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GAS-PHASE ELECTRON DIFFRACTION STUDIES OF SOME IRON CARBONYL COMPLEXES

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SUMMARY

Gas phase electron diffraction studies have been made of the complexes: butadieneiron tricarbonyl, cyclobutadieneiron tricarbonyl and ethyleneiron tetracarbonyl. In each instance the conformation was determined and values were obtained for the principal bond lengths and angles.

INTRODUCTION

Most of the known physical properties of olefin iron carbonyl complexes have been tabulated and discussed in one or other of three review articles[1-3]. Such relevant information as was available to us in the course of our investigations is summarized in the following paragraphs.

The structure of butadiene iron tricarbonyl had been investigated by X-ray crystallography[4]. The crystalline molecular conformation can be described in terms of a slightly distorted square-pyramidal arrangement of carbon atoms around the central iron atom (see Fig. 1). One of the carbonyl groups lies along the axis of the pyramid while the other two occupy corner sites. The other two corners are occupied by the terminal carbons of the *cis*-butadiene moiety. The four diene carbons lie in a plane which is nearly perpendicular to the basal plane of the pyramid. The C–C bonds of the complexed diene moiety were found to be nearly equal in length, in contrast to the situation in the free *trans* butadiene molecule[5].

The molecular structure of cyclobutadieneiron tricarbonyl had not previously been determined but the results of two X-ray studies of related compounds were available[6 7]. Cyclobutadiene itself is too unstable for structural study by any existing technique. The best evidence would appear to indicate that its ring is distinctly rectangular[2,8,9]. The X-ray studies show that in the complexes the cyclobutadiene is either square or only slightly rectangular. The results of a liquid crystal NMR study of cyclobutadiene iron tricarbonyl have also been interpreted in terms of square symmetry for the diene moiety[10].

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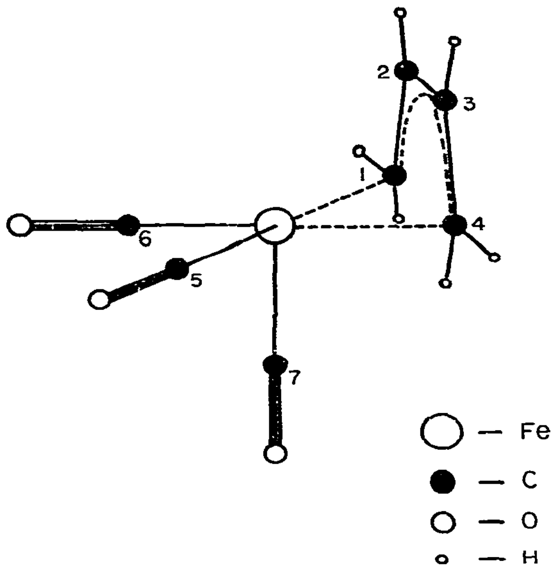

Fig. 1. Butadieneiron tricarbonyl.

In (tetraphenylcyclobutadiene)iron tricarbonyl, the four fold symmetry axis of the cyclobutadiene was found to coincide with the three fold axis of the $Fe(CO)_3$ group[6]. Of the possible orientations of the two groups with respect to each other, two possess mirror symmetry (see Fig. 2). That depicted in Fig. 2b was found for the tetraphenyl derivative[6].

The only published structural investigation of a mono-olefin iron tetracarbonyl is that of acrylonitrileiron tetracarbonyl by X-ray crystallography[11]. Its conformation was found to be roughly trigonal bipyramidal with the ethylene moiety occupying an equatorial site. The axial Fe–C bond length reported for that investigation is unusually long.

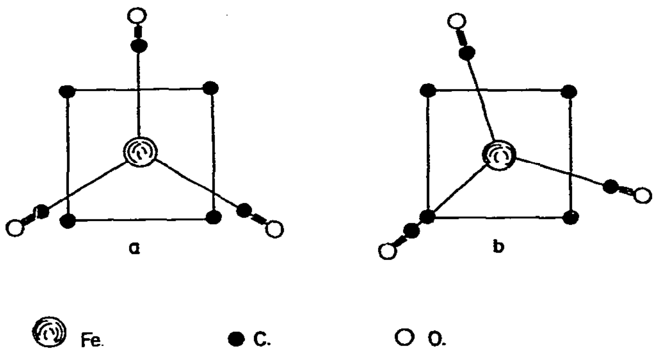

Fig. 2. Cyclobutadieneiron tricarbonyl. Internal rotation conformers.

EXPERIMENTAL

Materials

The samples of both dieneiron tricarbonyls were prepared in the laboratory of Professor R. Pettit. They were found to contain no detectable impurities. The samples were stored at -10°, in the dark, to avoid decomposition.

The sample of ethylene iron tetracarbonyl was synthesised by means of a procedure described by Murdoch and Weiss[12]. The proton magnetic resonance spectrum consisted of a single peak at τ 7.52 ppm (w.r.t. TMS). The sample was maintained at dry-ice temperature in the absence of light.

Data collection

Intensity data were collected photographically. The nozzle assembly was kept at 15–20° above the sample reservoir temperatures given in Table 1. Exposure times ranged from 20–120 sec.

TABLE 1

OPERATING CONDITIONS

Complex	Sample temp. (°C)	Nozzle to plate distances (cm)	deBroglie wavelength (Å)
Butadiene $Fe(CO)_3$	75	25, 50, 100	0.05629
Cyclobutadiene $Fe(CO)_3$	70	25, 50, 100	0.05662
Ethylene $Fe(CO)_4$	50	35, 50, 85	0.05662

Transmission values were obtained at an interval of 0.25 $Å^{-1}$ from traces of microdensitometer records. An exception was made for the longest camera distance data for ethyleneiron tetracarbonyl where Δs was reduced to 0.125 $Å^{-1}$ in an effort to improve the stability of the numerical background insertion procedure.

The transmission values were converted to electron intensities, using a correction curve for non-linear emulsion response. The intensities were further corrected for the use of a rotating sector.

DATA ANALYSIS AND STRUCTURE REFINEMENT

The basic procedures for structure analysis, used in this laboratory, have been described in a previous paper[13]. In an attempt to remove some of the errors in the higher s regions, where the molecular scattering constitutes an unfavorably low proportion of the total, certain of the curves were Fourier analyzed and the higher frequency components removed. The computational procedure was devised by R. F. Pohler and has been described by Fetzer[14].

Refinement procedures (general)

The number of parameters that are required to completely describe the structure of any one of these molecules is much larger than could possibly be extracted from our data. For each compound, it was found to be expedient to commence the analysis on the basis of the simplest possible model and to increase gradually the number of parameters in the refinement scheme until such time as the maximum level of reasonable flexibility had been attained.

Radial distribution curves were used to formulate the initial models, to give indications of further model changes and to provide periodic checks on the progress on the analyses. Refinements were carried out using the molecular scattering curves. A modified gradient method was used, in which the parameters were adjusted sequentially. Use was also made of a so-called direct search method which has been described by Wood[15] and by Hooke and Jeeves[16]. This method combines the simplicity of the gradient method with the larger steps obtainable with the method of steepest descents. The method of least squares[17] was used when it became apparent that most of the more prominent features of the experimental curves had been accounted for. At each stage and for each method of structure refinement several different starting models were employed.

It was evident that for each compound the function R*, used to evaluate the closeness of fit between the theoretical and experimental curves, possesses a fairly well defined minimum with respect to some of the parameters but not for others. There is strong correlation between several pairs of parameters. In two instances the nature of this interdependence was studied by computing contour maps of R as a function of a specific pair of parameters.

Estimation of confidence limits

The least-squares analysis procedure provides values for the standard errors of the parameters being refined[17]. These values were computed as if the data points were all independent, which is certainly not the case. Further, the computations did not make allowances for the constraints imposed upon the refinement of data in the form of assumptions concerning the nature of the model. The data points are correlated by virtue of the manner in which they are collected, and to some extent as a result of the background insertion and Fourier smoothing procedures. On the average it would probably be more realistic if one operated on the assumption that only every third or fourth point is strictly independent. Making that assumption, the least-squares standard errors were doubled to take into account data correlation and further multiplied by 2.5 to give the cited confidence limits.

The individual investigations

Butadieneiron tricarbonyl. Fifteen parameters are required to describe the skeletal equilibrium geometry with a further nine for the hydrogens; assuming the existence of a plane of mirror symmetry. There are not enough distinctive features in the radial distribution curve to allow for the unambiguous determination of anything like this many, particularly in view of the number of vibrational parameters also required.

The C–C bonds of the diene moiety were assumed to be of equal length. The

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$$R = \frac{\Sigma_s \left| M_A(s) - M_B(s) \right| P(s)}{\Sigma_s \left| M_A(s) \right| P(s)} \qquad (1)$$

where $M_A(s)$ and $M_B(s)$ are respectively the experimental and theoretical molecular scattering intensities[13]. The weighting function $P(s)$ was:

$$P(s) = s \cdot \exp\left[(\ln 5s_{max}) \cdot s^2/s_{max}^2\right] \qquad (2)$$

sharpness of their radial distribution peak indicates that this is close enough to the true situation as to make it impossible to make any meaningful distinction. The CCC bond angle was fixed at 120° in accordance with the X-ray and NMR evidence[4,18]. No distinction was made between the non-symmetry related Fe–C (carbonyl) bonds or between the Fe–C (diene) bonds. The $Fe(CO)_3$ group was constrained to have C_{3v} symmetry. The angle between the three-fold axis of the $Fe(CO)_3$ group and the plane of the diene carbons was allowed to vary (see Fig. 3). Deviations from linearity of the FeCO groups were permitted. Thus seven parameters were required to describe the equilibrium structure of the skeleton.

The C–H bond lengths were fixed at 1.094 Å. The inner CCH angles were assumed to be 120° and the terminal HCH angles 116°. One set of analyses was carried out on the basis of the assumption that the diene moiety is completely planar. A further set was carried out using two extra parameters (see Fig. 3) that allowed the terminal hydrogen atoms to lie out of the plane of the four diene carbons.

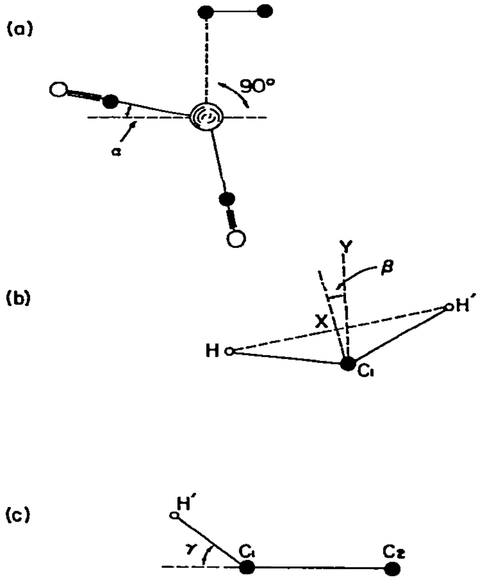

Fig. 3. Distortion angles in butadieneiron tricarbonyl. a. Projection along C_4–C_1. b. Projection along C_1–C_2. x is the midpoint of H–H′ and C_1–Y is perpendicular to the plane of the diene carbons. c. Projection along H–H′ and perpendicular to C_1–C_2.

It was assumed in all three investigations that all atom pairs with closely similar internuclear distances may be constrained to have identical vibrational amplitudes.

Theoretical and experimental versions of the radial distribution and molecular scattering curves are shown in Figs. 4 and 5. On this scale there is little, if any, discernible difference between the theoretical curves when the hydrogen positions are allowed to change. For $s > 20$ Å^{-1}, the level of correlation is less than desirable. The difference represents, however, a very small fraction of the total observed intensity.

Values for bond lengths, angular and vibrational parameters are given in Table 2. The confidence limits were assessed by the means outlined above.

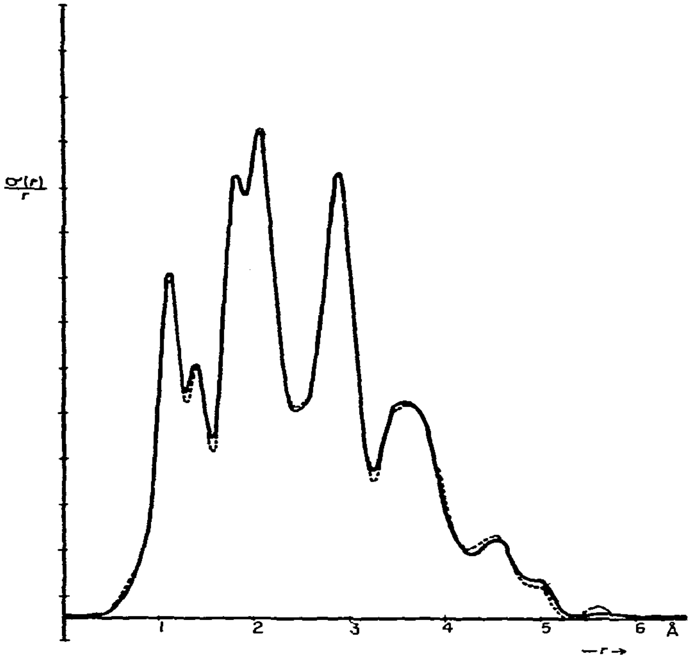

Fig. 4. Butadieneiron tricarbonyl. Radial distribution curves. ----- (exp.) —— (theor.) Damping factor $k = 0.003$.

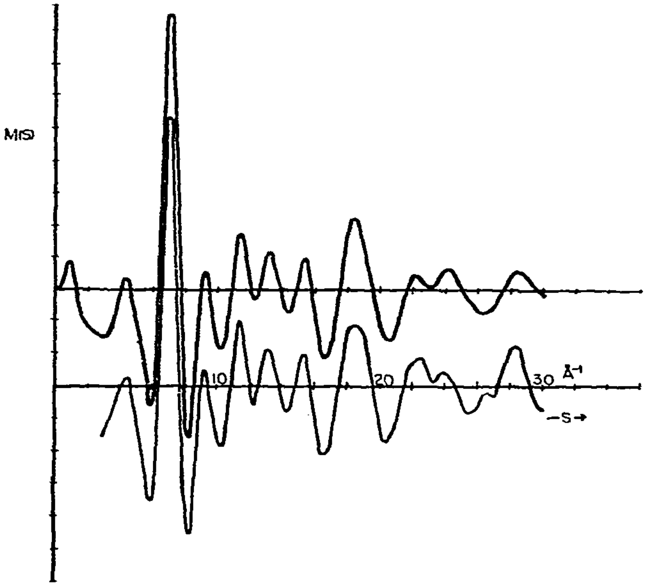

Fig. 5. Butadieneiron tricarbonyl. Molecular scattering curves. Upper curve theoretical, lower experimental.

TABLE 2

BUTADIENEIRON TRICARBONYL: RESULTS

Parameter	Model A	Model B
r(C–C)	1.410±0.015 Å	1.413±0.015 Å
r(Fe–C) diene	2.086±0.015	2.074±0.015
r(Fe–C) carbonyl	1.798±0.015	1.798±0.015
r(C=O)	1.134±0.010	1.137±0.010
∠CFeC [$Fe(CO)_3$]	98.9±3.0°	100.5± 5.0°
∠FeCO	180°[b]	178.3±10.0°
α[a]	4.5±5.0°	7.7± 5.5°
β	0°[b]	12.8± 7.5°
δ	0°[b]	2.9±11.0°
l(Fe–C) diene	0.087±0.015 Å	0.084±0.015 Å
l(Fe–C) carbonyl	0.054±0.015	0.060±0.015
l(Fe–C)	0.087±0.020	0.074±0.020
l(C=O)	0.053±0.015	0.054±0.015
l(C–C)	0.035[b]	0.022±0.035

[a] For explanation of symbols see Fig. 3. [b] Not treated as a refinement parameter.

Cyclobutadieneiron tricarbonyl. In this invesigation, the $Fe(CO)_3$ group was assumed to possess C_{3v} symmetry with its axis coincident with the four-fold axis of the cyclic diene moiety. The C–H bond length was set at 1.08 Å, with the hydrogen atoms assumed to be coplanar with the diene carbons. The contribution of the C–C bonds to the radial distribution curve is well enough isolated to allow for accurate determination of the average bond length. The sharpness of that peak excludes differences greater than 0.05 Å between adjacent C–C bond lengths. Any attempt to distinguish between the lengths of the C–C bonds would thus have been impracticable.

The theoretical curves are highly insensitive to the orientation of the $Fe(CO)_3$ group with respect to the diene moiety.

Theoretical and experimental versions of the radial distribution and molecular scattering curves are shown in Figs. 6 and 7. The results of the investigation are tabulated in Table 3.

TABLE 3

CYCLOBUTADIENEIRON TRICARBONYL: RESULTS

r(C–C)	1.456±0.015 Å	l(C–C)	0.040±0.015 Å
r(Fe–C) diene	2.063±0.010	l(Fe–C) diene	0.059±0.010
r(Fe–C) carbonyl	1.819±0.010	l(Fe–C) carbonyl	0.055±0.015
r(C=O)	1.131±0.010	l(C=O)	0.022±0.025
∠CFeC [$Fe(CO)_3$]	95.5±2.5°	l(Fe–O)	0.067±0.015

Ethylene iron tetracarbonyl. The radial distribution curves are consistent with a trigonal bipyramidal model, with the ethylene occupying an equatorial site (see Fig. 8). The proton NMR spectrum is consistent with C_{2v} symmetry. The FeCO groups were assumed to be linear, with the two axial groups colinear.

Attempts to reproduce our experimental curves on the basis of the unusually long axial Fe–C bonds, reported for acrylonitrileiron tetracarbonyl[11], were unsuccess-

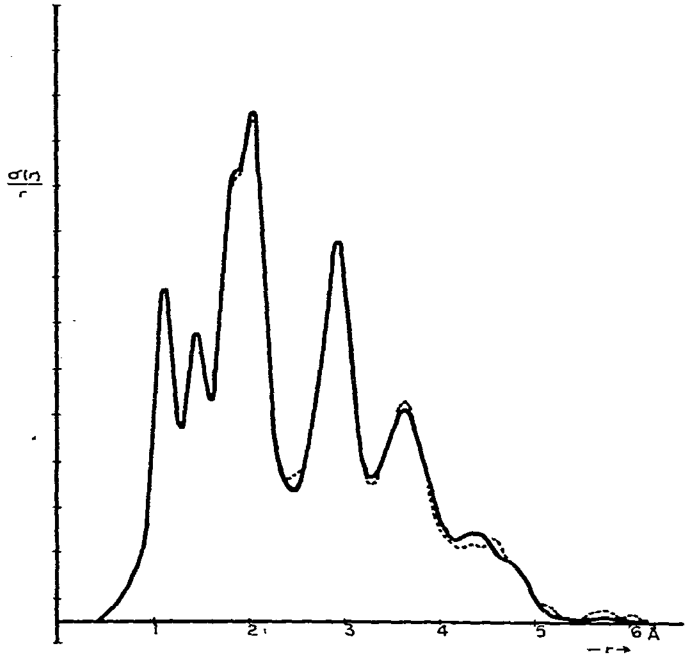

Fig. 6. Cyclobutadieneiron tricarbonyl. Radial distribution curves. ----- (exp.) —— (theor.). Damping factor $k = 0.003$.

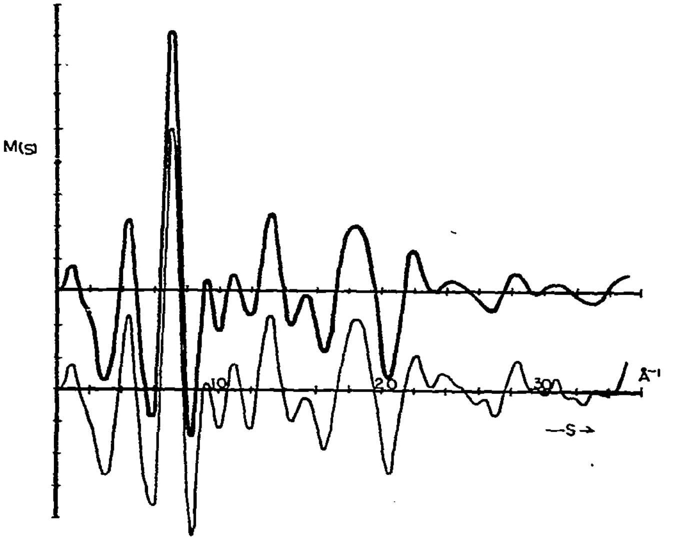

Fig. 7. Cyclobutadieneiron tricarbonyl. Molecular scattering curves. Upper curve theoretical, lower experimental.

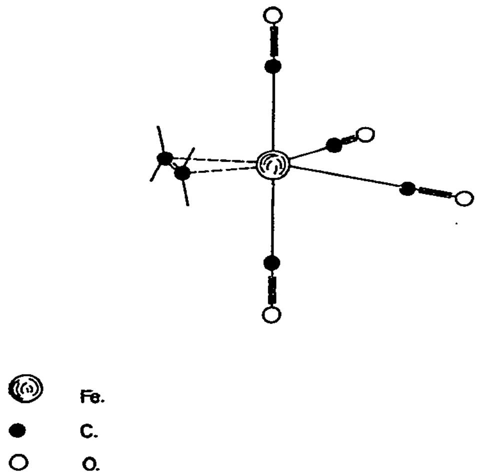

Fig. 8. Ethyleneiron tetracarbonyl.

ful. An attempt was made, however, to distinguish between the axial and equatorial Fe–C (carbonyl) bond lengths. The ethylene moiety was assumed to be planar, with the C–H bonds 1.08 Å in length and the HCH angles 116°.

The final results of this investigation are presented in Table 4. Theoretical and experimental versions of the radial distribution and molecular scattering curves are presented in Figs. 9 and 10.

TABLE 4

ETHYLENEIRON TETRACARBONYL: RESULTS

r(C–C)	1.46±0.06 Å	l(C=O)	0.030±0.020 Å
r(Fe–C) axial	1.796±0.035	l(Fe–C) carbonyl	0.058±0.030
r(Fe–C) equatorial	1.836±0.035	l(Fe–C) ethylene	0.110±0.020
r(Fe–C) ethylene	2.117±0.030	l(Fe–O)	0.070±0.025
r(C=O)	1.146±0.010	l(C–C)	0.040[b]
∠CFeC[a]	105.2±3.0°		

[a] Angle between the equatorial Fe–C (carbonyl) bonds. [b] Assumed.

DISCUSSION

For each of the three compounds studied, the electron diffraction data were found to be consistent with the molecular conformations anticipated on the basis of X-ray crystallographic work[4,6,11].

There is some question of whether the data might also be consistent with other conformations. In each instance, any significant departure from the reported $Fe(CO)_n$ geometry would have been discernible from the radial distribution curves. Concerning the relative orientations of the organic and iron-carbonyl moieties, we are on less certain ground. Here, in the absence of a sufficient number of isolated peaks, one's conclusions must be based upon the nature of the overall radial distribution curve profiles. We have been unable to conceive of any alternative models that would possess internuclear distances similar to those of the reported conformations.

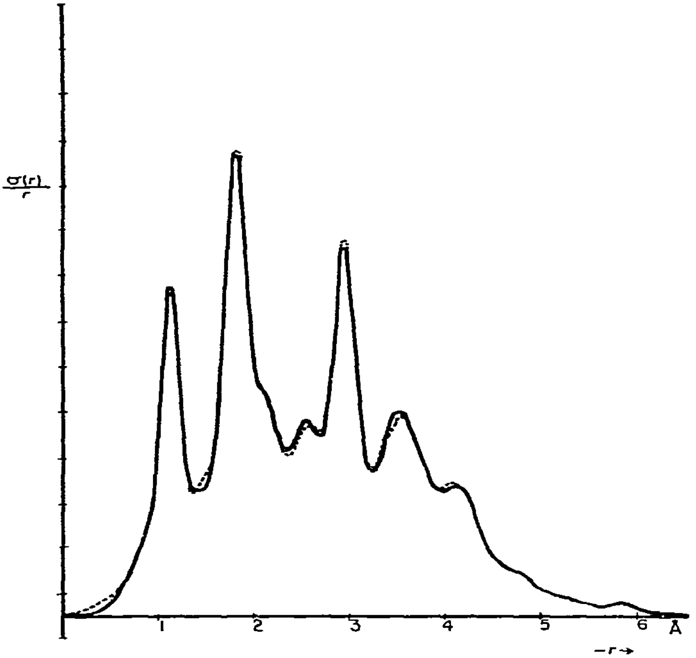

Fig. 9. Ethyleneiron tetracarbonyl. Radial distribution curves. ----- (exp.) —— (theor.) Damping factor $k = 0.003$.

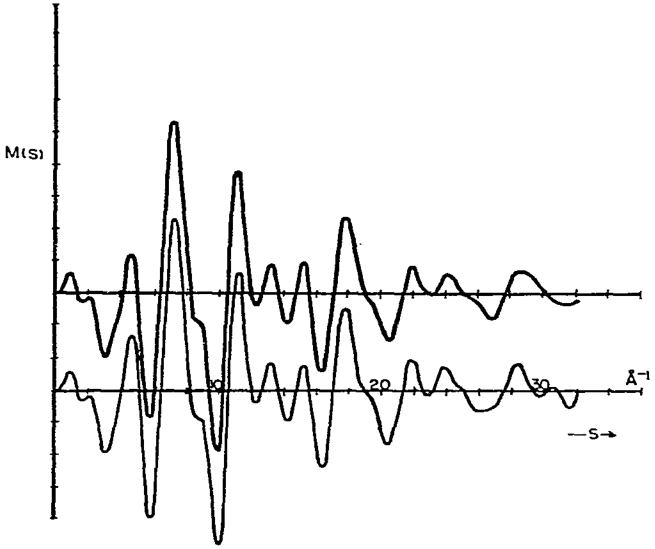

Fig. 10. Ethyleneiron tetracarbonyl. Molecular scattering curves. Upper curve theoretical, lower experimental.

Cyclobutadieneiron tricarbonyl

We can categorically rule out the possibility that in this complex the cyclobutadiene moiety possesses alternating single and double bonds, as has been proposed for the free molecule[8,9]. While our inclination is to consider that the diene moiety is square, the data is not inconsistent with a model in which alternating C–C bond lengths differ by a few hundredths of an Ångstrom.

There was no way in which we could ascertain whether or not the Fe(CO)$_3$ and diene groups undergo free rotation or have a preferred orientation. That the internuclear distances are so little changed with differing orientations is taken as a strong indication that in the gas phase free rotation is highly probable.

Our results are compared with those for the tetraphenyl derivative in Table 5.

TABLE 5

COMPARISON OF RESULTS FOR CYCLOBUTADIENEIRON TRICARBONYL AND (TETRAPHENYLCYCLOBUTADIENE)IRON TRICARBONYL

Parameter	Cyclobutadieneiron tricarbonyl (this work)	(Tetraphenylcyclobutadiene)iron tricarbonyl (ref. 6)
r(C–C)	1.456 Å	1.459 Å
r(Fe–C) diene	2.063	2.068
r(Fe–C) carbonyl	1.820	1.750
r(C=O)	1.131	1.179
r(Fe–O)	2.95	2.93
$\angle$CFeC [Fe(CO)$_3$]	95.6°	97.0°

We note that, while electron diffraction values for Fe–C (carbonyl) and C=O bond lengths are generally found to fall in the ranges 1.79–1.85 and 1.13–1.15 Å respectively[19,20], the X-ray studies have in most cases given shorter Fe–C and longer C–O values.

Ethyleneiron tetracarbonyl

Our results for this compound are presented with those for acrylonitrile iron tetracarbonyl in Table 6. The most significant difference is in the Fe–C (carbonyl)

TABLE 6

COMPARISON OF RESULTS FOR ETHYLENEIRON TETRACARBONYL AND ACRYLONITRILEIRON TETRACARBONYL

Parameter	Ethyleneiron tetracarbonyl	Acrylonitrileiron tetracarbonyl
r(C–C)	1.462 Å	1.40 Å
r(Fe–C) axial	1.796	1.99
r(Fe–C) equatorial	1.836	1.76
r(Fe–C) ethylene	2.117	2.10
r(C=O)	1.146	1.14
$\angle$CFeC[a]	105.2°	108°

[a] Angle between the equational Fe–C (carbonyl) bonds.

bond length values. We can find no logical reason for anticipating such a difference. We do not consider the difference between our values for the axial and equatorial Fe–C bond lengths to be significant.

The ethylene C–C bond length value of 1.46 Å is somewhat longer than that found in the acrylonitrile analogue. Its radial distribution curve contribution is so badly over-shadowed by those of the Fe–C bonds as to make our value of limited reliability.

The vibrational amplitude for the Fe-C (ethylene) bonds is quite a lot higher than its counterparts in the two diene complexes. The single peak in the proton resonance spectrum indicates that the two Fe–C bonds are equivalent. The high value must then arise from some sort of extra vibrational mobility.

Butadieneiron tricarbonyl

Our investigation of this compound was seriously hurt by the need to use oversimplified molecular models. The data were not adequate to provide the number of parameters required to give a reasonable description of the molecular geometry. Two of our assumptions were particularly unfortunate. From the accumulation of data in Table 7, it is clear that the two types of Fe–C (diene) bonds are not of equal length, as we felt we were obliged to assume. Further it would appear that these molecules possess $Fe(CO)_3$ groups which are distinctly distorted from C_{3v} symmetry. Despite these apparent model inadequacies, we were able to come close to reproducing the experimental radial distribution curve.

TABLE 7

A COMPARISON OF THE ELECTRON DIFFRACTION RESULTS FOR BUTADIENEIRON TRICARBONYL WITH THOSE OF X-RAY STUDIES OF RELATED COMPOUNDS[a]

	Butadieneiron tricarbonyl		A	B	C	D	E
	This work	Ref. 4					
r(Fe–C) diene	2.084	2.06[b]	2.05	2.06	2.09	2.05	2.045 Å
		2.14[c]	2.18	2.18	2.12	2.13	2.15
∠CFeC [$Fe(CO)_3$]	98.5°	93°[d]	93°	91°	[h]	80°	[h]
		102°[e]	101°	101.5°		89°	
r(Fe–C) carbonyl	1.801	1.76	1.80	1.77	1.78	1.76	1.73
r(Fe–O)	2.924	2.91	2.92	2.92	2.94	2.91	2.91
r(C–C)	1.409	1.45[f]	1.42	1.39	1.41	1.40	1.38
		1.46[g]	1.42	1.44	1.44	1.44	1.47

[a] A=$C_8H_8Fe(CO)_3$[21]; B=$C_8H_8[Fe(CO)_3]_2$[21]; C=$C_{16}H_{16}Fe(CO)_3$[22]; D=$C_7H_6OFe(CO)_3$[23]; E=$C_7(C_6H_5)_3H_3OFe(CO)_3$[24]. [b] Fe–$C_2$. [c] Fe–$C_1$. [d] C_5FeC_6. [e] C_5FeC_7=C_6FeC_7. [f] C_2–C_3. [g] C_1–C_2. [h] No value listed.

CONCLUSIONS

Clearly, these compounds are not ideally suited to the gas phase electron diffraction technique. The data are insufficient to provide the detailed structural description that is possible for smaller molecules. Consequently some of the items of structural information that would have been of interest were either not available at all, or, when available, of an ambiguous nature.

Most of the bond lengths and angular parameters were obtained within reasonable limits of confidence. The general conformational features were clearly established.

ACKNOWLEDGEMENTS

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