value for the molecular refraction was 117 for structure A and 125 for structure B.

The orientation polarization was calculated from the experimental molar polarization and the calculated molecular refraction. Values of 87 and 79 were obtained, depending upon whether structure A or B was used to calculate the molecular refraction. These values correspond to dipole moments of 2.1 and 2.0 D, respectively. The maximum error introduced by the calculation of the molecular refraction is estimated as 0.3 D.

Stability of Acetylenic Dicobalt Hexacarbonyls

Many acetylenic dicobalt hexacarbonyls decompose on exposure to air. When freshly prepared, the solid propargyl alcohol and 2-butyne-1, 4-diol dicobalt hexacarbonyls were readily soluble in organic solvents such as ethanol and diethyl ether. After a few days material insoluble in organic solvents was formed, indicating a chemical change on standing. Acetylene dicobalt hexacarbonyl and 2-butyne dicobalt hexacarbonyl, both liquids, formed solid material after exposure to air for a few hours. The infrared spectra of the acetylenic dicobalt hexacarbonyls that had been prepared from acetylenic carboxylic acids showed considerable change in cyclohexane or carbon disulfide solution during a period of a few hours or less. For example, after a solution of phenylpropiolic acid dicobalt hexacarbonyl in carbon tetrachloride had stood for one-half hour, its infrared spectrum no longer showed the presence of a carboxylic acid group, and absorption in the terminal carbonyl group region was very small. At the same time, new bands had appeared in the regions characteristic of the carbonyl anion.

To determine the importance of oxygen in these decompositions, solutions of 0.020 g. of diphenylacetylene dicobalt hexacarbonyl in 5 ml. of cyclohexane (purified by distillation and subsequent chromatoggraphy on activated carbon) were allowed to stand at room temperature in glass vials under oxygen, air, nitrogen (containing 0.2 percent oxygen), and synthesis gas (0.25 H_2:1CO). A second set of four similar samples was kept in the dark. The samples were then examined for decomposition, the criterion being visible formation of an insoluble, solid sediment. After 24 hours, decomposition had occurred in the solutions under air and oxygen but not under nitrogen and synthesis gas. No difference was apparent between samples kept in the dark and those exposed to light. After about 3 months the samples under oxygen were almost completely decomposed, as shown by the large amount of brown solid and the change in the color of the solution from dark red to pale yellow. Considerable decomposition of the samples occurred under air, slight decomposition under nitrogen, and no visible decomposition under synthesis gas. Again, there as no apparent difference between the samples kept in the dark and those exposed to light.

In a second series of experiments, solutions of 0.100 g. (2.15×10^{-4} moles) of diphenylacetylene dicolbalt hexacarbonyl in 50 ml. of cyclohexane were allowed to stand in stoppered flasks at room temperature for 1 month. Infrared spectroscopic analysis indicated that about 75 percent of the diphenylacetylene dicobalt hexacarbonyl had been decomposed and that benzil had been formed in about 28-percent yield. The identity of the benzil was confirmed by the formation of a benzil-mono-2,4-dinitrophenylhydrazone, which did not depress the melting point of an authentic sample. Preparation of benzil-2,4-dinitrophenylhydrazone according to the procedure of Shriner and Fuson (*122*) resulted in two isomeric mono-2,4-dinitrophenylhydrazones separated by fractional recrystallization from ethanol. The less soluble isomer, (A), melted at 192.0° to 192.8° C. after two recrystallizations from ethyl acetate-ethanol. The literature values for the melting point of benzil-2,4-dinitrophenylhydrazone are 185° (*4*) and 189° (*27*). The more soluble isomer, (B), melted at 161.8° to 162.8° C. after to recrystallizations from ethanol-water and then two recrystallizations from ethanol.

Calculated for benzil-mono-2,4-dinitrophenylhydrazone, $C_{20}H_{14}N_4O_5$:C, 61.55; H, 3.61.

Calculated for benzil-di-2,4-dinitrophenylhydrazone, $C_{26}H_{18}N_8O_8$:C, 54.75; H, 3.18.

Found for (A): C, 61.5; H, 3.6.

Found for (B): C, 61.5; H, 3.8.

To determine its thermal stability, a solution of 1.000 g. (2.15×10^{-3} moles) of diphenylacetylene dicobalt hexacarbonyl in 20 ml. of methylcyclohexane (boiling point 101° C.) was refluxed for 31 hours under an atmosphere of nitrogen. Infrared and ultraviolet spectroscopic analyses indicated that 86 percent of the diphenylacetylene dicobalt hexacarbonyl had been decomposed and that no diphenylacetylene had been formed.

Cobalt Hydrocarbonyl

PREPARATION

Cobalt hydrocarbonyl is obtained by preparing one of its salts, followed by acidification and condensation of the liberated cobalt hydrocarbonyl.

Where high-pressure equipment is not available, cobalt hydrocarbonyl may be prepared by absorption of carbon monoxide in an alkaline cobalto cyanide suspension (*13*).

$$12KOH+2K_4Co(CN)_6+11CO\rightarrow 3K_2CO_3+12KCN+6H_2O+2KCo(CO)_4 \quad (43)$$

and acidification of the resulting solution:

$$KCo(CO_4+HCl\rightarrow KCl+HCo(CO)_4. \quad (44)$$

Where high-pressure equipment is available, cobalt hydrocarbonyl may be prepared either from the cobalt salt of cobalt hydrocarbonyl,

$$3Co_2(CO)_8+12Pyr\rightarrow 2[Co(Pyr)_6][Co(CO)_4]_2+8CO \quad (45)$$

$$2[Co(Pyr)_6][Co(CO)_4]_2+8H_2SO_4\rightarrow 4HCo(CO)_4+2CoSO_4+6(PyrH)_2SO_4 \quad (46)$$

or from the pyridinium salt of cobalt hydrocarbonyl:

$$6CoCO_3+24CO+9H_2+6Pyr\rightarrow 6[PyrH][Co(CO)_4]+6H_2O+6CO_2 \quad (47)$$

$$6[PyrH][Co(CO)_4]+3H_2SO_4\rightarrow 6HCo(CO)_4+3(PyrH)_2SO_4. \quad (48)$$

To prepare cobalt hydrocarbonyl from the cobalt salts of cobalt hydrocarbonyl, dicobalt octacarbonyl (3.00 g.) is placed in a 300-ml. Erlenmeyer flask provided with a ground-glass joint. Twenty milliliters of chemically pure pyridine is added, and the flask is fitted with a male ground joint to which is sealed a U-tube filled with just sufficient mercury to make a seal. The mercury valve permits the escape of carbon monoxide and prevents access of air to the reaction mixture. The evolution of carbon monoxide is complete in a few minutes. The pyridine solution containing the salt $[Co(Pyr)_6][Co(CO)_4]_2$ may be stored, provided prolonged exposure to air is avoided. A short exposure to air, such as that required for the transfer of the solution, is not detrimental.

The apparatus for generation of cobalt hydrocarbonyl consists of a 500-ml., three-necked flask provided with an inlet tube (constricted at the tip which is placed close to the bottom of the flask), a dropping funnel, and an outlet tube. To the outlet tube is attached an absorption tube (35 by 110 mm.) filled with an intimate mixture of phosphorous pentoxide and glass beads. To the absorption tube is attached a cold trap (30 by 280 mm.) immersed in liquid nitrogen. To prevent clogging the inlet tube of the cold trap should be at least 15 mm. wide. The outlet tube of the cold trap is connected to a tube immersed in about 20 ml. of a solution of nickel o-phenanthroline chloride, prepared by dissolving 2.8 g. of o-phenanthroline monohydrate and 1.2 g. of nickel chloride hexahydrate in 400 ml. of water. This solution prevents access of air to the cold trap and indicates whether any cobalt hydrocarbonyl is carried past the cold trap. Traces of cobalt hydrocarbonyl form a voluminous precipitate according to the equation:

$$2HCo(CO)_4+[Ni(o\text{-}Phthr)_3][Cl]_2\rightarrow 2HCl+[Ni(o\text{-}Phthr)_3][Co(CO)_4]_2 \quad (49)$$

The three-necked flask, filled with a cold solution of 25 ml. of concentrated sulfuric acid and 75 ml. of water, is placed in an ice bath. The flask is then fitted with the inlet tube, the dropping funnel, and the outlet tube, and the pyridine solution is poured into the dropping funnel. The dropping funnel and the inlet tube are connected by a T-tube, and the system is purged with carbon monoxide. The pyridine solution is added drop by drop to the reaction flask. The rate of addition is regulated so that most of the oily droplets (cobalt hydrocarbonyl) forming on the surface of the aqueous solution have disappeared before more pyridine solution is added. If the solution is added faster than the hydrocarbonyl is removed, losses occur due to the decomposition of the hydrocarbonyl in the flask. If the gas flow is too fast, some hydrocarbonyl is carried past the cold trap. With the quantities just described, maximum yields in minimum time are obtained with a gas flow of about 300 ml. per minute and addition of the pyridine solution (20 ml.) during 45 to 60 minutes, followed by 15 minutes of sweeping.

From 3.00 g. of dicobalt octacarbonyl, the yield of pure cobalt hydrocarbonyl is 1.80 to 1.90 g., or 90 to 95 percent of theory (equations (45) and (46)).

To prepare cobalt hydrocarbonyl from the pyridinium salt of cobalt hydrocarbonyl, 20 g. of cobalt carbonate and 150 ml. of pyridine are placed in a 500-ml. stainless steel autoclave. The autoclave is flushed three times with about 200 p.s.i. of carbon monoxide and then pressured to 3,500 p.s.i. with an approximately equimolar mixture of hydrogen and carbon monoxide. After the rocking mechanism is started, the autoclave is heated to 155° to 160° C. and kept in this range for about 2 hours. The maximum pressure attained is about 4,000 p.s.i. at 140° C.; the pressure then falls to a constant value of about 3,100 p.s.i. at 155° C. The vessel is allowed to cool to room temperature, and the gases are vented. The yield of the pyridinium salt of cobalt hydrocarbonyl is about 90 percent, and the solution contains about 1.6 g. of hydrocarbonyl per 10 ml. of solution.

The solution of the pyridinium salt of the hydrocarbonyl is diluted with additional pyridine so that 20 ml. of the pyridine solution contains approximately 2 g. of the hydrocarbonyl. The pure hydrocarbonyl is prepared by dropping the pyridine solution into sulfuric acid as described in the preparation of cobalt hydrocarbonyl from the cobalt salt of cobalt hydrocarbonyl.

STABILITY

Although cobalt hydrocarbonyl decomposes (*66*) rapidly as a liquid above its melting point (−26° C.),

$$2HCo(CO)_4\rightarrow H_2+[Co(CO)_4]_2), \quad (50)$$

it is fairly stable in the gas phase. Hieber studied the decomposition in a closed vessel and emphasized that the last traces of cobalt hydrocarbonyl decomposed very slowly (*66*). Also, cobalt hydrocarbonyl can be carried through an adsorption train in a current of carbon monoxide (*13*) without noticeable decomposition. These facts implied, and previous workers assumed (*12*), that the presence of hydrogen and/or carbon monoxide somehow stabilized the hydrocarbonyl. Whereas carbon monoxide stabilizes dicobalt octacarbonyl,

$$2[Co(CO)_4]_2\rightleftharpoons[Co(CO)_3]_4+4CO, \quad (51)$$

it can stabilize the hydrocarbonyl only if equation (50) is reversible. Experimental data bearing on this point were secured as follows: To a gas mixture, containing equimolar (volume) quantities of hydrogen, deuterium, and carbon monoxide at room temperature, was added 1 volume-percent of gaseous cobalt hydrocarbonyl. If equation (50) were reversed under these conditions, some deuterocarbonyl would be expected:

$$D_2+[Co(CO)_4]_2\rightarrow 2DCo(CO)_4. \quad (52)$$

The decomposition of the deuterocarbonyl on collision with the hydrocarbonyl should provide HD

$$HCo(CO)_4+DCo(CO)_4\rightarrow HD+[Co(CO)_4]_2. \quad (53)$$

The gas mixture was allowed to stand 4 days at room temperature and then was analyzed in the mass spectrometer. No HD could be detected. Obviously the hydrocarbonyl is not

stabilized at room temperature and atmospheric pressure by carbon monoxide or hydrogen, and equation (50) is not an equilibrium reaction under these conditions.

Cobalt hydrocarbonyl may be relatively stable in the gas phase because its decomposition (equation (50)) is a second-order reaction. The rate of decomposition thus should be proportional to the square of its concentration,

$$-dHCo(CO)_4/dt=k[HCo(CO)_4]^{-2}. \quad (54)$$

This assumption was substantiated by a kinetic study. An evacuated gas cell was filled with gaseous cobalt hydrocarbonyl, and the rate of its decomposition at 25°±0.2° C. was determined by measuring the change in absorbance value (log I_0/I, where I_0 and I are the intensities of the incident and transmitted light, respectively) with time of an infrared absorption band at 5.01μ (table 12). Substitution of these data into the equation for a second-order rate constant indicates a second-order reaction.

TABLE 12.—*Specific reaction rate constant for the decomposition k, 10^3 x/t a(a−x)*

Time, minutes	a [1] − x [2]	x [2]	k, 10^3 x/t a(a−x)
0	0. 686	0. 000	
208	. 576	. 110	1. 34
1,397	. 313	. 373	1. 24
1,680	. 278	. 408	1. 27
3,000	. 212	. 474	1. 09
3,120	. 202	. 484	1. 12
4,160	. 161	. 525	1. 14
4,475	. 150	. 536	1. 16

[1] a = absorbance at time zero = 0.686.
[2] x = 0.686 minus absorbance at time t.

To obtain an estimate of the absolute magnitude of the second-order specific reaction rate constant, a 12-liter flask, filled with equal volumes of carbon monoxide and hydrogen at atmospheric pressure, and containing a known amount of cobalt hydrocarbonyl gas, was kept at 25°±1° C. for 5 days; then the amount of undecomposed cobalt hydrocarbonyl was determined. The specific reaction rate constant was found to be 3×10^{-3} (mole/liter)$^{-1}$ second^{-1}. In a similar experiment with helium as the diluent, the constant was of the same order of magnitude.

The experimental details of this kinetic study are described as follows:

A 12-liter, round-bottom flask fitted with a stopper and a three-way stopcock was evacuated and attached to the phosphorus pentoxide tube of the cobalt hydrocarbonyl generator. The apparatus was purged with synthesis gas (equal volumes of carbon monoxide and hydrogen), and the stopcock of the evacuated flask was turned to admit synthesis gas carrying cobalt hydrocarbonyl until the flask was filled (about 35 minutes), whereupon the flask was disconnected. After a few hours, small crystals of dicobalt octacarbonyl began to form on the wall of the flask.

The concentration of cobalt hydrocarbonyl was determined as follows: An evacuated 3-liter flask fitted with a stopper and stopcock was attached to the 12-liter flask, and the pressure was allowed to equilibrate. The 3-liter flask was removed, and a few milliliters of aqueous ammonia (concentrated ammonia and water, 1:1) was poured into the stopcock arm of the 3-liter flask. The stopcock was turned carefully to admit the solution to the flask without allowing any air to enter. This process was repeated until about 10 ml. of the ammonia solution had been added to the flask. (Heavy fumes of $NH_4Co(CO)_4$ were formed, similar to those observed on mixing ammonia and hydrogen chloride.) The flask was rotated and allowed to stand for 15 minutes to distribute the ammonia solution over a large area and to complete the absorption of gaseous cobalt hydrocarbonyl. Then 25 ml. of nickel o-phenanthroline chloride solution (*133*) was added through the stopcock to form the water-insoluble precipitate, $[Ni(o\text{-}phen)_3][Co(CO)_4]_2$. The flask was shaken for about 1 minute, the stopcock was opened, and the stopper was removed. About 50 ml. of water was added to the flask, and the amount of $[Co(CO)_4]^-$ in the precipitate was determined by a gasometric procedure (*133*). After standing at 25°±1°C. for 112 hours, the 12-liter flask was sampled again as just described.

A second, similar experiment was carried out with helium as the diluent. Black crystals of the tetramer, $[Co(CO)_3]_4$, deposited on the wall of the flask. The second gas sample was taken after the gas had remained at 25° ± 1° C. for 120 hours. The concentration of cobalt hydrocarbonyl in the 12-liter flask after removal of the first gas sample is given as initial concentration; the concentration before removal of the second sample is given as final concentration (see table 13). The rate constants were calculated from $k=[x/a(a-x)]t^{-1}$, where t is the time in seconds, a is the initial concentration, and a-x in the final concentration in moles per liter.

TABLE 13.—*Specific reaction rate constants of $(HCo(CO)_4$ decomposition*

Diluent	Concentration, 10^{-4} moles $Hco(CO)_4$/l.	Time, hours	Specific reaction rate constant, k, 10^{-3} (mole/l.)$^{-1}$ (sec.)$^{-1}$
$1H_2$:1CO	4. 45	0	3
	2. 77	112	
He	2. 39	0	6
	1. 43	120	

These results are semiquantitative, and no special significance should be attached to the difference in rate constants. The precision of sampling, analysis, and temperature control was only sufficient for an order of magnitude of the constant.

The relative stability of cobalt hydrocarbonyl in the gas phase compared with that in the liquid phase is now comprehensible. If the order and rate of the reaction in the liquid phase are the same as those in the gas phase, the half life of a 1- and a 9-molar solution of cobalt hydrocarbonyl may be computed from

$$t_{0.5}=1/ka, \quad (55)$$

where a=initial concentration (moles per liter) and k=(moles per liter)$^{-1}$ second^{-1}.

Substitution of $k=3\times10^{-3}$ into equation (55) gives a half life of 333 seconds for the 1-molar solution of cobalt hydrocarbonyl and 37 seconds for the 9-molar solution. This result agrees with the observation that a 1-molar solution of cobalt hydrocarbonyl in hexane decomposes within a few minutes and that liquid cobalt hydrocarbonyl (*68*), which is approximately 9 molar, is not stable at room temperature.

It has been stated that, according to its neutralization curve in aqueous acetone solution, cobalt hydrocarbonyl behaves like a strong acid (*30*). However, experimental details leading to this conclusion were not reported. To obtain data on the acid strength of cobalt hydrocarbonyl, an 0.02-molar aqueous solution of cobalt hydrocarbonyl was titrated potentiometrically with 0.1 *N* aqueous sodium hydroxide at room temperature. The pH of the solution before titration and the neutralization curve (fig. 7) corresponded to those of a strong acid such as hydrochloric acid. Phenolphthalein was a suitable indicator, whereas methyl orange and methyl red, contrary to published reports (*30*), could not be used since these azo-type indicators were immediately reduced by the hydrocarbonyl. The preparation and titration of the aqueous cobalt hydrocarbonyl solution are described as follows:

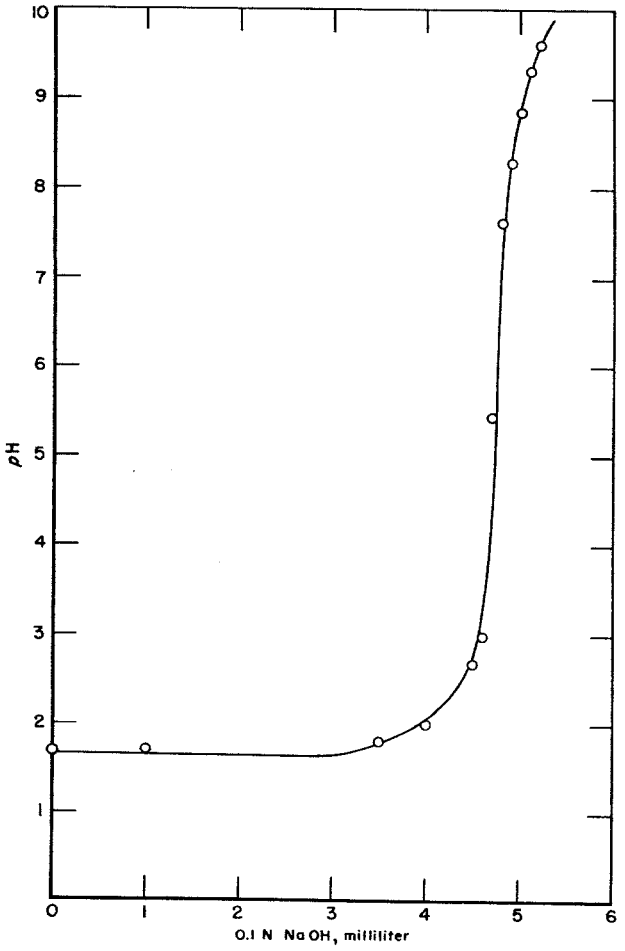


FIGURE 7.—Potentiometric Titration at 26° C. of 25 ml. of Aqueous HCo(CO)$_4$ with 0.1 *N* NaOH.

627136 O—62——3

Oxygen-free water (100 ml.) was placed in a 300-ml. Erlenmeyer flask fitted with a stopper, an inlet tube reaching to the bottom of the flask, and an outlet tube. Both inlet and outlet tubes were provided with stopcocks. The Erlenmeyer flask was attached to the cobalt hydrocarbonyl generator, and cobalt hydrocarbonyl diluted with synthesis gas was bubbled through the flask for 5 minutes. The flask was removed from the generator, and the solution was transferred to a burette in an atmosphere of nitrogen. The solution was titrated in a 100-ml. beaker fitted with a stopper provided with holes for two electrodes, a burette, an inlet tube, and an outlet tube. The inlet and outlet tubes were connected to a nitrogen cylinder and a mercury valve, respectively. This arrangement permitted the maintenance of an inert atmosphere during the titration. The aqueous cobalt hydrocarbonyl solution (25.00 ml.) was measured into the beaker, and a burette containing 0.1 *N* sodium hydroxide was inserted in the stopper. The data obtained at 26° C. with a Beckman pH meter (model H2) are plotted in figure 7. According to these data, the cobalt-hydrocarbonyl solution was 0.0192 molar. The pH of 1.65 indicates that the cobalt hydrocarbonyl is completely dissociated. (The pH of a completely dissociated 0.0192 molar solution would be 1.72.) After standing for 14 days at room temperature, the solution was titrated again and found to be 0.0148 molar.

Neither methyl orange nor methyl red could be used as indicators. They were discolored within a few seconds by both alkaline and acid solutions of cobalt hydrocarbonyl, possibly by reduction of the azo-group to a hydrazo-group. A good indicator is phenolphthalein: Fifty milliliters of aqueous cobalt hydrocarbonyl was titrated with 0.1 *N* sodium hydroxide in the presence of phenolphthalein. After titration, cobalt was determined by addition of ammonia and hydrogen peroxide, followed by treatment with concentrated sulfuric acid and electrolysis of the acid solution The amount of cobalt determined by titration was 0.1656 g and that determined by electrolysis was 0.1665 g.

Despite its acid strength, cobalt hydrocarbonyl is only sparingly soluble in water; its concentration at room temperature is 5.6×10^{-2} moles per liter.

The solubility of cobalt hydrocarbonyl in water was determined as follows: An Erlenmeyer flask, containing 50.0 ml. of distilled, oxygen-free water and phenolphthalein indicator, was fitted with a burette, an inlet tube, and an outlet tube, and attached to the cobalt hydrocarbonyl generator previously described. A current of carbon monoxide containing approximately 1 millimole of $HCo(CO)_4$ per liter was bubbled through the water at 25° C. and a rate of 300 ml. per minute. Cobalt hydrocarbonyl could be detected in the gas stream leaving the Erlenmeyer flask 5 minutes after the start of the experiment, and the experiment was continued for 15 minutes after this point had been reached. The flask was detached, and the solution was titrated with a 0.1 *N* NaOH solution; 28.0 ml. was required for neutralization. Thus, the saturated aqueous solution was 5.6×10^{-2} molar with respect to cobalt hydrocarbonyl.

In aqueous solution and in the absence of oxygen, cobalt hydrocarbonyl is fairly stable at room temperature. After 14 days the molarity of an aqueous solution of cobalt hydrocarbonyl had decreased from 0.0192

to 0.0148; hence, the accuracy of a titration at room temperature is not affected by decomposition of cobalt hydrocarbonyl.

The stability of the aqueous (ionized) solution of cobalt hydrocarbonyl is high compared with a half life of about 5 hours for a 0.02-molar solution of cobalt hydrocarbonyl in hexane.

REACTIONS OF $HCo(CO)_4$

Although, as just pointed out, cobalt hydrocarbonyl decomposes rapidly above −26° C., organic reactions with hydrocarbonyl may be conducted with surprising ease. The substrate is placed in a cold trap; cobalt hydrocarbonyl is condensed onto it; and the mixture is allowed to warm to room temperature.

The following preparation of cyclohexane-carboxaldehyde from cyclohexene and cobalt hydrocarbonyl serves as an example (*159*): Cobalt hydrocarbonyl (4.0 g., 0.023 mole) was collected in a liquid-nitrogen trap containing 7.0 g. (0.085 mole) of peroxide-free cyclohexene. On warming, the cobalt hydrocarbonyl dissolved in the olefin without noticeable decomposition. At about 15° C., the solution began to darken, a little gas was given off, and noticeable heat was evolved. Upon addition of 2,4-dinitrophenylhydrazine, the 2,4-dinitrophenylhydrazone of cyclohexanecarboxaldehyde was obtained in a yield of 60 percent, based on the amount of cobalt hydrocarbonyl used.

Maximum yields are obtained when the substrate is a liquid at or below 0° C. and is present in excess of cobalt hydrocarbonyl. A solid substrate should be dissolved in a low-melting, inert solvent such as hexane. Oxygenated solvents should be avoided, as they may retard the reaction or react with cobalt hydrocarbonyl. Thus, while triphenyl carbinol is readily reduced to triphenylmethane in acetone or isopropyl alcohol, benzhydrol is reduced to diphenylmethane in acetone but not in isopropyl alcohol.

The reactions between cobalt hydrocarbonyl and various substrates include isomerization, homologation, hydrogenolysis, hydrogenation, and hydroformylation. Examples for these types of reactions are summarized in the following:

Substrate	*Products*
Cyclohexene	Cyclohexanecarboxaldehyde.
Hexene-1 (excess)	C_7 aldehydes.
	Hexene-2.
	Hexene-3.
	No hexene-1.
α-Methylstyrene	Isopropylbenzene.
	C_{10} aldehyde.
Benzyl alcohol	Toluene.
Benzhydrol	Diphenylmethane.
Triphenyl carbinol	Triphenylmethane.

Dissociation of Iron Pentacarbonyl in Amines

DISSOCIATION IN PIPERIDINE

When iron pentacarbonyl is dissolved in piperidine, the solution becomes warm; at the same time it becomes conducting, indicating that ions have been formed. As no carbon monoxide is evolved on mixing the two compounds and as the solution is diamagnetic, ionization does not involve the formation of ferrous or ferric ions.

The susceptibility measurements were made with a Faraday-type magnetic balance (*134*) adapted for paramagnetic measurements. No paramagnetic effect was noted when a sample of piperidine was replaced by a solution consisting of 1.0 ml. of $Fe(CO)_5$ and 4.0 ml. of piperidine. The sensitivity of the balance was not sufficient for an exact measurement of the diamagnetic susceptability.

A postulate consistent with these facts and with the tendency of the metal carbonyls to form structures having the rare gas configuration is that iron pentacarbonyl dissociates in piperidine:

$$2Fe(CO)_5 \rightleftharpoons \underset{\text{XXIX}}{[Fe(CO)_6]^{++}} + \underset{\text{XXX}}{[Fe(CO)_4]^{=}} \quad (56)$$

The effective atomic number of iron in iron pentacarbonyl and in both of the ions XXIX and XXX is 36, which corresponds to the electronic configuration of krypton. Whereas the existence of the anion in its salts has been described (*44*, *71*, *76*), the existence of the positively charged iron carbonyl complex XXIX had not been proved.

The infrared spectrum of iron pentacarbonyl in piperidine corroborates the presence of these ions. The spectrum of $Fe(CO)_5$ in cyclohexane solution contains two bands in the C≡O triple bond region at 2,022 $cm.^{-1}$ and 2,000 $cm.^{-1}$. Both bands disappear when $Fe(CO)_5$ is dissolved in piperidine; in their place appear two new bands at 1,898 $cm.^{-1}$ and 2,016 $cm.^{-1}$. The band at 1,898 $cm.^{-1}$ may be attributed to XXX because cobalt carbonyl anion, $[Co(CO)_4]^-$, which is isoelectronic with XXX, gives rise to a single band located at the same position (*46*). By elimination, the band at 2,016 $cm.^{-1}$ must be due to XXIX.

The fact that XXIX and XXX each give rise to a single band is in agreement with group theory (*59*), which predicts a single infrared-active C≡O stretching frequency for an octahedral (*123*) as well as a tetrahedral (*34*) metal carbonyl. These predictions were verified for chromium carbonyl (*123*), $Cr(CO)_6$, which has an octahedral configuration (*17*), and for nickel carbonyl (*34*), $Ni(CO)_4$, which possesses a tetrahedral configuration (*77*). XXIX probably possesses an octahedral and XXX a tetrahedral configuration, as XXIX is isoelectronic with $Cr(CO)_6$ and XXX is isoelectronic with $Ni(CO)_4$.

The spectra of 0.161- and 1.48-molar solutions of $Fe(CO)_5$ in piperidine were determined within 1 hour from the time iron pentacarbonyl had been added to the amine. The spectrum of the 1.48-molar solution in piperidine showed only the cation and anion bands

at 2,016 cm.$^{-1}$ and 1,898 cm.$^{-1}$. The anion band was present in the spectrum of the 0.161-molar solution in piperidine, but the cation band at 2,016 cm.$^{-1}$ was obsecured by the two bands at 2,000 cm.$^{-1}$ and 2,022 cm.$^{-1}$ associated with $Fe(CO)_5$. An explanation of this phenomenon, that is, the incomplete dissociation of $Fe(CO)_5$ in dilute piperidine solution, must await further investigation.

EFFECT OF AMINE STRUCTURE ON THE DISSOCIATION OF $Fe(CO)_5$

An insight into the mechanism of the dissociation of iron pentacarbonyl in piperidine may be secured from the conductivity of iron pentacarbonyl in various amines.

The data shown in table 14 were obtained as follows: The electrodes were smooth platinum and the cell constant was 0.845 cm.$^{-1}$. A conductivity bridge permitted the determination of resistance values up to 2.5×10^6 ohms. Forty-five millileters of ice-cold amine was pipetted into the cell, which was immersed in an ice bath; 1.450 g. (1.0 ml.) of $Fe(CO)_5$ was added; and the solution was stirred under a blanket of nitrogen. The cell was then stoppered, and the first reading was taken 15 minutes after $Fe(CO)_5$ had been added to the solvent. The equivalent conductance of some of the solutions changed considerably during the first 2 hours. In these cases another reading was taken 18 hours after the start of the experiment to determine the extent of the change. In certain amines a precipitate began to form after 6 to 8 hours, probably owing to secondary reactions. These results are summarized in table 14. Except for those cases in which the conductivity did not change during the first 2 hours, no quantitative significance can be attached to the data.

The data in table 14 show that the ability of an amine to ionize iron pentacarbonyl

TABLE 14.—*Conductivities of 0.161-molar solutions of* $Fe(CO)_5$

Solvent	Molar conductivity [1] at O° C., ohms^{-1}		
	¼ hour	2 hours	18 hours
n-Butylamine	0. 500	0. 500	
Piperidine	. 233	. 496	1. 060
Morpholine [2]	. 150	. 344	. 760
Diethylamine [2]	. 008	. 294	. 350
Benzylamine	. 068	. 068	
tert-Butylamine [2]	. 036	. 046	. 131
4-Picoline	. 051	. 210	1. 165
Pyridine	. 019	. 086	. 396
2-Picoline	. 008	. 015	. 018
Pyrrole	. 0	. 0	
2,6-Lutidine	. 0	. 0	
Triethylamine	. 0	. 0	
Aniline	. 0	. 0	
di-n-Butylamine	. 0	. 0	
n-Butanol	. 0	. 0	

[1] The solutions were 0.161 molar with respect to $Fe(CO)_5$. However, since 2 moles of $Fe(CO)_5$ is involved in the ionization, molar conductivities are based on 2 moles of $Fe(CO)_5$: that is, on a molecular weight of 392.

[2] Formation of precipitate after standing 6–8 hours.

depends on two main factors: (1) Availability of the lone pair of electrons on nitrogen for bonding or charge neutralization—a polar effect; and (2) the presence of many or bulky substituents on nitrogen which prevent the pair of electrons from reaching the site of reaction—a steric effect. Brown (*18*) has shown that the extent of compound formation between an amine and a Lewis acid depends, among other things, upon the steric requirements of both amine and acid. The steric requirements of the amines listed in table 14 parallel those studied by Brown for compound formation with the reference acid triisopropylboron, $B(i\text{-}Pr)_3$.

The importance of electron availability and a favorable configuration at the nitrogen atom is well illustrated with the secondary amines. Both factors are conducive to ionization in piperidine and morpholine, but iron pentacarbonyl does not dissociate in either di-n-butylamine (high steric requirements) or in pyrrole (low electron availability).

To prove that the ions XXIX and XXX are strongly complexed with amine, iron pentacarbonyl was treated with excess monomethylamine, dimethylamine, and trimethylamine at −80° C.; the excess amine was allowed to evaporate; and the residue was weighed. With monomethylamine and dimethylamine, the weight increase corresponded to 4 to 5 moles of amine per mole of iron pentacarbonyl, but with trimethylamine, no weight increase was found. The infrared spectra of the residues obtained after treatment with monomethylamine and dimethylamine showed the typical cation and anion bands, whereas the residue obtained from treatment with trimethylamine proved to be unchanged iron pentacarbonyl. As indicated, the reactivity of these amines towards $Fe(CO)_5$ parallels their reactivity towards $B(i\text{-}Pr)_3$. Thus, compound formation takes place between monomethylamine or dimethylamine and $B(i\text{-}Pr)_3$, but not between trimethylamine and $B(i\text{-}Pr)_3$.

MECHANISM

The dissociation of iron pentacarbonyl (equation (56)) may be compared with that of phosphorous pentachloride:

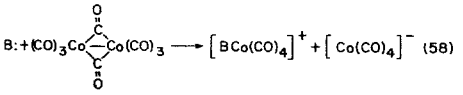
$$2PCl_5 \rightleftharpoons [PCl_4]^+ + [PCl_6]^- . \qquad (57)$$

Conductance measurements on solutions of PCl_5 have been reported by Payne, whose data indicate that the extent of dissociation of PCl_5 is determined by the ability of the solvent to stabilize the ionization by complex formation rather than through the effect of its dielectric constant (*106*). The same conslusions may be drawn for $Fe(CO)_5$. Thus, piperidine with a

dielectric constant of 5.8 causes ionization of $Fe(CO)_5$, whereas n-butanol with a dielectric constant of 19.2 does not.

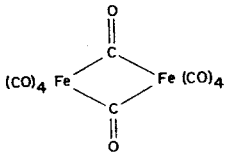
The effect of amine structure on the dissociation of the pentacarbonyl furnishes valuable information as to the mode of action of the solvent. For instance, steric hindrance between amine and $Fe(CO)_6^{++}$ could hardly be important if the amine acted chiefly on the carbonyl group of iron pentacarbonyl. However, stabilization of XXIX may be due to the transfer of positive charge from iron to nitrogen by a complex formation of the "ionic" or "outer complex" type (*22*). Since even weak bonding between nitrogen and iron necessitates a fairly close approach of nitrogen to iron, the configuration of the amine may be expected to play a role similar to that of a sterically hindered Lewis acid in compound formation with an amine (*18*). Stabilization of XXX could conceivably be achieved by the transfer of a negative charge through hydrogen bonding. Where hydrogen bonding is not possible, as in pyridine, the polarizability of the solvent may play a part in stabilizing XXX.

Some insight into the mechanism of the electron and carbonyl transfer involved in equation (56) may be obtained from the reaction between dicobalt octacarbonyl and piperidine (*158*). Dicobalt octacarbonyl, which was recently shown to possess the bridged structure XXXI (*23*, *46*), reacts with piperidine according to equation (58), where B is piperidine:



XXXI

Similarly, iron pentacarbonyl may dissociate via a bridged complex such as XXXII, followed by electron and carbonyl transfer. The fact that electrons are transferred much more efficiently by a bridged activated complex than by other available paths was shown by Taube and King for electron exchange between chromium (II) and monochlorochromium (III) ion (*137*). The facile conversion by light of iron pentacarbonyl to enneacarbonyl, which has three carbonyl bridges (*121*), indicates that bridged complexes are readily formed from $Fe(CO)_5$.



XXXII

The Iron Pentacarbonyl-Aqueous Alkali System

EVIDENCE FOR THE EXISTENCE OF BINUCLEAR IRON CARBONYL ANIONS

Solutions obtained by treating iron pentacarbonyl with aqueous alkali can convert olefins to the next higher alcohols (*116*),

$$H_2C{=}CH_2+3CO+2H_2O\rightarrow CH_3CH_2CH_2OH+2CO_2 \quad (59)$$

reduce nitrobenzene to aniline (*89*), benzil to benzoin (*89*), quinone to hydroquinone (*89*), and acetylene to ethylene (*129*).

Krumholz and Stettiner (*76*) have shown that the solutions obtained by treating iron pentacarbonyl with aqueous alkali contain $[HFe(CO)_4]^-$ and/or $[Fe(CO)_4]^=$, depending on the amount of alkali used. When 1 mole of $Fe(CO)_5$ is treated with 3 moles of NaOH, the anion $[HFe(CO)_4]^-$ is formed:

$$Fe(CO)_5+3NaOH=NaHFe(CO)_4+Na_2CO_3+H_2O. \quad (60)$$

Treatment with 4 or more moles of NaOH produces $[Fe(CO)_4]^=$:

$$Fe(CO)_5+4NaOH=Na_2Fe(CO)_4+Na_2CO_3+2H_2O. \quad (61)$$

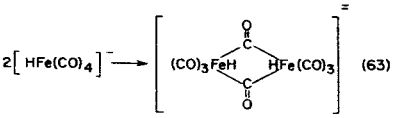
Since $Na_2Fe(CO)_4$ is hydrolyzed to some degree,

$$Na_2Fe(CO)_4+H_2O\rightleftharpoons NaOH+NaHFe(CO)_4, \quad (62)$$

$[HFe(CO)_4]^-$ ion is present even in strongly alkaline solution.

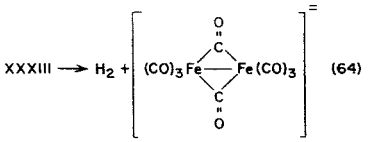
It will be shown that the solutions obtained according to equation (60) contain a dimer formed from $[HFe(CO)_4]^-$ and that this dimer accounts for the chemical properties of the iron pentacarbonyl aqueous alkali system.

When the light yellow aqueous solution obtained by treating 1 mole of $Fe(CO)_5$ with 3 moles of NaOH (equation (60)) is allowed to stand for a few days, it becomes dark red, even when oxygen is carefully excluded, and slowly gives off hydrogen. This behavior may be explained by the following: The color change is caused by dimerization of the anion, $[HFe(CO)_4]^-$,



XXXIII

and the evolution of hydrogen by the decomposition of XXXIII,



XXXIII → H_2 + [$(CO)_3Fe$—$Fe(CO)_3$ bridged by C=O] (64)

XXXIV

Evidence for the existence of XXXIII and XXXIV is based on the following observations:

Ether extraction of an aqueous solution prepared according to equation (60) yields a dark red pyrophoric solid. The iron and sodium contents of this solid indicate that it consists of a mixture of $NaHFe_2(CO)_8$, (XXXV), and a small amount of $H_2Fe_2(CO)_8$, (XXXVI); that is, the acid salt and free acid corresponding to XXXIV. When the mixture of XXXV and XXXVI is treated with excess acid, approximately one-half mole of hydrogen and one-third mole of iron tetracarbonyl, $[Fe(CO)_4]_3$, are formed per atom of iron present,

$$\underset{\text{XXXV}}{NaHFe_2(CO)_8} + HCl \rightarrow NaCl + \underset{\text{XXXVI}}{H_2Fe_2(CO)_8} \quad (65)$$

$$\underset{\text{XXXVI}}{H_2Fe_2(CO)_8} \xrightarrow{H^+} H_2 + \frac{2}{3}\underset{\text{XXXVII}}{[Fe(CO)_4]_3}. \quad (66)$$

Acidification of the monomeric, $NaHFe(CO)_4$, leads to an entirely different reaction. Iron hydrocarbonyl, $H_2Fe(CO)_4$, is liberated

$$NaHFe(CO)_4 + HCl \rightarrow H_2Fe(CO)_4 + NaCl \quad (67)$$

and decomposes according to (*69*)

$$2H_2Fe(CO)_4 \rightarrow 2H_2 + Fe(CO)_5 + Fe(CO)_3. \quad (68)$$

In this case 1 mole of hydrogen and one-half mole of $Fe(CO)_5$ and $Fe(CO)_3$ are obtained for each atom of iron present. No iron tetracarbonyl is formed.

The preparation, analysis, and acid treatment of the mixture of XXXV and XXXVI were carried out as follows:

When excess $Fe(CO)_5$ is treated with aqueous alkali, the reaction proceeds (*76*) until 1 mole of $NaHFe(CO)_4$ is formed for every 3 moles of NaOH (equation (60)). Thus, in the presence of excess $Fe(CO)_5$, 3 moles of NaOH form 1 mole of $NaHFe(CO)_4$.

Seven milliliters (52 millimoles) of $Fe(CO)_5$ was placed in an Erlenmeyer flask provided with a glass stopper, and 4.5 g. (112 millimoles) of NaOH dissolved in 50 ml. of oxygen-free water was added; the flask was stoppered at once and shaken vigorously for 48 hours at room temperature. After standing for another 48 hours, the dark red solution was extracted with low-boiling petroleum ether, to remove any unreacted $Fe(CO)_5$, and then with peroxide-free ethyl ether. The ethyl ether extract, which contained a large amount of water, was treated as follows: The bulk of the ether was removed in a current of inert gas at room temperature. To the residue was added sufficient Na_2SO_4 to absorb all of the liquid. The resulting mixture was allowed to stand in the refrigerator overnight and was extracted with anhydrous ether, and the ether was evaporated in a current of inert gas. After further evaporation at 1 mm. Hg and 100° C., the residue, a dark red pyrophoric powder, weighed 2.5 g. It was readily soluble in water, alcohol, or ether, and insoluble in petroleum ether or benzene.

Found: Fe, 30.14; Na, 6.42

Calculated for $NaHFe_2(CO)_8$: Fe, 31.05; Na, 6.39

Fe:Na ratio = 1.93:1

Analyses of subsequent preparations, however, did not give consistent results; that is, the ratio of Fe to Na was not always two, as required for $NaHFe_2(CO)_8$, XXXV, but varied from two to about three. The data in table 15 indicate that the high Fe:Na ratio is due to the presence of $H_2Fe_2(CO)_8$, XXXVI; that is, the free acid derived from XXXIV.

TABLE 15.—*Anaylsis of a mixture of* $H_2Fe_2(CO)_8$ *and* $NaHFe_2(CO)_8$

Found			Calculated		
Fe, percent	Na, percent	Fe:Na, atomic ratio	$NaHFe^2(CO)_8$, mole-percent [1]	Fe, percent [2]	Na, percent [2]
32.07	5.65	2.34	85.5	31.33	5.51
32.66	4.89	2.75	72.8	31.57	4.73
31.30	4.00	3.22	62.1	31.78	4.07

[1] Calculated from the atomic ratio (col. 3), assuming that the mixture consisted only of $H_2Fe_2(CO)_8$ and $NaHFe_2(CO)_8$.

[2] Calculated on the basis of the molar mixture (col. 4).

The observed iron-sodium ratios eliminate the possibility of the ether extract consisting of $NaHFe(CO)_4$, $Na_2Fe(CO)_4$, or a combination of these salts. The fact that the dried ether extract is soluble in absolute ether and water precludes the possibility of contamination by metals, metal salts, or metal carbonyls such as $Fe(CO)_5$, $Fe_2(CO)_9$, or $[Fe(CO)_4]_3$. When an aqueous solution of nickel o-phenanthroline chloride, $[Ni(o\text{-}Phthr)_3]Cl_2$, is added to an aqueous solution of the residue of the ether extract described previously, a dark-red precipitate is obtained. The dried precipitate is extremely pyrophoric and contains 0.08 percent of Na, 26.7 percent of Fe, and 4.9 percent of Ni, that is, iron and nickel in a mole ratio of 5.8. This ratio excludes the possibility of the precipitate being a nickel salt derived from either $[Fe(CO)_4)]^=$ or $[HFe(CO)_4]^-$. The salts derived from these two anions, $[Ni(o\text{-}Phthr)_3][Fe(CO)_4]$ and $[Ni(o\text{-}Phthr)_3][HFe(CO)_4]_2$, would have an iron-nickel ratio of 1 and 2, respectively. The nickel salt corresponding to $NaHFe_2(CO)_8$, XXXV, has the composition $[Ni(o\text{-}Phthr)_3][HFe_2(CO)_8]_2$; that is, an iron-nickel ratio of 4. The high Fe:Ni ratio found may be due to coprecipitation of $H_2Fe_2(CL)_8$.

A mixture of $NaH[Fe(Co)_4]_2$ and $[HFe(CO)_4]_2$, prepared as previously described, was dissolved in

ether; an aliquot of the ether solution contained 0.598 g. of iron (10.7 milliatoms).

Another aliquot was evaporated to dryness at room temperature in a current of helium, and the residue was dissolved in about 35 ml. of water. An Erlenmeyer flask, containing a glass-enclosed stirring bar, and provided with a ground joint and a sidearm with stopper for the addition of acid, was charged with the aqueous solution and attached to a gas burette. Through the sidearm was added 10 ml. of aqueous 6 *N* hydrochloric acid, and the contents of the flask were stirred. Soon after the acid had been added, gas was evolved and a small amount of dark green crystals formed. Gas evolution stopped after 4.95 millimoles of hydrogen and 0.32 millimole of carbon monoxide had been evolved during 3 hours. The rate of gas evolution was fast during the first hour and very slow at the end of the reaction. After completion of the reaction, the originally dark-red solution had become practically colorless, and a large amount of a dark-green crystalline precipitate had formed. The precipitate was filtered, washed with water, and, after drying over phosphorus pentoxide, weighed 1.436 g., corresponding to 2.85 millimoles $[Fe(CO)_4]_3$. The precipitate was identified as iron tetracarbonyl, $[Fe(CO)_4]_3$, by comparison of its infrared spectrum with that of an authentic sample. The filtrate and wash water contained 0.062 g. of iron. Accordingly, total iron in the filtrate and in $[Fe(CO)_4]_3$ was 0.540 g., or 90.5 percent of the iron in the aliquot. The balance is probably lost as $Fe(CO)_5$, which is formed in a side reaction. Some $Fe(CO)_5$ remains with the $[Fe(CO)_4]_3$ and is evaporated during drying. A small amount of $Fe(CO)_5$ was shown to have been formed: In a separate experiment, another aliquot was treated with excess acid as previously described. The reaction mixture was extracted with petroleum ether, and the amount of $Fe(CO)_5$ was determined by infrared analysis. Iron as $Fe(CO)_5$ was 4 percent of the iron in the aliquot.

According to equations (65) and (66), 0.50 mole of hydrogen and 0.33 mole of $[Fe(CO)_4]_3$ should be formed per atom of iron. Actually, 0.46 mole (92 percent of theory) of hydrogen and 0.27 mole (81 percent of theory) of iron tetracarbonyl, $[Fe(CO)_4]_3$, were found per atom of iron.

The decomposition of XXXVI in the presence of protons (equation (66)) requires an explanation. If the hydrogen atoms in XXXVI are surrounded by a large negative charge, as in cobalt hydrocarbonyl (*39*), they may behave like hydride ions and react with a proton to form hydrogen and a positively charged intermediate:

$$H^+ + \text{XXXVI} \rightarrow H_2 + [HFe_2(CO)_8]^+ \qquad (69)$$

which subsequently loses a proton,

$$[HFe_2(CO)_8]^+ \rightarrow H^+ + \frac{2}{3}\,\text{XXXVII}. \qquad (70)$$

Iron tetracarbonyl is formed from XXXVI (equation (66)) with evolution of hydrogen. The reaction is formally analogous to the formation of iron tetracarbonyl from the dimeric iron enneacarbonyl, which takes place with evolution of carbon monoxide:

$$Fe_2(CO)_9 \rightarrow CO + \frac{2}{3}[Fe(CO)_4]_3.\ \text{XXXVII} \qquad (71)$$

A freshly prepared solution of XXXIII absorbs at 4750 A., whereas a solution of XXXV and XXXVI absorbs at 5350 A. When the solution of XXXIII is allowed to stand, the band at 4750 A. is gradually replaced by that at 5350 A. The infrared spectrum of a solution of XXXV and XXXVI in ether contains only two sharp, strong bands at 4.98 and 5.04 μ. The spectrum of an ether extract of an aqueous solution containing XXXIII, on the other hand, shows three sharp, strong bands at 5.01, 5.07, and 5.27 μ, a broad band at 14.34 μ, and a shoulder at 5.20 μ.

The water and ether solutions of XXXIII and of the mixture of XXXV and XXXVI were prepared as follows:

A solution containing 7.5 millimoles of $NaHFe(CO)_4$ in 100 ml. of water was prepared according to equation (60). After standing for 3 days, 1 ml. of the solution was diluted with 20 ml. of distilled, oxygen-free water. The spectrum of the dilute solution showed a broad band at 4750 A. in the visible region. After 1 day, the intensity of the band had decreased, and a new one appeared at 5350 A. After 3 more days, the band at 4750 A. had disappeared, and the intensity of the newly formed band increased further.

A mixture of XXXV and XXXVI containing 0.047 g. (0.13 millimole) of $[Fe_2(CO)_8]^=$, XXXIV, was dissolved in 500 ml. of water. The spectrum of this solution contained a broad band at 5350 A. The molar extinction, based on $[Fe_2(CO)_8]^=$, was 1,800 g.-moles liter^{-1}.

A solution containing 75 millimoles of $NaHFe(CO)_4$ in 100 ml. of water was prepared according to equation (60). After standing for 4 days, the dark-red solution was extracted with ether, and the ether extract was treated with Na_2SO_4, as previously described. The infrared spectrum of the ether solution containing approximately 0.009 g. (0.023 millimole) of $[H_2Fe_2(CO)_8]^=$ per milliliter of ether was determined in a 0.032-mm. cell.

A mixture of XXXV and XXXVI containing 0.303 g. (0.84 millimole) of $[Fe_2(CO)_8]^=$ was dissolved in 40 ml. of anhydrous, peroxide-free ethyl ether, and the infrared spectrum was determined in a 0.032-mm. cell.

Equations (63) and (64) account for the chemical behavior of the solutions obtained by treating iron pentacarbonyl with aqueous alkali, as will be illustrated by the following examples:

Published accounts of the behavior of these solutions contain contradictory statements. Hieber and Leutert, for example, reported that in the absence of oxygen or oxidizing agents these solutions are stable and do not decompose even on boiling (*63*). Reppe and others, on the other hand, reported that an aqueous solution obtained by treating 1 mole of $Fe(CO)_5$ with 3 moles of NaOH was decomposed on boiling, with evolution of hydrogen and carbon monoxide (*115*). This discrepancy is readily explained if it is assumed that Hieber was referring to a strongly alkaline solution. In a strongly alkaline solution, the concentration of $[HFe(CO)_4]^-$ ions is low, according to equation (62). Consequently, dimer formation and hydrogen evolution (equations (63) and (64)) are slow. Reppe's solution, prepared according