

nickelate(0)²⁴ and tetracyanopalladate(0)²⁵ in which the metals are combined in zero oxidation state; and the lower halide complexes of tantalum and niobium, which contain metallic bonds.²⁶ From the position of platinum in the periodic system, it would appear more reasonable to place the compound in the first class, but some of its properties are more like those of the second class, which are colored, stable in aqueous solution, and highly soluble in ethanol. Chemical evidence at hand is insufficient to warrant an attempt to explain the

(24) J. W. Estes and W. M. Burgess, *THIS JOURNAL*, **64**, 2715 (1942).

(25) J. J. Burbage and W. C. Fernelius, *ibid.*, **65**, 1484 (1943).

(26) P. A. Vaught, J. H. Sturdivant and L. Pauling, *ibid.*, **72**, 5477 (1950).

manner in which the platinum, tin and chlorine are bound in the complex.

Very little evidence was obtained about the lower ratio reaction products and the products of the slow reactions; it is possible that these species may exist as polymers. As yet, it has not been possible to isolate any of the products in crystalline form for making X-ray examination. At least two of the other platinum metals, palladium and rhodium, react in solution with tin(II) chloride to form colored products the properties of which are not compatible with the formation of colloidal metals; a thorough study of these reactions might serve to clarify the observations made on the platinum system.

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[CONTRIBUTION OF BRANCH OF COAL-TO-OIL RESEARCH, BUREAU OF MINES]

The Dissociation of Iron Pentacarbonyl in Certain Amines

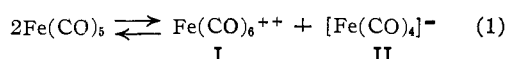
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Evidence for the dissociation of iron pentacarbonyl in certain amines according to $2\text{Fe}(\text{CO})_5 \rightleftharpoons [\text{Fe}(\text{CO})_6]^{++} + [\text{Fe}(\text{CO})_4]^{-}$ is presented and the effect of amine structure on this reaction discussed.

In connection with studies on the mechanism of catalysis by metal carbonyls and hydrocarbonyls, the reaction of iron pentacarbonyl with certain amines was investigated.

It was found that when iron pentacarbonyl is dissolved in piperidine, the solution becomes warm; at the same time it becomes conducting, indicating that ions have been formed. As no carbon monoxide is evolved on mixing of the two compounds and as the solution is diamagnetic, ionization does not involve the formation of ferrous or ferric ions. A postulate consistent with these facts and with the tendency of the metal carbonyls to form structures having the rare gas configuration is that iron pentacarbonyl dissociates in piperidine according to equation I



The effective atomic number of iron in iron pentacarbonyl and in both of the ions I and II is 36, which corresponds to the electronic configuration of krypton. Whereas the existence of anion II in its salts¹ has been described, no prior evidence has been shown for the existence of the positively charged iron carbonyl complex I.

The infrared spectrum of iron pentacarbonyl in piperidine corroborates the presence of these ions. The spectrum of $\text{Fe}(\text{CO})_5$ in cyclohexane solution contains two bands² in the $\text{C}\equiv\text{O}$ triple bond region at 2022 and 2000 cm^{-1} . Both bands disappear when $\text{Fe}(\text{CO})_5$ is dissolved in piperidine; in their place appear two new bands at 1898 and 2016 cm^{-1} . The band at 1898 cm^{-1} may be attributed to II

(1) H. Hock and H. Stulmann, *Ber.*, **61**, 2097 (1928); F. Feigl and P. Krumholz, *Z. anorg. allgem. Chem.*, **215**, 242 (1933); P. Krumholz and H. M. A. Stettiner, *THIS JOURNAL*, **71**, 3035 (1949).

(2) R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, unpublished work.

in view of the fact that cobalt carbonyl anion, $[\text{Co}(\text{CO})_4]^{-}$, which is isoelectronic with II, gives rise to a single band located at the same position.² By elimination, the band at 2016 cm^{-1} must be due to I.

The fact that I and II each give rise to a single band is in agreement with group theory³ which predicts a single infrared active $\text{C}\equiv\text{O}$ stretching frequency for an octahedral⁴ as well as a tetrahedral⁵ metal carbonyl. These predictions were verified in the case of chromium carbonyl,⁴ $\text{Cr}(\text{CO})_6$, which has an octahedral configuration,⁶ and in the case of nickel carbonyl,⁵ $\text{Ni}(\text{CO})_4$, which possesses a tetrahedral configuration.⁷ That I possesses an octahedral and II a tetrahedral configuration is likely as I is isoelectronic with $\text{Cr}(\text{CO})_6$ and II is isoelectronic with $\text{Ni}(\text{CO})_4$.

The Effect of Amine Structure on the Dissociation of $\text{Fe}(\text{CO})_5$.—An insight into the mechanism of the dissociation of iron pentacarbonyl in piperidine may be secured from the conductivity of iron pentacarbonyl in various amines. The data in Table I show that the ability of an amine to cause ionization of iron pentacarbonyl is dependent on two main factors: (a) The availability of the lone pair of electrons on nitrogen for bonding or charge neutralization, a polar effect; and (b) the presence of many or bulky substituents on nitrogen which pre-

(3) The applications of group theory to the determination of molecular structure are described by Gerhard Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(4) R. A. Friedel, S. L. Shufler and H. W. Sternberg, unpublished work.

(5) B. L. Crawford, Jr., and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938).

(6) L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(7) J. Ladell, B. Post and I. Fankuchen, *Acta Cryst.*, **5**, 795 (1952).

vents the pair of electrons from reaching the site of reaction, a steric effect. Brown and co-workers⁸ have shown that the extent of compound formation between an amine and a Lewis acid depends, among other things, upon the steric requirements of both amine and acid. The steric requirements of the amines listed in Table I parallel those studied by Brown for compound formation with the reference acid triisopropylboron, B(*i*-Pr)₃.

TABLE I
MOLAR CONDUCTIVITY OF 0.161 M SOLUTIONS OF Fe(CO)₅
IN VARIOUS AMINES AND IN BUTANOL

Solvent	Specific conductivity, mho/cm.	Molar conductivity, ^a ohms ⁻¹
<i>n</i> -Butylamine	4.02×10^{-4}	0.500
Piperidine	3.99×10^{-5}	.496
Morpholine	2.77×10^{-5}	.344
Diethylamine	2.36×10^{-5}	.294
Benzylamine	5.48×10^{-6}	.068
<i>t</i> -Butylamine	3.67×10^{-6}	.046
4-Picoline	1.69×10^{-6}	.210
Pyridine	6.93×10^{-6}	.086
2-Picoline	1.21×10^{-6}	.015
Pyrrrole	$<10^{-7}$	0
2,6-Lutidine	$<10^{-7}$	0
Triethylamine	$<10^{-7}$	0
Di- <i>n</i> -butylamine	$<10^{-7}$	0
Aniline	$<10^{-7}$	0
<i>n</i> -Butanol	$<10^{-7}$	0

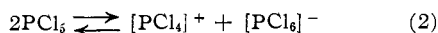
^a The solutions were 0.161 molar with respect to Fe(CO)₅. However, since 2 moles of Fe(CO)₅ is involved in the ionization, molar conductivities are based on 2 moles of Fe(CO)₅, *i.e.*, on a molecular weight of 392.

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

To prove that the ions I and II are strongly complexed with amine, iron pentacarbonyl was treated with excess mono-, di- and trimethylamine at -80° , the excess amine allowed to evaporate, and the residue weighed. With mono- and dimethylamine, the weight increase corresponded to 4–5 moles of amine per mole of iron pentacarbonyl, but with trimethylamine no weight increase was found. The infrared spectra of the residue obtained after treatment with mono- and dimethylamine showed the typical cation and anion bands, whereas the residuum obtained from the treatment with trimethylamine proved to be unchanged iron pentacarbonyl. As indicated, the reactivity of these amines toward Fe(CO)₅ parallels their reactivity toward B(*i*-Pr)₃. Thus, compound formation takes place between mono- or dimethylamine and B(*i*-Pr)₃ but not between trimethylamine and B(*i*-Pr)₃.

Discussion

The dissociation of iron pentacarbonyl (equation 1) may be compared with that of phosphorus pentachloride

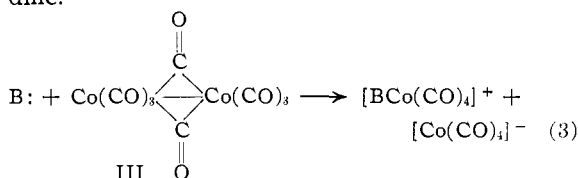


(8) H. C. Brown, *Science*, **103**, 385 (1946); H. C. Brown, *THIS JOURNAL*, **67**, 374 (1945).

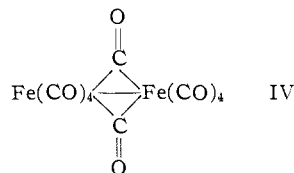
Conductance measurements on solutions of PCl₅ have been reported by Payne, whose data indicate that the extent of dissociation of PCl₅ is determined by the ability of the solvent to stabilize the ionization by complex formation rather than through the effect of its dielectric constant.⁹ The same conclusions may be drawn in the case of Fe(CO)₅. Thus, piperidine with a dielectric constant of 5.8 causes ionization of Fe(CO)₅ whereas *n*-butanol with a dielectric constant of 19.2 does not.

The effect of amine structure on the dissociation of the pentacarbonyl furnishes valuable information as to the mode of action of the solvent. For instance, steric hindrance between amine and Fe(CO)₅⁺⁺ could hardly be of importance if the chief action of the amine were on the carbonyl group of iron pentacarbonyl. However, stabilization of I may be due to the transfer of positive charge from iron to nitrogen by means of complex formation of the "ionic" or "outer complex" type.¹⁰ Since the formation of even a weak bond between nitrogen and iron necessitates a fairly close approach of nitrogen to iron, the configuration of the amine may be expected to play a role similar to that of an amine in compound formation with a sterically-hindered Lewis acid.⁸ Stabilization of II could conceivably be achieved by the transfer of negative charge through hydrogen bonding. Where hydrogen bonding is not possible, as in the case of pyridine, the polarizability of the solvent may play a part in the stabilization of II.

Some insight into the mechanism of the electron and carbonyl transfer involved in equation 1 may be obtained by considering the reaction between dicobalt octacarbonyl and piperidine.¹¹ Dicobalt octacarbonyl, which was recently shown^{2,12,13} to possess the bridged structure III, reacts with piperidine according to equation 3 where B is piperidine.



Similarly, it is conceivable that the dissociation of iron pentacarbonyl takes place *via* a bridged complex such as IV, followed by electron and carbonyl transfer.¹⁴



(9) D. S. Payne, *J. Chem. Soc.*, 1052 (1953).

(10) F. H. Burstall and R. S. Nyholm, *ibid.*, 3570 (1952).

(11) I. Wender, H. W. Sternberg and M. Orchin, *THIS JOURNAL*, **74**, 1216 (1952).

(12) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby and I. Wender, *ibid.*, **76**, 1457 (1954).

(13) J. W. Cable, R. S. Nyholm and R. V. Sheline, *ibid.*, **76**, 3373 (1954).

(14) That the electron transfer is very much more efficient by a bridged activated complex than by other available paths was shown by H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954), in the case of electron exchange between chromium(II) and monochlorochromium(III) ion.

The facile conversion by light of iron pentacarbonyl to enneacarbonyl, which has 3 carbonyl bridges,¹⁵ indicates that bridged complexes are readily formed from $\text{Fe}(\text{CO})_5$.

Experimental

Materials.—Aniline and piperidine, the latter prepared by catalytic hydrogenation of pyridine, were fractionated through a column rated at 90 theoretical plates. *n*-Butylamine was distilled from sodium through a Vigreux column, and a heart cut boiling within 1° was collected. All other amines and *n*-butanol were good quality commercial products that had been shaken with and stored over BaO. Iron pentacarbonyl was a commercial sample¹⁶ of better than 99.5% purity. The specific conductivities of all amines, of *n*-butanol, and of the iron pentacarbonyl were below 10^{-7} mho/cm.

Magnetic Susceptibility.—The susceptibility measurements were made with a Faraday-type magnetic balance¹⁷ adapted for paramagnetic measurements. No paramagnetic effect was noted when a sample of piperidine was replaced by a solution consisting of 1.0 ml. of $\text{Fe}(\text{CO})_5$ and 4.0 ml. of piperidine. The sensitivity of the balance was not sufficient for an exact measurement of the diamagnetic susceptibility.

Conductivity.—The electrodes were smooth platinum and the cell constant was 0.845 cm.^{-1} . A conductivity bridge, Model RC-16B, Industrial Instruments, Inc., permitted the determination of resistance values up to 2.5×10^6 ohm. Forty-five ml. of ice-cold amine was pipetted into the cell which was immersed in an ice-bath, 1.450 g. (1.0 ml.) of $\text{Fe}(\text{CO})_5$ added, and the solution stirred while the surface of the solution was kept under a blanket of nitrogen. The cell was then stoppered and the first reading taken 15 minutes after $\text{Fe}(\text{CO})_5$ had been added to the solvent. The equivalent conductance of some of the solutions changed considerably during the first two hours. In these cases another reading was taken 18 hours after the start of the experiment to determine the extent of the change. In certain amines a precipitate began to form after 6–8 hours, probably due to secondary reactions. These results are summarized in Table II. Except for those cases in which the conductivity did not change during the first two hours, no quantitative significance can be attached to the data. The measurements listed in Table I were made 2 hours after $\text{Fe}(\text{CO})_5$ had been added to the solvent.

Reaction of $\text{Fe}(\text{CO})_5$ with Mono-, Di and Trimethylamine.

—Weighed samples of iron pentacarbonyl were treated with excess amine, the excess allowed to evaporate at room temperature in an atmosphere of nitrogen, and the residue weighed as described previously.¹⁸ With monomethylamine

(15) R. K. Shelton and K. S. Pitzer, *THIS JOURNAL*, **72**, 1107 (1950).

(16) We are obliged to Antara Chemicals, Division of General Dyestuff Corp., for their liberal supply of iron pentacarbonyl.

(17) H. H. Storch, R. B. Anderson, L. J. E. Hofer, C. O. Hawk, H. C. Anderson and N. Golumbic, U. S. Bureau of Mines Tech. Paper 709, pp. 132–137, 1948.

(18) H. W. Sternberg, I. Wender, R. A. Friedel and M. Orchin, *THIS JOURNAL*, **75**, 3148 (1953).

TABLE II
CHANGE OF MOLAR CONDUCTIVITY WITH TIME OF 0.161
MOLAR SOLUTIONS OF $\text{Fe}(\text{CO})_5$

Solvent	Molar ^a conductivity, ohm ⁻¹ , at 0° after hours		
	1/4	2	18
<i>n</i> -Butylamine	0.500	0.500	
Piperidine	.233	.496	1.060
Morpholine ^b	.150	.344	0.760
Diethylamine ^b	.008	.233	.350
Benzylamine	.068	.068	
<i>t</i> -Butylamine ^b	.036	.046	.131
4-Picoline	.051	.210	1.165
Pyridine	.019	.086	0.396
2-Picoline	.008	.015	.018
Pyrrrole	.0	.0	
2,6-Lutidine	.0	.0	
Triethylamine	.0	.0	
Aniline	.0	.0	
Di- <i>n</i> -butylamine	.0	.0	
<i>n</i> -Butanol	.0	.0	

^a The solutions were 0.161 molar with respect to $\text{Fe}(\text{CO})_5$. However since 2 moles of $\text{Fe}(\text{CO})_5$ is involved in the ionization, molar conductivities are based on 2 moles of $\text{Fe}(\text{CO})_5$, *i.e.*, on a molecular weight of 392. ^b Formation of precipitate after standing 6–8 hours.

the weight increase corresponded to 5.5 moles, with dimethylamine to 4.4 moles of amine per mole of $\text{Fe}(\text{CO})_5$. In the case of trimethylamine the residue (4.141 g.) weighed less than the original sample (4.324 g.). This weight decrease was probably due to evaporation of some $\text{Fe}(\text{CO})_5$ with the trimethylamine. The residues obtained from the treatment with mono- and dimethylamine were light yellow, mobile oils whose spectra showed the typical cation and anion bands at 2016 and 1898 cm.^{-1} . The residue obtained after treatment with trimethylamine proved to be unchanged $\text{Fe}(\text{CO})_5$.

Infrared Spectra.—The spectra of 0.161 and 1.48 molar solutions of $\text{Fe}(\text{CO})_5$ in piperidine and *n*-butylamine were determined in a Perkin-Elmer Model 21 spectrophotometer. The spectra were determined within an hour from the time iron pentacarbonyl had been added to amine. The spectra of the 0.161 and 1.48 molar solutions in *n*-butylamine and the spectrum of the 1.48 molar solution in piperidine showed only the presence of the cation and anion bands at 2016 and 1898 cm.^{-1} . In the spectrum of the 0.161 molar solution in piperidine, the anion band was present but the cation band at 2016 cm.^{-1} was obscured by the two bands at 2000 and 2022 cm.^{-1} associated with $\text{Fe}(\text{CO})_5$. An explanation of this phenomenon, *i.e.*, the incomplete dissociation of $\text{Fe}(\text{CO})_5$ in dilute piperidine solution must await further investigation.

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