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A Gas Phase Electron Diffraction Investigation of Iron Pentacarbonyl

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The electron scattering pattern from gaseous iron pentacarbonyl has been recorded from $s=0.75$ Å^{-1} to $s=48.00$ Å^{-1}. The following bond distances are obtained by least-squares calculations on the intensity data (C–O)mean = 1.147 (0.002) Å and (Fe–C)mean = 1.832 (0.004) Å. It is concluded that Fe–C(eq) is between 0.000 Å and 0.050 Å longer than Fe–C(ax). The results are compared to those of a parallel study by Beagley, Cruickshank, Pinder, Robiette and Sheldrick.

Iron pentacarbonyl has recently been the subject of an electron diffraction investigation by Davis and Hanson [1,2] who concluded that the axial Fe–C bonds are 0.049 ± 0.020 Å shorter than the equatorial. Donohue and Caron [3,4] have pointed out that X-ray investigations of the crystal [5,6] yield a model in which the axial bonds are longer than the equatorial, though not significantly so. They also expressed doubt as to whether a difference of this magnitude can be determined by electron diffraction in a relatively complicated molecule like iron pentacarbonyl.

The problem is undoubtedly near the limit of the possible for electron diffraction at this time. Davis and Hanson therefore have asked us to duplicate their study. In addition to being a contribution towards the solution of the problem at hand, a duplicate study would serve as a check on the consistency of results obtained in different laboratories. For this reason we believe that double studies should be undertaken more often than is now the case.

We did not know that yet another electron diffraction study of iron pentacarbonyl was being carried out by Beagley, Cruickshank, Pinder, Robiette and Sheldrick [7] (hereafter referred to as BCPRS) before our study was completed.

EXPERIMENTAL AND CALCULATION PROCEDURE

Iron pentacarbonyl (purum) was purchased from Fluka AG and used without further purification. The scattering pattern from the gas was recorded on the Oslo electron diffraction units [8,9] with a nozzle temperature of 25°C. Exposures were made with four

nozzle to photographic plate distances, the four sets of plates thus obtained covered the diffraction ranges $s=0.75$ to 7.00 Å^{-1}, $s=1.50$ to 20 Å^{-1}, $s=7$ to 40 Å^{-1}, and $s=10$ to 50 Å^{-1}. $s=(4\pi/\lambda)\sin(\theta/2)$ when λ is the electron wavelength (determined by diffraction from gold foil) and θ the diffraction angle.

Four plates from each of the three first sets and two from the last were photometered and the traces read off by an $x-y$ reader. The data were corrected and processed in the usual way.[9]

The resulting modified molecular intensity points are shown in Fig. 1. They extend from 0.75 Å^{-1} to 47.75 Å^{-1}. Below 10 Å^{-1} the point density is eight per Å^{-1}, above 10 Å^{-1} four points per Å^{-1}.

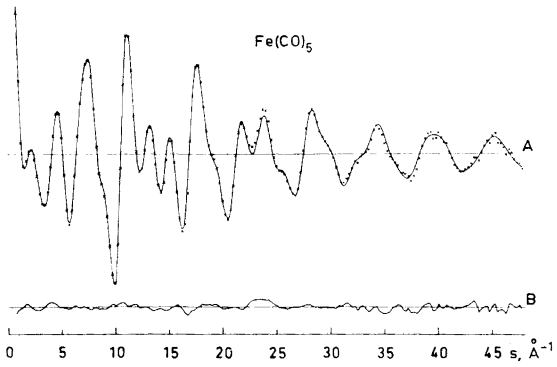

Fig. 1. A; experimental modified molecular intensity points and a theoretical modified molecular intensity curve calculated from the parameters in Table 1, column D and Table 2, column B. B; difference curve.

Theoretical curves were calculated from

$$I^{CC}(s) = \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_C(s)||f_C(s)|} \cos(\eta_i(s)-\eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2)$$

$$= \sum_{i \neq j} g_{ij/CC}(s) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2) \quad (1)$$

The sum extends over all atom pairs i,j in the molecule. R_{ij} is the internuclear distance, u_{ij} the root-mean-square amplitude of vibration. $f_j(s)=|f_j(s)|\exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j. It has been computed for Fe, C, and O by the partial wave approximation method with a program written by Peacher [10] and modified by Strand. The scattering potentials of C and O have been found by nonrelativistic Hartree-Fock,[11] the scattering potential of Fe by relativistic Hartree-Fock calculations.[12]

Radial distribution (RD) curves were obtained by Fourier inversion of experimental or theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$.

The molecular structure was refined by least-squares calculations on the intensity data [13] with a diagonal weight matrix.

STRUCTURE ANALYSIS

An experimental RD curve is shown in Fig. 2A. The three most prominent peaks are a C—O bond distance peak at 1.15 Å, a Fe—C bond distance peak at 1.83 Å and a nonbonded Fe···O distance peak at 2.97 Å.

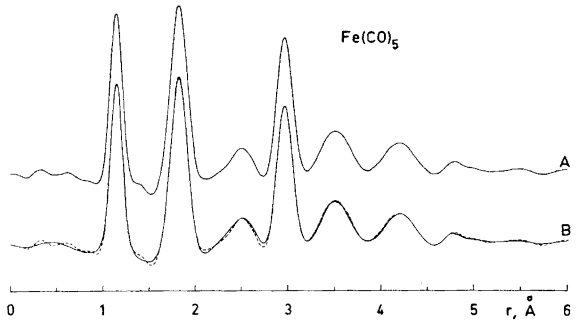

Fig. 2. A; Experimental RD curve. B; theoretical RD curve calculated from the parameters in Table 1, column D and Table 2, column B with the experimental curve stipled in. Artificial damping constant $k=0.0015$ Å^2.

Since the peaks corresponding to the two different Fe—C distances are not resolved, these distances (and the difference between them) can only be accurately determined by utilizing information contained in the outer part of the RD curve, that is by assuming functional relationships between the bond distances and the long nonbonded distances. It should be pointed out at the outset that the values obtained for the bond distances and their estimated standard deviations are accurate only insofar as these functional relationships are accurate.

We have assumed throughout this work that the equilibrium conformation of $Fe(CO)_5$ has D_{3h} symmetry. Furthermore, since a difference in the strength of the Fe—C(ax) and Fe—C(eq) bonds probably would have only a second order effect on the C—O bond distances, we have assumed that all C—O bonds have the same length. The molecular structure is then determined by three independent parameters; the two Fe—C distances and the C—O distance. The nonbonded distances were calculated from the three bond distances by the simple formulae suggested by D_{3h} symmetry.

When all vibrational amplitudes were treated as independent parameters, the least-squares calculations failed to converge. The number of unknown u-values was therefore reduced from sixteen to twelve by giving four pairs of distances the same u-value. These pairs were: the two C—O bond distances, the two Fe—C bond distances, the two Fe···O distances and the C(ax)···O(eq) and C(eq)···O(ax) distances.

Brunvoll [14] has calculated approximate symmetry force constants for iron pentacarbonyl from spectroscopic data by assuming zero value for all off-diagonal elements, and from this approximate forcefield he has calculated the vibrational amplitudes at 25°C. His results are listed in Table 1, column A. It is seen that the amplitudes calculated for the four pairs are very similar indeed; in all four cases is the difference between the two less than the standard deviation subsequently obtained by least-squares refinement of their mean. The calculated u-values therefore lend support to these assumptions.

Simultaneous least-squares refinement of the three bond distances and the twelve u-values gave the square-error sum and parameter values listed

Table 1. Root mean square vibrational amplitudes (u-values) and shrinkages in $Fe(CO)_5$ in Å. A; vibrational amplitudes at 298°K as calculated by Brunvoll.[14] B; vibrational amplitudes at 298 ± 10°K obtained in this work when shrinkages are not included. C; shrinkages at 298°K as calculated by Brunvoll.[14] D; vibrational amplitudes at 298 ± 10°K as obtained in this work when calculated shrinkages are included. E; vibrational amplitudes at 303°K as obtained by BCPRS.[7]

	A	B	C	D	E
C(ax)—O(ax)	0.0353	0.033 (0.001)		0.033 (0.001)	0.026 (0.007)
C(eq)—O(eq)	0.0348				
Fe —C(ax)	0.0506	0.057 (0.003)		0.057 (0.003)	0.048 (0.003)
Fe —C(eq)	0.0484				0.050 (0.003)
Fe ···O(ax)	0.0525	0.055 (0.006)	0.0044	0.055 (0.008)	0.054 (0.003)
Fe ···O(eq)	0.0503		0.0074		0.055 (0.003)
C(ax)···C(eq)	0.1490	0.125 (0.006)	0.0036	0.123 (0.005)	0.103 (0.007)
C(ax)···O(eq)	0.1818	0.152 (0.012)	0.0106	0.152 (0.010)	0.171 (0.005)
C(eq)···O(ax)	0.1795		0.0079		
O(eq)···O(ax)	0.2451	0.299 (0.034)	0.0151	0.270 (0.026)	0.321 (0.030)
C(eq)···C(eq)	0.1053	0.136 (0.023)	0.0070	0.112 (0.015)	0.179 (0.032)
C(eq)···O(eq)	0.1284	0.143 (0.011)	0.0161	0.149 (0.013)	0.153 (0.010)
O(eq)···O(eq)	0.1718	0.140 (0.008)	0.0263	0.231 (0.012)	0.171 (0.011)
C(ax)···C(ax)	0.0649	0.29 (0.22)	0.0193	0.20 (0.10)	0.30 (0.22)
C(ax)···O(ax)	0.0663	0.060 (0.009)	0.0286	0.068 (0.010)	0.057 (0.013)
O(ax)···O(ax)	0.0677	0.097 (0.033)	0.0414	0.093 (0.027)	0.049 (0.018)

in Table 2, column A and Table 1, column B. This minimum structure was obtained regardless of the relative magnitude of the two Fe—C bond distances in the start-model. Also listed in Table 2 is the mean Fe—C bond distance and Δ=(Fe—C(eq))—(Fe—C(ax)). The least-squares calculation gave a standard deviation for Fe—C(eq) equal to 0.0026 Å and a standard deviation for Fe—C(ax) equal to 0.0036 Å. The correlation coefficient $\varrho = -0.895$. The standard deviations of (Fe—C) mean and Δ were calculated from

$$\sigma(f(R_1,R_2)) = \left[\sigma_1^2\left(\frac{\partial f}{\partial R_1}\right)^2 + \sigma_2^2\left(\frac{\partial f}{\partial R_2}\right)^2 + 2\sigma_1\sigma_2\sigma_{12}\left(\frac{\partial f}{\partial R_1}\right)\left(\frac{\partial f}{\partial R_2}\right)\right]^{\frac{1}{2}}$$

σ((Fe—C)mean)=0.0007 Å and $\sigma(\Delta)$=0.0060 Å. Finally, the standard deviations for all parameters were expanded according to

$$\sigma^1(P) = [\sigma^2 + (0.0014 \cdot P)^2]^{\frac{1}{2}}$$

in order to account for an uncertainty of 0.0014 in the electron wavelength.[9] The expanded standard deviations are listed alongside the parameters in Tables 1 and 2.

It is common experience that the average value of the long nonbonded distances that is observed by electron diffraction is—because of molecular bending vibrations—shorter than the distance calculated from the bond distances by means of the simple formulae suggested by the equilibrium geometry.[15] Brunvoll has calculated these "shrinkages" in iron pentacarbonyl at 25°C from the approximate forcefield, the values are listed in Table 1, column C.

Table 2. Bond distances ($r_g(1)$[16]) in iron pentacarbonyl and their estimated standard deviations. Column A through E as obtained by different least-squares refinements on the intensity data in this study, F as obtained by BCPRS[7] and G as obtained by Davis and Hanson.[1,2] Column A; the independent interatomic distances ($r_g(1)$) are calculated from the three bond distances from the three bond distances (r_g) and calculated shrinkages[14] subtracted. C; the independent interatomic distances (r_g[16]) are calculated from the three bond distances (r_g) and calculated shrinkages subtracted. D and E; the two least-squares minima obtained when u(Fe−C(ax)) and u(Fe−C(eq)) are given the values calculated by Brunvoll,[14] other conditions as in B.

	A	B	C	D	E	F	G
C−O	1.146(0.002)	1.147(0.002)	1.147(0.002)	1.147(0.002)	1.147(0.002)	1.145(0.001$_9$)	1.136(0.001$_5$)
Fe−C(ax)	1.816(0.005)	1.820(0.005)	1.816(0.005)	1.797(0.004)	1.844(0.005)	1.806(0.003$_3$)	
Fe−C(eq)	1.830(0.004)	1.832(0.004)	1.834(0.004)	1.847(0.003)	1.816(0.004)	1.833(0.002$_5$)	
(Fe−C(eq))−(Fe−C(ax))	0.014(0.006)	0.012(0.006)	0.018(0.007)	0.050(0.004)	−0.028(0.006)	0.027(0.005$_0$)	0.049(0.020)
(Fe−C) mean	1.824(0.003)	1.827(0.003)	1.826(0.003)	1.827(0.003)	1.827(0.003)	1.822(0.001^4)	1.823(0.001^4)
$\sum W(I_{exp}-I_{calc})^2$	2.06	1.57	1.64	1.72	2.10		

A new least-squares refinement was carried out with the shrinkages being subtracted from the nonbonded distances calculated from the bond distances. The resulting square-error sum, the parameters and their expanded estimated standard deviations are listed in Table 2, column B and Table 1, column D. This minimum structure too was obtained regardless of the relative magnitude of the two Fe—C bond distances in the start model. A theoretical modified molecular intensity curve and a theoretical RD curve calculated from these parameters are shown in Fig. 1 and Fig. 2. The agreement with the experimental curves is excellent.

The least-squares refinement was repeated with yet another modification: The bond distances, $r_g(1)$,[16] were converted into r_g [16] through addition of u^2/R, the dependent distances were calculated from the r_g values of the bond distances by the formulae following from the molecular symmetry, the shrinkages subtracted, and all interatomic distances converted back into $r_g(1)$ through subtraction of u^2/R. Ideally this procedure should be more accurate. The resulting square error sum, bond distances and standard deviations are given in Table 2, column C. The parameters have changed only slightly, but the square error sum has increased from 1.57 to 1.64 indicating that this procedure is less favourable. The reason is probably that calculations based on $r_g(1)$ lead to fortuitous cancelling of some of the error introduced by the neglect of anharmonicity and asymmetry.[17]

Finally, two refinements were carried out with u(Fe—C(ax)) and u(Fe—C(eq)) fixed at the values calculated by Brunvoll. In this case two stable least-squares minima were obtained, one with Fe—C(ax) shorter than Fe—C(eq) (Table 2, column D) and one with Fe—C(ax) longer than Fe—C(eq) (Table 2, column F).

DISCUSSION

It is clear from the decrease of the square-error sum from 2.06 to 1.57 that inclusion of the calculated shrinkage effects improves the agreement quite considerably. However, it is seen from Table 1, columns B and D, and from Table 2, columns A and B, that the only parameter to change significantly is u(O(eq)···O(eq)) which changes from 0.140 (0.008) Å to 0.231 (0.012) Å. Obviously this parameter would be so sensitive to errors in the calculated shrinkage values that no significance can be attached to its estimated standard deviation. All the other parameters, however, change with an amount equal to or less than one standard deviation, and one might hope that these parameters would be correspondingly insensitive to errors in the calculated shrinkage values.

Since the lowest square-error sum was obtained by calculating the nonbonded distances from the $r_g(1)$ distances of the bonded distances and the subtraction of shrinkages we believe that the best estimate of the molecular parameters is found in Table 2, column B and Table 1, column D.

On the whole there is a reasonable agreement between the u-values calculated by Brunvoll and the u-values determined by us. The only instance when the difference is greater than three standard deviations (apart from u(O(eq)···O(eq))) is u(C(ax)···C(eq)). For this parameter the calculated value

is 0.1490 Å while we find 0.123 (0.005) Å. It should be noted, however, that BCPRS obtained 0.103 (0.007) Å which is in agreement with our result but significantly different from the calculated value. Since the u-values for non-bonded distances calculated from approximate forcefields are not always accurate, we believe that in this instance the calculated value may be in error.

Even though it is (barely) smaller than three standard deviations, the difference between the calculated values for the amplitudes of the Fe—C(eq) and the Fe—C(ax) distances, 0.0484 Å and 0.0506 Å, and the mean value determined by us, 0.057 (0.003) Å, is more disturbing: Calculated values for amplitudes of bonded distances are generally quite accurate. When the two u-values are fixed at the values calculated by Brunvoll, *two* stable least-squares minimum structures are obtained (Table 2, columns D and E). According to Hamilton's R-factor test [18] the lowest might be rejected at a significance level of about 0.005 the highest (by extrapolation of Hamilton's tables) at a significance level of about 10^{-5}.

We should, however, like to strike a note of caution at this point: Hamilton's test presupposes that there are no systematic errors, that the proper weighting-scheme has been used and that the observational equations are linear. Then conditions may not be entirely satisfied.

We believe that the disagreement is most probably due to the necessarily imperfect nature of our analysis; anharmonicity and asymmetry [17] has been neglected, approximate values for shrinkages have been used and the simplifying assumptions regarding the equility of C—O bond distances and various amplitudes of vibration have been made.

The electron diffraction study by BCPRS [7] has been carried out in a manner very similar to this study, the main differences being that their data do not extend beyond $s=30$ Å^{-1}, and that their least-squares calculations are superior to ours since they use a non-diagonal weight matrix. The parameter values and estimated standard deviations obtained by these workers are set out in Table 1, column E and Table 2, column F.

It is seen that at no point (always excepting u(O(eq)···O(eq)) is their result in disagreement with ours. The values obtained for the C—O bond distance and $(\text{Fe—C})_{\text{mean}}$ is 2.5 ppt lower than the values obtained by us, which indicates a scale difference of this magnitude. This is in agreement with observations made by Seip and coworkers in this laboratory who have carried out a series of studies on CO_2. They find bond distances that tend to lie 2.5 ppt above the spectroscopic.[19]

The bond distances obtained by Davis and Hanson [1,2] are set out in Table 2, column G. Since they have been obtained without the use of shrinkage they should be compared to those in column A. It is seen that their value for (Fe—C)mean is in good agreement with ours while their value for the C—O bond distance is significantly smaller than that obtained by us or by BCPRS.

Since Δ=(Fe—C(eq))—(Fe—C(ax)) is strongly correlated with the mean value for the Fe—C amplitude, and since this parameter was found to be rather different from the calculated amplitude, the value $\Delta=0.012$ (0.006) Å cannot be accepted without some reservation: Since it is obtained along with a mean Fe—C amplitude that is too large, the absolute value of Δ is probably too low. When the two Fe—C amplitudes were fixed at the values calculated by

Brunvoll, two minimum structures were obtained, one with $\Delta = 0.050$ (0.004) Å, the other with $\Delta = -0.028$ (0.006) Å. Hamilton's test indicates that the former can be rejected at a significance level of about 0.005 which the latter can be rejected at a significance level of about 10^{-5}. It is therefore very unlikely that Δ lies outside the range 0.000 to 0.050 Å. This conclusion, of course, is in excellent agreement with the values for Δ found by Davis and Hanson and by BCPRS.

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