Contribution from the Department of Chemistry,
the University of Akron, Akron, Ohio 44304, U.S.A.

Low-Temperature Studies on Dihalogenopentacarbonyliron(II)[1]

M. F. Farona and G. R. Camp

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Infrared spectral studies were carried out on the complexes $Fe(CO)_5X_2$ (X = Br, I, SCN) at temperatures ranging from −70°C to −30°C in CH_2Cl_2 solutions. The results are considerably different from those carried out in $CHCl_3/CH_2Cl_2$ solutions. Infrared and conductivity evidence in CH_2Cl_2 lead to the conclusion that the complexes are 7-coordinate, and possess a trigonal bipyramidal and/or capped octahedral structure. These complexes provide the first examples of mononuclear metal carbonyl compounds in which the effective atomic number is exceeded.

Introduction

The reaction between iron pentacarbonyl and halogens is known to proceed, at dry ice temperatures, by way of an intermediate dihalogenopentacarbonyliron(II) complex.[2] The $Fe(CO)_5X_2$ complexes undergo decomposition at higher temperatures (−35, −10, and 0°C for X = Cl, Br, I, respectively) to give the dihalogenotetracarbonyliron(II) compounds, $Fe(CO)_4X_2$. The tetracarbonyl complexes have been shown, by dipole[3] and infrared studies both in the carbonyl stretching[4] and Fe–C stretching and Fe–C–O bending regions,[5] to possess the *cis* configuration (C_{2v} symmetry). Iron carbonyl also reacts with thiocyanogen at low temperatures to give $Fe(CO)_5(SCN)_2$, but at 0°C this compound decomposes to liberate 5 CO molecules, and a tetracarbonyl complex is not formed.[6]

Until recently, the dihalogenopentacarbonyl derivatives had not been studied in any detail, but they were believed to be ionic compounds of C_{4v} symmetry, namely, $[Fe(CO)_5X]^+X^-$. This structure was deduced solely on effective atomic number (EAN) considerations, and in the above formulation, the EAN around iron is achieved.

While this work was in progress, a paper appeared which described the results of low-temperature infrared spectroscopy on $Fe(CO)_5X_2$ (X = Cl, Br, I) in $CHCl_3/CH_2Cl_2$ solutions.[7]

However, in this study where pure CH_2Cl_2 was used as a solvent, totally different observations were made from those in $CHCl_3/CH_2Cl_2$, leading to different conclusions as to the nature of $Fe(CO)_5X_2$ in the two media.

Experimental Section

Iron pentacarbonyl was obtained from McKay Chemical Company and used without further purification. The halogens employed in this work were of reagent grade. Thiocyanogen was prepared immediately before use in heptane or CH_2Cl_2 solutions from oxidation of $Pb(SCN)_2$ with Br_2.

The complexes $Fe(CO)_5X_2$ (X = Br, I, SCN) were prepared in heptane, from which they precipitate, by mixing solutions of $Fe(CO)_5$ and the appropriate halogen at −78°C. The precipitate was washed with heptane at −78°C several times to remove excess $Fe(CO)_5$, and then dissolved in CH_2Cl_2 at −78°C (only a small amount is soluble at this temperature). The above operations were carried out under a strong stream of dry nitrogen to prevent moisture in the atmosphere from condensing in the reaction mixture. The solution was transferred to the infrared cell, previously cooled to −70°C, in a dry, nitrogen atmosphere glove box, by means of a cooled syringe.

Solutions of the dihalogenopentacarbonyl complexes were also prepared directly in CH_2Cl_2 at −78°C, in one case with excess $Fe(CO)_5$ and a second time with excess halogen. In both cases a voluminous precipitation of $Fe(CO)_5X_2$ occurs, and the compound is only slightly soluble in CH_2Cl_2 at these temperatures. It was therefore necessary to apply ordinate expansion in order to obtain well-resolved infrared spectra. However, spectra of the complexes prepared by the various methods were always reproducible and identical.

Infrared spectra of each of the complexes were recorded several times at temperatures ranging from −70°C to −30°C on a Perkin-Elmer Model 521 Grating Spectrophotometer, using ordinate expansion of 3-5X. The infrared cell used for these studies was a Beckman variable temperature cell with AgCl windows. This cell was cooled by means of dry ice-isopropanol in the refrigerant vessel, and the temperature was calibrated with an iron-constantan thermocouple. The cell has temperature precision of ±0.5°C.

Conductivity studies were carried out at −30°C on an Industrial Instruments Model RCM15 conductivity bridge. The measurements were performed on

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[2] W. Hieber and G. Bader, *Z. Anorg. Chem.*, *190*, 193 (1930), *201*, 329 (1931).

[3] E. Weiss, *Z. Anorg. Chem.*, *287*, 223 (1956).

[4] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961).

[5] M. A. Bennett and R. J. H. Clark, *ibid.*, 5560 (1964).

[6] M. F. Farona and A. Wojcicki, *Inorg. Chem.*, *4*, 857 (1965).

[7] K. Noack, *J. Organometal. Chem.*, *13*, 411 (1968).

10^{-2}-10^{-4} M solutions of the complexes in CH_2Cl_2. A 10^{-3} M solution of $(C_6H_5)_4AsCl$ served as the 1:1 electrolyte standard, for which a value of 30 cm^2 ohm^{-1} mole^{-1} was obtained at −30°C.

Gas evolution measurements were carried out at −78°C by displacing mercury in a gas buret.

Results and Discussion

The only real difference between Noack's and our experimental techniques lies in the choice of solvents. In his study, a 2/3 chloroform/methylene chloride mixture was used as a solvent both in preparing the compounds and recording their spectra; in this work, pure methylene chloride was employed. This seemingly insignificant difference in the choice of solvent gives totally different products in the two investigations.

When $CHCl_3/CH_2Cl_2$ is used, the infrared spectra of the products obtained from the reaction of $Fe(CO)_5$ and Br_2 at −78°C indicates that two materials are present, and these have been formulated as $[Fe(CO)_5Br^+]Br^-$ (**I**) and $BrCOFe(CO)_4Br$(**II**). At about −40°C, **I** is converted entirely to **II**; upon further warming, the stable end product, $Fe(CO)_4Br_2$, is obtained. The distinguishing feature in the spectra of **I** and **II** is a band at 1665 cm^{-1}, which is indicative of the acyl type carbonyl in **II**. When the spectra of $Fe(CO)_5Br_2$ are obtained at various temperatures in pure CH_2Cl_2, then not only are there large differences in the frequencies of the CO stretching bands when compared to corresponding spectra in $CHCl_3/CH_2Cl_2$, but there is a total absence of the band in the 1600-1700 cm^{-1} region at any temperature between −70 and −30°C.

In an effort to resolve the differences between the two studies, we have carried out the reactions in the $CHCl_3/CH_2Cl_2$ mixtures and designed a variety of experiments to show if alternatives to the acyl type carbonyl could lead to the band at 1665 cm^{-1}. It was found that Noack's results are totally reproducible, and the 1665 cm^{-1} band could not be accounted for as arising from a source other than the acyl carbonyl. There is concurrence, therefore, not only with Noack's observations in $CHCl_3/CH_2Cl_2$, but in his interpretation of the data, as well.

Attesting to the differences in the nature of these compounds in the two media is the extremely interesting behavior of $Fe(CO)_5I_2$ at −78°C in the different solvent systems. In $CHCl_3/CH_2Cl_2$, $Fe(CO)_5I_2$ is unstable at −78°C and decomposes rapidly, evolving the theoretical amount of CO with production of the stable $Fe(CO)_4I_2$. However, in pure CH_2Cl_2, $Fe(CO)_5I_2$ exhibited no CO loss at −78°C for periods of at least 30 minutes. It is therefore possible to obtain meaningful spectra of the iodo derivative in CH_2Cl_2 solution, but it is not possible in $CHCl_3/CH_2Cl_2$ solution.

Additional evidence showing that different intermediates are obtained in the two solvent systems is afforded from solubility and color differences. The intermediates are much more soluble in $CHCl_3/CH_2Cl_2$ solution at −78° than they are in pure CH_2Cl_2. It is possible to obtain good infrared spectra in $CHCl_3/CH_2Cl_2$ without employing ordinate expansion; in order to obtain well-resolved spectra in CH_2Cl_2, ordinate expansion must be applied. Furthermore, the colors of the two solutions are different. In $CHCl_3/CH_2Cl_2$ solution, $Fe(CO)_5Br_2$ appears a light yellow orange, whereas its color in pure CH_2Cl_2 solutions is dark orange.

It was also found that in order to obtain Noack's results, $CHCl_3$ must be present at the time of mixing the halogen and $Fe(CO)_5$. When the precipitate of $Fe(CO)_5X_2$, obtained from heptane solutions or CH_2Cl_2 solutions (solubilities of these compounds are relatively low in CH_2Cl_2 solution at −78°C), is dissolved in $CHCl_3/CH_2Cl_2$ solutions, our observations, rather than Noack's, are obtained. If a solution of these compounds in CH_2Cl_2 is added to a $CHCl_3/CH_2Cl_2$ mixture so that the final ratio of $CHCl_3/CH_2Cl_2$ is 2/3, then again, our results are obtained, exclusively. It is apparent, therefore, that chloroform must somehow enter the reaction in the initial stages, and is the determining factor in the outcome of the structure of the intermediates formed. That haloforms can solvate certain species through hydrogen bonding is well known, and has recently been shown in the isolation of $(C_6H_5)_3PCl_2 . CHCl_3$.[8] It is possible that chloroform stabilizes the intermediates through hydrogen bonding, whereas in the absence of $CHCl_3$, different products are formed.

It should be pointed out that Noack also carried out low-temperature spectral studies of $Fe(CO)_5Br$ in CCl_4/C_2Cl_4 mixtures. Spectra obtained in this solution are considerably different from those obtained in either $CHCl_3/CH_2Cl_2$ or pure CH_2Cl_2 solutions, owing to the presence of a relatively large amount of the end-product, $Fe(CO)_4Br_2$. In CH_2Cl_2, two bands in the spectrum of $Fe(CO)_5Br_2$ are coincident with those of $Fe(CO)_4Br_2$, but the relative intensities are not similar. This occurrence in the similarity of frequencies of two bands in the spectra of $Fe(CO)_4Br_2$ and $Fe(CO)_5Br_2$ must be accidental; gas evolution studies show that no significant amount of CO is evolved until the temperature reaches about −10°C. Furthermore, a tetracarbonyl derivative is not obtained from $Fe(CO)_5(SCN)_2$; this compound decomposes at 0°C with loss of all 5 CO molecules, yet the low temperature infrared spectra of the thiocyanate and bromo derivatives are very similar (see Table I and the discussion which follows).

Figure 1 shows the spectrum of $Fe(CO)_5Br_2$ in the 2000-2300 cm^{-1} region at −50°C. It represents an average spectrum between the two extremes at −70° and −30°C. There are small changes in relative intensities of the bands with increasing temperature. The bands appearing in the CO stretching region of the pentacarbonyl complexes in CH_2Cl_2 solution are given in Table I.

The spectrum of $Fe(CO)_5Br_2$ changes with increasing temperature as follows. The 2200 cm^{-1} band does not appear at −70°C, appears as a weak band at about −55°C and remains essentially unchanged to −30°C. The 2164, 2120 and 2095 cm^{-1} bands

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[8] G. C. Arzorimanidis, *Chem. Comm.*, 217 (1969).

Table I. Infrared Spectra $Fe(CO)_5X_2$ Complexes in the Carbonyl Stretching Region in CH_2Cl_2 Solution

Complex	Bands in the 2000-2300 cm^{-1} region					
$Fe(CO)_5Br_2$ [a]	2200 w		2164 m	2150 s	2120 vs	2095 s
$Fe(CO)_5(SCN)_2$ [a]	2188 m	2172 (ν(CN)	2158 ms	2140 s	2125 vs	2110 s
$Fe(CO)_5I_2$ [b]	2158 w, sh		2148 ms	2162 w	2110 vs	2072 m

[a] Recorded at –50°C; [b] Recorded at –70°C Abbreviations: w = weak, m = medium, s = strong, v = very, sh = shoulder

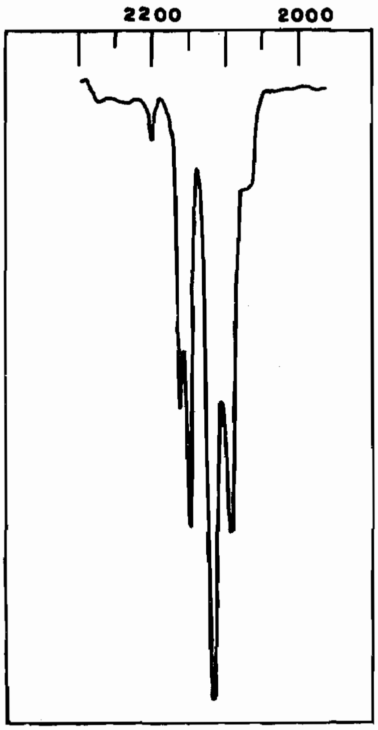

Figure 1. Infrared spectrum in the carbonyl stretching frequency region of $Fe(CO)_5Br_2$ in CH_2Cl_2 solution at –50°C. Ordinate expansion = 3X.

increase at various rates with increasing temperatures while the 2150 cm^{-1} band shows a small decrease in intensity. Analogous changes occur in the spectrum of $Fe(CO)_5(SCN)_2$ with increasing temperatures. Interestingly, the spectrum of $Fe(CO)_5I_2$ shows no relative intensity changes in the bands in the temperature range –70 to –30°C. The changes in the intensities of the carbonyl bands for the bromo and thiocyanato derivatives are not reversible; once the spectrum of these compounds is obtained at –30°C, it is maintained as the temperature is lowered again to –70°C.

If the band at 2172 cm^{-1} in the spectrum of $Fe(CO)_5(SCN)_2$ is assigned to the CN stretching frequency of the thiocyanato group, then the carbonyl stretching bands of the thiocyanate and bromo derivatives are analogous with respect to number, relative intensities, and positions of the bands. It would appear that these two complexes are of analogous structure, but different from that of the iodo derivative, since the infrared spectrum of the latter is considerably unlike those of the former in the CO stretching region. However, the changes in the spectra of the thiocyanato and bromo derivatives with increasing temperature are toward that of the spectrum of the iodo derivative; it appears that at higher temperatures (*ca.*, –30°), the three complexes are of analogous structures.

In an attempt to interpret the infrared spectra in terms of structures of the compounds, it may be immediately concluded that these complexes are not of molecular C_{4v} symmetry (*i.e.*, $[Fe(CO)_5X^+]X^-$), for which three infrared active bands are expected, $2A_1+E$. The fact that at least four CO stretching bands are observed for each complex at temperatures from –70°C to –30°C suggests that the complexes are molecular, rather than ionic, although this does not rule out, in itself, a mixture of ionic and molecular compounds contributing to the overall infrared spectra.

The molecular nature of $Fe(CO)_5X_2$ was confirmed by conductivity studies at –30°C in CH_2Cl_2, in which the compounds are much more soluble at this temperature than at –70°C. Solutions of these complexes in CH_2Cl_2 gave resistance readings which were virtually the same as that of the pure solvent ($>2.5\times10^6\Omega^{-1}$). The equivalent conductances did not change for solutions of these complexes in a range 10^{-2}–10^{-4} *M*. These measurements eliminate the possibility of the presence of ionic species, and the dilution studies rule out the possibility of any ion pair formation for these complexes at low temperature.

The possibility of bridging or acyl type carbonyls is eliminated by examination of the 1600-1900 cm^{-1} region; unlike the results found in $CHCl_3/CH_2Cl_2$ solution, no carbonyl absorption is found below 2070 cm^{-1} in the infrared spectra of these complexes.

There is a remote possibility that the initial products formed in the case of the bromo and thiocyanato derivatives is a halogen type complex, in which the halogen molecule is pi-bonded to the metal through vacant d orbitals on Br or S with non-bonding electrons on iron (no sigma bonding). This extra pi bonding could lead to an increase in the CO stretching frequencies even though iron is still in the zero oxidation state. However, it would seem unlikely that the increase in the CO stretching frequencies could be as large as 150 cm^{-1}. The CO stretching bands for these complexes are in the 2070-2200 cm^{-1} region, similar to those of $Fe(CO)_4X_2$, indicating a +2 oxidation state for iron. In $Fe(CO)_5$, the CO bands occur below 2030 cm^{-1}.

A better explanation, based on the available evidence, is that these complexes are 7-coordinate, and that the geometrical arrangement could be a pentagonal bipyramid where the halide ions occupy *cis* positions in the equatorial plane (C_{2v} symmetry). However, this structure cannot be distinguished from a « capped octahedral » arrangement[9] on the basis of infrared spectra alone, since group theoretical considerations predict 5 infrared CO bands to be active for both structures. In fact, in the sole x-ray structural determination of a 7-coordinate metal carbonyl complex, the compound was found to possess the capped octahedral structure.[10]

We feel that the changes in the spectra of the bromo and thiocyanato complexes represent a change in structure from a pentagonal bipyramid to a capped octahedron, or vice versa. The iodo complex assumes one structural arrangement at low temperatures, while the others show an initial, kinetically favored form and alter their structures with increasing temperatures to one similar to that of $Fe(CO)_5I_2$.

If these complexes are, indeed, 7-coordinate, then they provide the first examples of mononuclear metal carbonyl compounds in which the effective atomic number of the metal is exceeded. This means that the two « excess electrons » must be in antibonding orbitals, and this fact, perhaps, explains the extreme instability of the pentacarbonyl derivatives.

It is extremely unlikely that these complexes are anything other than mononuclear in nature. The conclusion is based not only on the lack of evidence for bridging CO groups, but also on the fact that bridging halogens or metal-metal bonds would require an even greater violation of the EAN rule than the mononuclear formulation.

The thiocyanato complex is tentatively assigned the S-attachment, mostly on the basis of negative evidence. Although the 680-720 and 780-860 cm^{-1} regions are somewhat obscured by solvent bands, no evidence of a CS stretch in the 780-860 cm^{-1} region was found, which suggests that the iron-thiocyanate attachment is through sulfur.

(9) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London) *21*, 130 (1967).
(10) M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Am. Chem. Soc.*, *90*, 2189 (1968).