[CONTRIBUTION FROM CENTRAL EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Binuclear Iron Carbonyls and Their Significance as Catalytic Intermediates[1]

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Evidence is presented for the existence of binuclear iron carbonyl ions formed by the dimerization of two $[HFe(CO)_4]^-$ ions: $2[HFe(CO)_4]^- \rightarrow [H_2Fe_2(CO)_8]^=$ (I) $\rightarrow H_2 + [Fe_2(CO)_8]^=$ (II). The chemical and catalytic properties of solutions obtained by treating $Fe(CO)_5$ with aqueous alkali can be explained on the basis of the existence of I and II. Previous explanations, which took into account only the existence of the mononuclear ions $[Fe(CO)_4]^=$ and $[HFe(CO)_4]^-$, are not in agreement with experimental facts. This is illustrated by a study of the stability and reducing properties of the $Fe(CO)_5$–aqueous alkali system. The structural similarity between I and II and dicobalt octacarbonyl, $Co_2(CO)_8$, led to the prediction that I and II should catalyze the isomerization of double bonds and the conversion of olefins to the next higher aldehydes. This prediction was found to be correct. In addition it is shown that iron hydrocarbonyl, $H_2Fe(CO)_4$, also possesses reducing properties and catalyzes the isomerization of double bonds. These properties probably are due to the formation of a binuclear intermediate: $2H_2Fe(CO)_4 \rightarrow [H_4Fe_2(CO)_8] \rightarrow 2H_2 + Fe(CO)_5 + Fe(CO)_3$.

Introduction

The solutions obtained by treating iron pentacarbonyl with aqueous alkali have intriguing chemical and catalytic properties, which include the conversion of olefins to the next higher alcohols[2] (equation 1)

$$H_2C{=}CH_2 + 3CO + 2H_2O \longrightarrow CH_3CH_2CH_2OH + 2CO_2 \quad (1)$$

the reduction of nitrobenzene to aniline,[3] benzil to benzoin,[3] quinone to hydroquinone[3] and acetylene to ethylene.[4] This paper deals with the nature of the catalytic species involved in these reactions.

Krumholz and Stettiner[5] have shown that the solutions obtained by treating iron pentacarbonyl with aqueous alkali contain the ions $[HFe(CO)_4]^-$ 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 according to equation 2

$$Fe(CO)_5 + 3NaOH = NaHFe(CO)_4 + Na_2CO_3 + H_2O \quad (2)$$

Treatment with 4 or more moles of NaOH produces the anion $[Fe(CO)_4]^=$ according to equation 3

$$Fe(CO)_5 + 4NaOH = Na_2Fe(CO)_4 + Na_2CO_3 + 2H_2O \quad (3)$$

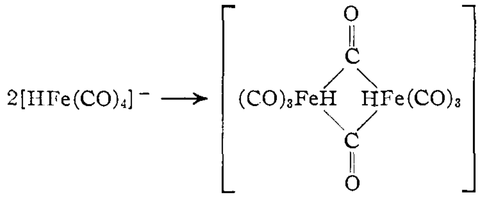
Since the dibasic salt $Na_2Fe(CO)_4$ is hydrolyzed to some degree according to equation 4

$$Na_2Fe(CO)_4 + H_2O \rightleftharpoons NaOH + NaHFe(CO)_4 \quad (4)$$

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

We have found that the chemical and catalytic properties of these solutions can be explained and new reactions predicted on the basis of the existence of binuclear iron carbonyl anions($[H_2Fe_2(CO)_8]^=$ and $[Fe_2(CO)_8]^=$) formed from iron hydrocarbonyl anion, $[HFe(CO)_4]^-$. Subsequent to our preliminary announcement[1] of the existence of these binuclear iron carbonyl anions, Hieber and Brendel, studying the reaction between polynuclear carbonyls and alcoholic alkali, provided independent and conclusive evidence for the existence of a binuclear iron carbonyl anion $[Fe_2(CO)_8]^=$.[6]

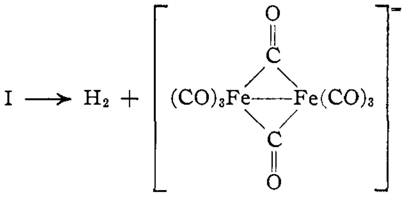
Dimerization of $[HFe(CO)_4]^-$.—When the light-yellow aqueous solution obtained by treating 1 mole of $Fe(CO)_5$ with 3 moles of NaOH (equation 2) is allowed to stand for a few days, it becomes dark-red, even when oxygen is carefully excluded, and slowly gives off hydrogen. This behavior may be explained in the following manner. The color change is caused by dimerization of the anion $[HFe(CO)_4]^-$ according to equation 5



(5)

I

and the evolution of hydrogen by the decomposition of I according to equation 6



(6)

II

Some evidence for the existence of I and II is provided by the following observations.

Evaporation of an ether extract of an aqueous solution prepared according to equation 2 yields a dark-red pyrophoric solid. The iron and sodium content of this solid indicates that it consists of a mixture of $NaHFe_2(CO)_8$ (III) and a small amount of $H_2Fe_2(CO)_8$ (IV), that is, the acid salt and free acid corresponding to II. When the mixture of III and IV is treated with excess acid, approximately one-half mole of hydrogen and one-third mole of iron tetracarbonyl,[7] $[Fe(CO)_4]_3$, is formed

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[1] For a previous communication on this subject see: H. W. Sternberg, R. Markby and I. Wender, THIS JOURNAL, **78**, 5704 (1956).

[2] W. Reppe and H. Vetter, *Ann.*, **582**, 133 (1953).

[3] German Patent to I. G. Farbenindustrie Akt.-Ges., 441,179 (January 18, 1925).

[4] H. W. Sternberg, R. A. Friedel, R. Markby and I. Wender, THIS JOURNAL, **78**, 3621 (1956).

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

[6] W. Hieber and G. Brendel, *Z. anorg. allgem. Chem.*, **289**, 324 (1957).

[7] The acidification of the monomeric $NaHFe(CO)_4$ leads to an entirely different reaction. Iron hydrocarbonyl, $H_2Fe(CO)_4$, is liberated

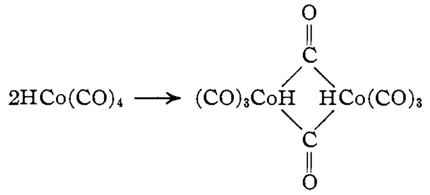
$$NaHFe(CO)_4 + HCl \longrightarrow H_2Fe(CO)_4 + NaCl$$

per atom of iron present according to equation 7

$$\underset{\text{II}}{[Fe_2(CO)_8]^{=}} + 2H^+ \longrightarrow H_2 + \underset{\text{V}}{2/3[Fe(CO)_4]_3} \quad (7)$$

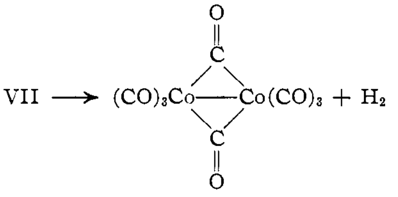
An aqueous solution containing **I** absorbs at 4750 Å. while a solution of III and IV containing II absorbs at 5350 Å. When the solution of I is allowed to stand, the band at 4750 Å. gradually is replaced by the band at 5350 Å. The infrared spectrum of a solution of III and IV in ether contains only two sharp, strong bands at 4.98 and 5.04 μ. The spectrum of an ether extract of an aqueous solution containing I, 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.

Further work will be necessary to establish definitely the manner in which the two monomeric units are joined. The present assignment of two carbonyl bridges is based on the similarity between the formation of $[Fe_2(CO)_8]^{=}$ (equations 5 and 6) and that of dicobalt octacarbonyl, $Co_2(CO)_8$, according to equations 8 and 9



$2HCo(CO)_4 \longrightarrow (CO)_3CoH\ HCo(CO)_3$ (8)

VI VII



$VII \longrightarrow (CO)_3Co—Co(CO)_3 + H_2$ (9)

VIII

Cobalt hydrocarbonyl (VI) and dicobalt octacarbonyl (VIII) are isoelectronic analogs of $[HFe(CO)_4]^-$ and $[Fe_2(CO)_8]^{=}$ (II). In the case of VIII, the bridged structure is well established.[8–10] Although the dimeric intermediate VII has not been prepared, an isoelectronic analog of VII, $H_2Ni_2(CO)_6$, has been isolated.[11]

Equations 5 and 6 account for the chemical behavior of the solutions obtained by treating iron pentacarbonyl with aqueous alkali, as will be illustrated by the following examples.

Stability of Solutions Containing $[HFe(CO)_4]^-$ **Ions.**—Published accounts of the behavior of these solutions contain contradictory statements. Hieber,[12] for example, reported that in the absence of oxygen or oxidizing agents these solutions are stable and do not decompose even on boiling. Reppe,[13] 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. This discrepancy is explained readily if it is assumed that Hieber was referring to a strongly alkaline solution. In strongly alkaline solution, the concentration of $[HFe(CO)_4]^-$ ions is low, according to equation 4. Consequently, the rate of dimer formation and hydrogen evolution (equations 5 and 6) is slow. Reppe's solution, prepared according to equation 2, contained a high concentration of $[HFe(CO)_4]^-$ and therefore decomposed rapidly.

That the rate of dimer formation depends on the concentration of $[HFe(CO)_4]^-$ ions was demonstrated as follows. Two 0.8 *M* solutions were prepared, one by treating 1 mole of $Fe(CO)_5$ with 3 moles of NaOH and the other by treating 1 mole of $Fe(CO)_5$ with 6 moles of NaOH. Both solutions were prepared and stored under helium. The first solution became deep red after two days, indicating dimer formation, and in the course of 2 weeks gave off 0.05 mole of hydrogen and 0.01 mole of carbon monoxide per mole of $Fe(CO)_5$ used. The second solution remained light-colored and did not give off any gas in the course of 2 weeks.

Reducing Properties.—The evolution of hydrogen[13] from and the reducing properties[12] of solutions obtained by treating $Fe(CO)_5$ with aqueous alkali were first attributed to the presence of $H_2Fe(CO)_4$. After it had been established[5] that $H_2Fe(CO)_4$ was not present, the reducing properties were attributed[14] to the oxidation reduction potential (equations 10 and 11)

$$3[Fe(CO)_4]^{=} \rightleftarrows [Fe(CO)_4]_3 + 6e,\ E_0 = 0.74 \quad (10)$$

$$3[FeH(CO)_4]^- \rightleftarrows [Fe(CO)_4]_3 + 3H^+ + 6e,\ E_0 = 0.35 \quad (11)$$

However, there is no evidence that iron tetracarbonyl is formed in alkaline solutions either from $[Fe(CO)_4]^{=}$ or from $[HFe(CO)_4]^-$. The preparation of iron tetracarbonyl by the action of oxidizing agents on solutions containing $[Fe(CO)_4]^{=}$ and $[HFe(CO)_4]^-$ ions always leads to dark-red solutions which yield the tetracarbonyl only on acidification.[15] The necessity for this acidification is not apparent from equations 10 or 11, but follows from equation 7. In the absence of a hydrogen acceptor I splits off hydrogen (equation 12), while in the presence of a hydrogen acceptor I acts as a hydrogen donor (equation 13)

$$I \longrightarrow II + H_2 \quad (12)$$

$$I + \text{Acceptor} \longrightarrow II + H_2\cdot\text{Acceptor} \quad (13)$$

Equation 13 implies that reduction of a substrate is achieved by the transfer of hydrogen from I to the substrate and not by the transfer of electrons (equations 10 or 11) with the subsequent addition

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and decomposes (see W. Hieber and H. Vetter, *Z. anorg. allgem. Chem.*, **212**, 145 (1933) according to

$$2H_2Fe(CO)_4 \longrightarrow 2H_2 + Fe(CO)_5 + Fe(CO)_3$$

In this case, one 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.

(8) J. W. Cable, R. S. Nyholm and R. K. Sheline, THIS JOURNAL, **76**, 3373 (1954).

(9) R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, *ibid.*, **77**, 3951 (1955).

(10) L. Cavalca and I. W. Bassi, *Ricerca Sci.*, **23**, 1377 (1953); reviewed in Science Abstracts, Section A, *Physics*, **57**, 893 (1954).

(11) H. Behrens, *Z. Naturforsch.*, **8b**, 691 (1953).

(12) W. Hieber and F. Leutert, *Z. anorg. allgem. Chem.*, **204**, 145 (1932).

(13) W. Reppe, *Ann.*, **582**, 116 (1953).

(14) W. Hieber and W. Hübel, *Z. Elektrochem.*, **57**, 331 (1953).

(15) W. Hieber, *Z. anorg. allgem. Chem.*, **204**, 165 (1932).

of protons. This transfer of hydrogen from metal atoms to a substrate may occur in a manner similar to that involved in heterogeneous catalysis. It is reasonable to assume that the distance between the iron atoms in I is close to that found[16] in $Fe_2(CO)_9$, that is, 2.46 Å. This is also the distance of closest spacing in a hydrogenation catalyst such as nickel.[17]

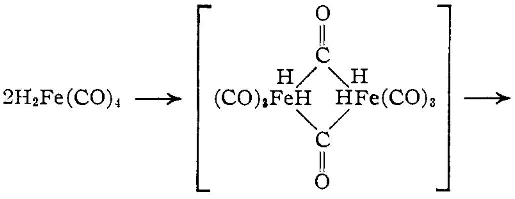
The existence of the binuclear anions I and II not only explains the properties of the iron pentacarbonyl–aqueous alkali system, as illustrated by the preceding examples, but permits one to predict new reactions as shown by the following examples.

Isomerization of Olefinic Double Bonds.—It is known that cobalt hydrocarbonyl (VI) catalyzes the double bond isomerization of olefins.[18] The catalytic intermediate in this reaction is probably the binuclear cobalt hydrocarbonyl VII.[19] On the basis of the structural similarity between VII and I we predicted that I should catalyze the isomerization of olefinic double bonds. This prediction proved to be correct. Treatment of 1-hexene at room temperature with an ether solution containing $[H_2Fe_2(CO)_8]^{=}$ (I) resulted in quantitative conversion to 2- and 3-hexene.

Hydrogenation and Double Bond Isomerization with Iron Hydrocarbonyl, $H_2Fe(CO)_4$.—Although the reducing properties of solutions prepared according to equation 2 or 3 have been attributed[12] to the presence of $H_2Fe(CO)_4$, no experiments have been reported in which $H_2Fe(CO)_4$ itself was used as a reducing agent. It was therefore of interest to determine whether or not $H_2Fe(CO)_4$ possesses reducing properties and is capable of isomerizing olefinic double bonds. The decomposition[7] of iron hydrocarbonyl according to equation 14

$$2H_2Fe(CO)_4 \longrightarrow 2H_2 + Fe(CO)_5 + Fe(CO)_3 \quad (14)$$

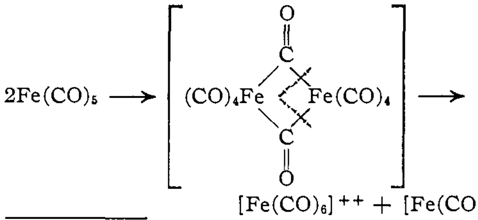
shows that this reaction involves transfer of a carbonyl group. It is reasonable to assume that this transfer takes place *via* a binuclear intermediate such as IX (equation 15)



IX

$$Fe(CO)_5 + Fe(CO)_3 + 2H_2 \quad (15)$$

A similar transfer of carbonyl groups in the case of iron pentacarbonyl, according to equation 16



$$[Fe(CO)_6]^{++} + [Fe(CO)_4]^{-} \quad (16)$$

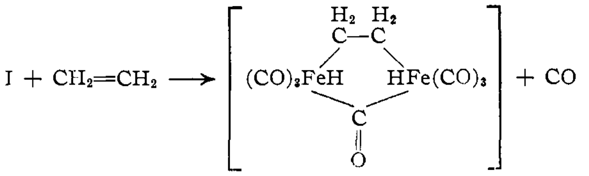
has been reported previously.[20] Since the intermediate $H_4Fe_2(CO)_8$ (IX) represents the acid derived from $[H_2Fe_2(CO)_8]^{=}$ (I), we predicted that $H_2Fe(CO)_4$ *via* the intermediate IX should effect hydrogenation and double bond isomerization in a manner similar to I. This prediction proved to be correct. Treatment of acetone with iron hydrocarbonyl, $H_2Fe(CO)_4$, 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,[5] it is unlikely that this double bond isomerization is acid catalyzed.

Conversion of Olefins to Alcohols.—Reppe and Vetter[2] have shown that the aqueous solutions prepared by treating $Fe(CO)_5$ with a base react with olefins at elevated temperature and carbon monoxide pressure to form the next higher alcohols. The reaction was thought to be due to the presence of $H_2Fe(CO)_4$ and formulated according to equation 17

$$H_2Fe(CO)_4 + 2CH_2{=}CH_2 + H_2O \longrightarrow 2CH_3CH_2CH_2OH + Fe(HCO_3)_2 \quad (17)$$

A modification of this reaction using catalytic amounts of iron pentacarbonyl in basic solutions was also reported by these authors and expressed by equation 1.

A recent study[19] of the hydroformylation reaction has shown that the addition of hydrogen and carbon monoxide to an olefinic double bond takes place within a complex derived from the olefin and $H_2Co_2(CO)_8$ (VII). The similarity between VII and $[H_2Fe_2(CO)_8]^{=}$ (I) indicated to us that the conversion of olefins to alcohols may proceed by a similar mechanism involving complex formation between the olefin and I. The analogy between the hydroformylation reaction and the conversion of olefins to alcohols becomes evident if the latter reaction is viewed as taking place in two separate steps. The first is the addition of hydrogen and carbon monoxide to the double bond and is analogous to the hydroformylation reaction. The second is the hydrogenation of the aldehyde. As in the case of the hydroformylation reaction, the first step may involve the displacement of a bridge carbonyl by the olefin (equation 18) to form complex X



X

(18)

which decomposes (equation 19) to give the next higher aldehyde and the unknown diiron hexacarbonyl anion XI

$$X \longrightarrow CH_3CH_2CHO + \underset{XI}{[Fe(CO)_3]_2^{=}} \quad (19)$$

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[16] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).

[17] G. H. Twigg and E. K. Rideal, *Trans. Faraday Soc.*, **36**, 533 (1940).

[18] I. Wender, H. W. Sternberg and M. Orchin, THIS JOURNAL, **75**, 3041 (1953).

[19] I. Wender and H. W. Sternberg, *Advances in Catalysis*, **9**, 594 (1957).

[20] H. W. Sternberg, R. A. Friedel, S. L. Shufler and I. Wender, THIS JOURNAL, **77**, 2675 (1955).

In the presence of carbon monoxide and water, I may be regenerated from XI according to equation 20

$$\text{XI} + 3\text{CO} + \text{H}_2\text{O} \longrightarrow \text{I} + \text{CO}_2 \qquad (20)$$

The aldehyde formed (equation 19) is then hydrogenated according to equation 13.

Reppe and Vetter did not report the presence of aldehydes in their reaction products. This failure to isolate any aldehydes may in part be due to the fact that they used rather strongly basic solutions prepared from iron pentacarbonyl and trimethylamine in a molar ratio of 1:4.4.

We have found that under certain conditions the aldehyde is formed exclusively. Thus, when cyclopentene was treated at elevated temperature and carbon monoxide pressure with an aqueous solution prepared from $Fe(CO)_5$ and NaOH in a molar ratio of 1:3, the reaction product contained only cyclopentanecarboxaldehyde and unchanged cyclopentene. When, on the other hand, cyclopentene was treated under similar conditions with a mixture of water, methanol, and iron pentacarbonyl and trimethylamine in a molar ratio of 1:4.4, cyclopentylcarbinol and only a small amount of the aldehyde were formed.

That aldehydes are reduced by solutions which catalyze the conversion of olefins to alcohols was demonstrated by treating excess benzaldehyde with an aqueous solution prepared according to equation 2. Benzyl alcohol was obtained in a yield of 33% based on I.

To determine whether double bond isomerization also takes place under the conditions reported by Reppe and Vetter, 1-octene was treated with a mixture of water, methanol, iron pentacarbonyl and trimethylamine at elevated temperature and carbon monoxide pressure. The reaction product contained 6% alcohol and 0.25% aldehyde based on the amount of 1-octene used. All of the recovered olefin was either 2-octene or 3-octene.

Experimental

All operations described below were carried out under helium.

Preparation and Extraction of an Aqueous Solution Containing $[HFe(CO)_4]^-$ Anion.—When excess $Fe(CO)_5$ is treated with aqueous alkali, the reaction proceeds[5] until 1 mole of $NaHFe(CO)_4$ is formed for every 3 moles of NaOH (equation 2). Thus, in the presence of excess $Fe(CO)_5$, 3 moles of NaOH will form one mole of $NaHFe(CO)_4$.

Seven milliliters (52 mmoles) of $Fe(CO)_5$ was placed in an Erlenmeyer flask provided with a glass stopper and 4.5 g. (112 mmoles) of NaOH dissolved in 50 ml. of oxygen-free water added; the flask was at once stoppered and shaken vigorously for 48 hours at room temperature. After standing for another 48 hours, the dark-red solution was first 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, extracted with anhydrous ether, and the ether evaporated in a current of inert gas. After further evaporation at 1 mm. and 100° the residue, a dark-red pyrophoric powder, weighed 2.5 g. It is readily soluble in water, alcohol or ether and insoluble in petroleum ether or benzene. The iron and sodium analyses[21] of this residue showed that iron and sodium were present in a ratio of 2:1.

Calcd. for $NaHFe_2(CO)_8$: Fe, 31.05; Na, 6.39. Found: Fe, 30.14; Na, 6.42; 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 2:1 as required for $NaHFe_2(CO)_8$ III, but varied from 2:1 to about 3:1. Inspection of the analytical data listed in Table I leads to the conclusion that the high Fe:Na ratio is due to the presence of $H_2Fe_2(CO)_8$ (IV), that is, the free acid derived from II.[22]

TABLE I

Found				Calcd.	
Fe, %	Na, %	Atomic ratio Fe:Na	Mole[a] % $NaHFe_2(CO)_8$	Fe, %[b]	Na, %[b]
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

[a] Calculated from the atomic ratio (column 3), assuming that the mixture consisted only of $H_2Fe_2(CO)_8$ and $NaHFe_2(CO)_8$. [b] Calculated on the basis of the molar mixture given in column 4.

The observed iron-to-sodium ratios eliminate the possibility of the ether extract consisting of either $NaHFe(CO)_4$ or $Na_2Fe(CO)_4$, 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 above, a dark-red precipitate is obtained. The precipitate showed signs of decomposition when dried over P_2O_5 in an atmosphere of helium and is extremely pyrophoric in the dried state. It contains traces (0.08%) of Na, 26.7% Fe and 4.9% Ni, that is, iron and nickel in a ratio of 5.8:1. 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-to-nickel ratio of 1:1 and 2:1, respectively.

Treatment of a Mixture of $NaHFe_2(CO)_8$ and $H_2Fe_2(CO)_8$ with Acid.—A mixture of $NaHFe_2(CO)_8$ and $H_2Fe_2(CO)_8$ prepared as described above was dissolved in ether and an aliquot of the ether solution analyzed for iron. The amount of iron contained in this aliquot was 0.598 g., corresponding to 10.7 milliatoms.

Another aliquot was evaporated to dryness at room temperature in a current of helium and the residue dissolved in about 35 ml. of water. An Erlenmeyer flask containing a glass-enclosed stirring bar and provided with a ground joint and a side arm with stopper for the addition of acid was charged with the aqueous solution and attached to a gas buret. Through the side arm was added 10 ml. of 6 *N* hydrochloric acid and the contents of the flask stirred. Soon after the addition of acid, gas was evolved and a small amount of dark-green crystals formed. The gas evolution stopped after a total of 4.95 mmoles of hydrogen and 0.32 mmole of carbon monoxide had been evolved in the course of 3 hours. The rate of gas evolution is 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 mmoles of $[Fe(CO)_4]_3$. That the precipitate formed in this reaction was iron tetracarbonyl, $[Fe(CO)_4]_3$, was verified by comparison of its infrared spectrum with that of an authentic sample. The filtrate and wash water contained 0.062 g. of iron. According to these data, the total amount of iron in the filtrate and in the form of $[Fe(CO)_4]_3$ was 0.540 g. or 90.5% of the amount of iron in the aliquot. The balance is probably lost as $Fe(CO)_5$ which is formed in a side reaction. Some of the $Fe(CO)_5$ remains with the $[Fe(CO)_4]_3$ and is evaporated during the drying operation. That a small amount of $Fe(CO)_5$ is formed in this reaction was shown as follows. In a separate

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(21) We wish to thank W. Dieter of these laboratories for the iron and sodium analyses.

(22) An alternate explanation for the observed high Fe to Na ratio is the assumption that some $NaHFe_3(CO)_{11}$ is present. The existence of this complex has been demonstrated recently by Hieber and Brendel.[6]

experiment, another aliquot was treated with excess acid, as described above, the reaction mixture extracted with petroleum ether and the amount of $Fe(CO)_5$ determined by infrared analysis. The amount of iron present as $Fe(CO)_5$ was 4% of the amount of iron in the aliquot.

According to equation 7, 0.50 mole of hydrogen and 0.33 mole of $[Fe(CO)_4]_3$ should be formed per atom of iron. In the present experiment there was formed 0.46 mole (92% of theory) of hydrogen and 0.27 mole (81% of theory) of iron tetracarbonyl, $[Fe(CO)_4]_3$, per atom of iron.

Spectra of I and II.—A solution containing 4.1 mmoles of $NaHFe(CO)_4$ in 100 ml. of water was prepared by shaking one ml. of $Fe(CO)_5$ with 100 ml. of an 0.125 *N* solution of NaOH for 24 hours. At this time the spectrum of the light yellow solution showed only a shoulder at 4750 Å. After standing 3 days the solution had turned dark red and the intensity of the band had increased to such an extent that an accurate value of the optical density could not be obtained. One ml. of the solution was diluted with 20 ml. of oxygen-free water. The spectrum of the dilute solution (0.002 *M*) with regard to $[HFe(CO)_4]^-$ showed a broad band at 4750 Å. After one day, the band at 4750 Å. had decreased and a new band at 5350 Å. had appeared. After 3 more days, the band at 4750 Å. had disappeared and the intensity of the newly formed band at 5350 Å. further increased.

A mixture of III and IV containing 0.044 g. (0.13 mmole) of the anion $[Fe_2(CO)_8]^=$ (II) was dissolved in 500 ml. of water. The spectrum of this solution contained a broad band at 5350 Å. The molar extinction coefficient based on $[Fe_2(CO)_8]^=$ was 1900 l. moles^{-1} cm.$^{-1}$.

A solution containing 75 mmoles of $NaHFe(CO)_4$ in 100 ml. of water was prepared according to equation 2 as described above. After standing for 4 days, the dark-red solution was extracted with ether, and the ether extract treated with Na_2SO_4, as described above. The infrared spectrum of the ether solution containing approximately 0.008 g. (0.024 mmole) of $[H_2Fe_2(CO)_8]^=$ per ml. of ether was determined in a 0.032 mm. cell.

A mixture of III and IV containing 0.282 g. (0.84 mmole) of $[Fe_2(CO)_8]^=$ was dissolved in 40 ml. of anhydrous, peroxide-free ethyl ether and the infrared spectrum determined in a 0.032 mm. cell.

Preparation[23] and Reactions of $H_2Fe(CO)_4$.—Twenty-five milliliters of an aqueous 6 *N* sodium hydroxide solution and 5.0 ml. (37 mmoles) of $Fe(CO)_5$ were placed in an erlenmeyer flask provided with a glass stopper. The air in the flask was displaced by carbon monoxide, the flask stoppered and shaken vigorously for 8 hours. The resulting clear solution contains the salt $Na_2Fe(CO)_4$, which on acidification yields hydrocarbonyl, $H_2Fe(CO)_4$.

The apparatus for the generation of $H_2Fe(CO)_4$ consisted of a 500-ml., 3-necked flask provided with an inlet tube whose constricted tip was placed close to the bottom of the flask, a dropping funnel and an outlet tube. To the outlet tube was attached an absorption tube (90 × 30 mm.) filled with $CaCl_2$. The absorption tube was connected to a cold trap (200 × 40 mm.) immersed in acetone–Dry Ice. The three-necked flask was filled with 100 ml. of ice-cold 6 *N* aqueous sulfuric acid and immersed in an ice-bath. The flask was then fitted with the inlet tube, the dropping funnel and the outlet. The solution of $NaHFe(CO)_4$ was poured into the dropping funnel. The dropping funnel and the inlet tube were connected by a T-tube and the apparatus purged with CO. After purging, the $NaHFe(CO)_4$ solution was added dropwise to the reaction flask in the course of about 1 to 1.5 hours in a current of CO gas of about 500 ml. per minute.

The $H_2Fe(CO)_4$ collected in the trap always contained appreciable amounts of $Fe(CO)_5$. To determine the amount of $H_2Fe(CO)_4$ present, the trap was allowed to warm to room temperature and the gas evolved measured. Since the amount of gas evolved corresponds to the amount of $H_2Fe(CO)_4$ present (1 mole of H_2 per mole of $H_2Fe(CO)_4$), the amount of $H_2Fe(CO)_4$ in the trap can be determined volumetrically. The yield of $H_2Fe(CO)_4$ determined in several experiments varied from 2.0–2.2 g. (12–13 mmoles) using 5.0 ml. (37 mmoles) of $Fe(CO)_5$ and employing the procedure described above.

The reduction of acetone was carried out as follows. Five ml. (68 mmoles) of acetone was placed in the cold trap and the cold trap attached to the apparatus. About 2 g. (12 mmoles) of $H_2Fe(CO)_4$ was generated as described above 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 mmoles) of isopropyl alcohol was present.

The reaction between $H_2Fe(CO)_4$ and 1-hexene was carried out in a similar way. Five ml. (40 mmoles) of peroxide-free 1-hexene was placed in the cold trap. After introducing about 2 g. (12 mmoles) of $H_2Fe(CO)_4$ as described above, the cold trap was disconnected and allowed to warm to room temperature. An infrared analysis of the reaction product showed that all of the 1-hexene had been converted to 2- and 3-hexene. That $Fe(CO)_5$ does not cause double bond isomerization was demonstrated by allowing a solution of 1 ml. $Fe(CO)_5$ in 25 ml. of 1-hexene to stand for 24 hours. Analysis of the solution showed that no 2- or 3-hexene was present.

Double Bond Isomerization.—A solution containing approximately 0.7 g. (2 mmoles) of $[H_2Fe_2(CO)_8]^=$ in 25 ml. of ether was prepared as described above. To this solution 5 ml. (40 mmoles) of 1-hexene was added, the mixture shaken at room temperature and a sample withdrawn after 25 hours. Infrared analysis showed only the presence of 2- and 3-hexene, that is, complete double bond isomerization.

Cyclopentanecarboxaldehyde from Cyclopentene.—Two hundred ml. of an aqueous solution prepared according to equation 2 and containing 150 mmoles of $NaHFe(CO)_4$ and 46 ml. (500 mmoles) of cyclopentene were placed in a rocking autoclave pressurized to 160 atmospheres with carbon monoxide and heated at 155° for 8 hours. After cooling, the reaction mixture was removed from the autoclave and separated into an upper, dark-red organic and a lower, practically colorless aqueous layer. Addition of a $[Ni(o\text{-Phthr})_3]Cl_2$ solution to the aqueous layer gave a voluminous orange-yellow precipitate, indicating the presence of $[HFe(CO)_4]^-$ ion. The fact that the aqueous layer was colorless showed that both I and II were absent. The red color of the organic layer could not have been due to the presence of salts derived from either I or II, since these salts are not soluble in hydrocarbon solvents. The dark-red solution containing I and II, obtained by treating 1 mole of $Fe(CO)_5$ with 3 moles of NaOH and allowing the solution to stand, cannot be extracted with hydrocarbon solvents. The absence of I and II in the reaction product explains the fact that the reaction stops at the aldehyde stage. Evidently, under the conditions of this experiment, I and II were used up in the formation of the aldehyde and not available for catalyzing the hydrogenation of the aldehyde (see below).

Infrared analysis of the organic layer showed that it consisted primarily of cyclopentene, together with a small amount of iron pentacarbonyl and aldehyde; no alcohol could be detected. The cyclopentanecarboxaldehyde present in the organic layer amounted to 2.57 g. (26.4 mmoles) and was determined by treating an aliquot of the organic layer with 2,4-dinitrophenylhydrazine in the usual manner and weighing the washed and dried hydrazone. The hydrazone melted at 160.5–161.5° (lit.[24] 160.5–161.5°).

Hydrogenation of Benzaldehyde.—To 25 ml. of an aqueous solution prepared according to equation 2 and containing 17.61 mmoles of $NaHFe(CO)_4$ (corresponding to 8.805 mmoles of I) was added 5 ml. (50 mmoles) of freshly distilled benzaldehyde. The mixture was shaken for 120 hours and then acidified in order to convert II, formed according to equation 13, to iron tetracarbonyl (equation 7).

The acidified reaction mixture was extracted with benzene to remove benzyl alcohol and unreacted benzaldehyde. Infrared analysis of the extract showed that 2.9 millimoles of benzyl alcohol had been formed. The iron tetracarbonyl $[Fe(CO)_4]_3$, formed during the acidification, was filtered off, washed with water and petroleum ether (35–55°) and dried. The weight of the tetracarbonyl formed was 1.82 g. (3.62 mmoles), corresponding to 5.43 mmoles of II.

Cyclopentylcarbinol from Cyclopentene.—Forty-six ml. of cyclopentene and a mixture consisting of 20 g. (0.1 mole) of $Fe(CO)_5$, 18 g. (1.0 mole) of H_2O, 26 g. (0.44 mole) of

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[23] Though methods for the preparation of iron hydrocarbonyl are described in the literature, yields have not been reported. The procedure described in the experimental part is a modification of the method described in "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., 1946, p. 243.

[24] A. A. Morton and H. P. Penner, THIS JOURNAL, **73**, 3300 (1951).

trimethylamine and 60 g. (1.9 moles) of methanol was placed in a rocking autoclave, pressurized to 160 atmospheres with carbon monoxide, and heated at 185° for 10 hours. After cooling, the reaction product was distilled and the amount of alcohol and aldehyde in the distillate determined by infrared analysis. The yield of cyclopentylcarbinol was 16.7% and that of the aldehyde 2.9%, based on the amount of cyclopentene used.

Nonyl Alcohol from Octene-1.—A mixture consisting of 66 ml. (0.42 mole) of 1-octene, 14 ml. (0.10 mole) of $Fe(CO)_5$, 18 ml. (1.0 mole) of water, 26 g. (0.44 mole) of trimethylamine and 60 g. (1.9 moles) of methanol was placed in a rocking autoclave and pressurized to 160 atmospheres with carbon monoxide. The autoclave was heated at 150–160° for 6 hours and then at 170–175° for 6 more hours. After cooling, the reaction mixture was distilled first at atmospheric pressure up to 122° and then from 90 to 120° at 2–6 mm. The amount of alcohol and aldehyde in the distillate was determined by infrared analysis and corresponded to a yield of 6% of alcohol and 0.25% of aldehyde based on the amount of olefin used. The recovered olefin consisted entirely of a mixture of 2-octene and 3-octene.

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Studies on Oxidation–Reduction Mechanism. II. The Anodic Oxidation of *p*-Aminophenol

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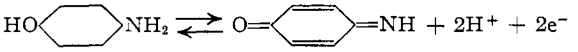
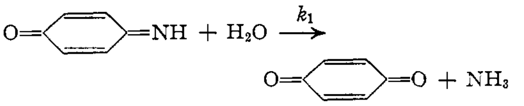
The anodic oxidation of *p*-aminophenol at *p*H 1.18 was studied by using Pt electrodes in an electrolytic cell through which flowed a small a.c. superimposed on a relatively large constant d.c. Both a.c. and d.c. voltages were obtained as functions of time by using a recording voltmeter. Theoretical mathematical equations were developed for the following possible mechanisms: (1) a reversible reaction, (2) a rate-controlling electron-transfer step, (3) a reversible electron-transfer followed by a rate-controlling hydrolysis. The experimental data were in accord with (3) but not with (1) and (2). The mathematical equations also made it possible to calculate: (1) $n = 2.0$ for the number of electrons transferred in the first step, (2) $E_0' = 0.711$ volt for the normal potential of the first step, (3) the first order rate-constant $k_1 = 0.020$ sec.$^{-1}$ for the second step, and (4) the diffusion coefficient $D_R = 0.946 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ for the participating species of the *p*-aminophenol. It was concluded that the mechanism is the same for the anodic as for the homogeneous reaction and that no mechanistic inversion occurs on lowering the *p*H to 1.18. It was emphasized that although mechanisms 2 and 3 are indistinguishable from the point of view of the theory of absolute reaction rates or experimentally by the Conant electrochemical technique, the voltammetric method used distinguishes between them in the case of the anodic reaction.

The mechanism of the oxidation of *p*-aminophenol (PAP) has been studied under a fairly wide range of conditions by several investigators. Wieland[2] suggested that quinone-imine is an intermediate in the oxidation of PAP. Since Willstätter[3] had shown that quinone-imine rapidly hydrolyzes to quinone in acid solution, Conant and Pratt[4] suggested the mechanism



(1a)



(1b)

In order to explain the observed dependence of oxidation rate on the reduction potential of the reversible oxidation–reduction system used as an oxidizing agent, they postulated that the first step is fast and reversible while the second step is slow and irreversible. They supplied evidence that quinone-imine is the intermediate in solutions of *p*H 7.8–11.3 by measuring potentiometrically the reduction potential of system 1a both by the titration method and the method of mixtures. These two methods gave concordant results within the limits of precision reasonably to be expected of such an unstable system. From the end-points of the titrations they deduced that the number of electrons involved in (1a) was $n = 2 \pm 0.2$. They also studied the rate of decay of potential in acidic solutions containing PAP and various oxidizing systems, expressing their results in terms of the "apparent oxidation potential" (A.O.P.) which was defined in terms of the reduction potential of (1a) and rate constant, k_1, of (1b). In general, neither of these quantities could be determined separately. They found that the over-all reaction rate is independent of the dilution thus showing k_1 to be a first-order rate constant.

Fieser[5] advanced Conant's work by devising his "method of discontinuous titrations." He found that potential–time plots were linear over only a limited range. Since linearity is demanded for a first order reaction, there is here clearly an implication that the kinetics of the follow-up step are complex, being first order only in the early stages. By extrapolation to zero time he was able to obtain values for the normal potential of (1a) at each *p*H (2.69 to 7.57) and very crude values for k_1.

In 1935, Bancroft and Magoffin[6] introduced their theory of the potential hump as an alternative explanation of the relation between potential (of a reagent *or an electrode*) and rate of electron transfer. They claimed that all of Conant's studies on irreversible electron transfers could be explained by their theory "if one rejects the two assumptions of a reversible electrolytic step and a practically irreversible, non-electrolytic step." This theory seems to have been in certain regards the qualitative equivalent of the theory of absolute reaction rates which

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[1] Based on the Ph.D. thesis of William K. Snead, Wayne State University, 1957.

[2] H. Wieland, *Ber.*, **43**, 718 (1910).

[3] R. Willstätter, *ibid.*, **42**, 2166 (1909).

[4] J. B. Conant and M. F. Pratt, THIS JOURNAL, **48**, 3178 (1926).

[5] L. F. Fieser, *ibid.*, **52**, 4915 (1930).

[6] W. D. Bancroft and J. E. Magoffin, *ibid.*, **57**, 2561 (1935).