also was obtained which, however, contained no nitrogen, and the triphenylamine was recovered unchanged.

Bis-(triphenylphosphine)-dicarbonyliron(III) pentaiodide.—A solution of iodine (2 g.) in anhydrous ether (100 ml.) was added drop by drop with stirring to a suspension of $((C_6H_5)_3P)_2Fe(CO)_3$ (1 g.) in 75 ml. of ether over a period of 30 min. The mixture then was stirred for 15 min. more. The chocolate-brown precipitate then was filtered, washed thoroughly with ether until the washings were colorless, and then vacuum-dried; yield, 1.85 g.; m.p. 121–122° dec. *Anal.* Calcd. for $((C_6H_5)_3P)_2Fe(CO)_2I_5$: Fe, 4.39; I, 49.93; mol. wt., 1271. Found: Fe, 4.33; I, 50.2; mol. wt., 1248 ± 1.5 (determined cryoscopically in nitrobenzene). The stoichiometry and slightly low molecular weight (indicating some ion-pair dissociation) suggest that the compound may be $(((C_6H_5)_3P)_2Fe(CO)_2I_2)I_3$.

Acknowledgment.—This work was supported by U. S. Borax Corporation and Sub-contract No. 3 under U. S. Air Force Contract No. AF 33 (616) 5931.

CONTRIBUTION FROM THE R. G. WRIGHT LABORATORY AND NUCLEAR SCIENCE CENTER,
RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, NEW JERSEY, AND
THE BELL TELEPHONE LABORATORIES, MURRAY HILL, NEW JERSEY

Mossbauer Effect in Iron Pentacarbonyl and Related Carbonyls

BY R. H. HERBER, W. R. KINGSTON, AND G. K. WERTHEIM

Received June 29, 1962

Four related iron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Fe(CO)_4I_2$, have been used as stationary absorbers in a Mössbauer experiment in which Co^{57} diffused into metallic chromium was employed as a source. All four absorbers show significant resonance absorption of the 14.4-kev. γ-ray of Fe^{57} at 78°K. The observed isomer shifts are interpreted in terms of the chemical bonding in transition metal–carbonyl compounds. The two major Mössbauer parameters (isomer shift and quadrupole splitting) in the case of $Fe(CO)_5$ and $Fe_2(CO)_9$ are in agreement with a trigonal bipyramid structure and a (3,3,3) structure, respectively. The data for $Fe_3(CO)_{12}$ strongly suggest the linear (3,3,3,3) structure and cannot be accounted for by the trigonal arrangement of the three iron atoms which has been proposed on the basis of X-ray data. The quadrupole splitting for $Fe(CO)_4I_2$ is essentially independent of temperature in the range 78 to 298°K., in contrast to the large temperature dependences which have been observed for some related Fe(II) compounds. The isomer shift is consistent with an assignment of +2 for the oxidation state of iron in this compound.

Introduction

As part of a continuing investigation[1–4] of the resonant absorption of γ-radiation in solids (Mössbauer effect), a number of iron carbonyl compounds have been studied as stationary absorbers at various temperatures.

The choice of iron carbonyl compounds as absorbers was prompted by the fact that a portion of the $Fe(CO)_n$ framework of these molecules survives in a number of the reactions which iron carbonyl compounds undergo, especially with olefinic hydrocarbons. Consequently, the eventual interpretation of the resonance spectra of these adducts, such as the $C_8H_8Fe(CO)_3$ and $C_8H_8[Fe(CO)_3]_2$ molecules reported earlier,[3] requires detailed knowledge regarding the contributions of the carbonyl groups to the characteristic parameters which can be extracted from the resonance data. In terms of molecular structure, the two parameters of major interest are the isomer shift, i.s., and the quadrupole splitting, ΔE.[5–7]

The isomer shift arises from differences in the interaction of the isomeric and ground states of the iron atom with the electronic charge densities at the nuclei in the source and in the absorber. The values of this parameter which have been observed for the four accessible oxidation states of the iron atom (metallic, +2, +3, and +6) not only permit the use of the isomer shift as a diagnostic measure of the oxidation state, but—for a given oxidation state—can be related[7] (at least qualitatively) to the effective contribution of bonding orbitals to the charge density at the nucleus. The quadrupole splitting of the resonance peak arises from the interaction between the nuclear quadrupole moment, Q, of the 3/2-excited state, and the electric field gradient tensor, q, due to inhomogeneities in the electrostatic field at the iron nucleus. When the iron atom is in a cubic environment (*e.g.*, tetrahedral or octahedral), the e.f.g. tensor vanishes and the upper nuclear state in the 14.4-kev. transition is fourfold degenerate. Under these conditions, no quadrupole splitting will be observed.

In the present study, both the isomer shift and the quadrupole splitting have been determined for four related iron carbonyls.

Experimental

The experimental techniques related to Mössbauer effect studies have been described in detail in previous communications.[8] All measurements were made with respect to a room tem-

---

[1] G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **36**, 2497 (1962).

[2] G. K. Wertheim, W. M. Robinson, and R. H. Herber, *ibid.*, **37**, 687 (1962).

[3] G. K. Wertheim and R. H. Herber, *J. Am. Chem. Soc.*, **84**, 2274 (1962).

[4] R. H. Herber and G. K. Wertheim, "The Mössbauer Effect," Proc. of the 2nd Intern. Conf. on the Mössbauer Effect, Saclay, September, 1961, J. Wiley and Sons, New York, N. Y., 1962, p. 105.

[5] O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters*, **4**, 412 (1960).

[6] S. DeBenedetti, G. Lang, and R. Ingalls, *ibid.*, **6**, 60 (1961).

[7] L. R. Walker, G. K. Wertheim, and V. Jaccarino, *ibid.*, **6**, 98 (1961).

[8] G. K. Wertheim, *J. Appl. Phys.*, **32**, 110S (1961).

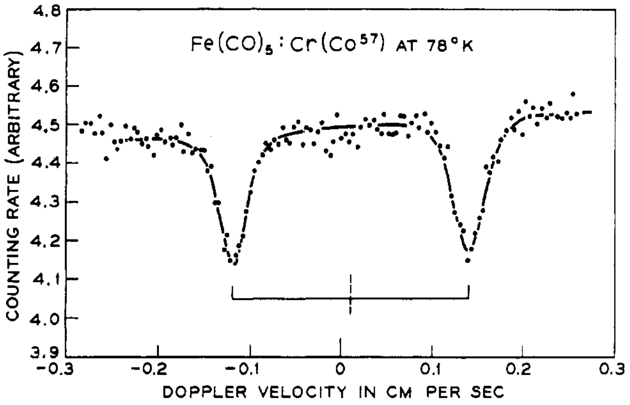

Fig. 1.—Resonant absorption of the 14.4-kev. gamma ray of Fe^{57} in iron pentacarbonyl.

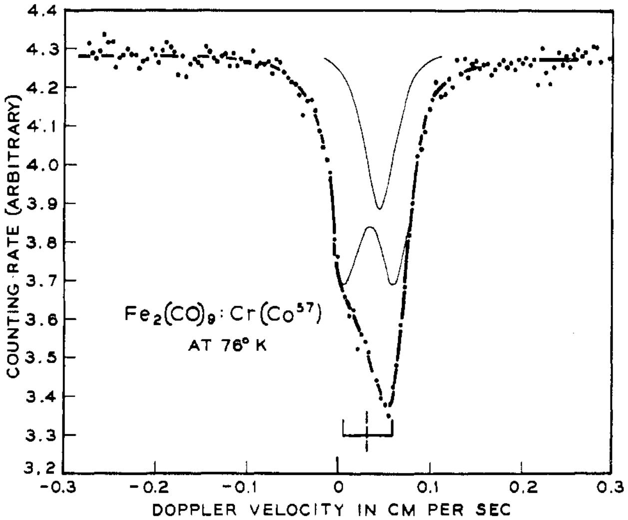

Fig. 2.—Resonant absorption of the 14.4-kev. gamma ray of Fe^{57} in iron nonacarbonyl. (The sample contains some Fe^{3+} contamination which produces an absorption at 0.05 cm. sec.$^{-1}$. The light lines indicate the resolution of the spectrum into its two components.)

perature source of Co^{57} diffused into metallic chromium. In the case of Fe(CO)$_5$, the absorber assembly consisted of two 5-mil glass windows cemented with epoxy resin adhesive to the two halves of the copper sample mount. A 10-mil lead spacer was placed on top of one of the glass windows, and the resultant circular volume was filled with liquid pentacarbonyl in an inert atmosphere and in subdued light. The other half of the absorber assembly was then placed on top, and the two halves were held together under moderate compression by four screws to form a leak-tight seal. The sample was stored in the dark in an inert (CO$_2$) atmosphere until it was finally mounted in the low-temperature dewar. To avoid condensation of moisture on the windows, the dewar was partially evacuated before the sample was cooled to 78°K. Final evacuation took place when the sample had been cooled to liquid nitrogen temperature. No significant loss of the volatile carbonyl was noted in using this procedure.

Iron nonacarbonyl was prepared using the method of Dewar and Jones,[9] in which dried ether is employed as the solvent. After being washed with 95% ethanol, the product was stored over calcium chloride in subdued light until it was transferred to the absorber assembly for measurement.

Iron dodecacarbonyl was prepared by the method of Hieber,[10] using ferrous sulfate to decompose the excess MnO$_2$ and ammonium chloride to control the pH. The solid was recrystallized three times from acetone–water solvent. The carbon analysis agreed within 0.21% with the theoretical value for Fe$_3$(CO)$_{12}$.

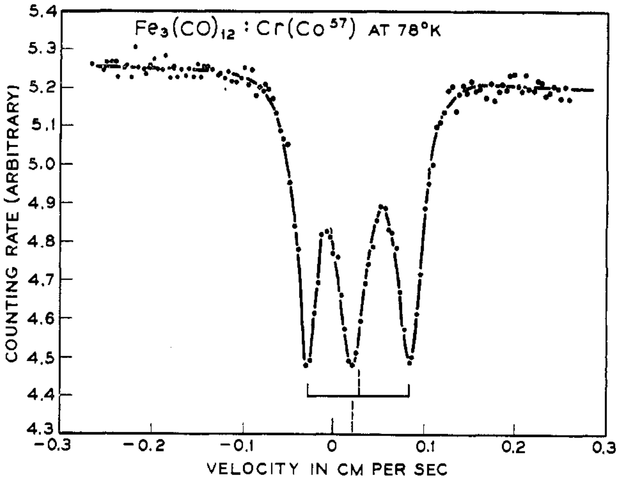

Fig. 3.—Resonant absorption of the 14.4-kev. gamma ray of Fe^{57} in iron dodecacarbonyl.

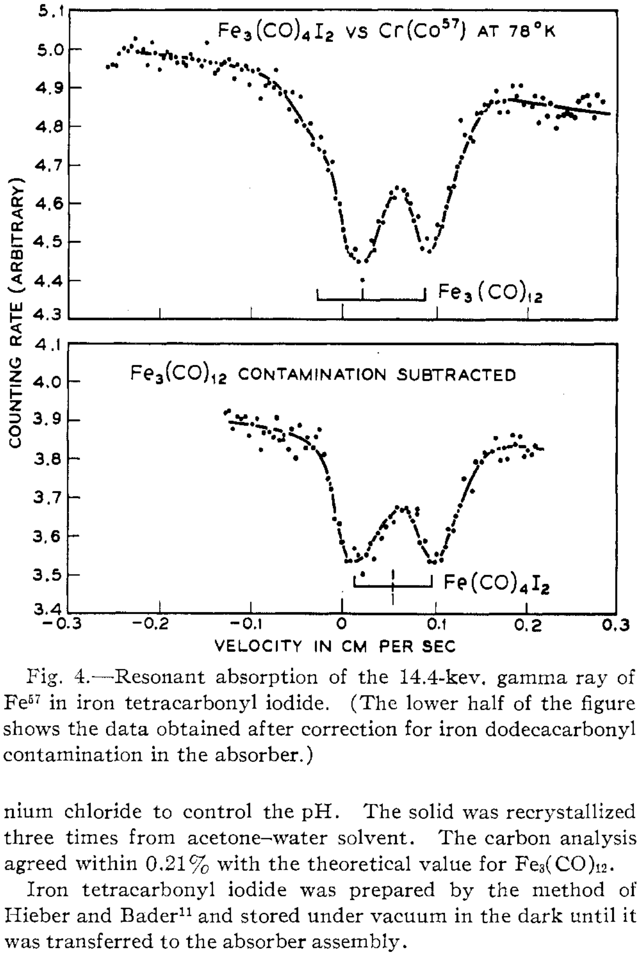

Fig. 4.—Resonant absorption of the 14.4-kev. gamma ray of Fe^{57} in iron tetracarbonyl iodide. (The lower half of the figure shows the data obtained after correction for iron dodecacarbonyl contamination in the absorber.)

Iron tetracarbonyl iodide was prepared by the method of Hieber and Bader[11] and stored under vacuum in the dark until it was transferred to the absorber assembly.

Results and Discussion

The resonant γ-ray absorption spectra are shown in Fig. 1 to 4, and the pertinent parameters extracted from these spectra are summarized in Table I.

Fe(CO)$_5$.—The Mössbauer parameters for iron pentacarbonyl at 78°K. are in good agreement with the values reported by Epstein.[12] The very small isomer

---

[9] J. Dewar and H. O. Jones, *Proc. Roy. Soc.* (London), **A76**, 573 (1905).

[10] W. Hieber, *Z. anorg. allgem. Chem.*, **203**, 165 (1932).

[11] W. Hieber and G. Bader, *Ber.*, **61B**, 1717 (1928).

[12] L. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).

TABLE I

Absorber	Temp., °K.	Isomer shift[a] i.s., mm. sec.$^{-1}$	Quadrupole splitting ΔE, mm. sec.$^{-1}$	Full width at half height $\Gamma_{1/2}$
$Fe(CO)_5$	78	$+0.085 \pm 0.043$	2.57 ± 0.04	0.43 ± 0.04
$Fe_2(CO)_9$	78	$+0.282 \pm 0.043$	0.541 ± 0.043	0.43 ± 0.04
$Fe_3(CO)_{12}$	78	$+0.280 \pm 0.043$	1.115 ± 0.043	0.365 ± 0.043
		$+0.208 \pm 0.043$	0	0.48 ± 0.04
$Fe(CO)_4I_2$	78	$+0.55 \pm 0.08$	0.85 ± 0.08	0.636 ± 0.08
	298	$+0.54 \pm 0.08$	0.72 ± 0.08	0.76 ± 0.12

[a] Relative to Fe^{57} in metallic chromium. Subtract 0.050 mm. sec.$^{-1}$ to convert to stainless steel as reference substance.

shift—which corresponds to $+0.035 \pm 0.047$ mm. sec.$^{-1}$ with respect to 310 stainless steel—suggests[7] essentially covalent bonding between the ligands and the iron atom. It is likely, however, that augmentation of the 3d electron density due to dsp^3 hybridization reduces somewhat the 4s electron density at the nucleus of the zero-oxidation state iron atom in this compound.

A number of proposals concerning the structure of this compound have been made.[13] The evidence for a tetragonal pyramid structure[14] is based largely on dipole moment data[15] which also can by accounted for[16] on the basis of atomic polarizations of the trigonal bipyramid structure. The indirect Raman spectroscopic evidence of Stammreich, *et al.*,[17] and the definitive X-ray structure determination by Hanson[18] leave no doubt regarding the correctness of the trigonal bipyramid structure in the range -70 to $-110°$.

The small isomer shift (0.085 ± 0.043 mm. sec.$^{-1}$) (0.035 ± 0.043 mm. sec.$^{-1}$ with respect to a stainless steel source[12]) for $Fe(CO)_5$ in the present study is consistent with the dsp^3 hybridization implied by the trigonal bipyramid structure. The e.a.n. of the iron atom in this compound corresponds to an inert gas configuration ($Z = 36$) with complete occupancy of the bonding orbitals. As compared to the electron configuration of metallic iron ($3d^74s$), the dsp^3 bonded atom configuration ($3d^{10}4s^24p^6$) shows an increase in both the 3d and the 4s orbital occupancy, and it is clear from the present data that the increase in the 4s electron density—which by itself is expected to change the isomer shift toward negative values—is just offset by the increase in the 3d electron density. This latter d-orbital augmentation due to bonding leads to increased shielding of the nuclear charge with respect to the 4s electrons and hence an expansion of the 4s electron wave function. This expansion in turn reduces the electron density at the nucleus to almost the value found for metallic iron, despite the fact that, at least formally, the 4s electron density has increased by a whole charge unit.

$Fe_2(CO)_9$.—The structure of iron nonacarbonyl has been discussed by Powell and Ewens[19] on the basis of their X-ray spectroscopic study. From their model it is seen that the molecule is nearly symmetrical with respect to a plane passing through the mid-point, with (possibly) 3° rotation around the threefold axis of one half of the molecule with respect to the other. The two iron atoms are equivalent in every way, but the nine carbonyl groups fall into two chemically and spectroscopically distinct groups. The CO distance for the bridging groups is 1.3 ± 0.1 Å. and 1.15 ± 0.05 Å. for the six terminal carbonyls; moreover the C–Fe–C bond angle for the bridging groups is $87 \pm 4°$, while for the terminal groups it is $94 \pm 4°$. In view of the known diamagnetism of this compound, it has been suggested that the single unpaired electron on one iron atom interacts sufficiently strongly with that on the other so that spin pairing is attained.

Although such an iron–iron bond is expected to contribute to the quadrupole splitting which is observed in the Mössbauer spectrum of this compound, it is likely that the major contribution to the e.f.g. tensor at the iron nucleus arises from the non-identity of the two types of carbonyl ligands. The fact that the total field gradient at the iron nucleus is small is seen from the magnitude of the quadrupole splitting, 0.541 ± 0.043 mm. sec.$^{-1}$, which is only 20% of that observed in $Fe(CO)_5$, and is consistent with the small departure from octahedral symmetry found in the X-ray structure determination.

The observed isomer shift in $Fe_2(CO)_9$—0.282 mm. sec.$^{-1}$ compared to 0.085 mm. sec.$^{-1}$ for $Fe(CO)_5$—reflects both the change from penta- to hexacoördination and the fact that the e.a.n. is reduced by one. The electron distribution in $Fe_2(CO)_9$ is satisfactorily accounted for if each of the three terminal carbonyl groups is assumed to donate two electrons to the bonding orbitals of its iron atom while each of the three bridging carbonyls donates a single electron to each of the two iron atoms. Hence, one of the bonding orbitals is singly occupied (if the possible contribution of Fe–Fe bonding, which can have only a very minor effect on the electron density at the iron atom, is ignored). The change in the isomer shift can be accounted for if formally three electrons are assigned to one 3d and one 4s orbital, although this formalism fails to provide d^2sp^3 hybridization which usually is associated with the near-octahedral symmetry of the six nearest neighbor carbonyl groups. Since the i.s. values arising from Mössbauer spectra are a measure of the differences in the contribution of the 4s electrons to the charge densities at the nuclei in the source and the absorber, the present results may be taken as an effective demonstration of the inadequacy of the L.C.A.O. treatment of bonding in these compounds. Clearly the d^2sp^3 hybridization suggested by the molecular structure could be attained by promoting three of the 3d nonbonding electrons into half-filled bonding orbitals. However, this would provide an electron configuration of $3d^94s^24p^6$ and hence a smaller shielding by the 3d electrons of the nuclear charge from the two 4s electrons than in $Fe(CO)_5$. This in turn would lead to a larger electron density at the nucleus due to the 4s electrons

---

(13) R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

(14) M. F. O'Dwyer, *J. Mol. Spectry.*, **2**, 144 (1958).

(15) E. Bergmann and L. Engel, *Z. physik. Chem.*, **B13**, 232 (1931); W. Graffunder and E. Heymann, *ibid.*, **B15**, 377 (1932).

(16) E. Weiss, *Z. anorg. allgem. Chem.*, **287**, 223 (1956).

(17) H. Stammreich, O. Sala, and Y. Tavares, *J. Chem. Phys.*, **30**, 856 (1959).

(18) A. W. Hanson, *Acta Cryst.*, in press.

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

than in the pentacarbonyl and hence a *smaller* i.s., in contrast to the *larger* i.s. actually observed. The most plausible rationalization of the near-octahedral symmetry is based on treating the interaction of the three bridging carbonyls with each iron atom as due to an overlap between the π-electron density of the ligands and the available d-orbitals of the transition metal. This ferrocenoid bonding then may be assumed to yield the observed molecular structure as a configuration of maximum overlap rather than as an *a priori* bond orientation demanded by the hybridization of particular atomic orbitals. The present data suggest that this d–π overlap significantly reduces the charge density at the iron nucleus of the total electron wave function compared to $Fe(CO)_5$ but a quantitative correlation between this charge density and the bonding interaction must await a more comprehensive theoretical treatment of the bonding.

$Fe_3(CO)_{12}$.—Although no accurate bond distance data have been reported for this compound, several proposals concerning the structure of iron dodecacarbonyl have received widespread attention. The X-ray data of Mills[20] have been discussed by Brown,[21] who has carried out molecular orbital calculations on the six-bridged structure (3,3,3,3)[22] and finds this structure consistent with the reported magnetic properties of $Fe_3(CO)_{12}$, which, like the other three iron carbonyl compounds described, is diamagnetic. On the other hand, Sheline[23] has interpreted the infrared spectrum of this compound in terms of the (4,2,2,4) structure suggested earlier by Brill.[24] Although this interpretation has been questioned by Cotton and Wilkinson[25] on the basis of a redetermination of the infrared bands in the rock salt and LiF region, these authors do not suggest an alternative model. Moreover, their interpretation does not support the (3,3,3,3) structure as claimed by Brown.[21] Such support, at least for the species present in solution can, however, be drawn from the kinetic data of Keeley and Johnson,[26] who studied the isotopic $C^{14}O$ exchange between gaseous carbon monoxide and benzene solutions of the iron carbonyl compound. These data show that six of the twelve carbonyl groups of $Fe_3(CO)_{12}$ exchange at a more rapid rate than the others, and on this basis a (3,3,3,3) structure is suggested.

The seemingly most unambiguous determination of the structure of $Fe_3(CO)_{12}$ is the X-ray work of Dahl and Rundle,[27] which is supported by considerations of the infrared spectrum of this compound by the same authors.[28] The structure proposed by them is a trigonal ring arrangement of the three iron atoms with a single Fe–Fe distance of 2.75 to 2.85 Å. A similar structure has recently been proposed[29] for $Os_3(CO)_{12}$.

The Mössbauer spectrum of $Fe_3(CO)_{12}$ (Fig. 3) shows three resonance maxima of equal intensity. Since the presence of three electronically different iron atoms, each in a cubic environment, most probably can be ruled out, the likeliest interpretation is that the two resonance maxima at +0.847 and −0.287 mm. sec.$^{-1}$ represent two halves of a quadrupole split line with an isomer shift of +0.280 ± 0.043 mm. sec.$^{-1}$, while the maximum at +0.208 ± 0.043 mm. sec.$^{-1}$ represents a single unsplit line. Such a spectrum arises if the central iron atom is in an essentially octahedral environment while the two "outside" iron atoms are situated at a point where the e.f.g. tensor is not zero. The near identity of the isomer shift of the "outside" iron atoms with that observed for Fe_2CO_9 is in agreement with the postulate that in both cases the iron atom "sees" three terminal and three bridging carbonyl groups. In addition, the assignment of the quadrupole splitting to the two "outside" iron atoms is consistent with the equal intensity of the resonance line assigned to the single central iron atom and the split line assigned to the two "outside" iron atoms.

While the present data do not constitute a structure proof, they are clearly inconsistent with the interpretation of the X-ray data of Dahl and Rundle,[27] which implies an equivalence of the three iron atoms on the basis of the unique Fe–Fe bond distance reported by them. A distortion of the three-membered ring to give an isosceles triangle in which the disposition of the ligands about the central atom is such as to constitute effectively an octahedral environment would have to be well outside the 0.1 Å. range reported for the Fe–Fe distance.

The fact that the quadrupole splitting of the resonance peak assigned to the "outside" iron atom in $Fe_3(CO)_{12}$ is significantly larger than that observed in $Fe_2(CO)_9$ is readily understood on the basis of the known infrared data for these compounds. Sheline and Pitzer[30] have reported two carbonyl frequencies in the infrared spectrum of the nonacarbonyl: that at 2000 cm.$^{-1}$ is assigned to the terminal $C\equiv O$ groups (in $Fe(CO)_5$ this band occurs at 2030 cm.$^{-1}$) while that at 1828 cm.$^{-1}$ is assigned to the bridging $C=O$ groups. Cotton and Wilkinson[25] have similarly ascribed the bands at 2043 and/or 2020 cm.$^{-1}$ to the terminal $C\equiv O$ groups in $Fe_3(CO)_{12}$ but consider the very weak band at 1828 cm.$^{-1}$ (which has an intensity of $\sim$1/20 that of the terminal carbonyl band) to be due to non-fundamental infrared active modes. They assign no frequency to the $C=O$ bridging groups, although they report a strong band at 1997 cm.$^{-1}$.

From these data it is clear that the bridging carbonyls in the dodecacarbonyl are significantly different from either the bridging carbonyls in $Fe_2(CO)_9$ or the terminal carbonyls in $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$. This difference is readily evident from the most straightforward electron bookkeeping for these compounds.

---

(20) O. S. Mills, *Chem. Ind.* (London), **3**, 73 (1957).

(21) D. A. Brown, *J. Inorg. Nucl. Chem.*, **5**, 289 (1958).

(22) F. A. Cotton, A. D. Liehr, and G. Wilkinson, *ibid.*, **2**, 141 (1956).

(23) R. K. Sheline, *J. Am. Chem. Soc.*, **73**, 1615 (1951); J. W. Cable and R. K. Sheline, *Chem. Rev.*, **56**, 1 (1956).

(24) R. Brill, *Z. Krist.*, **77**, 36 (1931).

(25) F. A. Cotton and G. Wilkinson, *J. Am. Chem. Soc.*, **79**, 752 (1957).

(26) D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).

(27) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

(28) L. F. Dahl and R. E. Rundle, *ibid.*, **27**, 323 (1957).

(29) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

(30) R. K. Sheline and K. S. Pitzer, *J. Am. Chem. Soc.*, **72**, 1107 (1950).

If it is assumed that formally each bridging carbonyl supplies one electron to each of the two iron atoms, the e.a.n. of the iron atom is 35 in the case of $Fe_2(CO)_9$, but only 32 in the case of the central iron atom in $Fe_3(CO)_{12}$. Clearly the nature of the bonding between the bridging carbonyls and these two distinct kinds of iron atoms will be different.

The present data suggest that there is considerable contraction of the central iron atom–"outside" iron atom distance by virtue of a stronger bonding interaction between the central iron atom and the six bridging carbonyl groups. (This decrease in the Fe–Fe distance would be expected to increase the magnitude of the e.f.g. tensor at the "outside" iron atom and hence would account for the twofold increase in the quadrupole splitting assigned to this atom as compared to $Fe_2(CO)_9$.) Moreover, the broadening of the central resonance line suggests that while there is no major distortion from octahedral symmetry for the nearest neighbor environment of the central iron atom, the symmetric bond shortening does cause an observable departure from perfect octahedral symmetry.

As in the case of the nonacarbonyl, the octahedral symmetry of the six bridging ligands about the central iron atom in $Fe_3(CO)_{12}$ cannot be rationalized in terms of the usual d^2sp^3 hybridization. This octahedral symmetry again can be envisioned as arising from the condition of maximum overlap between the two π-electron distributions of the two groups of carbonyl ligands, and the available orbitals of the central iron atom. Indeed the similarity of the bonding in $Fe_3(CO)_{12}$ and the ferrocene-like compounds is emphasized by the fact that the six bridging carbonyls assume a staggered configuration with respect to the Fe–Fe–Fe axis, much as the two cyclopentadienyl groups assume a non-eclipsing configuration in ferrocene.

The difference between the isomer shift observed for the "outside" iron atom in $Fe_3(CO)_{12}$ and the iron atom in either $C_8H_8Fe(CO)_3$ or $C_8H_8[Fe(CO)_3]_2$ is consistent with our earlier interpretation[3] of the Mössbauer spectral data for the cyclooötatetraene compounds. In each case the iron atom is bonded to three terminal carbonyl groups and a molecular configuration which can be formally regarded as contributing four bonding electrons. The smaller isomer shift observed for $C_8H_8Fe(CO)_3$ (0.23 ± 0.01 mm. sec.$^{-1}$) and $C_8H_8[Fe(CO)_3]_2$ (0.18 ± 0.01 mm. sec.$^{-1}$) as compared to the dodecacarbonyl arises from the greater delocalization of electronic charge in bonding to the butadiene residue of the C_8H_8 ring, compared to the π-electron density of the three carbonyl groups. This greater delocalization in turn reduces the shielding provided by the bonding electrons between the nuclear charge and the 4s wave function, and hence brings about an increase in the electron density at the nucleus. This increase is observable as a smaller isomer shift than that assigned to "outside" iron atoms in $Fe_3(CO)_{12}$.

This effect of charge delocalization also accounts for the fact that the isomer shift for the central iron atom ($+0.208 \pm 0.043$ mm. sec.$^{-1}$) is smaller than that of the "outside" iron atom ($+0.282 \pm 0.043$ mm. sec.$^{-1}$), since again the greater p–π, d–π electron delocalization in the former is expected to provide a smaller shielding of the nuclear charge, and hence a larger contribution by the 4s electrons to the charge density at the nucleus, than in the case of the d–π bonding ascribed to the "outside" iron atom.

$Fe(CO)_4I_2$.—The octahedral iron tetracarbonyl iodide is known to have the *cis* configuration[31] in consonance with its dipole moment of 3.6 D. The unavailability of the corresponding *trans* compound has been ascribed by Weiss to the mechanism of CO elimination which presumably proceeds *via* a heptacoördinate transition state to give exclusively the *cis* product.

Wojcicki and Basolo[32] have studied the $C^{14}O$ exchange between $Fe(CO)_4I_2$ and carbon monoxide in toluene solution at 31.8°. Their results indicate that all four carbonyls exchange at the same rate *via* an SN2 mechanism in contrast to the SN1 exchange mechanism which has been proposed[29] for the compound $Mn(CO)_5I$. From these data it is clear that the four carbonyl groups are kinetically, and hence presumably sterically, identical, and that the *trans* effect due to the two iodine atoms is negligibly small.

The Mössbauer spectrum of $Fe(CO)_4I_2$ is shown in the upper half of Fig. 4. The asymmetry of these data suggests contamination by another iron compound. The most likely contaminant is $Fe_3(CO)_{12}$, which is known to be formed under the conditions of the synthesis procedure.[11] The bottom half of Fig. 4 shows the spectrum which results when the known spectrum of $Fe_3(CO)_{12}$ (see Fig. 3) is subtracted from the gross $Fe(CO)_4I_2$ spectrum until a symmetrical line shape is obtained. The parameters for the carbonyl iodide compound here reported are those extracted from the corrected spectrum.

The isomer shift in $Fe(CO)_4I_2$, uncorrected for second-order Doppler shifts, is seen from the data in Table I to be essentially temperature-independent in the range 78 to 298°K., and corresponds[7] to an effective 4s electron density at the nucleus of $\sim 35\%$. This value is in modest agreement with a value extrapolated from the available data for FeF_2 (1.40 ± 0.05) and $FeCl_2 \cdot 4H_2O$ (1.30 ± 0.05), provided that the four carbonyl groups contribute the same electron density as four liganded water molecules. The more strongly covalent character of the Fe–I bond compared to those of Fe–Cl and Fe–F is in consonance with the prediction based on the usual considerations of electronegativity differences as related to bond character.[33] A rigorous test of this assumption lies in the measurement of isomer shifts for FeI_2 and $FeI_2 \cdot 4H_2O$ and their comparison with the results of the present study. Such measurements are now underway in these Laboratories.[34]

Acknowledgments.—The authors are indebted to

---

[31] E. Weiss, *Z. anorg. allgem. Chem.*, **287**, 223 (1956).

[32] A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

[33] L. Pauling, "The Nature of the Chemical Bond," Second Ed., Cornell University Press, Ithaca, N. Y., 1944.

[34] G. K. Wertheim, W. R. Kingston, and R. R. Herber, to be published.

D. N. E. Buchanan for assistance with some of the measurements and to the Antara Chemicals Division, General Aniline and Film Corporation, for a generous gift of $Fe(CO)_5$. We are especially grateful to Professors R. E. Rundle and L. F. Dahl for a number of illuminating discussions related to their X-ray results and to Dr. A. W. Hanson for permitting us to read his manuscript prior to publication. This research was supported in part by the U. S. Atomic Energy Commission.

Contribution from the Department of Chemistry,
The University of California, Los Angeles, California

Infrared Spectra and Structure of the Tetracarbonyl Halide Dimers of Manganese, Technetium, and Rhenium

By M. A. El-Sayed and H. D. Kaesz

Received May 28, 1962

The high resolution infrared spectra in the C≡O stretching region are discussed for the tetracarbonyl halides $[M(CO)_4X]_2$, M = Mn, Tc, and Re, and X = Cl, Br, and I. These compounds show three strong absorptions and a relatively weak high-energy band, in the carbonyl stretching region. The relative intensity of the latter band is found to increase as the size of M is decreased or the size of the halogen increased. This behavior leads to the conclusion that while this band most probably is due to a fundamental mode, because of symmetry, the moments created from the oscillating local CO dipoles cancel for the most part, similar in behavior to a previously observed high-energy band in the case of the derivatives $M(CO)_5X$. The four observed bands in the C≡O stretching region could be accounted for by a structure with either D_{2h} or C_{2h} symmetry. The observed infrared spectrum in the M—C≡O bending region for $[Mn(CO)_4I]_2$ can be readily interpreted on the basis of the D_{2h} structure (halogen bridging). The four observed fundamental bands in the C≡O stretching region have been qualitatively assigned for the modes of the D_{2h} structure by the use of both the oscillating dipole picture as well as valence force potential arguments.

Introduction

The infrared spectrum of $[M(CO)_4X]_2$ where M = Mn[1] and Re[2] and X = Cl, Br, and I have been reported previously in the C≡O stretching region. Four bands have been reported for the case of M = Mn[1] and three for M = Re.[2] For the latter, the authors mentioned that the observed three bands are in agreement with a structure in which two octahedra are connected at an edge through halogen bridges (D_{2h} structure). Simple group theoretical predictions show that such a structure requires four (not three) infrared active C≡O stretching modes. These authors[1b,2] also suggested the possibility of structures with M–M bridges. This gives rise to D_{4h}, C_{2h}, and C_{2v} structures, none of which predict three infrared active C≡O stretching bands. The lowest energy absorption of the reported four bands by these authors for the case when M = Mn[1a] can be shown to be due to the ^{13}CO mode of the strong absorption band next to it. These conflicting results have stimulated this research, in which the high resolution spectra of the whole series of compounds, including the derivatives of technetium,[3] are obtained and examined. The observed trends and the behavior of the bands in comparison with those observed in the monomeric pentacarbonyl halides[4,5] are found helpful in assigning the fundamental bands. It is found that a new band at high energy, *not reported previously for the dimer*, behaves as a similar band in the derivatives $M(CO)_5X$ which has been assigned[4,5] to a fundamental mode, which because of cancellation of local moments has a weak intensity. A simple oscillating local dipole picture is applied here (as was done for the pentacarbonyl halides[5]) and the results are in good agreement with the observed behavior of the bands. The possible structures are discussed not only in terms of the allowed number of modes, but also in terms of the position, intensity, and behavior of the observed bands.

Experimental

The derivatives of technetium were prepared according to the procedures reported elsewhere,[3] similar to the techniques used for the analogous derivatives of manganese[1a] and rhenium.[2]

Infrared spectra in the carbonyl stretching region were obtained with a double beam Beckman Model IR4 spectrophotometer with a lithium fluoride prism, at a spectral slit width of about 1 cm.$^{-1}$ in the region of interest. The low energy region (down to 250 cm.$^{-1}$) was scanned with a Beckman Model IR7 spectrophotometer, equipped with a CsI prism, made available through the courtesy of the manufacturer, in Fullerton, California. Only one compound, $[Mn(CO)_4I]_2$, was investigated in the latter region in CCl_4 solution. In order to obtain a more concentrated amount of material in the same path length, a Nujol mull was used, which has the advantage of being essentially transparent in the region 700–250 cm.$^{-1}$.

---

[1] (a) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959); (b) E. W. Abel, M. A. Bennett, and G. Wilkinson, *Chem. Ind.* (London), 442 (1960).

[2] E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958).

[3] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962); for preliminary communication, *cf.*, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

[4] L. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

[5] M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962).