[CONTRIBUTION FROM THE INSTITUTE FOR NUCLEAR STUDIES, UNIVERSITY OF CHICAGO]

The Spectra and Structure of Iron Carbonyls. II. Iron Tetracarbonyl

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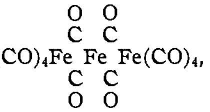
The infrared absorption spectra of iron tetracarbonyl were obtained with NaCl prism optics over the region 2–15 μ and the visible and ultraviolet absorption spectra of iron carbonyl, iron enneacarbonyl and iron tetracarbonyl were taken from 2180–7000 Å. Narrowing of the extremely intense band beyond 2180 Å. in $Fe(CO)_5$ when it is cooled so that the tail of this band does not appear in the visible is hypothesized as the explanation for the disappearance of color in $Fe(CO)_5$ when it is cooled to −196°.

A D_{2d} structure for iron carbonyl,  $(CO)_4Fe\overset{\overset{O}{C}}{\underset{\underset{O}{C}}{}}Fe\overset{\overset{O}{C}}{\underset{\underset{O}{C}}{}}Fe(CO)_4$, is strongly indicated by a diamagnetic susceptibility, by X-ray diffraction studies, by the presence of a ketone like carbonyl band at 1833 cm.$^{-1}$, and by the existence at 2835 Å. of a forbidden electronic transition found in aldehydes and ketones. The diversity of the physical properties of the iron carbonyls, the unusual solubility of iron tetracarbonyl and the 6080 Å. transition all support the D_{2d} structure. Evidence is presented which suggests a Fe–C–Fe bond angle of approximately 90° in the bridge carbonyl and a carbonyl bond which is very much like that in organic aldehydes or ketones with considerable ring strain. Finally the evidence indicates that the end carbonyls are little modified carbon monoxides bonded to the iron atoms.

In the first article of this series[1] the infrared spectra of iron carbonyl, $Fe(CO)_5$, and iron enneacarbonyl, $Fe_2(CO)_9$, were observed and found to be in substantial agreement with the electron and X-ray diffraction, respectively. In the case of iron tetracarbonyl, $Fe_3(CO)_{12}$, even the gross geometrical structure is lacking. It is therefore the purpose of this investigation to determine a structure for iron tetracarbonyl and to interpret if possible some of the finer details such as the nature of the bonding within the carbonyl groups.

Since the infrared spectra proved to be unique in confirming the structure of iron enneacarbonyl, it seemed advisable to obtain the infrared spectrum for iron tetracarbonyl. The diversity of color in the three compounds suggests that the comparison of their visible and ultraviolet spectra might be revealing. Accordingly the infrared, visible and ultraviolet spectra were obtained for iron tetracarbonyl.

Experimental

(a) **Preparation of Sample.**—The iron tetracarbonyl was prepared from iron enneacarbonyl which had previously been prepared from iron carbonyl by the following sequence. Ten cc. of purified $Fe(CO)_5$ was dissolved in 40 cc. of reagent grade ether dried with sodium or in glacial acetic acid. This solution was sealed off in an evacuated tube and exposed to the sunlight or a photo flood light. It was found that the yield of iron enneacarbonyl could be considerably increased if the evacuated tube were placed in an ice-bath so arranged as to allow a maximum light intensity to pass through the ice-bath into the $Fe(CO)_5$ solution. After a 6–10-hour exposure to the light source, the iron enneacarbonyl was filtered and washed with additional solvent. $Fe_2(CO)_9$ and sodium dried toluene were then placed in a carefully dried and evacuated tube (1 g. of $Fe_2(CO)_9$ for every 20 g. of toluene). The tube was heated to 90° and allowed to cool slowly. The dark green or black prisms of iron tetracarbonyl were filtered and recrystallized from toluene or acetone.

(b) **Infrared Spectrum.**—Measurements were made on a saturated solution in toluene and on the solid using a liquid cell fitted with KBr windows and the Perkin–Elmer 12B automatic prism spectrometer. All spectral data were obtained at room temperature. The calibration of the spectrometer was checked several times during the period of operation and the data from it are probably accurate to ±8 cm.$^{-1}$ at 2000 cm.$^{-1}$. The absorption curve is given in Fig. 1. In the case of the solid spectrum the iron tetracarbonyl was ground into a fine powder and spread uniformly over the KBr plate. The usual Christiansen filter effect is observed in Fig. 1. The spectrum of solid $Fe_2(CO)_9$ is included in Fig. 1 for comparison. The similarity with the exception of relative intensities is very great. The greater complexity of the solid spectrum band over that of the solution at ∼ 2000/cm.$^{-1}$ is unexplained.

(c) **Visible and Ultraviolet Spectra.**—Measurements were made on all three carbonyls with both the Carey and the Beckman spectrophotometer. These spectra are shown in Figs. 2 and 3. In the case of $Fe(CO)_5$ solutions of three different concentrations, 1.9×10^{-5}, 4.75×10^{-4} and 1.19×10^{-2} molar in isoöctane were run. With the exception of a band at about 2480 Å. with an extinction coefficient of approximately 3700 the visible and ultraviolet spectrum of $Fe(CO)_5$ decreases monotonously. The orange color of iron carbonyl is only the tail of extremely strong band which lies somewhere beyond 2180 Å. However, it would appear to be precisely this point which would explain the interesting decolorization of $Fe(CO)_5$, as it is cooled down to −196°. As shown in Fig. 2 with the dotted line, it is highly probable that this color change is the result of a very slight amount of narrowing of the very intense band beyond 2180 Å. so that its tail does not extend into the visible. The results for finely ground $Fe_2(CO)_9$ are disappointing in that very little structure is observed. It seems highly probable that the nature and uniformity of the solid film are quite inadequate for the experiment. Finally the spectra of iron tetracarbonyl have two bands not appearing in the $Fe(CO)_5$ spectra. These bands will be discussed in detail in a later part of this paper.

Discussion

Hieber,[2] Brill[3] and others have proposed various structures for iron tetracarbonyl. The three most promising of these structures are shown in Fig. 4 (3, 4 and 5). Certain physical information other than spectra is available for the structural analysis. Freudlich and Cuy,[4] Berkman and Zocher,[5] and Cutforth and Selwood[6] have all shown that iron tetracarbonyl is diamagnetic. The susceptibility when corrected for ferromagnetic impurity is -0.07×10^{-6}. This criterion alone makes structure 3 of Fig. 4 highly improbable. In structure 3 (Fig. 4) the central iron obtains one electron from the covalent bond with each of the other two iron atoms. Therefore it has 26 + 8 = 34 electrons, two short of filling the 4*p* orbitals to complete to

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[1] R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950). Herewith designated I.

[2] W. Hieber and E. Becker, *Ber.*, **63B**, 1405 (1930).

[3] R. Brill, *Z. Krist.*, **77**, 36 (1931).

[4] H. Freudlich and E. J. Cuy, *Ber.*, **B56**, 2264 (1923).

[5] S. Berkman and H. Zocher, *Z. physik. Chem.*, **124**, 318 (1926).

[6] H. G. Cutforth and P. W. Selwood, THIS JOURNAL, **65**, 2414 (1943).

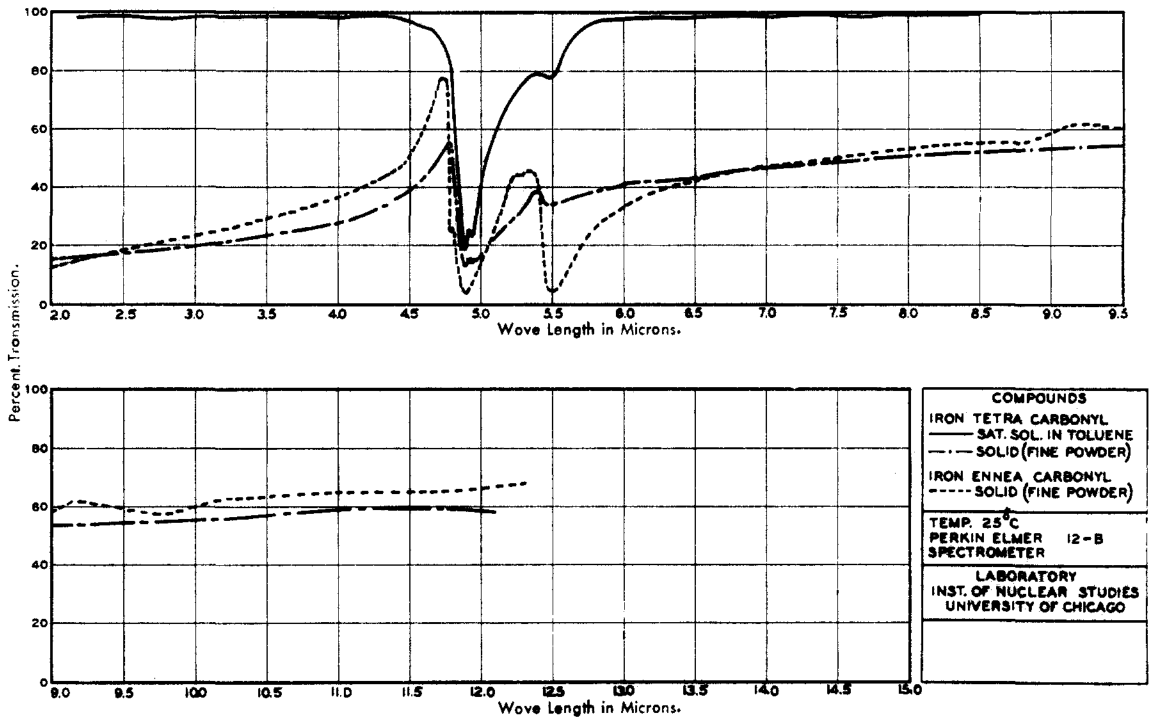

Fig. 1.—The infrared spectra of iron enneacarbonyl and iron tetracarbonyl.

the krypton structure. Structure three would be paramagnetic unless the unusual antiparallel pairing of electron spins occurs rather than the more normal filling of the p orbitals one at a time. In iron enneacarbonyl, Fig. 4 (2), the arrangement of the CO's about the irons is very similar to that of the central iron in structure 3 of iron tetracarbonyl. If antiparallel pairing occurs in the central iron atom of the iron tetracarbonyl molecule, a dsp^2 hybridization with a different arrangement of CO's should obtain. The choice between a hybridization scheme which will not give structure 3 or one which gives paramagnetism in the face of observed diamagnetism leaves no alternative but to discard structure 3 in spite of its interesting structural analogy to iron enneacarbonyl. Anderson[7] has stated that the observed diamagnetism of iron tetracarbonyl violates structure 5 also because the central iron atom has an effective atomic number of 30 which Anderson suggests would be paramagnetic. However, on closer scrutiny it becomes obvious that an effective atomic number of 30 for the central iron atom will leave it diamagnetic. Twelve electrons beyond the argon closed shell structure of 18 added in the normal way to the $3d$, $4s$ and $4p$ orbitals fill up completely through the $4s$ orbital and leave the $4p$ orbitals completely empty giving a ^1S diamagnetic configuration for the iron. Therefore structure 5 is not excluded by magnetic criteria. Brill[3] has done a crystal analysis on iron tetracarbonyl. He finds that it crystallizes in a monoclinic prismatic crystal in group C^6_{2h}. The dimensions of the unit cell are a = 13.00 Å., $b = c$ = 11.41 Å. Since Brill's work was done without taking account of the diamagnetism, he suggests that either structure 3 or 5 would satisfy his data. However, he favors structure 5 because the square pyramids would pack in such a way as to give 2 equal sides in the unit cell as observed.

The infrared spectra of iron tetracarbonyl in Fig. 1 indicate the usual strong carbon monoxide type carbonyl bands at 2020 and 2043 cm.$^{-1}$. They also indicate that there is a ketone-like carbonyl band at 1833 cm.$^{-1}$. This corresponds very closely to the bridge ketone carbonyl in iron enneacarbonyl at 1828 cm.$^{-1}$. In the ultraviolet spectrum of iron tetracarbonyl there is a weak band at 2835 Å. with an extinction coefficient of approximately 400 which does not occur in the ultraviolet spectrum of $Fe(CO)_5$. This is the precise region in which one expects the forbidden non-bonding electron transition ($n \rightarrow \pi^*$) for ketone carbonyls. If one considers the fact that there are four ketone bridge carbonyls in structure 5, this would give an extinction coefficient of 100 per carbonyl group. This is a very reasonable value for this forbidden transition and establishes in conjunction with the infrared data the strong probability that iron tetracarbonyl contains ketone like bridge carbonyls. Since this criterion eliminates structure 4 and structure 3 has been eliminated by a magnetic criterion, structure 5 seems to be the correct structure by default. It should be pointed out here that the fact that no higher member of the series of iron carbonyls has been found suggests termination of the series by ring closure (structure 4). However, the number of additional factors which structure 5 appears to satisfy is significant. For example, the series of carbonyls have such different physical properties. The correct structures for the carbonyls (1, 2 and 5) indicate a diversity of structure which might be expected to show a diversity of physical properties. In particular it seems strange that

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(7) J. S. Anderson, *Quart. Rev.*, **1**, 355 (1947).

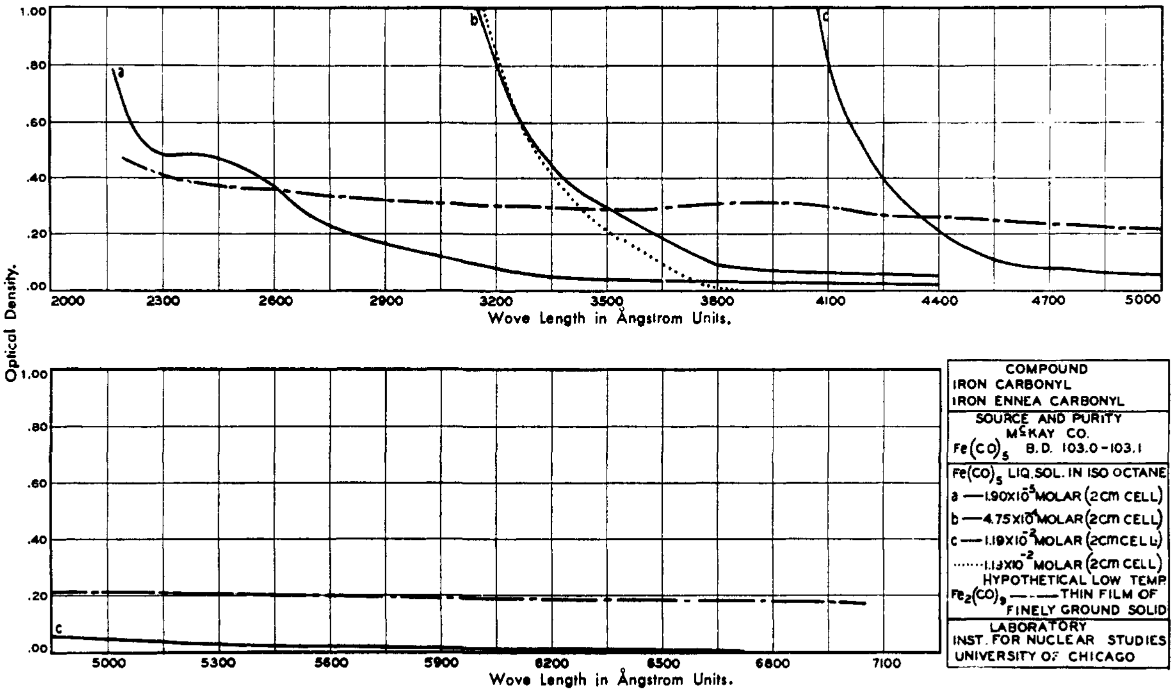

Fig. 2.—The visible and ultraviolet spectra of iron carbonyl and iron enneacarbonyl.

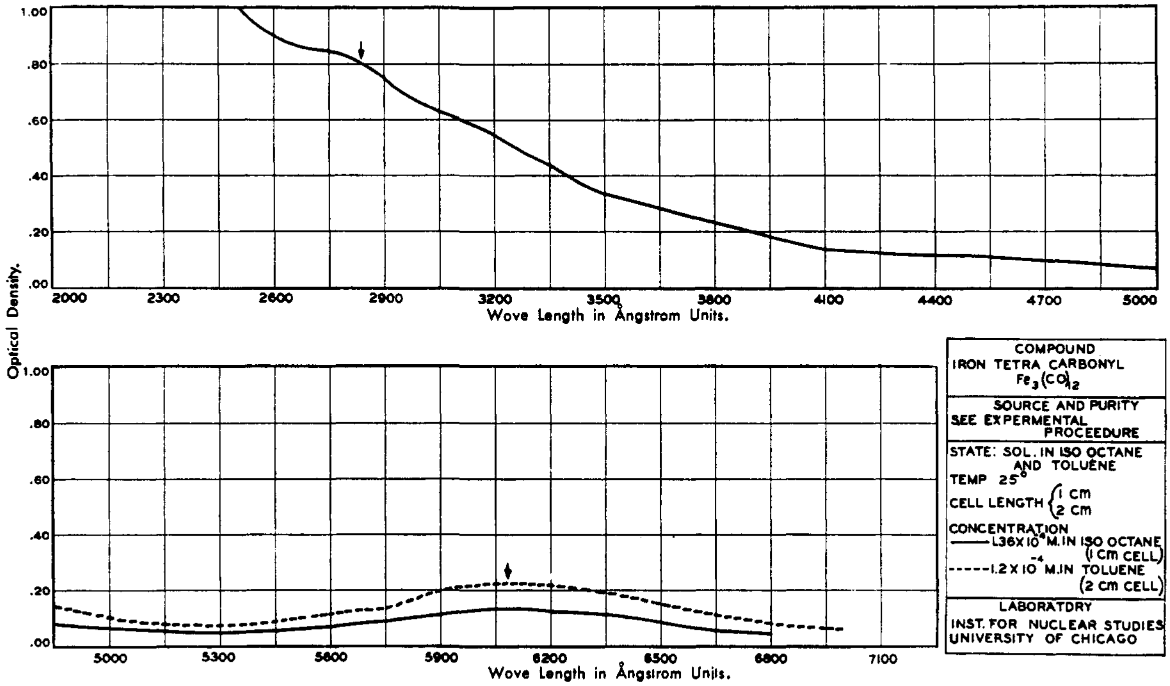

Fig. 3.—The visible and ultraviolet spectra of iron tetracarbonyl.

iron tetracarbonyl should be soluble in so many organic solvents whereas iron enneacarbonyl, also a solid containing ketone and carbon monoxide type carbonyls, should be so insoluble. It is possible that the three empty 4*p* orbitals of the central iron atom of iron tetracarbonyl offer to the solvent a convenient set of non-specific bonding orbitals with which it can solvate this molecule. The three empty *p* orbitals are interesting in another regard. The band at 6080 Å. in iron tetracarbonyl is unexplained. It is possible that it is the transition of one of the electrons from the 4*s* to the energetically easily available 4*p* orbitals. Since the central iron is perturbed by four electrons more than a neutral iron atom, it is not easy to suggest what energy a transition from a 4*s* to a 4*p* orbital would require. However, as a first approximation we might look at iron itself. The lowest 4*s* to 4*p* transition in iron as listed by Bacher and Goudsmit[8] is 19,350 cm.$^{-1}$ whereas 6080 Å. corre-

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[8] R. F. Bacher and S. Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., Inc., New York, N. Y., 1932.

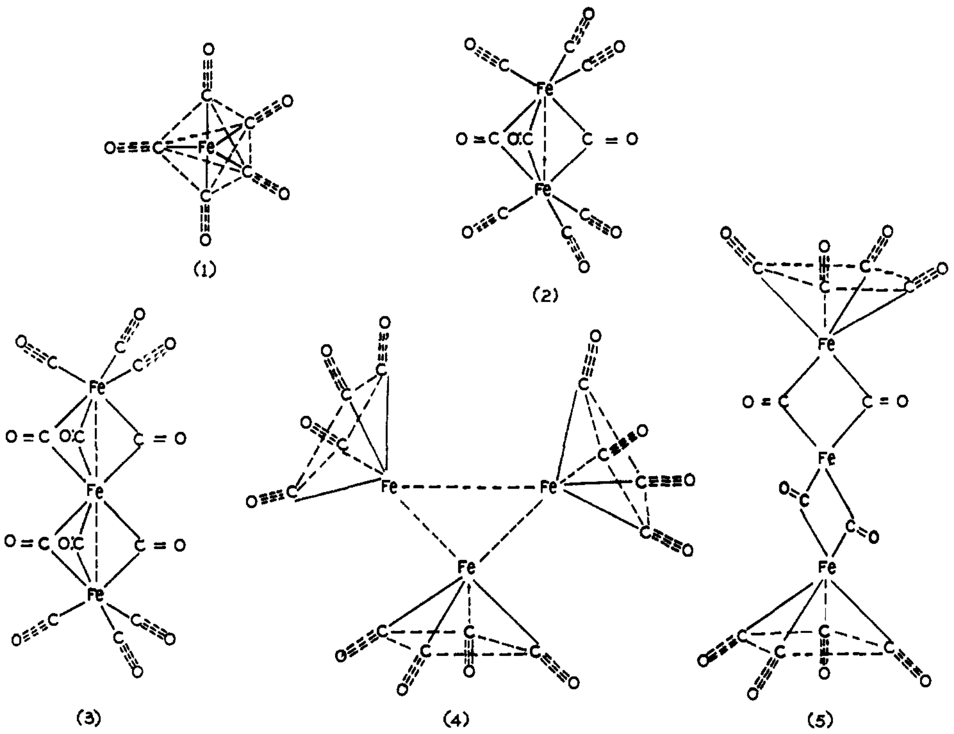

Fig. 4.—Iron carbonyl structures.

sponds to 16,350 cm.$^{-1}$. It is therefore not unreasonable to expect that the transition at 6080 Å. may be a $4s$–$4p$ transition in a somewhat perturbed iron atom. With this body of supplementary information it is very probable that the D_{2d} structure shown in Fig. 4 (5) is correct.

Carbonyl Bond Angle and the Nature of the Carbonyl Bond

Rasmussen and Brattain[9] have given the infrared carbonyl stretching frequencies for ketones and lactones. Their pertinent data indicate that the CO stretching frequencies increase regularly as the ring angle decreases. This is even more evident in work on the infrared spectra of 4, 5 and 6 membered lactam rings.[10] Powell and Ewens[11] in their X-ray diffraction found a $\rangle$C=O angle in the carbonyl bridge of 87°. It is therefore not surprising that the carbonyl stretching frequency is 1828 cm.$^{-1}$ in $Fe_2(CO)_9$. In fact it fits in surprisingly well with the data of Rasmussen and Brattain. Since the bridge carbonyl stretching frequency in iron tetracarbonyl is 1833 cm.$^{-1}$, very close to that in $Fe_2(CO)_9$, it is probable that the bond angles Fe–C–Fe are approximately 90°. It is also highly probable that the bridge carbonyls in both iron enneacarbonyl and iron tetracarbonyl are very much like those in organic ketones or aldehydes in which there is considerable ring strain. It is to be noted that the stretching frequencies of the end carbonyls at 2020 and 2043 cm.$^{-1}$ are similar to that of carbon monoxide at 2155 cm.$^{-1}$. Furthermore any structure for iron tetracarbonyl which gives pure or high percentage double bond character to the carbonyl group forces additional electrons on the outer irons and destroys the hybridization scheme. It is therefore probable that the two sets of four end carbonyls are little modified carbon monoxides coördinately bonded to the irons.

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(9) R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

(10) R. R. Brattain, Shell Development Co., Emeryville, Cal., private communication.

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