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A study of iron pentacarbonyl as a solvent and reaction medium

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A STUDY OF IRON PENTACARBONYL AS A SOLVENT AND REACTION MEDIUM

by

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I. INTRODUCTION

Just fifty years ago iron pentacarbonyl was first discovered and since then an interesting body of literature has been published concerning the preparation of this compound, its constitution, properties, derivatives, and uses. However, no work has been or done on the study of iron pentacarbonyl as a solvent or reaction medium. Only a few organic solvents are mentioned which will dissolve the iron pentacarbonyl and an investigation has not been made of the possibility of the use of iron pentacarbonyl, since it is a liquid, as a solvent for other substances.

Several investigators found that iron pentacarbonyl formed a dark red substance when treated with amines. Their work, however, was confined to the use of ethylenediamine, ortho phenanthroline, and pyridine. This investigation has extended this study to include the amine derivatives of the lower hydrocarbons and other solutes.

The generally accepted idea of the constitution of iron pentacarbonyl as a coördination compound has created an interest as to its reactivity. This phase has not been extensively studied. One would expect to find derivatives in which the carbon monoxide is replaced by other groups. A large number of such compounds has been prepared. The derivatives are generally of two types, addition compounds and substitution compounds.

II. REVIEW OF LITERATURE

Encouraged by their success in preparing nickel carbonyl in 1890, Mond and his coworkers, Langer and Quincke, (67) immediately attempted to prepare carbonyls from all the metals at their disposal. However, it was Berthelot (2) who first announced the formation of a volatile compound of carbon monoxide and iron on June 15, 1891. Fourteen days later, on June 29, 1891, Mond and Quincke (68) disclosed their independent discovery of a volatile iron carbonyl. Later the same year, Mond and Quincke (69) made another report on the compound. The formula which they published at the time was incorrect and later in the year Mond and Langer (66) announced the formula to be $Fe(CO)_5$ and named it iron pentacarbonyl. In 1892, Berthelot (3) again published an article on the compound, agreeing to the formula assigned to it by Mond and Langer.

The early preparations of iron pentacarbonyl were made by reacting freshly reduced iron with carbon monoxide. Ferric oxide or ferrous oxalate, which had been dried, was heated in a combustion tube in a current of hydrogen. The finely divided iron thus obtained was subjected to an atmosphere of carbon monoxide, with one end of the combustion tube closed, for a period of about 24 hours. Then the tube

was heated to about 120°C. and the iron carbonyl distilled over. When no more iron carbonyl distilled over, the tube was allowed to cool and connected with the source of carbon monoxide, which was absorbed as before.

Berthelot reported 45°C. as the optimum temperature for the reaction between iron and carbon monoxide, while Mond and his associates worked at slightly higher temperatures. In 1911, Staffel (75) found that 80°C. was optimum at atmospheric pressure, that hydrogen sulfide inhibited the reaction, and that ammonia accelerated it. Three years later (76) he found that the optimum reaction temperature could be raised to 100°C. by the application of four or five atmospheres of pressure. In 1922, Mond and Wallis (70) published data indicating yields over a wide range of temperatures and pressures. They found that the yield increased greatly with increase in pressure but decreased with a temperature above 200°C. Fieldner and Jones (11) stated that iron carbonyl could form only at temperatures below 250°C.

As early as 1891, Roscoe and Scudder (72) studied the reactions between iron and carbon monoxide. The reaction products together with the temperature range in which each takes place are shown in Table I.

TABLE I

Reactions of Iron and Carbon Monoxide

$Fe + 5CO = Fe(CO)_5$	Room temperature to about 250°C.
$Fe + CO = FeO + C$	330° - 500°
$FeO + CO = Fe + CO_2$	200° - 800°
$FeO + C = Fe + CO$	Very high temperature
$3Fe + C = Fe_3C$	Very high temperature

These data give a clear indication that there is a definite upper limit for the temperature at which the reaction will proceed.

In one industrial process for the manufacture of iron pentacarbonyl, carbon monoxide is passed at pressures varying from 50 to 200 atmospheres over iron, obtained by the reduction of ferric oxide, which is held at temperatures between 100° and 200°C. The same results may be obtained by the use of water-gas, which contains hydrogen and carbon monoxide. The exothermal reaction between the carbon monoxide and the iron supplies the heat necessary to maintain the temperature required for the production of the carbonyl. The flow of gases may reach five hundred liters an hour. The iron pentacarbonyl, constituting about ten per cent of the gas issuing from the reaction chamber, is condensed, and the excess carbon monoxide is returned to the reaction vessel.

The liquid carbonyl is usually purified by distillation in a low boiling hydrocarbon such as benzene or kerosene, forming a solution in which the carbonyl is marketed.

The presence of oxygen hinders the reaction, as does also an oxide coating on the iron. Addition of finely divided alumina, bismuth, nickel, or copper prevents sintering of the metal and accelerates the reaction. Ammonia, hydrogen, and small quantities of sulfur compounds in the carbon monoxide exert a favorable influence on the rate of formation of the carbonyl.

Iron turnings and scrap iron have been utilized for the commercial preparation of iron pentacarbonyl. These forms of iron may be oxidized by air, or steam, or both, and then reduced, either with hydrogen or directly with carbon monoxide. Pyrites, FeS_2, may be converted in the presence of wood charcoal at 1000°C. into Fe_2O_3, which is subsequently reduced by carbon monoxide. The use of ashes to support the metal is said to increase the yield. Iron ores also may be reduced by means of solid or liquid carbonaceous materials. In these processes, the carbon monoxide which is formed produces the carbonyl in one operation.

The chemists who discovered iron pentacarbonyl found it was not stable in daylight but did not discover the compound formed from such decomposition. Dewar and Jones (7) studied the effect of sunlight on iron pentacarbonyl

and concluded that the following equation described the reaction:

$$2Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO$$

He called this compound differononacarbonyl but the name most commonly accepted is iron enneacarbonyl. Two years later, Dewar and Jones (8) published considerable data on the physical and chemical properties of both iron pentacarbonyl and iron enneacarbonyl. They also announced their discovery of a third carbonyl of iron, namely, iron tetracarbonyl. The formula given was $Fe_3(CO)_{12}$ indicating a polymerized compound.

Iron pentacarbonyl is a clear, colorless liquid; however, the presence of small amounts of the enneacarbonyl frequently gives it a yellow or orange color. The iron enneacarbonyl is an orange-red crystalline compound and the tetracarbonyl is dark green and of crystalline form. Dewar and Jones obtained a dark green colored body when a solution of iron enneacarbonyl was heated and assumed that the following equation described the reaction:

$$Fe_2(CO)_9 \longrightarrow Fe(CO)_5 + Fe(CO)_4$$

Garratt and Thompson (16) found that in light of wavelength shorter than 4100Å., that is in the violet and ultra-violet range, iron pentacarbonyl decomposes to form the enneacarbonyl. They suggest the following equations for the reaction:

$$Fe(CO)_5 + h\nu \longrightarrow Fe(CO)_4 + CO$$

$$Fe(CO)_4 + Fe(CO)_5 \longrightarrow Fe_2(CO)_9$$

Freundlich and Cuy (13) became interested in the compound in 1923 and confirmed the work of Dewar and Jones. They found that iron pentacarbonyl reacted with iodine in sunlight or in alcohol solution. Iron tetracarbonyl was prepared by the action of heat or alkaline reagents on the pentacarbonyl. They concluded that iron-carbon monoxide complexes are stable only in alkaline solution. Working with Malchow, Freundlich (14) concluded that iron tetracarbonyl immediately polymerized to a molecule containing three iron atoms. This report relates a method of forming the tetracarbonyl by the action of alcoholates and subsequent neutralization of the pentacarbonyl. With Wosnessensky, Freundlich (15) prepared ferric oxide of colloidal particle size from iron pentacarbonyl.

Hock and Stuhlmann published a series of three papers (49, 50, 51), starting in 1928, covering the reactions of iron pentacarbonyl with mercury salts. The following equations are a summary of the reactions they were able to carry out:

$$Fe(CO)_5 + 2HgCl_2 + H_2O = Fe(CO)_4Hg_2Cl_2 + CO_2 + 2HCl$$

$$Fe(CO)_5 + HgSO_4 + H_2O = Fe(CO)_4Hg + H_2SO_4 + CO_2$$

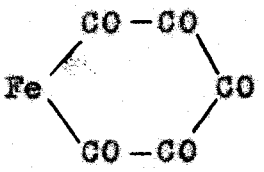
$$Fe(CO)_5 + Hg_2SO_4 + H_2O = Fe(CO)_4Hg + CO_2 + H_2SO_4 + Hg$$

$$Fe(CO)_4Hg + 4I = Fe(CO)_4I_2 + HgI_2$$

$$2Fe(CO)_5 + Hg(CH_3COO)_2 + 2CH_3OH = 2Fe(CO)_5 \cdot Hg(OCH_3)_2 + 2CH_3COOH$$

None of the compounds is particularly stable. $Fe(CO)_4Hg_2Cl_2$ can be crystallized from acetone but starts to decompose with the liberation of carbon monoxide below 140°C. Neither this compound nor $Fe(CO)_4I_2$ is stable in the presence of white light, the latter decomposing to FeI_2 and CO. This work is interesting in connection with the discoveries of Hieber and his associates in their extensive study of the reactions and derivatives of iron pentacarbonyl.

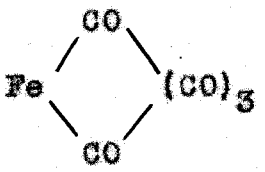
Mention of compounds of the type in the preceding paragraph immediately causes speculation as to the structure of the compound. Mond (63) proposed a ring structure for iron pentacarbonyl in 1893.



Mond's Ring Structure

Armstrong (1), Gladstone (17), and Friend (12) substantiated this structure but the evidence to support it was not strong since there had been little research done on the reactions of the compound. However, it is significant to note that as early as 1896 da Silva (74) did not agree with Mond and

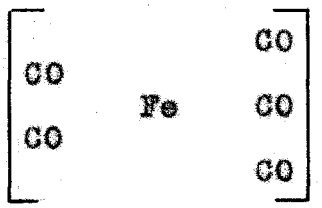
and offered the following structure instead



da Silva's Modified Ring Structure

He later indicated his belief that the carbon atoms do not form a chain but are connected directly to the metal atom.

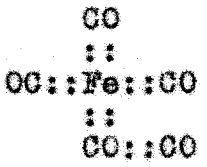
Werner, in the publication of his theory of coördination compounds in 1909 (81), gave iron pentacarbonyl the following structure:



Werner's Coördination Structure

L. Mond (65) agreed at once with Werner's idea for the constitution of iron pentacarbonyl, but in a report in 1930, his son, Robert L. Mond (64), refers again to evidence favoring the ring formula. Manchot and Gall (60) worked with the carbonyls and found evidence to support the coördination compound theory. Manchot added additional evidence while working with the nitrous oxide compounds of iron which he found very similar to the carbonyl compounds in many reactions (58).

Hieber and his associates (24, 41, 42) were in agreement with Werner and Manchot. The more modern structural formula representing the theory of these three investigators follows:

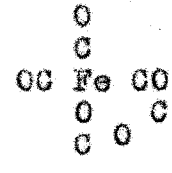


Manchot's Coördination Structure

Still another theory as to the structure of the carbonyls arises from Langmuir's (56) idea that the molecules of iron, nickel, and molybdenum carbonyls all have eighteen electrons in the outer layer, the same number as the atom of the next inert gas. Sidgwick and Bailey (73) point out that carbon monoxide is the electron donor and occupies one coördination position in the metal. This view is supported by electric dipole moments of the symmetrical carbonyls (which are nearly zero), by interatomic distances, by the heats of formation, by the force constants of the bonds, and by the parachor. This view is also in agreement with Langmuir's theory of the structure of carbon monoxide (55). The electronic conception of carbon monoxide may be represented in two ways, :C:::O: or $\overset{+}{C}\equiv\overset{-}{O}$, where the triple bond between carbon and oxygen is indicated. When the carbon monoxide forms a coördinate link with the metal atom and acts as donor of the pair of

electrons, the structure of such a bond may be represented similarly: M:C::O: or $M\text{-}C\equiv O$. It is not clear whether the carbon monoxide is coordinated through the carton atom or through the oxygen atom. In any event, the M:C:::O: group must be co-linear, otherwise rotation of the groups would give rise to an electric moment. Since carbon monoxide will replace water or ammonia from complex compounds, the coordinate link of carbon monoxide to metal must be by means of a single electron pair. Furthermore, Raman spectra data have shown that in the metallic carbonyls, the carbon is joined to the oxygen by a triple link. In view of these facts, Sidgwick regards the structure M:C:::O: as reasonably well established.

Blanchard and Gilliland (5) in 1926 suggested a coordination compound structure for iron pentacarbonyl and found evidence from the carbonyl hydrides, which had not been discovered at the earlier date, to support such a structure (6). Blanchard's formula is



Blanchard's Structural Formula

In general, the Werner-Hieber-Manchot theory of structure, so called by Trout (78), has the support of the majority of

the workers in this field today. Studying the magnetochemical properties of iron carbonyls and similar compounds, Klemm, Jacobi, and Tilk (53) confirmed the coördination structure. Graffunder and Heymann (18) measured the dipole moment of iron pentacarbonyl and their results support the theory that the carbon monoxide groups are not symmetrically arranged about the iron atom.

Eyber (10) studied the photochemical decomposition of iron pentacarbonyl and agreed with the equation of Dewar and Jones (8) which was given previously. Eyber (10) investigated the absorption spectrum of hexane solutions of iron pentacarbonyl and found strong absorption of light of wave lengths below 4600Å. The decomposition of the vapor of iron pentacarbonyl by light of wave lengths over 4000Å was noted. The quantum efficiency was 2. Thompson and Garratt (16) were in agreement with these investigators on the wave length of light which caused the decomposition but felt that the absorption of light was through the carbonyl radical. Without considering the correctness of either of the two proposed mechanisms for the photochemical decomposition of the compound, the work does indicate that either the Werner-Hieber-Manchot theory or the Blanchard theory of structure is correct since it is evident that one, and only one, of the carbonyl radicals in linked differently from the other four. Therefore, we can possibly represent the composition of this coördinated compound by the formula, $[Fe(CO)_4]CO$.

The chemical reactions of the iron carbonyls have been studied quite extensively by Hieber and his associates. One of the compounds which they formed is iron carbonyl hydride, $Fe(CO)_4H_2$, (29, 31, 46). This is a very volatile compound, boiling at -70°C, and the vapor decomposed rapidly at atmospheric pressure. It is prepared by the action of bases on iron pentacarbonyl and then distilled off in a high vacuum. Hieber explains this reaction by stating that carbon monoxide coördinately bound to salts or metals is highly reactive and is easily oxidized in the presence of alkalies

$$Fe(CO)_5 + 2\bar{O}H = \bar{\bar{C}}O_3 + Fe(CO)_4H_2$$

Iron carbonyl hydride or iron hydrocarbonyl is a colorless liquid. It is a strong reducing agent and readily decomposes when in the pure form to give the pentacarbonyl of iron and the tricarbonyl, or its polymer, with the liberation of hydrogen. At room temperature, it is a light yellow colored liquid having an obnoxious odor. In air it explodes.

Iron carbonyl hydride was prepared by reacting barium hydroxide or iron pentacarbonyl. After the reaction was complete, the hydride was distilled from the mixture under a pressure less than one millimeter. Hieber also prepared this compound by the reaction of sodium methylate on iron pentacarbonyl, as shown by the following reaction:

$$Fe(CO)_5 + CH_3ONa + H_2O = Fe(CO)_4H_2 + CH_3O\cdot CO\cdot ONa$$

The latter compound is precipitated by the addition of anhydrous ether. The reaction is dependent on traces of water and is a sensitive test for water in methyl alcohol. $Fe(CO)_4H_2$ in alkaline solution has strong reducing action on organic substances such as nitrobenzene, quinone, and dyes, such as indigo.

Among the other reactions investigated by Hieber and his associates were the reactions of halides, hydrazine, amines, nitric oxide and some organic sulfur compounds on the pentacarbonyl and tetracarbonyl of iron (19 to 48 inc.). The halides prepared had the same structure as those prepared by Hock and Stuhlmann (49, 50, 51) and were considered of the type $Fe(CO)_4X_2$. The structure and volatility were accounted for by the assumption of a symmetrically closed electron configuration. Hieber made a study of the heats of reaction of chlorine, bromine, and iodine with iron pentacarbonyl. These halide derivatives lose carbon monoxide at room temperature and are decomposed by water. If they are heated in the presence of ammonia, carbon monoxide is eliminated and hexammine-ferrous halides are produced. Amines, alcohols, esters, aldehydes, and ketones cause decomposition of these salts and light causes complete elimination of carbon monoxide.

The work of Hieber and his associates with the reaction of iron pentacarbonyl with amine was confined to ethylene-

diamine, ortho phenanthroline, and pyridine. They referred to the products of these reactions as complexes. Due to their instability and the difficulty in isolating these products, the results along this line were not very satisfactory. They found that ethylenediamine formed an addition product with iron pentacarbonyl, but in the presence of pyridine, the ethylenediamine substituted for the carbon monoxide. When iron pentacarbonyl was heated with pyridine in the mol proportion of one to four at 80° to 85°C. for a period of time from 50 to 60 hours, di-iron tripyridine tetracarbonyl was formed. Light increased the reaction velocity. The pyridine in the above compound could be substituted by ammonia and the carbon monoxide could be substituted by the action of halogens and nitric oxide. They found that iron tetracarbonyl was more reactive with pyridine than iron pentacarbonyl. Blanchard (4) in a review article lists several complexes formed from iron pentacarbonyl with pyridine, ethylenediamine, and ortho phenanthroline.

Hieber and Sonnekalb (41) studied the reaction between hydrazine and iron pentacarbonyl. They obtained from this reaction a blood red sirupy solution which contained colorless prismatic crystals of semicarbazide. On treatment of this sirup with an acid, carbon monoxide and hydrogen were evolved. If the dark red sirup was extracted with ether, iron

tetracarbonyl was obtained.

Manchot (58) reported on the similarity of nitrosyl and carbonyl compounds of iron. Manchot and Enk (59) prepared iron tetranitrosyl, $Fe(NO)_4$, by carefully heating $Fe(CO)_5$ and NO under pressure in an autoclave at 44-45°C. It is a black crystalline substance which fumes in the air. Manchot and Gall (61) studied the reaction between nitric oxide and iron pentacarbonyl at room temperature in the presence of methyl alcohol. They obtained a black, unstable, microcrystalline substance which they supposed to have the following composition $FeNO \cdot nCH_3OH$. It decomposes on contact with air and loses part of the combined methanol at 80°C and the remainder above 200°C. Mond (70), at an earlier date, had reported on the reaction of nitric oxide with iron enneacarbonyl. He reported the formation of a red liquid at 70°C. having the composition of $FeNO \cdot 3Fe(CO)_5$. Anderson and Hieber (22) passed nitric oxide gas into a mixture of iron pentacarbonyl and iron tetracarbonyl at 95°C. in an atmosphere of nitrogen for several hours. They reported the finding of a solid which they obtained by filtering through a porous glass plate and then fractionating by steam distilling under reduced pressure. The solid they obtained had a melting point of 18.5°C., a vapor pressure of 4.5 mm. at 0°C., and a density at 18°C. of 1.568. It started to decompose at 15°C. in vacuo and was rapidly oxidized by air.

Hieber and Spacu (44) made a study of the effect of organic sulfur compounds on the carbonyls of iron and cobalt. They report the formation of the following compounds from the reaction of thiophenol with iron tetracarbonyl and ethanethiol reacting with iron enneacarbonyl:

$$Fe(CO)_4 + HSC_6H_5 = Fe(CO)_3.SC_6H_5 + CO + 1/2\ H_2$$

$$Fe_2(CO)_9 + 2HSC_2H_5 = [Fe(CO)_3.SC_2H_5]_2 + 3CO + H_2$$

Hieber and his associates (26) also describe the reaction between the dicarbonyl compounds of ferrous halides with dithioglycol ether, $C_2H_4(SC_2H_5)_2$. The product obtained was supposed to have the following formula: $Fe(CO)_2I_2.C_2H_4(SC_2H_5)_2$. The stability of the compounds diminished in the order of iodide, bromide, chloride.

TABLE II

Some Properties of Iron Carbonyls

Compound	$Fe(CO)_5$	$Fe_2(CO)_9$	$Fe_3(CO)_{12}$
Discoverer and Date	Berthelot (Mond) 1891	Mond, Langer 1891	Dewar, Jones 1905
Color and State	Water-clear liquid	Golden or orange-yellow hexagonal plates	Dark green tables with square borders
Melting Point °C.	-19.5°	Decomposed at 100°	Decomposed at 140°-150°
Boiling Point °C.	104.6°		
Vapor Pressure mm.	25.9 at 16.1°	Not measurable	
Specific Gravity	1.453 at 20°	2.085 at 18°	1.996 at 18°
Temperature of Formation	173° at 200 atm. (Mond)	Light on $Fe(CO)_5$ at room temp. (Mond)	From $Fe_2(CO)_9$ at 60° (Dewar)
Decomposition	To $Fe_2(CO)_9$ by light. To CO and Fe above 130°	To $Fe(CO)_5$, Fe, and CO at 100°. To $Fe(CO)_5$ in soln. at 95°	To Fe and CO at 150°

The metal carbonyls early attracted the attention of investigators in industrial laboratories, who have secured a large number of patents covering proposed uses of these compounds. Although only a few of the suggested applications

of iron carbonyls have become important economically, interest in the compounds continues and we find a number of patents concerning them issued each year. A great deal of study has been made of the use of iron carbonyls as antiknock agents in fuels for internal combustion engines. De Langeron (54) published on the uses of iron pentacarbonyl as an antiknock agent in 1927. The compound was then being sold under the trade name "Motaline" in Germany. He could find little difference between iron pentacarbonyl and tetraethyl lead as an antiknock. The chief difficulty in the way of substituting iron pentacarbonyl for tetraethyl lead is the sensitivity of the iron pentacarbonyl to light. Leady (57) made a study of stabilizers which would decrease or stop the photochemical decomposition of the carbonyl. He reports that none of the so-called inhibitors have proven satisfactory. He also finds that iron pentacarbonyl is the most important of the three carbonyls of iron as an antiknock agent.

Considerable difference of opinion is found among the investigators concerning the effects of the residue left in a motor when using iron pentacarbonyl in the fuel. Leahy states clearly that iron pentacarbonyl does not leave any harmful deposits in the combustion chamber of the motor. Trout (80) reported a private communication from T. A. Boyd of the General Motors Corporation claiming that the deposits

in the cylinder head first affect the spark plugs and finally get into the lubricating oil leading to undue cylinder wear.

As early as 1892, Berthelot (3) mentioned the possibility of preparing iron with a very high degree of purity from iron carbonyl. Since that time, there has been some mention made of this in the foreign literature but very little work has been done along this line in the United States. However, in the June 25, 1941 issue of the News Edition of the American Chemical Society, page 723, there is a notice that the General Aniline Works at Grasselli, New Jersey, is now producing carbonyl iron powder. This iron powder is destined principally for use in electrical devices. Mittasch (62) described the process of preparing finely divided iron and its properties. Iron pentacarbonyl decomposes at atmospheric pressure at temperatures ranging from 140° to 160°C. Decomposition at this temperature, however, leaves rather large amounts of carbon-oxygen compounds in the finished product. Mittasch found that an iron of much higher purity could be prepared by decomposing the iron pentacarbonyl at a temperature of 250°C. Iron prepared in this manner contains no metal impurities, but does contain about one per cent of carbon, being purer than iron prepared by many other processes. The electrical and magnetic properties are superior to those of electrolytic iron.

In his book, "Powder Metallurgy", Jones (52) covers the uses of finely divided iron very thoroughly. Some of the

more significant uses will be mentioned. Perhaps the outstanding use to which iron powder has been put is in the manufacture of molds for metal and plastic casting. The powder can be sintered in such a manner as to make almost any degree of porosity and extremely high thermal conductivities. Molds of such materials are superior to sand molds in strength, speed of molding, and freedom from surface contamination.

Porous iron catalysts have been prepared by the thermal decomposition of iron pentacarbonyl (9). It is possible to manufacture porous iron plates with ninety per cent porosity by first heating powdered iron in an oxidizing atmosphere or mixed with some ferric oxide at about 600°C. It is also possible to reduce oxides of chromium, tungsten, and silicon by mixing them with powdered iron and heating in a hydrogen atmosphere. Powdered iron is also especially valuable in the production of magnetic steels. Welding rods of superior quality can be manufactured from iron powder, due to the absence of foreign metals.

Patents have been taken out for quite a varied list of uses of iron pentacarbonyl. One is the preparation of hydrocarbons by heating the carbonyl in hydrogen. Due to the decomposition of iron pentacarbonyl in the light, a process utilizing this fact has been patented for the manufacture of blueprints. The paper is soaked in iron pentacarbonyl which forms a brown deposit of iron enneacarbonyl.

This deposit is turned blue by washing with a slightly acid solution of potassium ferrocyanide, forming insoluble Prussian blue. Another unusual patent is for the use of metal pentacarbonyls, or their decomposition products, as plant stimulants. The patent suggests that the carbonyl may be either added to the soil or to the seeds of the plants, and that it may be used alone or in fertilizers.

III. EXPERIMENTAL

A. Preparation of Iron Pentacarbonyl for use in Testing

The iron pentacarbonyl used in this experimental work was purchased from the Ferroline Sales Company Incorporated, Shreveport, Louisiana. This company is manufacturing iron pentacarbonyl and selling it as an antiknock agent in the motor fuel market under the trade name of "Ferroline". They use a high grade of purity of iron, most of which was imported from Sweden, and obtain their carbon monoxide by the reduction of carbon dioxide obtained by the volatilization of dry-ice. The carbon monoxide is preheated from 200° to 300°C. and compressed to about 700 pounds pressure per square inch. It is then passed downward over the crushed iron in a vertical tower. This reaction tower is maintained at a constant temperature of about 300°C. by means of a jacket of steam coils. The iron pentacarbonyl is removed from the chamber by the constant stream of carbon monoxide entering the chamber. The carbon monoxide which fails to react is recirculated through the pre-heater and finally re-enters the reaction chamber.

The iron pentacarbonyl is purchased in tin cans of quart

size. Every effort must be made to avoid exposure to the light in order to avoid the decomposition into the enneacarbonyl. The iron pentacarbonyl was distilled before using in the experimental work and only that amount to be used at once was prepared as it decomposes on standing. The condenser, receiving flask, and connections were of glass but painted black with a thick oil paint so as to exclude the light. The distillation flask was heated in an oil bath and the distillation conducted under a reduced pressure, obtained by a water pump connected to the receiving flask. In between the pump and receiving flask was connected a gas-wash bottle containing a small amount of sulfuric acid. The purpose of this was to absorb any uncondensed vapors. The water pump was regulated so as to give only a slight reduction in pressure and a uniform rate of flow of bubbles through the acid in the gas-wash bottle.

The temperature of the oil bath during the distillation was kept at a temperature of 115° to 120°C. The iron pentacarbonyl distilled over at 103° to 104°C. It had a slight orange color due to traces of the enneacarbonyl and the residue in the distilling flask consisted of a black crusty deposit of iron. At the end of the distillation, the black-painted receiving flask was disconnected and stoppered. Quantities of 50 to 100 milliliters were distilled at a time.

B. Study of Solubilities

In studying the solubility of various substances in iron pentacarbonyl, a small quantity, usually 5 milliliters, was placed in a test tube and the other substance added in small amounts. The test tube was then stoppered and the mixture shaken before making further additions. If the iron pentacarbonyl remained clear, the substance was considered soluble in the iron pentacarbonyl. A record was kept of the amount added until the formation of two layers or a cloudiness was observed in the carbonyl. This work was done in a darkened room to avoid as much decomposition of the iron pentacarbonyl due to light as possible.

A liquid substance was considered soluble in iron pentacarbonyl if equal volumes of the two formed a clear mixture and did not separate into layers. Any soluble amount less than the volume of iron pentacarbonyl used was considered as partly soluble. In the case of solid substances, a very small amount was added and the mixture well shaken before further additions were made. The amount added until a cloudiness was produced or until the substance remained undissolved was noted. In some cases a very evident reaction took place, such as the formation of a gas, a precipitate, or a decided change in color.

This study of solubilities of chemical substances in

iron pentacarbonyl has been made using 252 different compounds and elements. It was necessary to use anhydrous substances because water is not soluble in iron pentacarbonyl and any water present affected the solubility.

The results of the testing of the solubilities of the different substances are given in Table III. The results have been groups in the following divisions: soluble, partly soluble, insoluble and reactive. The compounds have been listed in sections consisting of similar types of compounds.

TABLE III

SOLUBLE

Acetic acid	CH_3COOH
Acetic anhydride	$(CH_3CO)_2O$
Butyric acid	$CH_3(CH_2)_2COOH$
Caproic acid	$CH_3(CH_2)_4COOH$
Isobutyric acid	$(CH_3)_2 \cdot CH_2COOH$
Isovaleric acid	$(CH_3)_2CH \cdot CH_2 \cdot COOH$
Propionic acid	CH_3CH_2COOH
Valeric acid	$CH_3(CH_2)_3COOH$
Butyl alcohol	$CH_3(CH_2)_2CH_2OH$
Hexyl alcohol	$CH_3(CH_2)_4CH_2OH$
Isobutyl alcohol	$(CH_3)_2CH \cdot CH_2OH$
Sec.-butyl alcohol	$CH_3CH_2 \cdot CHOH \cdot CH_3$
Tert.-butyl alcohol	$(CH_3)_3COH$
Allyl ethyl ether	$CH_2:CH \cdot CH_2 \cdot O \cdot C_2H_5$
Butyl benzyl ether	$C_4H_9 \cdot O \cdot CH_2 \cdot C_6H_5$
Ethyl ether	$(C_2H_5)_2O$
Isoamyl ether	$(C_5H_{11})_2O$
Amyl acetate	$CH_3COOC_5H_{11}$
Benzyl formate	$HCOOCH_2 \cdot C_6H_5$
Beta-bromoethyl acetate	$CH_3COO \cdot CH \cdot Br \cdot CH_3$
Butyl acetate	$CH_3COO\ C_4H_9$
Butyl benzoate	$C_6H_5COOC_4H_9$
Diethyl oxalate	$(COOC_2H_5)_2$
Ethyl acetate	$CH_3COOC_2H_5$
Ethyl acetoacetate	$CH_3COCH_2COOC_2H_5$
Ethyl benzoate	$C_6H_5COOC_2H_5$
Ethyl chloroacetate	$CH_2Cl \cdot COOC_2H_5$
Ethyl chlorocarbonate	$C_2H_5 \cdot O \cdot C(O)Cl$

TABLE III (Cont.)

SOLUBLE

Acetone	$CH_3 \cdot CO \cdot CH_3$
Acetophenone	$CH_3 \cdot CO \cdot C_6H_5$
Ethyl methyl ketone	$C_2H_5 \cdot CO \cdot CH_3$
Parabromoanisole	$Br \cdot C_6H_4 \cdot OCH_3$
Alphachloronaphthalene	$C_{10}H_7\ Cl$
Benzene	C_6H_6
Bromobenzene	C_6H_5Br
Iodobenzene	C_6H_5I
Nitrobenzene	$C_6H_5NO_2$
Parabromochlorobenzene	$Br \cdot C_6H_4 \cdot Cl$
Petroleum ether	$C_3H_8 - C_4H_{10}$
Toluene	$C_6H_5CH_3$
Turpentine	$C_{10}H_{16}$
Allyl bromide	$CH_2:CH \cdot CH_2Br$
Amyl cyamide	$C_5H_{11}CN$
Butyl bromide	C_4H_9Br
Butyl chloride	C_4H_9Cl
Carbon tetrachloride	CCl_4
Chloroform	$CHCl_3$
Ethyl bromide	C_2H_5Br
Ethylene bromide	$CH_2Br \cdot CH_2Br$
Isopropyl bromide	$CH_3 \cdot CHBr \cdot CH_3$
Methylene bromide	CH_2Br_2
Nitro methane	CH_3NO_2
Propyl bromide	$C_2H_5CH_2Br$
Sec.-butyl bromide	$C_2H_5 \cdot CHBr \cdot CH_3$
Tert.-butyl bromide	$(CH_3)_3CBr$
Tetrachloroethylene	$CCl_2:CCl_2$
Trichloroethane	$CCl_3 \cdot CH_3$
Triethyl amine	$(C_2H_5)_3N$

TABLE III (Cont.)

SOLUBLE

Arsenic trichloride	$AsCl_3$
Carbon bisulfide	CS_2
Phosphorus trichloride	PCl_3

PARTLY SOLUBLE

Benzoic acid	C_6H_5COOH (very slightly)
Oleic acid	$C_{17}H_{33}COOH$ (1 ml. in 10 ml.)
Stearic acid	$C_{17}H_{35}COOH$ (very slightly)
Ethyl alcohol	C_2H_5OH (0.5 ml. in 10 ml.)
Isopropyl alcohol	$CH_3 \cdot CHOH \cdot CH_3$ (2 ml. in 10 ml.)
Propyl alcohol	C_3H_7OH (2 ml. in 10 ml.)
Azobenzene	$C_6H_5N:NC_6H_5$ (0.2 gm. in 5 ml.)
Chloroacetophenone	$CH_3COC_6H_4Cl$ (very slightly)
Diphenyl amine	$(C_6H_5)_2:NH$ (slightly)
Naphthalene	$C_{10}H_8$ (slightly)
Orthobromo-anisole	$Br \cdot C_6H_4 \cdot OCH_3$ (0.5 ml. in 5 ml.)
Parabromo-aniline	$Br \cdot C_6H_4 \cdot NH_2$ (very slightly)
Parabromochlorobenzene	$Br \cdot C_6H_4 \cdot Cl$ (0.5 gm. in 5 ml.)

REACTIVE

Antimony pentachloride	$SbCl_5$
Bromine	Br_2
Chlorine	Cl_2
Hydrogen peroxide (30%)	H_2O_2
Iodine	I_2
Nitric acid (cond. soln.)	HNO_3
Phosphorus tribromide	PBr_3
Sodium peroxide	Na_2O_2

TABLE III (Cont.)

REACTIVE

Stannic chloride	$SnCl_4$
Sulfur monochloride	S_2Cl_2
Sulfuric acid (conc.soln.)	H_2SO_4
Thionyl chloride	$SO\ Cl_2$
Acetaldehyde	CH_3CHO
Amyl bromide	$C_5H_{11}Br$
Benzaldehyde	C_6H_5CHO
Ethyl sulfate	$(C_2H_5)_2SO_4$
Paraldehyde	$(CH_3CHO)_3$
Allylamine	$CH_2:CH\cdot CH_2NH_2$
Aniline	$C_6H_5\cdot NH_2$
Butylamine	$C_4H_9NH_2$
Ethanolamine	$NH_2\cdot CH_2\cdot CH_2OH$
Ethylamine	$C_2H_5NH_2$
Diethylamine	$(C_2H_5)_2NH$
Dimethylamine	$(CH_3)_2NH$
Hydrazine	$NH_2\cdot NH_2$
Methylamine	CH_3NH_2
Methylaniline	$C_6H_5\cdot NH\cdot CH_3$
Paraphenetidine	$C_2H_5\cdot O\cdot C_6H_4\cdot NH_2$
Phenylhydrazine	$C_6H_5\cdot NH\cdot NH_2$

INSOLUBLE

Aluminum	Al
Aluminum chloride	$AlCl_3$
Ammonia	NH_3
Ammonium acetate	CH_3COONH_4
Ammonium bromide	NH_4Br
Ammonium hydroxide	NH_4OH
Ammonium thiocyanate	NH_4SCN

TABLE III (Cont.)

INSOLUBLE

Antimony trichloride	$SbCl_3$
Antimony potassium tartrate	$SbK(C_4H_4O_6)_2$
Arsenious acid (anhydride)	As_2O_3
Barium hydroxide	$Ba(OH)_2$
Bismuth chloride	$BiCl_3$
Boric acid	H_3BO_3
Calcium	Ca
Calcium chloride	$CaCl_2$
Chromic acid (anhydride)	CrO_3
Cupric oxide	CuO
Cupric sulfate	$CuSO_4$
Cyanamide	$CN \cdot NH_2$
Hydrogen chloride (dry gas)	HCl
Hydrogen cyanide (dry gas)	HCN
Iron (powder)	Fe
Mercury	Hg
Mercuric chloride	$HgCl_2$
Mercurous sulfate	Hg_2SO_4
Mercurous iodide	Hg_2I_2
Molybdic acid (anhydride)	MoO_3
Phosphoric acid (ortho)	H_3PO_4
Phosphorus tribromide	PBr_3
Phosphorus pentasulfide	P_2S_5
Phosphomolybdic acid	$H_3PO_4 \cdot 12MoO_3 \cdot 12H_2O$
Potassium bromate	$KBrO_3$
Potassium carbonate	K_2CO_3
Potassium hydroxide	KOH
Potassium iodate	KIO_3
Potassium acid phthalate	$C_6H_4(COO)_2HK$
Potassium sulfate	K_2SO_4
Sodamide	$NaNH_2$
Sodium	Na
Sodium acetate	CH_3COONa

TABLE III (Cont.)

INSOLUBLE

Sodium amalgam	Na-Hg
Sodium bismuthate	$NaBiO_3$
Sodium cyanide	NaCN
Sodium hydroxide	NaOH
Stannous chloride	$SnCl_2$
Sulfur dioxide	SO_2
Thorium nitrate	$Th(NO_3)_4 \cdot 12H_2O$
Titanium trichloride	$TiCl_3$
Uranium acetate	$(CH_3COO)_2UO_2 \cdot 2H_2O$
Zinc	Zn
Zinc chloride	$ZnCl_2$
Acetyl salicylic acid	$C_6H_4 \cdot (COOH) \cdot O \cdot COCH_3$
Aminobenzoic acid	$NH_2 \cdot C_6H_4 \cdot COOH$
Chlorobenzoic acid	$Cl \cdot C_6H_4 \cdot COOH$
Citric acid	$C_3H_4(OH)(COOH)_3$
Diphenyl acetic acid	$(C_6H_5)_2CH \cdot COOH$
Formic acid (85% soln.)	HCOOH
Gallic acid	$(HO)_3 \cdot C_6H_2 \cdot COOH$
Glycollic acid	$CH_2(OH)COOH$
Lactic acid	$CH_3 \cdot CHOH \cdot COOH$
Maleic acid	$HOOC \cdot CH:CH \cdot COOH$
Malonic acid	$CH_2(COOH)_2$
Nitrobenzoic acid	$NO_2 \cdot C_6H_4 \cdot COOH$
Oxalic acid	$(COOH)_2$
Palmitic acid	$C_{15}H_{31}COOH$
Phthallic acid	$C_6H_4(COOH)_2$
Pyruvic acid	$CH_3 \cdot CO \cdot COOH$
Salicylic acid	$HO \cdot C_6H_4 \cdot COOH$
Succinic acid	$(CH_2COOH)_2$
Tartaric acid	$HOOC \cdot (CHOH)_2 \cdot COOH$

TABLE III (Cont.)

INSOLUBLE

Allyl alcohol	$CH_2 \cdot CH \cdot CH_2OH$
Benzyl alcohol	$C_6H_5 \cdot CH_2OH$
Benzohydrol	$(C_6H_5)_2CHOH$
Cinnamyl alcohol	$C_6H_5 \cdot CH{:}CH \cdot CH_2OH$
Ethylene alcohol	$CH_2{:}CHOH$
Ethylene glycol	$HOCH_2 \cdot CH_2OH$
Eugenol 1, 4, 3	$C_3H_5 \cdot C_6H_3(OH)(OCH_3)$
Glycerol	$C_3H_5(OH)_3$
Guaiacol	$CH_3O \cdot C_6H_4 \cdot OH$
Methyl alcohol	CH_3OH
Naphthol (alpha)	$C_{10}H_7OH$
Phenol	C_6H_5OH
Propylene glycol	$CH_3 \cdot CH(OH) \cdot CH_2OH$
Pyrogallol	$C_6H_3(OH)_3$
Quinhydrone	$C_6H_4 \cdot O_2 \cdot C_6H_4(OH)_2$
Resorcinol (meta)	$C_6H_4(OH)_2$
Butyl nitrite	$C_4H_9NO_2$
Isoamyl nitrite	$(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot NO_2$
Paranitro diphenyl	$C_6H_5 \cdot C_6H_4 \cdot NO_2$
Paranitrophenol	$NO_2 \cdot C_6H_4 \cdot OH$
Acetamide	$CH_3 \cdot CO \cdot NH_2$
Acetyl paratoluidine	$CH_3CONHC_6H_4CH_3$
Acetanilide	$C_6H_5 \cdot NH \cdot COCH_3$
Alphanaphthylamine	$C_{10}H_7NH_2$
1-amino anthroquinone	$NH_2 \cdot C_6H_3{:}(CO)_2{:}C_6H_4$
Amino azobenzene hydrochloride	$C_6H_5 \cdot N{:}N \cdot C_6H_4 \cdot NH_2 \cdot HCl$
2-amino 5-azotoluene hydrochloride	$HCl \cdot NH_2(CH_3)\ C_6H_3 \cdot N{:}N \cdot C_6H_4 \cdot CH_3$
Benzene sulfonamide	$C_6H_5 \cdot SO_2 \cdot NH_2$
Benzylaniline	$C_6H_5 \cdot NH \cdot CH_2 \cdot C_6H_5$

TABLE III (Cont.)

INSOLUBLE

Benzyl-phenyl nitrosoamine	$C_6H_5.N(NO)CH_2.C_6H_5$
Chloramine T	$CH_3.C_6H_4\ SO_2.N(Cl)Na$
Chloroacetamide	$CH_2Cl.CONH_2$
Dicyandiamide	$NH_2.C(:NH)NHCN$
Dimethylglyoxime	$(CH_3)_2.C_2.(NOH)_2$
Formamide	$HCONH_2$
Hexamethylene tetramine	$C_6H_{12}N_4$
Hydroxylamine hydrochloride	$NH_2OH.HCl$
Metanitroaniline	$NO_2.C_6H_4.NH_2$
Methylamine hydrochloride	$CH_3NH_2.HCl$
Methyl bromide (25% soln. in C_2H_5OH)	CH_3Br
Ortho-nitroaniline	$NO_2.C_6H_4.NH_2$
Para-amino acetanilide	$NH_2.C_6H_4.NH.COCH_3$
Para-amino acetophenone	$NH_2.C_6H_4.COCH_3$
Para-amino azobenzene	$NH_2.C_6H_4.N:N.C_6H_5$
Para-amino biphenyl	$C_6H_5.C_6H_4.NH_2$
Para-amino dimethylaniline hydrochloride	$NH_2.C_6H_4.N(CH_3)_2.HCl$
Parabromoacetanilide	$Br.C_6H_4.NH.COCH_3$
Parabromodimethylaniline	$Br.C_6H_4.N(CH_3)_2$
Paraiodoacetanilide	$I.C_6H_4.NH.COCH_3$
Paraphenylene diamine	$NH_2.C_6H_4.NH_2$
Paranitroacetanilide	$NO_2.C_6H_4.NH.COCH_3$
Paranitroethylacetanilide	$NO_2.C_6H_4.N(C_2H_5)(COCH_3)$
Paratoluidine	$CH_3.C_6H_4.NH_2$
Phenyl-alphanaphthalene	$C_{10}H_7.NH.C_6H_5$
Phenyl-hydrazine hydrochloride	$C_6H_5.NH.NH_2.HCl$
Phthalimide	$C_6H_4(CO)_2NH$
Quinoline	C_9H_7N
Thioacetamide	$CH_3.CS.NH_2$
Triethanolamine	$N(CH_2CH_2OH)_3$

TABLE III (Cont.)

INSOLUBLE

Nitrourea	$NH_2CO.NH.NO_2$
Thiourea	$NH_2.CS.NH_2$
Urea	$NH_2.CO.NH_2$
Dextrin	$(C_6H_{10}O_5)_x$
Levulose	$C_6H_{12}O_6$
Sucrose	$C_{12}H_{22}O_{11}$
Anthracene	$C_6H_4.(CH)_2.C_6H_4$
Benzil	$C_6H_5.COCO.C_6H_5$
Benzoin	$C_6H_5.CHOH.CO.C_6H_5$
Diphenyl sulfide	$(C_6H_5)_2S$
Formaldehyde	$HCHO$
Furfural	C_4H_3OCHO
Potassium ethyl xanthate	C_2H_5OCSSK
Quinone	$C_6H_4.O_2$
Sodium valerate	$CH_3.(CH_2)_3.COONa$
Vanillin	$CH_3O(OH)C_6H_3.CHO$

An effort was made to see if some of the substances which reacted with iron pentacarbonyl, or were insoluble in it, could be dissolved in a liquid which was soluble in the iron pentacarbonyl. The resulting solution was then added to the iron pentacarbonyl and the extent of the solubility of the mixture was observed.

Butylamine, allylamine, diethylamine, ethylaniline, methylaniline, paraphenetidine, and phenylhydrazine, all of

which form dark red liquids with iron pentacarbonyl, are soluble in ether. The solutions of each of these in ether was added to iron pentacarbonyl and the mixture shaken. The same reaction took place as without the presence of ether. However, the dark-red liquid did not separate but instead a uniform mixture of all the materials was obtained. Ethanolamine, which reacts with iron pentacarbonyl, was dissolved in chloroform and this solution added to the iron pentacarbonyl and the same reaction took place as without the presence of chloroform. Quinoline, which is insoluble in the carbonyl, was dissolved in ether and the resulting solution was found to be soluble in iron pentacarbonyl. Triethanolamine, which is insoluble in the carbonyl, was dissolved in acetone and the resulting solution added to a sample of iron pentacarbonyl. The triethanolamine remained insoluble and separated from the mixture.

C. Reactions of Amines and Nitrogen Compounds with Iron Pentacarbonyl

Hieber and Sonnekalb (41, 42) report on the reaction of ethylenediamine and hydrazine with iron pentacarbonyl to form a blood-red sirupy solution. This investigation was extended to a large group of amines and related compounds. Those which reacted with the carbonyl are listed in Table III

under the reactive group of compounds.

The reaction between iron pentacarbonyl and normal butylamine is exothermic and it is necessary to cool the reacting mixture with tap water. To 20 milliliters of iron pentacarbonyl were added small portions of butylamine until a total of 10 milliliters of the amine was added. The mixture was thoroughly agitated and frequently cooled during the process of mixing. A total of 12.5 milliliters of a thick, dark-red liquid was obtained which separated on top of the iron carbonyl. Ammonia was evolved during the reaction. This dark-red liquid was removed by means of a separatory funnel and treated with a fresh 10 milliliter portion of iron pentacarbonyl. The excess carbonyl was removed and this step was repeated six times.

The dark-red substance was analyzed for iron and nitrogen. The iron was determined by dissolving the sample in hydrochloric acid. A few drops of nitric acid were added to oxidize the iron. The iron was then precipitated as ferric hydroxide upon the addition of ammonium hydroxide and filtered on ashless filter paper. The precipitate was ignited to constant weight and weighed as ferric oxide, from which the percentage of iron was determined.

The nitrogen was determined by means of the modified Kjeldahl method. The sample was dissolved in 25 milliliters of concentrated sulfuric acid to which was added 10 grams

of anhydrous potassium sulfate to raise the boiling point of the acid. A few crystals of selenium oxide were added to accelerate the process of digestion. The mixture was heated until the liquid becamse clear, showing that the sample was completely dissolved and the carbon had been oxidized. The acid solution was allowed to cool and 100 milliliters of water were added, a little at a time and with frequent shaking, and cooling the flask under the tap. To the cool mixture were added 100 milliliters of a saturated solution of sodium hydroxide so as to form a separate layer and not mix with the acid solution. A small piece of paraffin was added to prevent foaming when the two layers were mixed. The flask was then connected to the distillation apparatus and the acid solution mixed with the base by a gentle swirling motion. The ammonia was distilled over into 50 milliliters of standard 0.1 N hydrochloric acid until about half of the solution was distilled. The excess acid was then titrated with a standard solution of sodium hydroxide, using methyl orange as an indicator. A blank was run on the reagents at the same time. The percentage of nitrogen in the sample was calculated from the amount of ammonia.

From the percentages of iron and nitrogen in the sample, the ratio of the atoms of the two elements was calculated. This indicated the mol ratio of the carbonyl and amine in

in the substance.

Since this dark-red liquid is quite viscous and sticks to the walls of the separatory funnel, efforts were made to find other means of separating it from the excess carbonyl. No solvent could be found that would dissolve one and not the other. A definite separation could not be obtained by cooling the mixture with ice or solid carbon dioxide.

This dark-red product formed from the reaction of iron pentacarbonyl with an amine was apparently not affected by light but did decompose on exposure to the atmosphere. The samples were weighed in small stoppered bottles,which could be put immediately into the dissolving acid upon removal of the stopper. The substance decomposed upon heating and did not have a definite boiling point. Efforts were made to distill this dark-red liquid under reduced pressure but even then decomposition took place.

This study was repeated on the products of the reaction between iron pentacarbonyl and ethylamine, methylamine and hydrazine. The hydrazine was prepared from hydrazine hydrate by mixing 100 grams of the hydrate with 100 grams of sodium hydroxide (in pieces the size of a pea) in a distilling flask which had a long side tube. The mixture was heated on an oil bath so that a temperature of 113°C. was attained in 2 hours. At this point, the temperature of the bath was further raised to 150° and the anhydrous hydrazine, $NH_2.NH_2$, distilled over. It is a colorless liquid which

boils at 113.5° C. and has a specific gravity of 1.011 at 15° C.

The analysis of the dark-red liquid formed from the reaction of butylamine with iron pentacarbonyl gave 8.57 per cent iron and 8.56 per cent nitrogen which gives a proportion of the atoms of iron to the atoms of nitrogen to be in the ratio of one to four. The percentages of each of these two elements confirmed the compound to have the composition represented by the formula, $Fe(CO)_3.4(C_4H_9)_2NH$. The Hinsberg test using benzenesulfonyl chloride confirmed the presence of a secondary amine. The following equation is proposed for the reaction since ammonia is evolved.

$$Fe(CO)_5 + 8C_4H_9NH_2 = Fe(CO)_3.4(C_4H_9)_2NH + 4NH_3 + 2CO$$

The dark-red product from the reaction of ethylamine with iron pentacarbonyl gave an analysis of 9.02 per cent iron and 9.15 per cent nitrogen which is a ratio of one atom of iron to four atoms of nitrogen. The percentages of the two elements would indicate a compound of the type represented by the formula $Fe(CO)_5.4(C_2H_5)_3N$. Calculated from this formula, this compound has 9.33 per cent each of iron and nitrogen. The reaction could be represented by the following equation:

$$Fe(CO)_5 + 12C_2H_5NH_2 = Fe(CO)_5.4(C_2H_5)_3N + 8NH_3$$

Constant results were not obtained for the percentages

of iron and nitrogen in the dark-red product formed by the reactions of methylamine with iron pentacarbonyl. Evidently the compound was unstable.

Hieber and Sonnekalb (41) report the reaction between iron pentacarbonyl and hydrazine to form a blood red sirupy solution which contains colorless prismatic crystals of semicarbazide, $NH_2NHCONH_2$. This result was checked by treating a sample of hydrazine with an excess of iron pentacarbonyl. The mixture obtained was analyzed for the percentages of iron and nitrogen. The analysis gave 16.25 per cent of iron and 13.61 per cent of nitrogen. These percentages give a ratio of 1 to 3.34 of iron atoms to nitrogen atoms. If the dark-red liquid was an addition compound of the type represented by the formula $Fe(CO)_5.NH_2NHCONH_2$, then the percentage of iron would be 20.6 and the nitrogen 15.8 per cent.

The product from the reaction between iron pentacarbonyl and normal butylamine was treated with oxygen by bubbling the gas through the liquid. The gas was collected in a gas burette having a leveling tube and an analysis made for carbon monoxide, carbon dioxide, and oxygen. The gases from a measured volume of the mixture were absorbed in suitable reagents in Hempel absorption pipettes containing suitable reagents and the loss in volume was measured. The results of the analysis were computed in percentages by volume.

The gas mixture was first treated with a sulfuric acid solution to absorb any ammonia and gaseous amines. The gas mixture was next treated with a 33 per cent, by weight, solution of potassium hydroxide to absorb the carbon dioxide. The oxygen was then absorbed in an alkaline pyrogallol solution. This solution was made by dissolving 2.5 grams of pyrogallol in 100 milliliters of a potassium hydroxide solution of a specific gravity of 1.55. Lastly, the carbon monoxide was absorbed in an acid solution of cuprous chloride. This solution was made by dissolving 18 grams of cuprous chloride in a solution of 30 milliliters of concentrated hydrochloric acid mixed with 60 milliliters of water. Copper wire was placed in a stoppered bottle of the solution and the solution was not used until it became colorless on standing.

The results of bubbling oxygen through a 5 milliliter sample of the compound formed from butylamine and iron pentacarbonyl, $Fe(CO)_3.4(C_4H_9)_2NH$, are given in Table IV. The first 100 milliliters of gas collected is called sample I, and samples II and III refer to further samples obtained by treating the same sample with more oxygen. The figures given refer to volume per cent in the mixture.

TABLE IV

Sample	I	II	III	Av.
Soluble in H_2SO_4 (NH_3, Amines, etc.)	1.0	0.0	0.0	0.33
Soluble in KOH (CO_2, trace of Fe)	4.5	2.5	7.6	4.9
Soluble in alkaline pyrogallol (O_2)	71.5	84.7	82.3	79.5
Soluble in Cu_2Cl_2 (CO)	16.4	8.8	5.5	10.2
Volume of sample left	6.6	4.0	3.6	4.7
Total	100.0	100.0	100.0	

C. Reactions of Oxidizing and Reducing Agents on Iron Pentacarbonyl

A powdered form of iron, called carbonyl iron, has been reported by Mittasch (62). It was produced by heating iron pentacarbonyl to around 250° C. In an effort to produce the iron in a pure form from the pentacarbonyl by some method other than thermal decomposition, a study was made of the effect of oxidizing and reducing agents on iron pentacarbonyl.

Dry sulfur dioxide gas was passed through iron pentacarbonyl but no reaction could be observed. The sulfur

dioxide was prepared by the action of concentrated sulfuric acid on sodium sulfite and the gas was dried over concentrated sulfuric acid.

Sulfur monochloride, S_2Cl_2, and thinoyl chloride, $SOCl_2$, were tried with the iron carbonyl. Each of these liquids was found to be extremely reactive. When the vapors came in contact with the vapor from the iron pentacarbonyl, a dense smoke was formed varying in color from yellow to brown. When either sulfur monochloride or thionyl chloride is mixed with iron pentacarbonyl, a heavy yellow to brown vapor is formed which settles over the apparatus and neighboring objects. This sediment and the residue in the reacting mixture was found to be chlorides of iron.

Anhydrous stannous chloride and titanium trichloride do not react with iron pentacarbonyl. The anhydrous stannous chloride was prepared by passing dry hydrogen chloride gas over heated tin in a combustion tube. The anhydrous stannous chloride condensed into a white glassy solid in the cool portion of the tube.

Titanium trichloride was prepared by dissolving metallic titanium in hydrochloric acid. The nascent hydrogen reduces the titanium to the trivalent form, giving a purple colored solution of $TiCl_3$. This solution was saturated with hydrogen chloride gas while in an ice-salt-water mixture and violet crystals of titanium trichloride separated. These

were centrifuged from the liquid and dried over sulfuric acid in a vacuum desiccator.

Antimony pentachloride, stannic chloride, sodium peroxide, and a solution of hydrogen peroxide were also used with iron pentacarbonyl. These reagents were obtained from the regular stock of the chemical supply room.

Carbonyl iron was not obtained from iron pentacarbonyl by use of oxidizing and reducing agents. Sulfur monochloride and thionyl chloride are extremely reactive with iron carbonyl and form the chlorides of iron. Antimony pentachloride and stannic chloride also react to form the chlorides of iron. Stannous chloride and titanium trichloride do not react with iron pentacarbonyl. Sodium peroxide reacts only very slowly and after several hours, a small amount of a black precipitate of iron is obtained. The solution of hydrogen peroxide reacts slowly and after two or three hours, a brown precipitate is formed in the hydrogen peroxide layer. Freundlich (15) referred to this as a ferric oxide solution.

E. Study of the Electrical Conductivity of Iron Pentacarbonyl

The apparatus used for the determination of the electrical conductivity was of the standard type consisting of a cell for holding the liquid, a resistance box, an electrically

driven tuning fork, ear-phones, and a Wheatstone bridge. The cell was a glass-stoppered bottle having two platinized plates, each one centimeter square, and placed one centimeter apart. The connections to the plates are made by platinum wires sealed through the glass and leading into wells containing mercury by which contact can be made with copper leads to the apparatus.

The cell constant was first determined by using a 0.02 molar solution of potassium chloride in the cell. This solution has a specific conductance of 0.002761 reciprocal ohms at 25° C. When using iron pentacarbonyl or solutions of arsenic trichloride, antimony trichloride, sodium chloride, acetic acid,and acetic anhydride in iron pentacarbonyl, it was necessary to increase the known resistance to 250,000 ohms in order to balance the resistance of the cell containing the liquid. A decrease in the humming sound could only then be noticed when the ratio on the adjustable bridge was made extremely large in order to be proportional to the ratio of the resistances.

The specific electrical conductance of iron pentacarbonyl is very small. The cell constant, using a 0.02 molar solution of potassium chloride with a specific conductance of 0.002761 reciprocal ohms, was found to be 0.347. The resistance of the cell containing iron pentacarbonyl was found to be 24,700,000 ohms. This gives a specific conductance for iron

pentacarbonyl of 0.000000014 reciprocal ohms. A carbonyl solution of arsenic trichloride, acetic acid, or acetic anhydride, or iron pentacarbonyl containing crystals of sodium chloride or antimony trichloride would not show any electrical conductivity greater than the iron carbonyl alone.

F. Action of Iron Pentacarbonyl Vapors on Metallic Aluminum and Zinc

Iron pentacarbonyl vapors were passed over metallic aluminum and zinc in an effort to determine if any reaction would take place. Since no reaction took place when the metals were cold, the metals were kept hot in the glass tube by means of a gas burner. This method allowed the tube to get too hot, which caused the iron pentacarbonyl to decompose forming an iron mirror on the walls of the tube.

The glass tube containing the metal was then jacketed with a larger size glass tube through which was circulated oil kept constant at a temperature of 110°C. This temperature was high enough to keep the iron pentacarbonyl in a vapor state and yet not high enough to cause it to decompose.

The iron pentacarbonyl was heated in a flask, by means of an oil-bath, at a temperature around 120°C. The aluminum used was in the form of turnings and the zinc was in the form of shot. The vapors of iron pentacarbonyl after

passing over the metal were condensed in a water jacketed condenser.

There is no reaction between vaporized iron pentacarbonyl and metallic aluminum or zinc. There was no deposit of iron on the metals and no trace of aluminum or zinc could be found in the condensed iron pentacarbonyl.

G. Study of the Decomposition of Iron Pentacarbonyl to give a Deposit of Iron on Cloth

In an effort to see if a deposition of iron could be formed on cloth from the decomposition of iron pentacarbonyl, several different methods were tried. One piece of cloth was moistened with the carbonyl and then allowed to dry in the air. It was again wetted and allowed to dry and this process repeated several times. Another piece was suspended over iron pentacarbonyl and allowed to stand over night. Another piece was suspended over heated iron pentacarbonyl, causing its decomposition. Oxygen was bubbled through iron pentacarbonyl in which was immersed a piece of cloth. A piece was moistened with the dark-red liquid formed from the reaction of butylamine and iron pentacarbonyl and the cloth allowed to dry in the air.

When a piece of cloth is repeatedly moistened with iron pentacarbonyl and allowed to dry in the air, a deposit of

iron oxides is obtained on the cloth. There was no deposit of iron formed on the cloth when suspended over evaporating iron carbonyl or even when the carbonyl was heated. A reddish brown deposit of iron oxides was formed on the cloth when a stream of oxygen was bubbled through iron pentacarbonyl in which a piece of cloth was immersed. The vapor from this oxidation would explode and cause the iron carbonyl to burn. $Fe(CO)_3.4(C_4H_9)_2NH$ was allowed to evaporate in the air on a piece of cloth and it only formed a tarry-like crust and did not give free iron.

IV. DISCUSSION OF RESULTS

The results of the experimental work on the determination of the solubilities of various chemical substances in iron pentacarbonyl show that a great many organic compounds and only a very few inorganic compounds are soluble. Practically all of the compounds which are soluble are liquids. Only a few solids were found to be soluble and their solubilities varied from a trace up to 0.5 grams in 5 milliliters of iron pentacarbonyl. The latter value is the solubility of parabromochlorobenzene, which is the most soluble solid found.

The liquids which are soluble in iron pentacarbonyl to any great extent are all of low viscosity and most of them also have a low density. Since water is not soluble in iron pentacarbonyl, no water solutions or hydrates were found to be soluble in the carbonyl.

Only two inorganic compounds were found to be soluble in iron pentacarbonyl and they were arsenic trichloride and phosphorus trichloride. Both of these compounds are liquids at ordinary room temperature and are not oxidizing agents. Liquid oxidizing agents react with iron pentacarbonyl to cause decomposition.

No particular class of compounds in general was found to be soluble. The main characteristics of a substance which is soluble in iron pentacarbonyl appear to be of a physical nature; namely, an anhydrous liquid of low viscosity and perhaps having a low specific gravity.

The solubility of a substance in iron pentacarbonyl does not seem to be increased or changed by the use of a solvent in which both the carbonyl and substance are soluble. Only in the case of quinoline, which is insoluble, was an ethyl ether solution found to be soluble in the carbonyl.

Practically all of the amines and hydrazines react with iron pentacarbonyl to form an unstable complex compound having a blood-red color. The primary amines are converted to secondary or tertiary amines with the evolution of ammonia. The complex compound may either be of the substitution or addition type of compound with iron pentacarbonyl. It is difficult to get a good separation of these complex compounds because of their instability. They are of a sirupy consistency and have a foul odor. They decompose in air and oxygen and dissolve in hydrochloric acid with the liberation of phosgene, $COCl_2$.

The only satisfactory method of obtaining carbonyl iron from iron pentacarbonyl is by heating the compound above 200° C. The vapor mixed with air is explosive. Any oxidizing agent sufficiently stron g nough to decompose the compound also

oxidizes the iron or forms a compound with the iron.

Iron pentacarbonyl is a nonconductor of electricity and solutions of the two inorganic compounds, arsenic trichloride, will not conduct an electrical current. Vaporized iron pentacarbonyl is no more reactive with metals then the liquid carbonyl.

V. CONCLUSIONS

1. A great many liquid organic compounds are soluble in iron pentacarbonyl.

2. Only two inorganic compounds, arsenic trichloride and phosphorus trichloride, are found to be soluble in iron pentacarbonyl.

3. Iron pentacarbonyl reacts with amines and hydrazine to form a blood-red complex compound having a sirupy consistency. The compound formed from the reaction between normal butylamine and iron pentacarbonyl is found to have the composition represented by the formula, $Fe(CO)_3.4(C_4H_9)_2NH$. With ethylamine, the complex compound formed is found to be $Fe(CO)_5.4(C_2H_5)_3N$. The reaction with hydrazine forms a mixture of a liquid complex addition compound and crystals of semicarbazide, $NH_2NHCONH_2$.

4. Iron pentacarbonyl cannot be decomposed by oxidizing and reducing agents to give the element iron in a pure form.

5. Iron pentacarbonyl is a nonconductor of electricity and solutions of which it is the solvent do not possess electrical conductivity.

6. Iron pentacarbonyl is characterized by its general inertness. It does not react in either the liquid or gaseous state with metals. It is decomposed by oxidizing agents.

VI. SUMMARY

1. In this investigation the solubilities of 252 different chemical substances in iron pentacarbonyl have been tested.

2. A great many liquid organic compounds were found to be soluble in iron pentacarbonyl. These substances were of no particular type of compound but mainly liquids of low viscosity and low specific gravity.

3. A few solid organic compounds were found to be sparingly soluble in iron pentacarbonyl.

4. Only two inorganic compounds, arsenic trichloride and phosphorus trichloride, were found to be soluble in iron pentacarbonyl and both of these compounds are liquids at room temperature.

5. Iron pentacarbonyl reacts with amines and hydrazine to form an unstable blood-red complex compound having a sirupy consistency.

a. The compound formed from the reaction between iron pentacarbonyl and normal butylamine has the composition represented by the formula, $Fe(CO)_3.4(C_4H_9)_2NH$. The reaction is accompanied with the evolution of ammonia and carbon monoxide as is indicated by the following equation. $Fe(CO)_5 + 8C_4H_9NH_2 = Fe(CO)_3.4(C_4H_9)_2NH + 4NH_3 + 2CO$

b. With ethylamine, iron pentacarbonyl formed the unstable addition product represented by the formula, $Fe(CO)_5.4(C_2H_5)_3N$, the primary amine being converted to the tertiary amine with the evolution of ammonia.

c. With hydrazine, iron pentacarbonyl forms a mixture containing crystals of semicarbazide and a complex addition compound of the carbonyl and hydrazine.

6. In this investigation no oxidizing or reducing agents were found which were capable of decomposing the iron pentacarbonyl to give the free element iron. Any oxidizing agent sufficiently strong to decompose the compound also formed a compound with the iron.

7. Iron pentacarbonyl has such a low specific electrical conductivity that it can be considered a non-conductor. None of the solutions made by dissolving a substance in iron pentacarbonyl had a greater electrical conductivity than the carbonyl alone.

8. Iron pentacarbonyl did not react in the vapor state with metallic aluminum or zinc. Its vapor mixed with air will ignite with a slight explosion at a temperature around 120°C. or above. Oxygen bubbled through liquid iron pentacarbonyl caused spontaneous combustion of the vapor accompanied by a detonation.

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