

succinic acid and a Cr(III) complex of the organic free radical.

In region B the main reaction has been completed and the observed change in absorption can be attributed to the hydrolysis of the red complex. The chromatographic experiments indicate that there are three species in region B. In this region the ranks of the optical density matrices become two. One linear relationship between the concentrations of these species is, therefore, still holding. A very likely explanation is that the hydrolysis involves, as a first step, the change from the chelated succinate complex to the monodentate form. In that case the linear relationship existing between the three species present is the constant ratio between the concentration of the  $\text{Cr}_{\text{aq}}^{3+}$  and the sum of the concentrations of the two forms of the succinate complex. Run 14, where the reaction mixture was exposed to the air after all  $\text{Cr}^{2+}$  had been consumed, also gives a matrix of rank two. After the hydrolysis has been completed (run 20) the rank becomes again one, because there are only two linearly dependent concentrations.

The rank of the matrix for fumaric acid in region A is also one. A mechanism similar to the one proposed for maleic acid, with a slower rate-determining step, is also proposed for fumaric acid. In the maleic ester, chelation, even after the formation of the free radical, is inhibited and the mechanism seems to be different. If

a formally similar mechanism to the one proposed for the acid is also adopted for the ester, it has to be assumed that the intermediate formed in reaction 1 is less reactive toward  $\text{Cr}^{2+}$  than the corresponding intermediate formed with the acid, accumulating and giving, in region A, matrices of rank two. This hypothesis is consistent with runs 18 and 19 of Table I, although a more complicated process cannot be excluded. Hydrolysis, in particular, cannot be excluded. The fact that hydrogen ion concentration does not seem to change during the reaction may simply mean that the amount of  $\text{H}^+$  consumed in the reduction of the double bond equals the amount of  $\text{H}^+$  formed in the hydrolysis.

If the mechanism proposed for the reduction of maleic acid by chromous ion is accepted, it is not surprising that no isomerization to fumaric acid was observed. In the cases where activation for isomerization takes place,<sup>6</sup> evidence has been presented that an intermediate is formed containing both the oxidizing and reducing metal ions, directly bonded to the organic ligand.

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## The Reaction of Metal Carbonyls and Amines. I. Iron Carbonyl with Piperidine and *n*-Butylamine. The Initial Stages of the Reaction<sup>1,2</sup>

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*The reaction between  $\text{Fe}(\text{CO})_5$  and amines was studied with particular attention to the *n*-butylamine and piperidine systems. Three different iron carbonyl species, I-III, have been observed, appearing successively in time in the reaction mixture at room temperature. The infrared bands arising from modes in these species appear about  $100 \text{ cm}^{-1}$  lower than the  $\text{Fe}(\text{CO})_5$  values, indicating the presence of negative charge on the iron carbonyl moiety, but they do not correspond to the values from the known polynuclear carbonylferrates. II is ionic; I is either an ion of low conductivity in piperidine solutions or is nonionic. While the evidence is less certain, III appears to be nonionic. I is formed almost instantaneously in the pure amines but its formation may be reversed to  $\text{Fe}(\text{CO})_5$  and amine by the addition of non-polar solvents. I was identified as  $\text{Fe}(\text{CO})_5(\text{NHC}_5\text{H}_{10})_3$  in the case of piperidine. Its structure and bonding are*

*considered. II was found to be  $\text{HFe}(\text{CO})_4^-$  and the other species formed with it were identified. III is postulated to be  $\text{Fe}(\text{CO})_4(\text{NHC}_5\text{H}_{10})$ . The reaction paths by which these species are formed are considered.*

It has been proposed that  $\text{Fe}(\text{CO})_5$  disproportionates into  $\text{Fe}(\text{CO})_6^{2+}$  and  $\text{Fe}(\text{CO})_4^{2-}$  in various amines such as piperidine.<sup>4</sup> Two infrared bands, 2016 and 1898  $\text{cm}^{-1}$ , were observed for such solutions and were assigned to the first and second ions, respectively. A substance analyzed as  $\text{Fe}(\text{CO})_5 \cdot 3\text{C}_5\text{H}_{10}\text{NH}$  was obtained from the reaction of  $\text{Fe}(\text{CO})_5$  and piperidine at liquid nitrogen temperatures and viewed as a loose association of the reagents which gave the spectrum of unmodified  $\text{Fe}(\text{CO})_5$  and piperidine when dissolved in cyclohexane or ether.<sup>5</sup> It was proposed that the "adduct," when dissolved in piperidine, was converted

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(2) Supported by a contract with the Atomic Energy Commission.

(3) Fulbright Postdoctoral Fellow, 1959-1961.

(4) H. W. Sternberg, R. A. Friedel, S. L. Shuffer, and I. Wender, *J. Am. Chem. Soc.*, **77**, 2675 (1955).

(5) W. Hieber and N. Kahlen, *Chem. Ber.*, **91**, 2223 (1958).

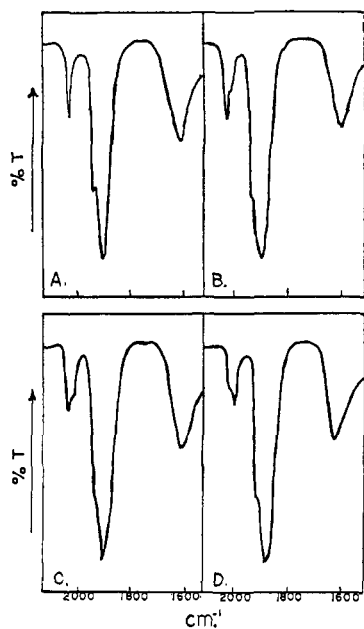


Figure 1. Infrared spectra of the reaction mixture of  $\text{Fe}(\text{CO})_5$  and  $n$ -butylamine at  $25^\circ$ ,  $5\text{-}\mu$  region: A, 1 hr. after mixing; B, after 35 hr.; C, after 53 hr.; D, after 196 hr.

by a disproportionation into the mononuclear carbonylferrate anion and a cationic iron carbonyl complex.<sup>5,6</sup> Attack of the amine on the cationic complex was said to liberate CO and result in the immediate formylation of the amine while the mononuclear carbonylferrate anion was transformed rapidly into polynuclear carbonylferrates.

The above infrared assignments seemed reasonable when proposed. However, molecular orbital considerations of the variation of the participation of the antibonding  $\pi_{\text{CO}}$  orbitals in the bonding of the various metal carbonyl species and the resulting effects upon the infrared spectra<sup>7,8</sup> make it implausible to assign the  $2016\text{-cm}^{-1}$  band to  $\text{Fe}(\text{CO})_6^{2+}$ . Moreover, the  $1898\text{-cm}^{-1}$  band cannot be assigned to  $\text{Fe}(\text{CO})_4^{2-}$  on experimental grounds.<sup>9</sup>

Thus, difficulties and conflicting views exist about the nature of the reaction between  $\text{Fe}(\text{CO})_5$  and amines. This reaction has been studied in this laboratory with particular attention to the piperidine and  $n$ -butylamine systems. Emphasis was placed upon measuring the conductance and the infrared spectrum.

When  $\text{Fe}(\text{CO})_5$  and  $n$ -butylamine were mixed at room temperature, the spectrum, taken within 2 min. after mixing, showed no trace of unreacted  $\text{Fe}(\text{CO})_5$ . Instead, three bands were observed in the carbonyl stretching region of the spectra at 2017 (m), 1921 (m), and 1895 (s)  $\text{cm}^{-1}$ , while bands at 677 (m), 627 (s), and 608 (w)  $\text{cm}^{-1}$  were found in the middle-frequency region. These bands faded with time while bands at 2006 (w), 1913 (m), 1887 (s), 695 (s), 617 (m), and 586 (w)  $\text{cm}^{-1}$  appeared and grew to dominant status. Characteristic spectra of this reaction mixture

(6) W. Hieber and R. Werner, *Chem. Ber.*, **90**, 286 (1957).

(7) W. F. Edgell, Abstracts, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1958; talks before various ACS local sections 1958–1959; Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., 1961.

(8) W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *J. Am. Chem. Soc.*, **82**, 1254 (1960).

(9) John P. Thomas, Ph.D. Thesis, Purdue University, June 1962.

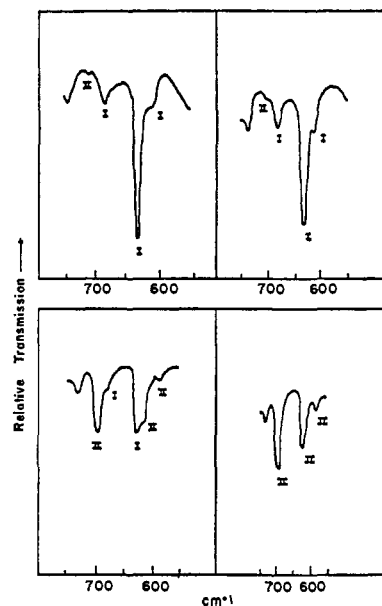


Figure 2. Infrared spectra of the reaction mixture of  $\text{Fe}(\text{CO})_5$  and  $n$ -butylamine at  $25^\circ$ , middle-frequency region: A, 1 hr. after mixing; B, after 3 hr.; C, after 50 hr.; D, after 475 hr.

are shown in Figures 1 and 2. It is possible to make reasonable estimates of the peak intensities of the bands in the  $2000\text{--}2020\text{-}$  and  $575\text{--}700\text{-cm}^{-1}$  regions by correcting for overlap. This is not possible, however, for the bands clustered about  $1890\text{-cm}^{-1}$ . Correction for the moderate variation in sample thickness from run to run was made by taking the ratio of the carbonyl bands to that of the  $1588\text{-cm}^{-1}$  band of the  $n$ -butylamine solvent. The resulting relative intensities for the  $2017\text{-}$ ,  $2006\text{-}$ ,  $695\text{-}$ , and  $627\text{-cm}^{-1}$  bands are plotted against time in Figure 3. Analogous results are obtained for the other bands. The intensities of the bands at  $2017$ ,  $677$ ,  $627$ , and  $608\text{-cm}^{-1}$  decreased with time in a similar manner while those at  $2006$ ,  $695$ ,  $617$ , and  $586\text{-cm}^{-1}$  increased together. Clearly, at least two metal carbonyl species are present. Since there is no positive evidence in these data that requires more than two species, the simplest assumption will be made for the present. The species giving rise to the bands at  $2017$ ,  $1921$ ,  $1895$ ,  $677$ ,  $627$ , and  $608\text{-cm}^{-1}$  is designated as I while that giving rise to  $2006$ ,  $1913$ ,  $1887$ ,  $695$ ,  $617$ , and  $586\text{-cm}^{-1}$  is called II.

The species found in the reaction mixture of  $\text{Fe}(\text{CO})_5$  and  $n$ -butylamine show their main C–O stretching vibrations at frequencies approximately  $100\text{-cm}^{-1}$  lower than those for  $\text{Fe}(\text{CO})_5$ . Shifts in this direction have been shown to result from the presence of negative charge on the metal carbonyl moiety and are due to an increase in the  $\pi_{\text{CO}}^*$  participation in the bonding.<sup>7–9</sup> This charge may be an anionic charge or it may result from the presence of one or more ligands which transfer negative charge to the iron carbonyl moiety. In order to answer the question whether I and II are neutral or ionic, the conductance of the reaction mixture was measured with time at  $25^\circ$ . The molar conductances increased steadily from a value of  $0.500\text{ mho cm}^2/\text{mole}$  obtained 20 min. after mixing to  $3.75\text{ mhos cm}^2/\text{mole}$  obtained 22 hr. later. The conductance increase paralleled the gain in the intensity of the bands associated with II and the decrease in the intensity of those

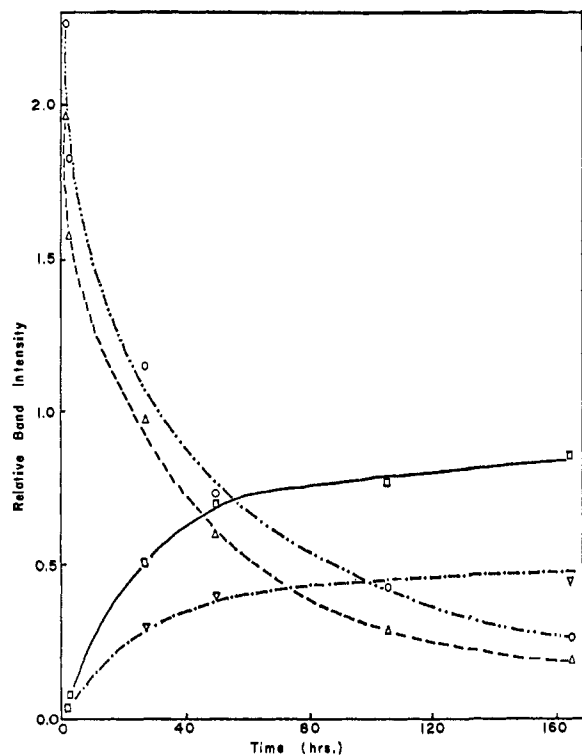


Figure 3. Change of relative intensity of the carbonyl bands of the reaction mixture of  $\text{Fe}(\text{CO})_5$  and *n*-butylamine at  $25^\circ$ : (—)  $695\text{-cm}^{-1}$  band; (---)  $627\text{-cm}^{-1}$  band; (-·-·-)  $2006\text{-cm}^{-1}$  band; (-·-·-)  $2017\text{-cm}^{-1}$  band.

associated with I in the infrared spectra. These data indicate that II is ionic and that I is either nonionic or a slightly conducting ion.

The infrared spectrum of  $\text{Fe}(\text{CO})_5$  in piperidine at 0, 25, 35, and  $60^\circ$  was studied. The results were similar to those obtained with *n*-butylamine, especially at the lower temperatures. Bands in the  $5\text{-}\mu$  region at  $2010$  (m),  $1918$  (m), and  $1895$  (s)  $\text{cm}^{-1}$  were associated with I, while bands at  $1995$  (w),  $1909$  (m), and  $1880$  (s)  $\text{cm}^{-1}$  were assigned to II. The initial intensities of the bands of II were successively stronger with increasing temperature. The decrease in the concentration of I, as measured by band intensities, took place slowly at  $0^\circ$  and became increasingly faster at higher temperatures. For example, I was still observable after 400 hr. at  $0^\circ$  but disappeared completely in 70 hr. at  $35^\circ$  and in 25 hr. at  $60^\circ$ . A third species (designated as III) with bands at  $2038$  (w),  $1945$  (m), and  $1916$  (s)  $\text{cm}^{-1}$  appeared at later stages of the reaction at higher temperatures. III was not distinctly observed after 400 hr. at  $0^\circ$ ; it appeared about 20 hr. after mixing at  $35^\circ$  and after 35 min. at  $60^\circ$ . Figure 4 shows the variation with time of the spectrum in the  $5\text{-}\mu$  region of the mixture at  $60^\circ$ .

No evolution of gas was observed while only I and II were present. Some gas evolution accompanied the appearance of III at elevated temperatures and was identified as CO. No gas was observed at room temperature; however, only small amounts of III were formed in the time interval studied.

The conductance of the reaction mixture of  $\text{Fe}(\text{CO})_5$  and piperidine at  $0^\circ$  was measured at various times after mixing. The initial value was  $0.10$  mho  $\text{cm}^2/\text{mole}$  obtained 20 min. after mixing. It slowly rose to a

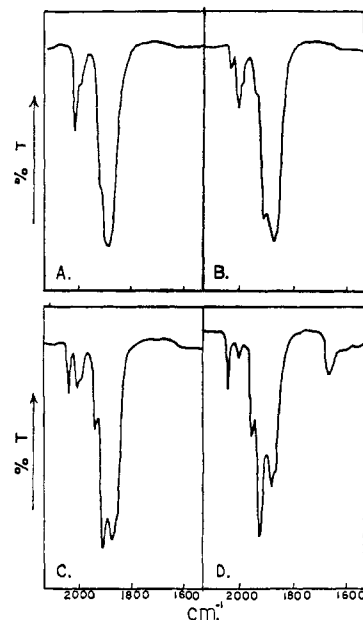


Figure 4. Infrared spectra of the reaction mixture of  $\text{Fe}(\text{CO})_5$  and piperidine at  $60^\circ$ ,  $5\text{-}\mu$  region: A, 3 min. after mixing; B, after 30 min.; C, after 3 hr.; D, after 25 hr.

value of  $0.44$  mho  $\text{cm}^2/\text{mole}$  after 250 hr. although 80% of the increase occurred in the first 25 hr. After 250 hr. II was the dominant species present. The results lead to the same conclusion arrived at in the *n*-butylamine experiment, namely, II is ionic and I is nonionic or a slightly conducting ion. The conductance of  $\text{Fe}(\text{CO})_5$  and piperidine was also measured at  $35^\circ$ . It started (a few minutes after mixing) at a larger value than found at  $0^\circ$ , increased rapidly, and leveled off within an hour. The appearance of modest amounts of III in the later stages of the reaction coincided with a modest decrease in the conductance of the mixture. These results are also consistent with the proposed nature of I and II and suggest that III may be nonionic.

The spectra of species I, II, and III show the presence of negative charge on the iron carbonyl moiety. None of them shows the properties which have been ascribed to  $\text{Fe}(\text{CO})_5 \cdot 3\text{C}_5\text{H}_{10}\text{NH}$  in solution, *viz.*, the spectrum of unmodified  $\text{Fe}(\text{CO})_5$  and piperidine.<sup>5</sup> However, it has been indicated that  $\text{Fe}(\text{CO})_5 \cdot 3\text{C}_5\text{H}_{10}\text{NH}$  was rapidly converted into polynuclear carbonyl ferrates when dissolved in piperidine. Consequently, salts of the polynuclear carbonylferrates were prepared by the methods in the literature<sup>10-13</sup> and analyzed, and their spectra were obtained in dimethylformamide (DMF) for the purpose of comparing with those of species I-III. The results are collected together in Table I.<sup>14</sup> It is clear that neither species I, II, nor III has the same spectrum as any of the polynuclear ions.

The formation of I was demonstrated to be reversible. When a large quantity of a nonpolar solvent, *e.g.*, *n*-heptane or cyclohexane, was added to reaction mixtures of  $\text{Fe}(\text{CO})_5$  and piperidine having I as the dom-

(10) W. Hieber and F. Sonnekalb, *Ber.*, **61**, 558 (1928).

(11) W. Hieber and R. Werner, *ibid.*, **90**, 286 (1957).

(12) W. Hieber, J. Sedlmeier, and R. Werner, *ibid.*, **90**, 278 (1957).

(13) J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 4623 (1960).

(14) The frequencies in piperidine are expected to be within several wave numbers of the values in DMF as shown by solvent studies on the  $\text{HFe}(\text{CO})_4^-$  and the  $\text{Co}(\text{CO})_4^-$  ions.

Table I. Infrared Absorption Bands of Carbonylferrate Anions<sup>a</sup>

$\text{Fe}(\text{CO})_4^{-2}$			1730(s)		
$\text{HFe}(\text{CO})_4^-$	2008(w)	1914(m)	1880(s)		
$\text{Fe}_2(\text{CO})_8^{-2}$		1916(m)	1866(s)	1842(w)	
$\text{HFe}_2(\text{CO})_8^-$	1998(w)	1980(m)	1930(s)	1906(m)	1873(w)
$\text{Fe}_3(\text{CO})_{11}^{-2}$			1941(s)	1913(m)	1884(w)
$\text{HFe}_3(\text{CO})_{11}^-$		2070(vw)	2004(s)	1980(m)	1950(w)
$\text{Fe}_4(\text{CO})_{13}^{-2}$		2030(vw)	1967(s)	1950(m)	1829(vw)

<sup>a</sup> DMF solution; 5- $\mu$  region.

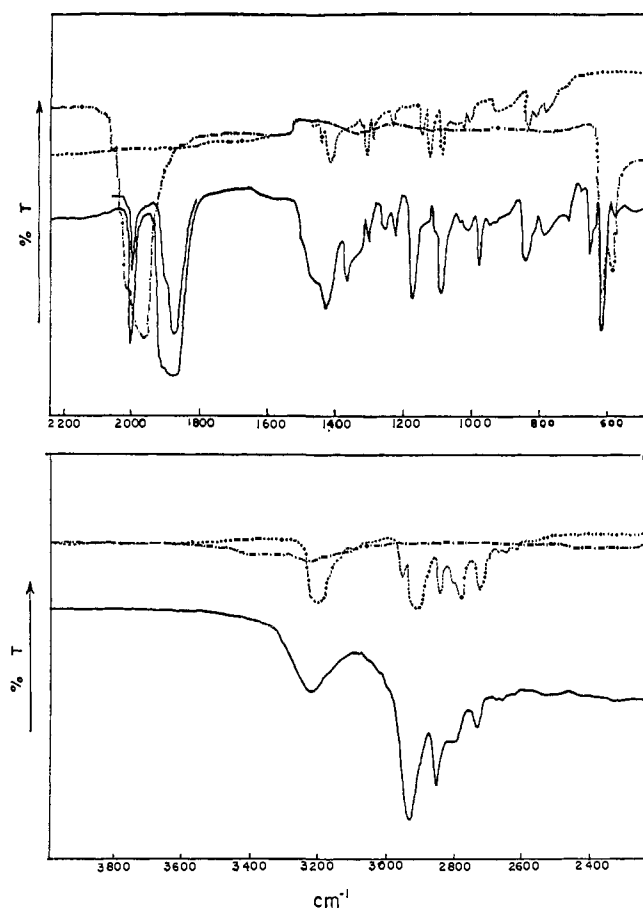


Figure 5. Solid film spectra at  $-78^\circ$ : (—)  $\text{Fe}(\text{CO})_5(\text{NHC}_5\text{H}_{10})_3$ ; (---)  $\text{Fe}(\text{CO})_5$ ; (- - -) piperidine.

inant species present, the spectrum shifted to that of unmodified  $\text{Fe}(\text{CO})_5$  (bands at 2022 (s) and 2000 (vs)  $\text{cm}^{-1}$ ). Thus, the equilibrium in the formation of I from  $\text{Fe}(\text{CO})_5$  and the amine is far to the right in an excess of piperidine and shifts to the left in nonpolar solvents.

These results raise the possibility that the spectrum of  $\text{Fe}(\text{CO})_5 \cdot 3\text{C}_5\text{H}_{10}\text{NH}$  may not be almost the same as that of  $\text{Fe}(\text{CO})_5$  and  $\text{C}_5\text{H}_{10}\text{NH}$ ,<sup>5</sup> but that the compound may dissociate into these substances in those solvents (cyclohexane, ether) which were used to obtain its spectrum. If this were the case, then one of the species observed in the piperidine solution could actually be this compound. The compound was prepared and dissolved in piperidine. The resulting spectrum was an exact replica of that of a freshly prepared mixture of  $\text{Fe}(\text{CO})_5$  and excess piperidine. The spectrum of a solid film of the compound at  $-78^\circ$  was then obtained (Figure 5). It proved to be the same as the spectrum of I. Thus, species I (in piperidine) is fundamentally

the same chemical substance as Hieber's compound,  $\text{Fe}(\text{CO})_5 \cdot 3\text{C}_5\text{H}_{10}\text{NH}$ .

As can be seen in Figure 5, no band corresponding to unaltered  $\text{Fe}(\text{CO})_5$  was observed either in the 5- $\mu$  region or between 550 and 800  $\text{cm}^{-1}$  for the solid  $\text{Fe}(\text{CO})_5 \cdot 3\text{C}_5\text{H}_{10}\text{NH}$ . Many bands corresponding to piperidine were altered and shifted, though the presence of unreacted piperidine could be traced among the weak bands. Moreover, the spectrum of a concentrated liquid reaction mixture containing only small amounts of II in the presence of large amounts of I shows changes in the regions corresponding to NH stretching, NH deformation, and skeletal motions<sup>15</sup> from that of pure piperidine. Now, it has been supposed that the attack of the amine on a cationic complex resulted in the immediate formylation of the amine.<sup>6</sup> This raised the question of whether the modifications of the piperidine spectrum are caused by the presence of formylpiperidine. This compound was prepared and found to have a strong C=O stretching band at 1670  $\text{cm}^{-1}$ . No such band occurred in the above spectra and formylpiperidine is eliminated as the source of the modifications. The conclusion is that amine participates in the bonding. Thus the compound  $\text{Fe}(\text{CO})_5 \cdot 3\text{C}_5\text{H}_{10}\text{NH}$  is not  $\text{Fe}(\text{CO})_5$  and  $\text{C}_5\text{H}_{10}\text{NH}$  loosely held together and essentially unmodified from the starting materials but a substance in which the C-O and Fe-C bonds of the metal carbonyl moiety are substantially modified and in which at least one of the amine moieties participates rather directly. It seems better, therefore, to formulate this compound at present as  $\text{Fe}(\text{CO})_5(\text{NHC}_5\text{H}_{10})_3$ . The question of its structure is considered below.

Several experiments were carried out to shed light on the nature of II and III and on their formation. The rate of the formation of these species with piperidine was found to be affected by the nature of the reaction media. In the presence of a small amount of water, the formation of II is accelerated with the faster consumption of I. When water constituted about half of the reaction medium, no formation of III was observed. In the presence of a nonpolar solvent, e.g., *n*-hexane, the unmodified bands of  $\text{Fe}(\text{CO})_5$  are present and persist for some time with a resulting retardation of the formation of I. The concentration of II was consistently low and III was the main product observed. In the late stages of the reaction, only the spectrum of III was observed. At the same time, a few droplets of immiscible oil settled down to the bottom of the flask. The behavior of II and III in different media agrees well with the finding of the conductance data, viz., II is ionic and III is probably nonionic. Thus the ionic II is predominantly formed in water while III

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 14.

is the main product in *n*-hexane. The immiscible droplets found in the nonpolar solvent are believed to be piperidine solutions of II.

We turn now to the question of the identification of II. Its infrared spectrum in the 5- $\mu$  region resembles that of the  $\text{HFe}(\text{CO})_4^-$  ion in aqueous solution<sup>8,9</sup> except that the band positions are shifted about 20  $\text{cm}^{-1}$  toward lower frequencies. Solutions of  $\text{KHF}(\text{CO})_4$  in piperidine and in *n*-butylamine were prepared according to the method of Edgell and Thomas.<sup>16</sup> The resulting spectra were the same as those of II in the same media both in the 5- $\mu$  region and between 550 and 700  $\text{cm}^{-1}$ . Confirmation of II as  $\text{HFe}(\text{CO})_4^-$  was made by examination of the far-infrared spectra of piperidine-iron carbonyl solutions containing only II. Bands are found at 505 (w), 474 (m), and 346 (w)  $\text{cm}^{-1}$  in this region and correspond to those of  $\text{HFe}(\text{CO})_4^-$ .

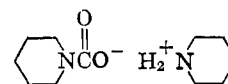
The conductance measurements as well as the effect of solvent character on its formation suggest that III may be nonionic. Since CO evolution was observed along with its formation, we were led to examine the spectra of  $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})_4$ ,  $(\text{C}_6\text{H}_5)_3\text{AsFe}(\text{CO})_4$ , and  $(\text{C}_6\text{H}_5)_3\text{SbFe}(\text{CO})_4$ .<sup>17</sup> Three bands were observed in the 5- $\mu$  region for each of these compounds when dissolved in piperidine or in DMF; the band positions and intensities are: 2046.8 (m), 1974.8 (m), and 1940.5 (s); 2045.8 (m), 1973.1 (m), and 1944 (s); and 2051.1 (m), 1966.4 (m), and 1935.6 (s)  $\text{cm}^{-1}$  for the same order as the compounds are named above. The 5- $\mu$  spectrum pattern of III is quite similar to that of these compounds although its frequencies appear at slightly lower values. Thus, a possibility for III is  $\text{C}_5\text{H}_{10}\text{HNFe}(\text{CO})_4$ . The somewhat lower frequencies in III compared to those in the above compounds can be readily understood. In the phosphine, arsine, and stibine derivatives, the 3d and 4d orbitals of the P, As, and Sb atoms are partly available for  $\pi$ -bonding with the Fe atom, removing some of the charge transferred to the iron carbonyl group by the  $\sigma$ -bonds. In the amine derivative, however, these orbitals would be of relatively higher energy, and one would expect less  $\pi$ -bonding to the iron. The greater accumulation of charge in the iron carbonyl moiety which would result for III would give more  $\pi_{\text{CO}}^*$  participation in the metal carbonyl bonding and hence lower C-O stretching frequencies. For the time being, it is postulated that III is  $\text{C}_5\text{H}_{10}\text{HNFe}(\text{CO})_4$ .

The identification of II as  $\text{HFe}(\text{CO})_4^-$  posed two challenging problems: what has happened to the other CO group of the original  $\text{Fe}(\text{CO})_5$  molecule and, perhaps more puzzling, where did the H atom in the  $\text{HFe}(\text{CO})_4^-$  ion come from? It is questionable whether any likely reaction intermediate here could abstract H from the amine substrate. In any event, no evidence was found for reaction products which might be expected to follow such a reaction step. It should be noted that to follow the reaction spectroscopically, it was necessary to work with quite small amounts of iron carbonyl in large amounts of piperidine. This is due to the very great intensity of the metal carbonyl stretching bands. With these quantities of reactants, traces of water which might have survived the drying process

for the amines might become significant with respect to the quantity of iron carbonyl present. The amines used in the experiments described above had been dried in a standard procedure with fused KOH (method I, Experimental). To investigate the possibility that the H atom in the  $\text{HFe}(\text{CO})_4^-$  might have its origin in such traces of water, a more complex drying procedure (see method II, Experimental) was tried. The results were quite dramatic. In the infrared spectrum of the  $\text{Fe}(\text{CO})_5$ -piperidine system, the bands of II were missing for the first time. At room temperature III appeared slowly, as it had before, with concurrent diminution in the intensity of the bands of I. If, however, a small amount of water was added to a solution of I, the bands of II appeared at once. The behavior of the *n*-butylamine system was analogous. Thus, the evidence points to II as being due to a reaction of I with water. The H atom of the  $\text{HFe}(\text{CO})_4^-$  ion was coming from a water molecule.<sup>18</sup>

The consequences of the absence of traces of water were equally apparent in the conductivity. The *n*-butylamine system, which had showed a conductivity change of 700% in 18 hr., now showed a change of only 9% in the same period. Moreover, the value never rose above that of the initial value obtained in the amine containing traces of water. Similarly, the conductivity in piperidine was nearly constant over a period of 24 hr. at a conductance at 21.5° of 0.15 mho  $\text{cm}^2/\text{mole}$ . This may be compared with the results of Sternberg<sup>4</sup> at 0° which showed an initial value of 0.11 rising to 0.51 after 18 hr. and with Hieber's single measurement of 0.52 at 0° or our own data for solutions in amines dried by method I cited above. It would appear that the conductivities reported by Hieber and by Sternberg are those of mixtures with amines containing traces of water which reacted to form  $\text{HFe}(\text{CO})_4^-$ . In light of the results presented here, one might question whether the conductivity of  $\text{Fe}(\text{CO})_5$  in various amines has yet been established.<sup>4,5</sup>

The question remains as to what had happened to the other CO group of the  $\text{Fe}(\text{CO})_5$  molecule when II was formed. A band at 1540  $\text{cm}^{-1}$  which appeared with II led us to investigate the possibility of a carboxylate group being present in the reaction mixture. It was speculated that this might be the carbamate of piperidine



This compound was prepared and every band in its infrared spectrum in piperidine was found in reaction mixtures containing II. Reaction mixtures more concentrated in  $\text{Fe}(\text{CO})_5$  were prepared and known amounts of water were added. A crystalline product formed which, upon purification, proved to be piperidine carbamate. Quantitative analysis of several such reaction mixtures showed that 1 mole of  $\text{HFe}(\text{CO})_4^-$  and 1 mole of carbamate were formed for every mole of  $\text{Fe}(\text{CO})_5$ . To obtain these results, it was necessary to rigorously exclude oxygen from every operation in the analysis.

(16) W. F. Edgell and J. P. Thomas, to be published; see also ref. 9. Similar results were also obtained with amine solutions prepared by extraction of the ion from aqueous solutions; see ref. 1.

(17) These compounds were kindly supplied by Dr. A. Clifford, Purdue University.

(18) It proved difficult to keep all traces of water out of a system closed with a rubber stopple through which samples were periodically withdrawn for observation. Thus, the strong bands of II could generally be detected in the spectrum after several days but they never grew to prominence when the amine was dried by method II.

**Table II.** Classification of the C–O Stretching Vibrations for Some Possible Structures of I

	Structure	Idealized point group <sup>a,c</sup>	Classification <sup>a,c</sup>
A		D <sub>3h</sub>	E' + A <sub>2</sub> ' + (2A <sub>1</sub> ') <sup>b</sup>
B		C <sub>4v</sub>	E + 2A <sub>1</sub> + (B <sub>1</sub> ) <sup>b</sup>
C		C <sub>2v</sub>	B <sub>1</sub> + B <sub>2</sub> + 2A <sub>1</sub>
D		C <sub>3v</sub>	E + 2A <sub>1</sub>
E		D <sub>4h</sub>	E <sub>u</sub> + (B <sub>1g</sub> + A <sub>1g</sub> ) <sup>b</sup>
F		C <sub>2v</sub>	B <sub>1</sub> + B <sub>2</sub> + 2A <sub>1</sub>
G		C <sub>2v</sub>	B <sub>1</sub> + 2A <sub>1</sub>
H		C <sub>3v</sub>	E + A <sub>1</sub>
J		C <sub>s</sub>	A'' + 2A'
K		C <sub>2v</sub>	B <sub>1</sub> + 2A <sub>1</sub>
L		D <sub>3h</sub>	E' + (A <sub>1</sub> ') <sup>b</sup>

<sup>a</sup> Ligands considered as points and as equivalent to each other. <sup>b</sup> Infrared inactive vibrations enclosed in parentheses. <sup>c</sup> Deviations caused by breakdown of idealizations considered in text.

Sufficient data are available to say something about the structure of I. The most direct evidence is spectroscopic. The shift to lower frequencies of about 100 cm.<sup>-1</sup> from those in Fe(CO)<sub>5</sub> implies the presence of about one unit of negative charge on the metal carbonyl moiety, which has responded by a marked increase in the participation of the π\*-orbitals of the metal carbonyl CO groups. The presence of three piperidine units per Fe(CO)<sub>5</sub> unit in the stoichiometry of solid I does not necessarily mean that all three amines are bonded in the same way. And, of course, some of the original metal carbonyl CO groups may have been converted into other structural units. However, the presence of three infrared bands near 5 μ, not only for solid I but especially for its amine solutions, requires the presence of at least three metal carbonyl type CO groups per molecule and may require more if I is highly symmetrical.

The number of infrared bands expected in this region for structures containing three to five metal carbonyl CO groups may be obtained from Table II. The metal atom has a very small amplitude relative to that of the C and O atoms in vibrations of this type as shown, for example, by the Coriolis constant found in Ni(CO)<sub>4</sub>.<sup>19</sup> Consequently, the effective potential energy for these vibrations contains very little contribution from the portion of the molecule outside of the metal carbonyl moiety. Therefore the relevant ligands (L, L', L'') are treated as equivalent points; only those ligands are shown which tend to define the configuration of the metal carbonyl. The expectations are given for the

(19) W. F. Edgell and R. Moynihan, *J. Chem. Phys.*, **27**, 155 (1957).

basic or idealized structures. Where the ligands are sufficiently bulky or asymmetric to cause deviations from these structures, the effects upon the spectra are expected to be readily recognized perturbations of the basic patterns. Thus, inactive vibrations may appear weakly in the spectra and, to a lesser extent, the type E bands may be split into a pair of very close and almost equally intense bands.

The metal carbonyl group of compound I could have the structure A of Table II if the amine ligands were bound to the iron atom by outer orbitals. In that event, one would expect the basic pattern of infrared bands to be like that of monomeric Fe(CO)<sub>5</sub>.<sup>20</sup> Thus one expects two strong bands separated by roughly 35 cm.<sup>-1</sup> with the possible addition of two quite weak bands, one near the high frequency strong band and the other roughly 115 cm.<sup>-1</sup> to the high frequency side of the first strong band. This is clearly not the pattern and structure A is eliminated. If an amine were added to an Fe(CO)<sub>5</sub> molecule in a way that would bring about a rearrangement into the octahedral configuration, structure B would result. The 5-μ spectra of a number of compounds of this configuration have been discussed.<sup>21-25</sup> These results lead one to expect the pattern: medium (A<sub>1</sub>), strong (E), weak-medium (A<sub>1</sub>) reading from low to high frequency. Sufficient distortion could cause the B<sub>1</sub> mode to appear as a quite weak band between the last two bands and perhaps split the E band. This is not the observed pattern. Both theory and experiment<sup>24,26-29</sup> lead to a pattern of four bands for structure F: medium-strong (B<sub>2</sub>), strong (B<sub>1</sub>), medium-strong (A<sub>1</sub>), weak-medium (A<sub>1</sub>). Although no experimental data are yet available, one expects a similar pattern for structure C. Structures H and L may also be eliminated because they lead to the respective basic patterns: strong (E), medium (A<sub>1</sub>) and strong (E), weak (A<sub>1</sub>). All the remaining structures lead to three bands. E is readily eliminated because one expects strong (E<sub>u</sub>), very weak (B<sub>1g</sub>), very weak-medium (A<sub>1g</sub>) for it. Making use of the fact that a ligand *trans* to a CO in octahedral molecules lowers its force constant leads one to expect the pattern: medium (A<sub>1</sub>), strong-medium (B<sub>1</sub>), weak-medium (A<sub>1</sub>) for G and this is supported by the available data<sup>27,30</sup>; this also disagrees with the observations. The metal carbonyl part of the molecule in structure K is geometrically the same as in structure G. Moreover, replacing two planar CO groups by non-π-acceptor ligands should lower the force constant for the remaining planar CO from that in Fe(CO)<sub>5</sub>. Since the planar (A<sub>1</sub>) and the *trans* (B<sub>1</sub>) modes correspond to the E' and A<sub>2</sub>' modes of Fe(CO)<sub>5</sub>, respectively, this effect should make the A<sub>1</sub>-B<sub>1</sub> frequency difference greater than the E'-A<sub>2</sub>' difference in Fe(CO)<sub>5</sub>. On the other

(20) W. F. Edgell and J. Cengel, to be published; see also *J. Phys. Chem.*, **68**, 452 (1964).

(21) M. A. El-Sayed and H. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962).

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(24) C. S. Kraihanzel and F. A. Cotton, *ibid.*, **2**, 533 (1963).

(25) J. B. Wilford and F. G. A. Stone, *J. Organometal. Chem. (Amsterdam)*, **2**, 371 (1964).

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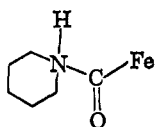
(28) H. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962).

(29) B. Ross, J. Grasselli, W. Ritchey, and H. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963).

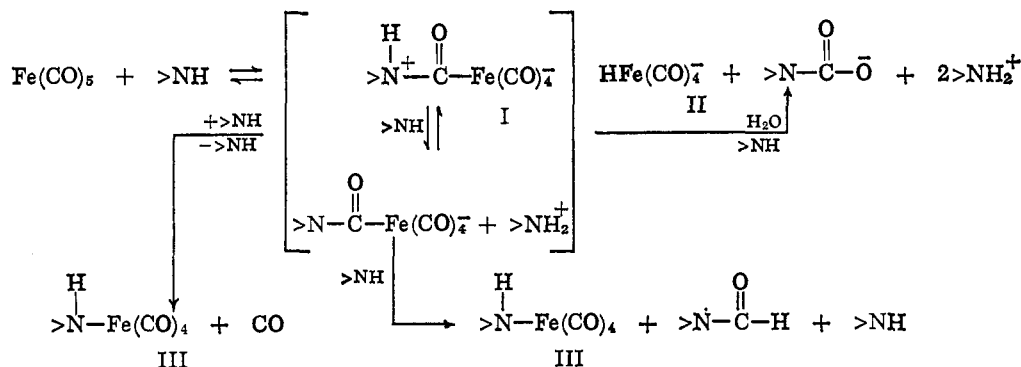
(30) F. A. Cotton, *ibid.*, **3**, 702 (1964).

hand, the effect of the loss of the coupling with the other planar CO groups will be to move the planar  $A_1$  frequency to higher values while leaving the  $B_1$  mode unchanged. Considering the frequency separation in  $\text{Fe}(\text{CO})_5$ , it is probable that the planar  $A_1$  mode will lie at a lower frequency than the  $B_1$  mode to give the pattern: medium ( $A_1$ ), strong-medium ( $B_1$ ), weak-medium ( $A_1$ ) for K. Structure J is an interesting case. Consider the planar CO groups as distorted from a *trans* position relative to each other. Then the considerations should be similar to those for K except that one expects less difference between the force constants. The resultant pattern could be similar to K but might become: strong-medium ( $A''$ ), medium (axial  $A_1$ ), medium (planar  $A_1$ ), in which case it would correspond to the observations. The pattern expected for structure D and found experimentally in compounds of the type  $\text{LFe}(\text{CO})_4$  is<sup>31</sup>: strong (E), medium (axial  $A_1$ ), weak-medium (planar  $A_1$ ). This is in exact agreement with the observations for the substance I. It may be concluded from the above considerations that the metal carbonyl group in I most probably has the configuration D. A less probable configuration is J, while K is an outside possibility.

Turn now to the question of the nature of the ligand L. Since the products of the hydrolysis of I are  $\text{HFe}(\text{CO})_4^-$  and piperidine carbamate, it seems reasonable to formulate it as a compound in which the lone pair on a piperidine nitrogen has attacked a C atom of the metal carbonyl species. The resulting hydrolysis is then postulated as cleaving the C-Fe bond to give the observed products. This formulation of I is consistent with recent calculations<sup>32</sup> that show that the carbon atom is the most electron-deficient point in  $\text{Ni}(\text{CO})_4$ . Such an attack would convert a metal carbonyl CO group into a C=O unit to make the ligand



Spectral evidence for a C=O unit in the molecule is found in the presence of a weak band at  $1640\text{ cm}^{-1}$  in the less dilute solutions of I in piperidine. One cannot be certain of the position of the H atom. To



be sure, the infrared spectrum of solid I shows the presence of an N-H bond but then there are three piperidine units per  $\text{Fe}(\text{CO})_5$  unit in the solid. The position of the  $5\text{-}\mu$  band shows that the iron carbonyl

group bears a unit negative charge and this would place a positive charge on the N atom in the above ligand. Under these conditions the proton might be lost to the basic substrate and then I would be an anion.

With these data, one is led to formulate a different mechanism from that proposed previously.<sup>5,6</sup> In this reaction sequence (see below),  $\text{Fe}(\text{CO})_5$  and amine react almost instantaneously and *reversibly* to form I. In the case of *n*-butylamine the equilibrium position is such that no spectroscopically measurable amount of  $\text{Fe}(\text{CO})_5$  is present. However, with piperidine there is spectroscopic evidence for the presence of a small fraction of the metal carbonyl as unreacted  $\text{Fe}(\text{CO})_5$  at equilibrium. In the presence of water (even traces), I is hydrolyzed to piperidine hydrogen tetracarbonylferrate (II) and piperidine carbamate. III is slowly formed at the expense of I together with gas evolution and the growth of a band at  $1670\text{ cm}^{-1}$ . A mechanism consistent with the data is that I reacts with amine by *two* paths to form III. In one, CO is liberated, and, in the other, formylpiperidine is formed.

Further study of this reaction in these and other systems is in progress.

## Experimental

**Chemicals.** The  $\text{Fe}(\text{CO})_5$  used was a product of Antara Chemicals and was specified as better than 99.5%  $\text{Fe}(\text{CO})_5$ . Impurities in this reagent have been found to be negligible,<sup>33</sup> and it was used without further purification. Purified or reagent grade piperidine and *n*-butylamine were used. In method I, they were dried over fused KOH and distilled in a current of  $\text{N}_2$  immediately before use. In method II they were dried by a sequential procedure involving storage over  $\text{CaH}_2$  for several weeks, transfer to Linde 4A Molecular Sieves for at least 24 hr., and finally deaeration and distillation *in vacuo* onto fresh molecular sieves. All sieves were regenerated before use by heating to at least  $300^\circ$  while pumping. Hexanes and heptanes were freshly distilled over  $\text{LiAlH}_4$  in a current of  $\text{N}_2$ . DMF was dried over anhydrous BaO and distilled in a current of  $\text{N}_2$ . Water which had been passed over Amberlite MB-3 mixed anion-cation-exchange resin was deaerated *in vacuo* before use. All preparations and handlings

of the iron carbonyls were performed under the rigorous exclusion of air.

**Infrared Spectra.** The infrared spectra were taken with Perkin-Elmer Model 421, Model 221, Model 112G,

(31) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).  
 (32) W. C. Nieuwoort, private communication.

(33) R. Summitt, Ph.D. Thesis, Purdue University, Aug. 1961.

or Beckman IR-5A infrared spectrometers. They were equipped, respectively, with an automatically interchangeable double grating coupled with filters, a sodium chloride prism, a grating blazed for  $6\ \mu$  with a sodium chloride foreprism, and a CsBr prism. Absorption bands of atmospheric moisture, DCl gas, and polystyrene film were used for wave length calibration. Demountable KBr and CsBr cells were used for solutions in organic solvents. For mixtures containing water, BaF<sub>2</sub> plates were used as windows. The cell thickness was adjusted freely to obtain sharp, well-resolved bands, except in the quantitative measurements. The first spectrum was taken within 2–6 min. after the reagents were mixed. The subsequent spectra were taken intermittently over a period of several hundred hours.

**Conductance Measurements.** An inductively coupled, ratio arm bridge was constructed by N. K. The initial capacitance balance of the bridge was performed with two variable air condensers (maximum capacitance 130  $\mu\mu\text{f.}$ ) in each side of the bridge. The range of conductance measurement was extended to  $10^{-2}$  mho with an extension decade conductance box. The extension conductor was coupled with a General Radio Co. polystyrene decade capacitor (Type 1419-A) and a General Radio Co. variable air precision capacitor (Type 722-CB) for extended capacitance balance. An R-C oscillator (Type 1210-C) and an amplifier and null detector (Type 1231-B), both of General Radio manufacture, were used as the signal source and the detector, respectively. Power was supplied by a General Radio Co. power supply (Type 1203-B). The conductance was measured at 1 kc.

Two conductance cells consisting of two parallel, bright, platinum electrodes sealed into a spherical glass bulb were used. Two glass outlets, one at the bottom and one at the top of the bulb, were used to facilitate flushing with nitrogen.

**Reaction Mixture of Fe(CO)<sub>5</sub> and Amines.** For the infrared spectra and the conductance measurements, 0.20 ml. (1.48 mmoles) of Fe(CO)<sub>5</sub> was mixed with 10 ml. (ca. 100 mmoles) of the amine. More concentrated samples containing up to 1 ml. of Fe(CO)<sub>5</sub>/3 ml. of piperidine were prepared to get more information about the nature of I. Typical results are shown in Figures 1, 2, and 4.

**Demonstration of the Participation of Piperidine in the Reaction.** Fe(CO)<sub>5</sub> (0.50 ml., 3.7 mmoles) was mixed with 2.0 ml. (20 mmoles) of piperidine at 0°. The resultant spectrum was taken 3 min. after mixing.

**The Effect of a Nonpolar Solvent.** Fe(CO)<sub>5</sub> (0.20 ml.) was added to a mixture containing 20 ml. of *n*-hexane and 10 ml. of piperidine. A spectrum taken within 2 min. showed the presence of II and III along with a large quantity of unreacted Fe(CO)<sub>5</sub> (i.e., two strong bands at 2020 and 2000  $\text{cm.}^{-1}$ ). Complete consumption of Fe(CO)<sub>5</sub> took 2 hr. Meanwhile, droplets of yellow oil settled down to the bottom of the flask. In the supernatant fluid, III appeared to gain intensity very rapidly with the decrease in intensity of II. After 13 hr., virtually only III was observed.

**Demonstration of the Reversibility of the Formation of I.** *n*-Heptane (8.0 ml.) was added to a reaction mixture of 0.20 ml. of Fe(CO)<sub>5</sub> and 2.0 ml. of piperidine at 0°.

Before the addition of *n*-heptane, the spectrum in the  $5\text{-}\mu$  region showed largely I with a slight amount of II. After the addition, the strong bands of Fe(CO)<sub>5</sub> at 2020 and 2000  $\text{cm.}^{-1}$  appeared. Similar results were obtained with cyclohexane.

**Isolation and Characterization of Fe(CO)<sub>5</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>3</sub>.** Fe(CO)<sub>5</sub> (2 ml.) was mixed with 10 ml. of piperidine at 0°. The yellow-orange viscous solution was kept at 0° for 3 days in the dark. A voluminous colorless solid was formed. The spectrum of the supernatant liquid appeared to be the same as that of the freshly prepared mixture at 0°. The solid was washed with several 4-ml. portions of ice-cold piperidine until the washings were colorless. The spectrum of the last washing was similar to that of the original supernatant liquid. The solid was dried by evacuating under high vacuum for 2 hr. The composition of Fe(CO)<sub>5</sub>-(NHC<sub>5</sub>H<sub>10</sub>)<sub>3</sub> was determined spectrophotometrically. Solid I dissociates into its components, Fe(CO)<sub>5</sub> and piperidine, when dissolved in an inert solvent such as cyclohexane. The amounts of these two components in the compound were determined by comparing the intensities of the 740- $\text{cm.}^{-1}$  band of Fe(CO)<sub>5</sub> and the 617- $\text{cm.}^{-1}$  band of piperidine in a cyclohexane solution of the compound with those of solutions containing known amounts of the individual reagents in the same solvent. The molar ratio of piperidine to Fe(CO)<sub>5</sub> in I was thus determined to be 3.3:1.

**Solid Film Spectra of Fe(CO)<sub>5</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>3</sub>.** The solid film spectrum of Fe(CO)<sub>5</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>3</sub> was obtained by subliming the solid onto a KBr plate in a cold temperature cell, which was similar in design to that described by Lord, *et al.*<sup>34</sup> The KBr plate was kept cold with a Dry Ice-trichloroethylene mixture. Solid films of Fe(CO)<sub>5</sub> and piperidine were also laid down in separate experiments, and their spectra were taken for comparison. The results are shown in Figure 5.

**Identification of I as Fe(CO)<sub>5</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>3</sub>.** Solid Fe(CO)<sub>5</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>3</sub> prepared as above was dissolved in piperidine and its spectrum taken immediately. It was identical with the spectrum associated with I in piperidine.

**Preparation of the KHF<sub>e</sub>(CO)<sub>4</sub> Solutions in Amines.** Solid K<sub>2</sub>Fe(CO)<sub>4</sub> was prepared as described previously.<sup>9</sup> Excess solid was shaken with 2.0 ml. of an amine while 0.25 ml. of water was dropped into the mixture. The saturated solutions of KHF<sub>e</sub>(CO)<sub>4</sub> in DMF, piperidine, and *n*-butylamine thus prepared contained only a trace amount of water and K<sub>2</sub>Fe(CO)<sub>4</sub> as shown spectroscopically.

**The Effect of Water on the Reaction between Fe(CO)<sub>5</sub> and Piperidine.** Water (0.1, 1.0, and 5.0 ml.) was added to piperidine to make up 10.0 ml. which was, in turn, mixed with 0.2 ml. of Fe(CO)<sub>5</sub>. In the presence of 0.1 ml. of water, I disappeared in 13 min. I was not observed for the mixtures containing 1.0 and 5.0 ml. of water in the spectra taken within 2 min. after mixing. In all of these mixtures, HFe(CO)<sub>4</sub><sup>-</sup> and piperidine carbamate were always present. III was not observed in these mixtures in the later stages of the reaction.

**Isolation and Identification of Piperidine Carbamate.** Water (0.2 ml.) was added to a solution of I prepared

(34) R. C. Lord, R. S. McDonald, and F. A. Miller, *J. Opt. Soc. Am.*, **42**, 149 (1952).



from 1 ml. of  $\text{Fe}(\text{CO})_5$  and 3.3 ml. of piperidine. Initially, the reaction mixture showed a rise in temperature. White crystals appeared upon gradual cooling to room temperature; these were purified by vacuum sublimation.

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{22}\text{N}_2\text{O}_2$ : C, 61.6; H, 10.3; N, 13.1. Found: C, 60.4; H, 10.6; N, 12.0.

Pure piperidine carbamate was prepared by bubbling  $\text{CO}_2$  through a solution of piperidine and water in ether according to the method of Faurholt, *et al.*<sup>35</sup> The crystals were filtered, dried, and stored in a desiccator containing concentrated  $\text{H}_2\text{SO}_4$ . The infrared spectra in a Nujol mull of crystals prepared in this manner was identical in every respect with that of the crystals isolated from the reaction mixtures. In addition, both compounds melted at 75–77°.

*Determination of Moles of  $\text{HFe}(\text{CO})_4^-$  Formed/Mole of  $\text{Fe}(\text{CO})_5$  Added.* Quantitative analysis for  $\text{HFe}(\text{CO})_4^-$  was performed gravimetrically by precipitating  $\text{Ni}(\text{o-phen})_3(\text{HFe}(\text{CO})_4)_2$ <sup>36</sup> from the reaction mixtures.  $\text{Ni}(\text{o-phen})_3\text{Cl}_2$  in aqueous solution was de-aerated and added to the reaction mixtures until precipitation of the insoluble  $\text{HFe}(\text{CO})_4^-$  derivative appeared to cease. The precipitate was filtered, sucked dry, collected, and weighed. When the precipitation was carried out under  $\text{N}_2$  with the subsequent operations in air, the result was 0.69 mole of  $\text{HFe}(\text{CO})_4^-$ /mole of  $\text{Fe}(\text{CO})_5$ . When all operations were carried out under  $\text{N}_2$ , the results were 0.971 and 0.990 mole of  $\text{HFe}(\text{CO})_4^-$ /mole of  $\text{Fe}(\text{CO})_5$ . It was found that  $\text{Ni}(\text{o-phen})_3(\text{HFe}(\text{CO})_4)_2$  occasionally burns in air, and some caution must therefore be executed in handling this compound and in disposing of samples.

*Determination of Moles of Piperidine Carbamate/Mole of  $\text{Fe}(\text{CO})_5$  Added.* The carbamate analysis was done by a Beer's law plot of a characteristic carbamate

(35) C. Faurholt and A. Jensen, *Acta Chem. Scand.*, **6**, 1073 (1952).

(36) W. Hieber and E. Fack, *Z. anorg. allgem. Chem.*, **236**, 83 (1938).

band at 1250  $\text{cm}^{-1}$ . Several standard solutions containing between 0.04 and 0.07 g./ml. of piperidine carbamate were prepared and their absorbances measured at 1250  $\text{cm}^{-1}$  in a 0.015-mm. path length cell. A plot of  $\log I_0/I$  vs. concentration in g./ml. gave a good straight line of slope 6.7. Typical analyses of reaction mixtures showed 0.99 and 1.0 mole of carbamate/mole of  $\text{Fe}(\text{CO})_5$ .

*Preparation and Spectra of N-Formylpiperidine.* N-Formylpiperidine was prepared by the reaction of piperidine and ethyl formate.<sup>37</sup> N-Formylpiperidine, 0.88 mmole, was dissolved in 10 ml. of piperidine. Infrared spectra were taken using the usual cells used for the spectra of the reaction mixtures of  $\text{Fe}(\text{CO})_5$  and piperidine. In the 0.015-mm. cell, the transmittance of the band center at 1670  $\text{cm}^{-1}$  was approximately 90% and in the 0.05-mm. cell, 67%.

*The 6- $\mu$  Band of N-Formylpiperidine in the Presence of  $\text{Fe}^{2+}$  and Various Solvents.*  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 0.1 mole, was mixed with 0.6 mole of formylpiperidine in the presence of 70 ml. of water. The resulting light green solution was evacuated under a high vacuum. After 3 days, a light brown sirup was obtained. The spectrum of this heavy liquid showed a band at 1640  $\text{cm}^{-1}$  with shoulders at 1655 and 1668  $\text{cm}^{-1}$  indicating that Hieber's assignment of the 1640- $\text{cm}^{-1}$  band to the coordinated formylpiperidine might be correct. However, when 20 ml. of piperidine was added to the sirup, evolution of heat occurred and the spectrum of the resulting dark brown solution showed only a band at 1668  $\text{cm}^{-1}$  which belongs to free formylpiperidine.

*CO Evolution at Higher Temperatures.*  $\text{Fe}(\text{CO})_5$  (1 ml.) was added to 6 ml. of piperidine in a reaction vessel connected to a vacuum system. After heating at 60°, for 50 hr., the reaction mixture was frozen in a liquid nitrogen bath. The noncondensable gas which remained was transferred to a 10-cm. infrared gas cell. Its spectrum was that of carbon monoxide.

(37) M. Auerbach and R. Wolfenstein, *Ber.*, **32**, 2518 (1899).

## Radiation-Induced Ammonolysis of Carbon Tetrachloride

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The major products formed in the  $\gamma$ -radiolysis of carbon tetrachloride and ammonia solutions are ammonium chloride, ammonium dicyanamide, and hexachloroethane. Minor products include cyanoguanidine, guanidine hydrochloride, and nitrogen. The *G* values of these products are as follows: ammonium chloride, 25.3; ammonium dicyanamide, 2.36; hexachloroethane, 2.13; cyanoguanidine, 0.48; guanidine hydrochloride, 0.53; and nitrogen, 0.80. A reaction scheme is given which explains the formation of these products on the basis of a common precursor, cyanogen chloride. Such a precursor seems to account for both the large yield of ammonium chloride and the great abundance of nitrile

groups found in stable products. A comparison with the thermally induced reactions studied earlier by Watt and Hahn reveals that in both cases the same reaction scheme appears to be applicable.

### Introduction

The results of the present studies show that from the  $\gamma$ -radiolysis of simple molecules like carbon tetrachloride and ammonia some unusual and rather complex organic nitrogen compounds can be synthesized. It has been reported<sup>1</sup> that, under normal laboratory

(1) H. H. Anderson, *J. Am. Chem. Soc.*, **74**, 1421 (1952).