals which, after washing with a few milliliters of cold ether and drying in a vacuum desiccator over Drierite, melted at 155.2° to $156.4^\circ C$. Recrystallization from ether did not change the melting point. The yield was 4.66 g., or 44 percent of theory. The mother liquor yielded 2.33 g. (22 percent) of crystals melting at 154° to $156^\circ C$.

¹¹ Reference to specific brands is made to facilitate understanding and does not imply endorsement of such items by the Bureau of Mines.

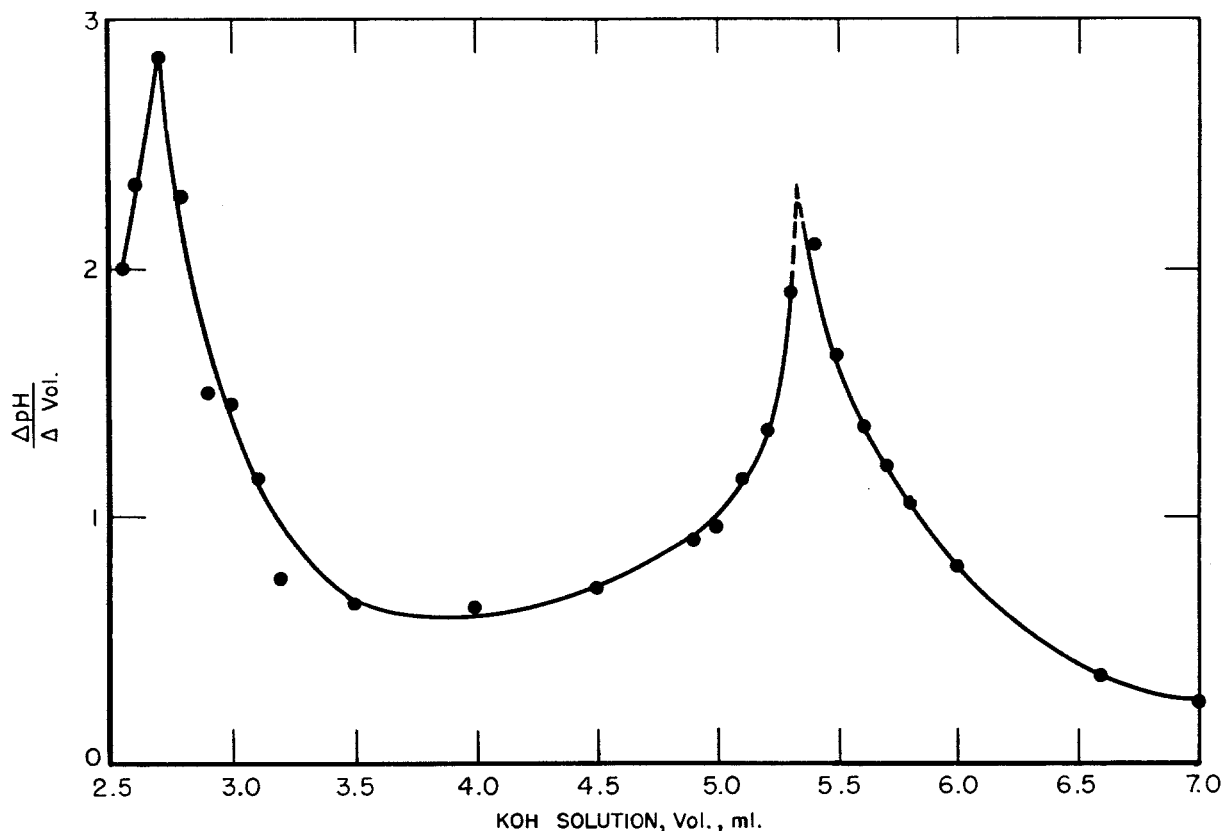


FIGURE 8.—Potentiometric Titration of 0.0181 Molar $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ With 0.50 N KOH; Initial Volume 75 ml.

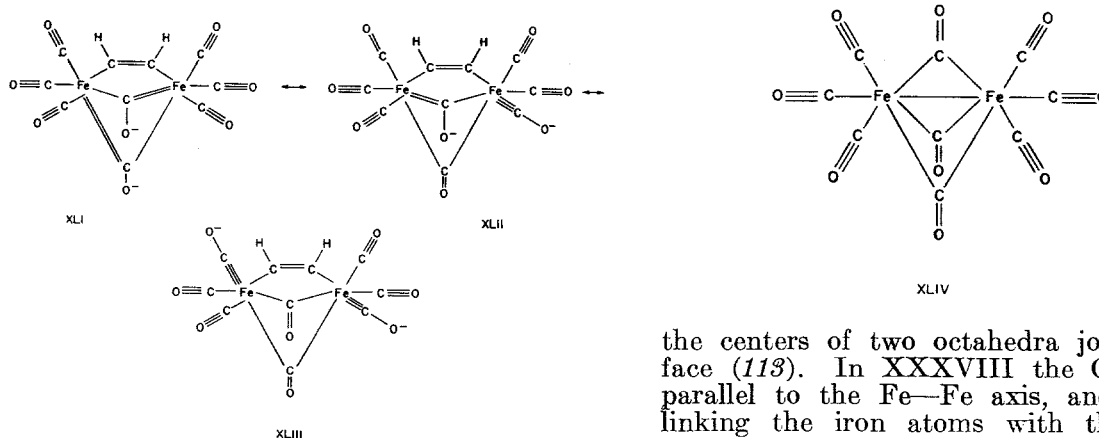
Calculated for $\text{Fe}_2\text{C}_{12}\text{H}_6\text{O}_8$: C, 36.77; H, 2.04; Fe, 28.52.

Found: C, 36.90; H, 2.20; Fe, 28.47.

In a strong amine, such as butylamine, the iron complex would probably dissociate completely, so the spectrum would be that of the doubly charged anion XLI. It may be further assumed that the $>\text{C}-\text{O}^-$ single bond would acquire a considerable double-bond character owing to the many possible resonance forms, two of which are shown in XLII and XLIII.

$\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ in carbon disulfide with that of a solution of $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ in n-butylamine (fig. 10). The latter spectrum lacks the bands attributable to $-\text{OH}$ and $\text{C}-\text{O}$; its complexity, that is, the number of infrared-active carbonyl stretching vibrations in the $1,900$ to $2,100 \text{ cm.}^{-1}$ region, has increased.

The configuration of XXXVIII is assumed to be analogous to that in iron enneacarbonyl (XLIV), where the iron atoms are located at



These assumptions are supported by a comparison of the spectrum of a solution of

the centers of two octahedra joined face to face (113). In XXXVIII the $\text{C}-\text{C}$ axis is parallel to the $\text{Fe}-\text{Fe}$ axis, and the bonds linking the iron atoms with the acetylene group are shown as localized bonds. Two other structures (not shown) are possible where the $\text{C}-\text{C}$ axis is perpendicular to the $\text{Fe}-\text{Fe}$

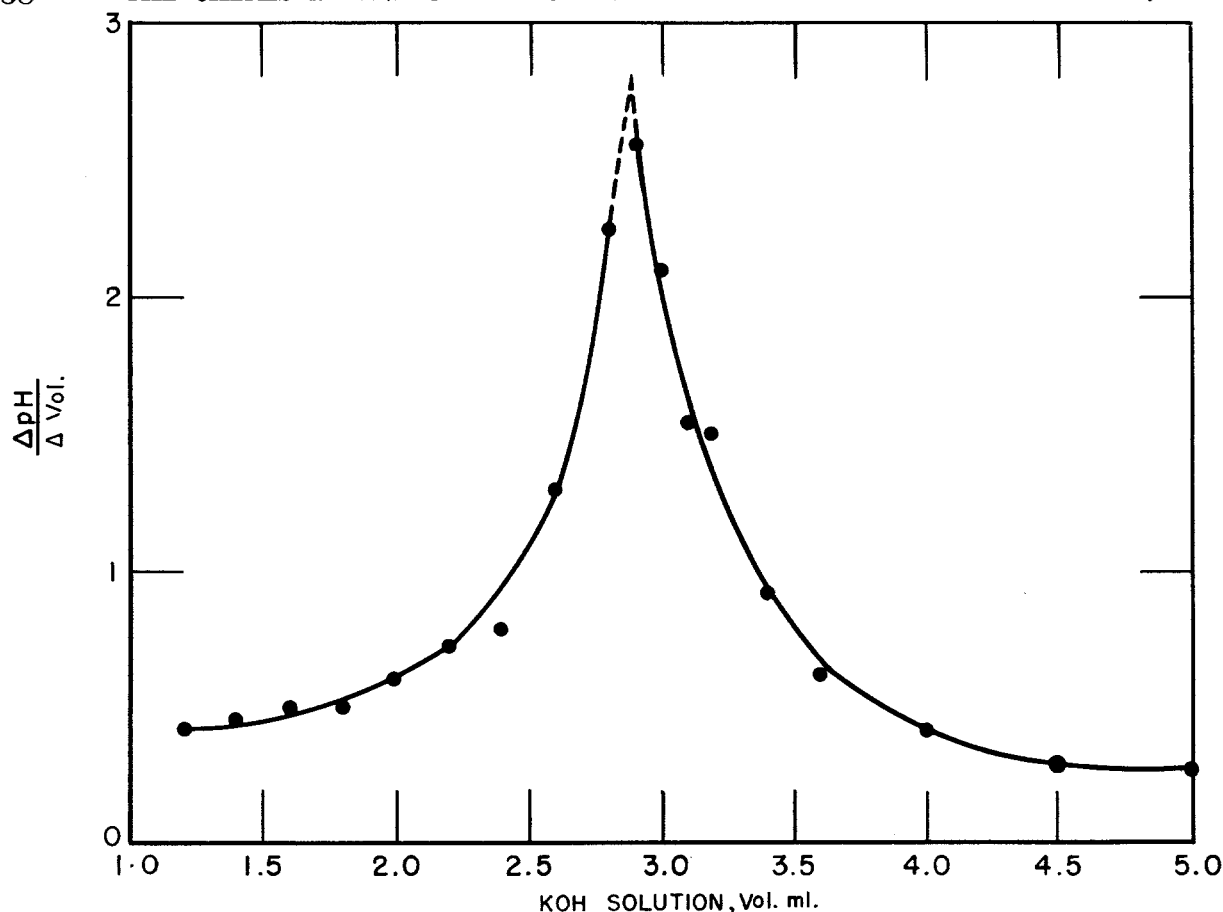


FIGURE 9.—Potentiometric Titration of 0.00145 Molar $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ With 0.050 N KOH; initial Volume 100 ml.

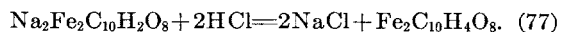
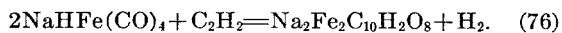
axis and in the same or a different plane. Neither structure can be expressed in terms of localized bonds.

The assignment of structure XXXVIII merely implies that the acetylene group occupies a place between the two iron atoms. Since the infrared spectrum of $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ does not show any bands which may be unambiguously attributed to either a C—C or a C—H linkage, speculation on the type of C—C bonding in the acetylene group in $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ appears fruitless.

It is of interest to note that XXXVIII contains an M—C—OH grouping, a type of linkage postulated in surface intermediates in the Fischer-Tropsch reaction (135).

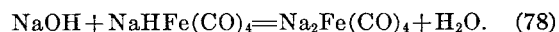
PREPARATION AND PROPERTIES

The iron complex is obtained by treating an alkaline aqueous solution of $\text{NaHFe}(\text{CO})_4$ with acetylene and acidifying the reaction mixture after the uptake of acetylene is completed:

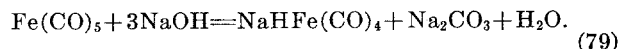


Equation (76) indicates that the presence of

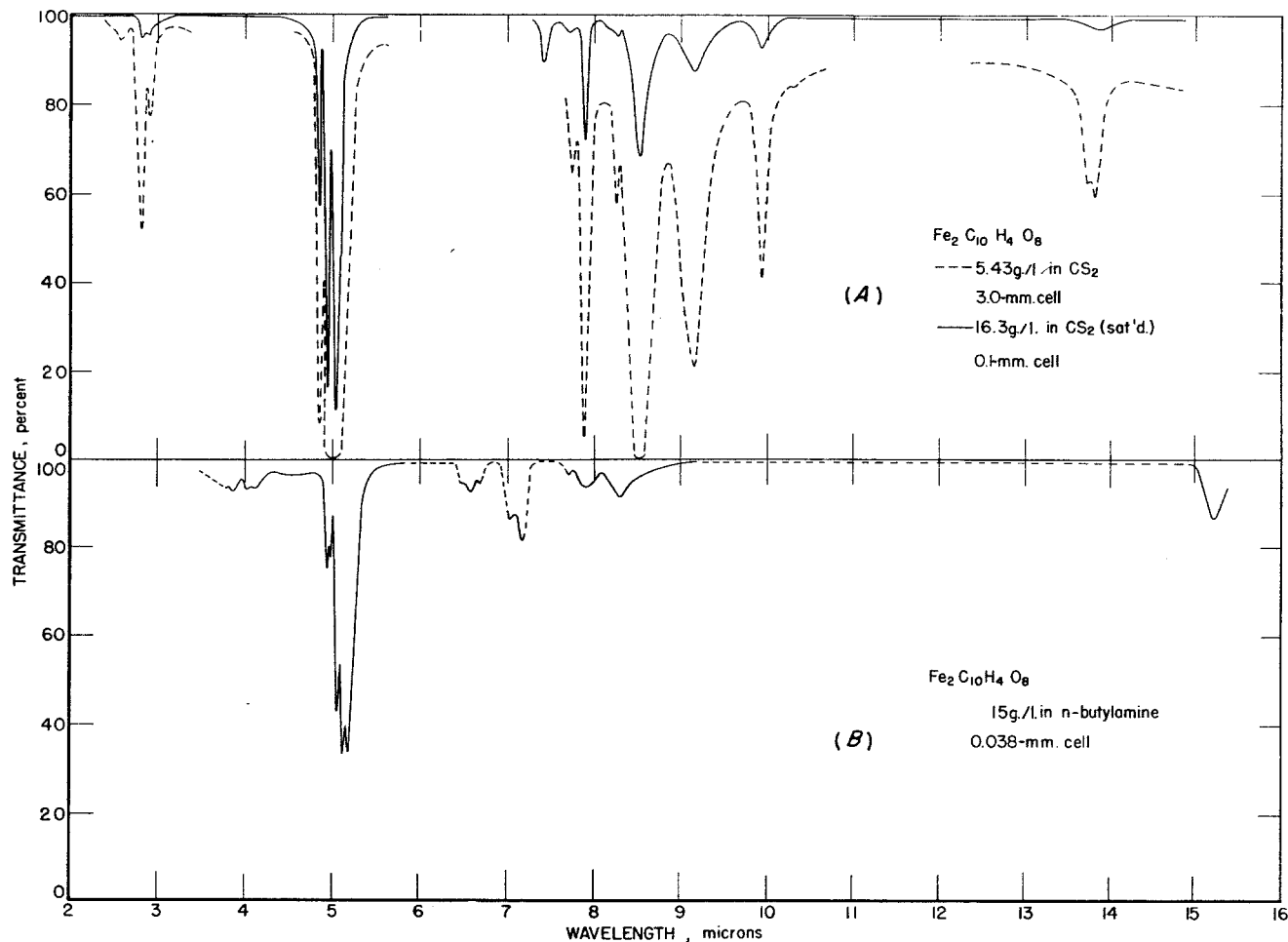
$[\text{HFe}(\text{CO})_4]^-$ is essential for the reaction. This assumption is supported by the fact that the uptake of acetylene is extremely slow in the presence of excess alkali where, according to equation (78), most of the ion $[\text{HFe}(\text{CO})_4]^-$ is



converted to the ion $[\text{Fe}(\text{CO})_4]^-$ (76). Hence, excess alkali should be avoided, and the solution of $\text{NaHFe}(\text{CO})_4$ should be prepared according to the stoichiometry expressed in equation (79):



Reppe and Vetter reported that a 1-molar solution of $\text{NaHFe}(\text{CO})_4$, when treated in a rocking autoclave with acetylene at 15 atm. and 45° to 50° C., took up about 0.5 mole of acetylene per mole of $\text{NaHFe}(\text{CO})_4$ in 16 hours and gave crude $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ in a yield of 45 percent, based on the $\text{NaHFe}(\text{CO})_4$ used (116). In a typical experiment at atmospheric pressure and room temperature, it was found that a 1-molar solution of $\text{NaHFe}(\text{CO})_4$ took up 0.6 mole of acetylene per mole of $\text{NaHFe}(\text{CO})_4$ in 9 hours and gave crude $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ in a yield

FIGURE 10.—Infrared Spectra of $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$.

of 70 percent. These results indicate that elevated temperatures are not required and may even be detrimental for the formation of the complex.

The $\text{NaHFe}(\text{CO})_4$ solution was prepared and treated with acetylene in the absence of air in a 250-ml. Erlenmeyer flask provided with the necessary sidearms, ground joints, and stopcocks. Fifty milliliters of oxygen-free water, containing 4.44 g. (111 millimoles) of NaOH , was placed in the flask, which was purged with helium and stoppered after addition of 5 ml. (37 millimoles) of $\text{Fe}(\text{CO})_5$. The flask was attached to a mechanical shaker, shaken for 24 hours, and opened while a current of helium was passed through one of the sidearms; a glass-enclosed stirring bar was then placed in the flask, and the flask was attached to a gas burette. After the flask and burette had been purged with acetylene, the gas volume was recorded, and the contents of the flask were stirred by a magnetic stirrer. The uptake of gas, which is rapid at the start—about 150 ml. per hour—slowed down gradually and finally stopped. In 9 hours 488 ml. (S.T.P.) (21.8 millimoles) of gas was absorbed. Mass spectroscopic analysis of the residual gas showed that 1.5 millimoles of ethylene had been formed and that 2.0 millimoles of hydrogen had evolved. Since evolution of hydrogen is accompanied by volume increase, whereas formation of ethylene from acetylene and hydrogen is not, 23.8 millimoles of acetylene had been adsorbed.

After gas adsorption had stopped, the flask was detached from the gas burette, and the reaction mixture was poured into a mixture of 80 g. of ice and 20 ml. of concentrated HCl . After a few hours the precipitate was filtered, washed with water, and dissolved in dilute aqueous NaOH . The alkaline solution was extracted several times with benzene and filtered, and the filtrate was collected in a flask containing dilute HCl . All these operations should be carried out in a well-ventilated hood, since acidification of the reaction mixture may produce considerable $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$. The yellow crystalline precipitate, $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8 \cdot \text{H}_2\text{O}$, was filtered and after drying over P_2O_5 weighed 4.8 g., corresponding to a yield of 71 percent, based on the amount of $\text{Fe}(\text{CO})_5$ used. If necessary, the iron complex may be further purified by repeating the precipitation from its alkaline solution as previously described. In alkaline solution the iron complex is rather sensitive towards oxygen. It should therefore be filtered under nitrogen, and the time for dissolving the iron complex in alkali should be minimized. The anhydrous complex is prepared by drying the filtered and washed precipitate, $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8 \cdot \text{H}_2\text{O}$, in a vacuum desiccator over P_2O_5 for 4 to 8 hours. The anhydrous complex, $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$, consists of light-yellow needles which melt at 80° to 85° C. with decomposition. It is hygroscopic and much less stable than the monohydrate. To obtain the latter, the anhydrous complex is placed in a desiccator containing some water, and the air in the desiccator is replaced by helium. After about 8 hours

the required amount of water to form the monohydrate is taken up, and the weight of the sample has become constant. The monohydrate forms light yellow-to-orange needles which melt in a vacuum capillary at 104° to 110° C. with decomposition.

Analytically calculated for $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8 \cdot \text{H}_2\text{O}$: C, 31.45; H, 1.58; Fe, 29.25.

Found: C, 31.40; H, 1.64; Fe, 29.06.

Both the anhydrous complex and the monohydrate are sparingly soluble in water and readily soluble in ether and alcohol. They differ considerably in their solubilities in other organic solvents, as shown in table 18.

TABLE 18.—*Solubility of the iron carbonyl-acetylene complex and its monohydrate at 25° C., g./100 ml. of solvent*

Solvent	$\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$	$\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8 \cdot \text{H}_2\text{O}$
Petroleum ether (35°–55° C.)	0.23	0.013
n-Hexane	.41	.014
Carbon disulfide	1.63	.025
Benzene	5.82	.188
Water		.055
Ethanol	(1)	(1)
Ether	(1)	(1)
Acetone	(1)	(1)

¹ Very soluble.

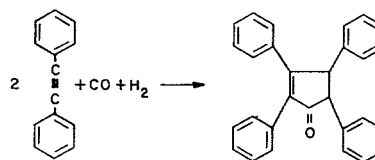
Equation (76) shows that hydrogen is liberated by the reaction of acetylene with $\text{NaHFe}(\text{CO})_4$. In addition to acetylene and hydrogen, a sample gas mixture also contained ethylene, an indication that some of the hydrogen had reacted with acetylene to give ethylene. The total hydrogen evolved (hydrogen plus hydrogen used in the formation of ethylene from acetylene) is considerably less than that required by equation (76); this is indicated in table 19. Thus, 0.57 mole more of acetylene

TABLE 19.—*Products and yields from the reaction between $\text{NaHFe}(\text{CO})_4$ and C_2H_2 .*

	Moles of reagents		Moles of products		
	$\text{NaHFe}(\text{CO})_4$	C_2H_2	$\text{Na}_2\text{Fe}_2\text{C}_{10}\text{H}_2\text{O}_8$	H_2	C_2H_4
Used	2.00	1.28			
Formed			0.71	0.1	0.08
Calculated from equation (76)	2.00	1.00	1.00	1.0	.00

was absorbed and 0.53 mole less of total hydrogen (hydrogen plus hydrogen in ethylene) was evolved than expected on the basis of 0.71 mole of reaction product. The differences may be caused by a side reaction in which hydrogen and acetylene react in the presence of a metal carbonyl to give condensation products. Thus, G. P. Mueller and F. L. MacArtor (88) found that treatment of diphenylacetylene with nickel carbonyl and hydrochloric acid in dioxane-

ethanol gave 2,3,4,5-tetraphenylcyclopenta-2-en-1-one:



In its crystalline form and in the absence of oxygen, the monohydrate is stable to light. A sample of the monohydrate that had been crystallized several times was stored under helium at room temperature for 6 months without showing any signs of decomposition. In aqueous solution in the presence of oxygen, the complex decomposes within a few days. The monohydrate readily loses 1 mole of water when placed in a vacuum desiccator over phosphorous pentoxide (116). In contrast to the monohydrate, the anhydrous complex, is considerably less stable and shows signs of decomposition after 12 hours, even when stored in the dark and in the absence of air. The anhydrous complex melts at 80° to 85° C. with decomposition. Reppe and Vetter reported a melting point of 110° to 111° C. (with decomposition) but did not specify whether this melting point referred to the monohydrate or to the anhydrous complex. Their statements concerning the stability and solubility of the complex indicate that they were dealing with the monohydrate. The monohydrate is probably soluble in these solvents only to the extent to which it is dissociated into anhydrous complex. This assumption is supported by the identical infrared spectra of solutions in carbon disulfide of monohydrate and anhydrous complex. Both are readily soluble in alcohol and ether and sparingly soluble in water.

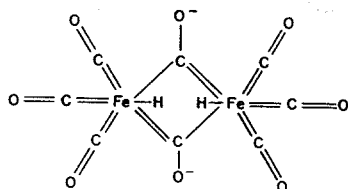
To determine whether the same type of complex could be obtained from a substituted acetylene, the reaction between methylacetylene and an aqueous solution of $\text{NaHFe}(\text{CO})_4$ was studied. Although methylacetylene was absorbed, a complex could not be isolated under these conditions. However, when methylacetylene was allowed to react for 3 weeks with an aqueous solution of $\text{Na}_2\text{Fe}(\text{CO})_4$ containing 30 percent methanol, the corresponding methyl derivative, $\text{Fe}_2\text{C}_{11}\text{H}_6\text{O}_8$, was obtained as follows:

A solution of $\text{Na}_2\text{Fe}(\text{CO})_4$ was prepared by shaking 5 ml. (37 millimoles) of $\text{Fe}(\text{CO})_5$ and 5.92 g. (148 millimoles) of NaOH in 50 ml. of water for 24 hours. After addition of 25 ml. of methanol, the solution was treated with acetylene as previously described. In 3 weeks 31 millimoles of acetylene was absorbed. The mixture, treated as just described, yielded 1.27 g. (18 percent) of crude material. Sublimation of the crude product at 70° C. and 10^{-5} mm. Hg yielded yellow crystals which melted at 100° to 105° C. with decomposition.

Calculated for $\text{Fe}_2\text{C}_{11}\text{H}_6\text{O}_8$: C, 34.96; H, 1.60; Fe, 29.56.

Found: C, 34.67; H, 1.58; Fe, 29.30.

The evolution of ethylene may provide a clue to the mechanism of the formation of $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$. If a bridged complex such as XLV is formed from two $[\text{HFe}(\text{CO})_4]^-$ ions in the first



XLV

step of the reaction (131), interaction of acetylene with the two iron and hydrogen atoms could either yield ethylene or result in substitution of acetylene for hydrogen and then evolution of the latter.

Iron Hydrocarbonyl $\text{H}_2\text{Fe}(\text{CO})_4$

PREPARATION

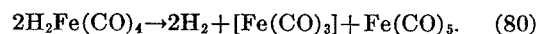
Two methods have been described for preparing $\text{H}_2\text{Fe}(\text{CO})_4$; neither includes a statement on yields (12, 69). One method (69) is reported to give pure $\text{H}_2\text{Fe}(\text{CO})_4$, but it is complicated and time consuming. The purity of $\text{H}_2\text{Fe}(\text{CO})_4$ obtained by the other, less complicated method (12) is not indicated. This method was modified, and the purity and yield of $\text{H}_2\text{Fe}(\text{CO})_4$ were determined.

Twenty-five milliliters of an aqueous 6-N sodium hydroxide solution and 5.0 ml. (37 millimoles) $\text{Fe}(\text{CO})_5$ are placed in an Erlenmeyer flask with a glass stopper. Air in the flask is displaced by carbon monoxide, and the flask is stoppered and shaken vigorously for 8 hours. The resulting clear solution contains $\text{NaHFe}(\text{CO})_4$, which yields $\text{H}_2\text{Fe}(\text{CO})_4$ on acidification.

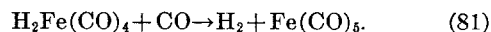
The apparatus for generating $\text{H}_2\text{Fe}(\text{CO})_4$ consists of a 500-ml., three-necked flask with an inlet tube whose constricted tip is placed close to the bottom of the flask, a dropping funnel, and an outlet tube. The outlet tube is attached to an absorption tube (90 by 30 mm.) filled with CaCl_2 . The absorption tube is connected to a cold trap (200 by 40 mm.) immersed in acetone-dry ice. The three-necked flask is filled with 100 ml. of ice-cold 6-N aqueous sulfuric acid and immersed in an ice bath. The flask is then fitted with the tubes and the funnel. The solution of $\text{NaHFe}(\text{CO})_4$ is poured into the funnel. The funnel and inlet tube are connected by a T-tube, and the apparatus is purged with CO. After purging, $\text{NaHFe}(\text{CO})_4$ is added drop by drop to the flask for 1 to 1½ hours in a current of CO of about 500 ml. per minute.

The $\text{H}_2\text{Fe}(\text{CO})_4$ collected in the trap contains appreciable amounts of $\text{Fe}(\text{CO})_5$. To determine the amount of $\text{H}_2\text{Fe}(\text{CO})_4$ present, the trap was warmed to room

temperature, and the evolved gas was measured. Since this gas corresponds to the amount of $\text{H}_2\text{Fe}(\text{CO})_4$ present (1 mole of H_2 per mole of $\text{H}_2\text{Fe}(\text{CO})_4$), the amount of $\text{H}_2\text{Fe}(\text{CO})_4$ in the trap can be determined volumetrically. The yield of $\text{H}_2\text{Fe}(\text{CO})_4$ determined in several experiments varied from 2.0 to 2.2 g. (12 to 13 millimoles) when 5.0 ml. (37 millimoles) of $\text{Fe}(\text{CO})_5$ was used. Subtraction of the $\text{H}_2\text{Fe}(\text{CO})_4$ from the total weight of products [$\text{Fe}(\text{CO})_5 + \text{H}_2\text{Fe}(\text{CO})_4$] in the trap yielded the $\text{Fe}(\text{CO})_5$, which varied from 1.0 to 0.8 g. The presence of $\text{Fe}(\text{CO})_5$ in the trap cannot be due to entrainment of $\text{Fe}(\text{CO})_5$ formed in the reaction flask from the decomposition of $\text{H}_2\text{Fe}(\text{CO})_4$:



This was demonstrated when $\text{Fe}(\text{CO})_5$ was placed in the reaction flask, along with the usual amount of aqueous HCl solution, and the apparatus was swept with synthesis gas at a high rate. Only a negligible amount of $\text{Fe}(\text{CO})_5$ was carried over into the trap. The $\text{Fe}(\text{CO})_5$ in the trap must have resulted from gas-phase decomposition:



The yield of $\text{H}_2\text{Fe}(\text{CO})_4$ is greatly affected by the presence of CO. The following yields were obtained in a series of experiments made under identical conditions except for the gas used as a sweeping agent.

Gas used	Yield of $\text{H}_2\text{Fe}(\text{CO})_4$, percent
Carbon monoxide (no oxygen).....	36.2
Synthesis gas 1:1 (no oxygen).....	32.4
Helium (no oxygen).....	17.6
Hydrogen (0.08 percent oxygen, maximum)....	5.9

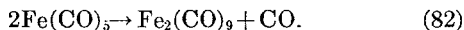
The lower yields in the helium and hydrogen runs were apparently caused by decomposition in the gas phase, since a heavy red-black solid deposit formed on the glass surface of the entire apparatus; in the presence of CO, on the other hand, only a little light-yellow solid (apparently Fe_2CO_9) deposited. Whether the lower yields in the hydrogen runs (as compared with the helium runs) are due to hydrogen or to the presence of oxygen cannot be decided on the basis of these experiments.

DECOMPOSITION IN THE GAS PHASE

Additional evidence in support of equation (81) was obtained as follows:

Iron hydrocarbonyl was swept into an evacuated 12-liter flask in a current of 1:1 synthesis gas. Infrared analysis showed the presence of $\text{Fe}(\text{CO})_5$ and $\text{H}_2\text{Fe}(\text{CO})_4$. After a few days a layer of green and yellow crystals had collected on the walls of the flask. The green solid— $[\text{Fe}(\text{CO})_4]_3$, as judged from its color and solubility in benzene, pentane, acetone, and alcohol—was extracted. By far the larger portion of the residue was $\text{Fe}_2(\text{CO})_9$, as judged from its crystal form, light golden-yellow color, and insolubility in benzene, acetone, and alcohol. As very little of the dark polymeric carbonyls, $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$, was formed, $\text{H}_2\text{Fe}(\text{CO})_4$ in the presence of CO probably decomposes according to equation (81). The presence of $\text{Fe}_2(\text{CO})_9$

is probably due to a secondary reaction, decomposition of $\text{Fe}(\text{CO})_5$ in light:



In the absence of carbon monoxide large amounts of dark-red material were deposited (as previously described) on the apparatus for generating $\text{H}_2\text{Fe}(\text{CO})_4$. In the absence of carbon monoxide, $\text{H}_2\text{Fe}(\text{CO})_4$ probably decomposes according to equation (80). The dark-red deposit presumably was $\text{Fe}(\text{CO})_3$ polymer. Thus, $\text{H}_2\text{Fe}(\text{CO})_4$ may decompose according to equation (80) or (81), depending on the presence of CO. Although equation (81) was discussed by Hieber (70), this is the first evidence for decomposition of $\text{H}_2\text{Fe}(\text{CO})_4$ according to (80).

DECOMPOSITION IN SOLUTION

As hydrogen is one of the products of decomposition of $\text{H}_2\text{Fe}(\text{CO})_4$, its collection and periodic measurement serve to determine the rate and order of the reaction.

The apparatus consists of a 250-ml. Erlenmeyer flask with a long neck (the overall length of the flask and the neck is 30 cm.) with an outlet tube. The neck is clamped in a shaking mechanism, with the flask proper immersed in a constant-temperature bath. The bottom of the flask is covered with glass beads so that shaking permits the gas to escape from the solution as rapidly as it is formed. A gas-measuring burette is attached to the outlet tube by Tygon tubing.

One hundred milliliters of n-heptane was placed with the glass beads in the flask. Iron hydrocarbonyl from 2 ml. of $\text{Fe}(\text{CO})_5$ was collected in this flask by the method described under preparation of iron carbonyl. (later decomposition showed this to be 5.76 millimoles of $\text{H}_2\text{Fe}(\text{CO})_4$, a yield of 38.9 percent.) The outlet tube of the flask was connected to the gas-measuring burette, and the entire apparatus was purged with helium, with the flask still immersed in the acetone-dry ice bath that was used in preparing the iron hydrocarbonyl. The dry-ice bath was then removed, and when the solution approached room temperature, the flask was fitted in the shaking mechanism and constant-temperature bath (25.0 to 25.1° C.). The volume of gas was read periodically as hydrogen evolved. Concentrations of $\text{H}_2\text{Fe}(\text{CO})_4$ remaining were calculated in moles per liter.

The reaction-rate constants were calculated from the kinetic equation for a reaction of the first order,

$$k = (2.303/t) \log [a/(a-x)],$$

where t is time, a is initial concentration, and $a-x$ is concentration after time t .

A constant k was obtained for 56 percent of the total reaction (table 20).

The decomposition of iron hydrocarbonyl in heptane solution is accompanied by a change from amber to dark red and finally, after the solution has stood for several hours, to dark green. When the heptane solution is decanted, a dark red-green residue remains that colors the

solvent dark green even after repeated extractions with fresh heptane. Therefore, a large

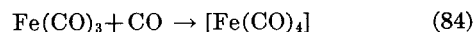
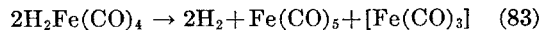
TABLE 20.—Spontaneous decomposition of iron hydrocarbonyl in heptane solution at 25° C.

Time, minutes	Concentration, $a-x$, moles $\text{H}_2\text{Fe}(\text{CO})_4$ per liter heptane	Specific reaction rate constant, k , minutes ⁻¹
0	0.0576	-----
20	.0396	1.86×10^{-2}
30	.0320	1.96
40	.0267	1.93
50	.0226	1.87
60	.0188	1.86
70	.0158	1.85
80	.0132	1.84
90	.0109	1.85
100	.00904	1.85
110	.00753	1.85

proportion of the residue must consist of the trimer $[\text{Fe}(\text{CO})_4]_3$.

Mass spectrometric analysis of the gas evolved during decomposition showed that CO had been evolved with H_2 . The ratio of CO to H_2 was 1:14. This result indicates that the decomposition of $\text{H}_2\text{Fe}(\text{CO})_4$ does involve the evolution of some CO and thus does not proceed strictly according to equation (80).

The tricarbonyl $[\text{Fe}(\text{CO})_3]$ formed can combine with gaseous CO at atmospheric pressure: Iron hydrocarbonyl in heptane solution was decomposed, and the gas was collected in a gas burette. The volume of gas corresponded to the decomposition of 12.7 millimoles of $\text{H}_2\text{Fe}(\text{CO})_4$. After decomposition was complete, the apparatus was purged and filled with CO. In 4 days, 3.5 millimoles of CO was absorbed, equivalent to 0.28 mole of CO absorbed per mole of $\text{H}_2\text{Fe}(\text{CO})_4$ originally present. A possible reaction sequence such as



indicates that 0.5 mole of CO could be absorbed per mole of $\text{H}_2\text{Fe}(\text{CO})_4$.

The decompositions of $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$ are compared in table 21.

REACTION WITH ACETONE AND 1-HEXENE

Although the reducing properties of solutions of $\text{NaHFe}(\text{CO})_4$ have been attributed to the presence of $\text{H}_2\text{Fe}(\text{CO})_4$ (63), no experiments

TABLE 21.—*Reactions of $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$ at atmospheric pressure and room temperature*

$\text{H}_2\text{Fe}(\text{CO})_4$	$\text{HCo}(\text{CO})_4$
Decomposition in gas phase, in presence of CO	
$\text{H}_2\text{Fe}(\text{CO})_4 + \text{CO} \rightarrow \text{H}_2 + \text{Fe}(\text{CO})_5$	$2\text{HCo}(\text{CO})_4 \rightarrow \text{H}_2 + \text{Co}_2(\text{CO})_8$
Decomposition in gas phase, in absence of CO	
$2\text{H}_2\text{Fe}(\text{CO})_4 \rightarrow 2\text{H}_2 + \text{Fe}(\text{CO})_5 + [\text{Fe}(\text{CO})_3]$	$4\text{HCo}(\text{CO})_4 \rightarrow 2\text{H}_2 + \text{Co}_4(\text{CO})_{12} + 4\text{CO}$
Decomposition in liquid phase	
$2\text{H}_2\text{Fe}(\text{CO})_4 \rightarrow 2\text{H}_2 + \text{Fe}(\text{CO})_5 + [\text{Fe}(\text{CO})_3]$	$2\text{HCo}(\text{CO})_4 \rightarrow \text{H}_2 + \text{Co}_2(\text{CO})_8$
Absorption of CO	
$[\text{Fe}(\text{CO})_3] + \text{CO} \rightarrow [\text{Fe}(\text{CO})_4]$	Neither $\text{Co}_2(\text{CO})_8$ nor $\text{Co}_4(\text{CO})_{12}$ absorbs CO at atmospheric pressure and room temperature, but both do so at elevated pressure and temperature.

have been reported in which $\text{H}_2\text{Fe}(\text{CO})_4$ was used as a reducing agent. We therefore determined whether $\text{H}_2\text{Fe}(\text{CO})_4$ possesses reducing properties and is capable of isomerizing olefinic double bonds in a manner similar to $\text{HCo}(\text{CO})_4$.

Treatment of acetone with iron hydrocarbonyl, $\text{H}_2\text{Fe}(\text{CO})_4$, at room temperature gave isopropyl alcohol, and treatment of 1-hexene resulted in complete isomerization to 2- and 3-hexene. Since iron hydrocarbonyl is a weak acid (76), this double-bond isomerization is not likely to be acid catalyzed.

Acetone was reduced as follows: 5 ml. (68 millimoles) of acetone was placed in the cold trap, and the cold trap was attached to the apparatus. About 2 g. (12 millimoles) of $\text{H}_2\text{Fe}(\text{CO})_4$ was generated, as previously described, and collected in the cold trap. The cold trap was then disconnected from the apparatus and allowed to warm to room temperature. Infrared analysis of the reaction product showed that 0.16 g. (2.7 millimoles) of isopropyl alcohol was present.

The reaction between $\text{H}_2\text{Fe}(\text{CO})_4$ and 1-hexene was carried out similarly. Five milliliters (40 millimoles) of peroxide-free 1-hexene was placed in the cold trap. After introducing about 2 g. (12 millimoles) of $\text{H}_2\text{Fe}(\text{CO})_4$ as previously described, the cold trap was disconnected and allowed to warm to room temperature. An infrared analysis of the product showed that all of the 1-hexene had been converted to 2- and 3-hexene. It was demonstrated that $\text{Fe}(\text{CO})_5$ does not cause double-bond isomerization by allowing a solution of 1 ml. of $\text{Fe}(\text{CO})_5$ in 25 ml. of 1-hexene to stand for 24 hours. No 2- or 3-hexene was present in the solution.