Infrared Spectrum of Matrix Isolated Tricarbonyliron

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Prolonged u.v. photolysis of the matrix isolated complex [Fe(CO)$_5$] results in formation of the fragment [Fe(CO)$_3$]. Isotopic substitution indicates a pyramidal C_{3v} structure. Possible reasons for this structure are discussed. Further u.v. photolysis produces Fe(CO)$_x$ species ($x < 3$).

IT has already been reported that u.v. photolysis of matrix-isolated pentacarbonyliron results in the formation of a tetracarbonyl species, and that subsequent irradiation with longer wavelength light regenerates the parent pentacarbonyl.[1] The structure of the [Fe(CO)$_4$] fragment was distorted from tetrahedral, possibly as a result of Jahn–Teller effects. In this paper it is shown that prolonged u.v. photolysis of the complex [Fe(CO)$_5$] removes more than one CO ligand to form [Fe(CO)$_3$], and small amounts of lower carbonyl fragments.

Figure 1(a) shows the i.r. spectrum of [Fe(CO)$_5$] isolated in a CH$_4$ matrix (1 : 10 000) at 20 K. Although only two i.r. active bands ($A_2'' + E'$) are expected for a D_{3h} pentacarbonyl in the C–O stretching region, three strong bands were observed. The extra band has been assigned to ' matrix effects '.[1]

After u.v. photolysis for 1 min with a medium pressure mercury arc [Figure 1(b)], the [Fe(CO)$_5$] bands were reduced in intensity and those of [Fe(CO)$_4$] (labelled 4) appeared. In addition two † other bands (labelled 3) were observed. On further photolysis these bands continued to grow until after 5 min, the band at 1930 cm^{-1} was the strongest in the spectrum [Figure 1(c)]. At the same time both the [Fe(CO)$_5$] and [Fe(CO)$_4$] bands decreased in intensity. With longer wavelength photolysis ($\lambda > 320$ nm), or on annealing the matrix, the intensity of the ' **3** ' bands decreased and that of the [Fe(CO)$_5$] and [Fe(CO)$_4$] bands increased (not illustrated).

The most obvious assignment of the ' 3 ' bands is to an [Fe(CO)$_3$] species. Isotopic substitution confirms this assignment and distinguishes between the possible structures of the fragment. The use of C^{18}O to characterize matrix-isolated carbonyl species has been described at length by Darling and Ogden.[3] Although they did not specifically consider distorted M(CO)$_3$ species, the method used here is essentially the same. By means of the Cotton–Kraihanzel CO factored force field,[4] the expected positions of the bands of the isotopically substituted [Fe(CO)$_3$] fragments can be predicted for each structure.

Since two i.r. bands were observed for the unsubstituted molecule a planar D_{3h} structure (one active mode) can be eliminated. A planar tricarbonyl can undergo distortion to a C_{3v} structure (two active modes $A_1 + E$), a C_{2v} or a C_s structure (three active modes, $2A_1 + B_1$ and $2A' + A''$). Figure 2 shows the C–O stretching bands of [Fe(CO)$_3$] generated from ^{13}CO substituted [Fe(CO)$_5$] (the bands drawn in broken lines are due to [Fe(CO)$_5$] and [Fe(CO)$_4$] species). A C_{3v} tricarbonyl would have two CO force constants (one stretching and one interaction constant) while C_{2v} or C_s structures would have four (two stretching and two interaction constants). Using two force constants, the agreement between the calculated and observed spectra is so close (see Table 1) that there is little doubt that the bands are due to a C_{3v} [Fe(CO)$_3$] fragment.

In a C_{3v} tricarbonyl, the relative intensities of the A_1

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† A third band at *ca.* 1950 cm^{-1} was also produced and will be discussed fully in a separate paper (ref. 2). It is assigned to an [Fe(CO)$_4$CH$_4$] species.

[1] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, **1973**, 1351.
[2] M. Poliakoff and J. J. Turner, unpublished work.
[3] J. H. Darling and J. S. Ogden, *J.C.S. Dalton*, **1972**, 2496.
[4] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

and E modes are independent of force field and can be used to estimate the bond angle between the CO groups.[5]

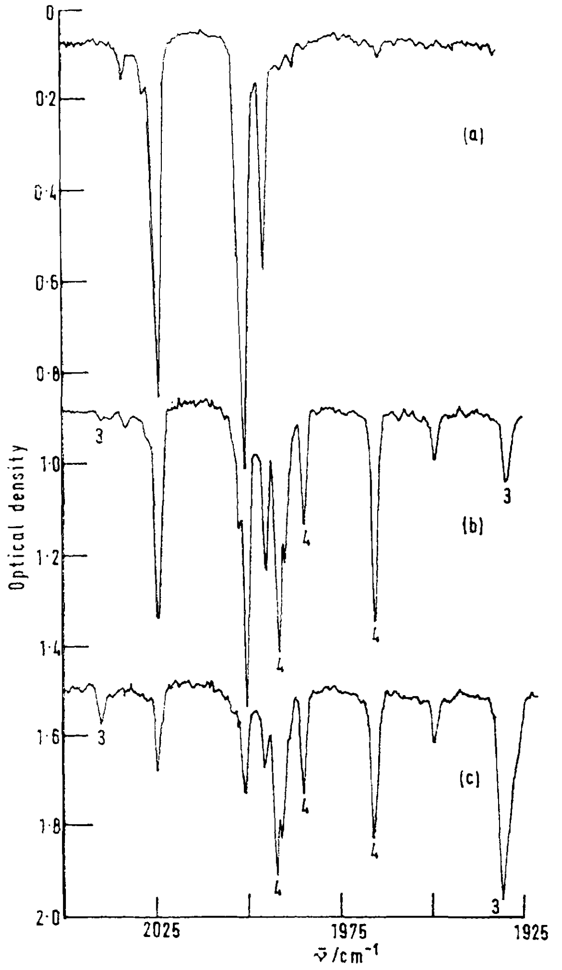

FIGURE 1 I.r. spectra of $[Fe(CO)_5]$ in a CH_4 matrix at 20 K; (a) after deposition; (b) 1 min. u.v. photolysis; (c) 5 min. u.v. photolysis

Using the observed ratio $A_1 : E$ for the unsubstituted molecule ($1 : 8 \pm 1$) the estimated angle is *ca.* 108 ± 3°, very close to that in a tetrahedron. The intensities of the isotopic bands were also consistent with such a distortion.

The complex $[Fe(CO)_3]$ was produced in several other matrices to see whether this distortion was a general effect. In xenon (1 : 4000) the spectrum was similar to methane. In krypton (1 : 10 000) a high frequency band was observed but the overall yield was much lower than in methane or xenon. This band appeared to be slightly less intense relative to the low frequency band than in the other matrices. Unfortunately, in argon not only was the yield still lower but also other bands obscured the region where the high frequency band would be expected. However, using isotopic data from the low frequency region the expected positions of the high frequency bands could be calculated with an uncertainty of 2 cm^{-1}. The band of the disubstituted molecule (*ca.* 2014 cm^{-1}) should have been observable under the conditions of the experiment, but it was not seen. However, the weakness of the bands involved prevents this result from being used as evidence for a planar structure. Photolysis of $[Fe(CO)_5]$ in solid nitrogen at 20 K produced the two bands of $[Fe(CO)_3]$, both split, at rather higher wavenumbers than in other matrices.

TABLE 1

Wavenumbers of ^{13}CO substituted $[Fe(CO)_3]$ species in CH_4 matrix at 20 K

	Observed	Calculated
$[Fe(CO)_3]$	2040·1	2039·8
	1930·4 [b]	1930·1
$[Fe(CO)_2(^{13}CO)]$	2027·9	2028·1
	1930·4 [b]	1930·1
	1897·9	1898·0
$[Fe(CO)(^{13}CO)_2]$	2013·9	2013·9
	1911·3	1911·3
	1887·1 [b]	1887·1
$[Fe(^{13}CO)_3]$	*a*	1994·3
	1887·1 [b]	1887·1

Average error in wavenumbers 0·007 per cent; $k = 15{\cdot}627 \pm 0{\cdot}002$ mdyn Å^{-1}; $k_i = 0{\cdot}586 \pm 0{\cdot}002$ mdyn Å^{-1}.

[a] Region obscured by $[Fe(CO)_4]$ band. [b] Included only once in 'least-squares' refinement as the wavenumber is necessarily degenerate.

These bands were related to weak absorptions (2189, 2184 cm^{-1}) in the N–N stretching region and were probably due to an $[Fe(CO)_3N_2]$ complex similar to the complex $[Ni(CO)_3N_2]$, recently reported by Rest.[6] The wavenumbers and force constants of all these species are summarized in Table 2.

The results suggest that in most, if not all, the matrices $[Fe(CO)_3]$ has a C_{3v} structure. Kettle[7] has considered the shapes of simple $M(CO)_x$ moieties using a perturbation model, and predicted that the carbonyls should adopt the most symmetrical and stereochemically least

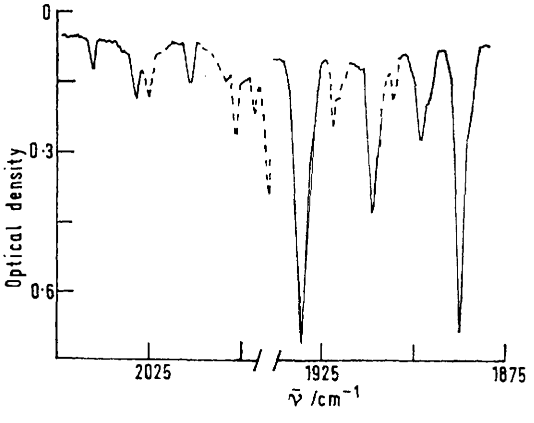

FIGURE 2 I.r. spectrum of a mixture of $[Fe(^{12}CO)_{3-x}(^{13}CO)_x]$ species (x = 0—3) in a CH_4 matrix at 20 K. Bands shown in broken lines due to $[Fe(CO)_4]$ and $[Fe(CO)_5]$

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[5] L. M. Haines and M. B. H. Stiddard, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

[6] A. J. Rest, *J. Organometallic Chem.*, 1972, **40**, C76.

[7] S. F. A. Kettle, *J. Chem. Soc.* (*A*), 1966, 420.

hindered structure (*i.e.* D_{3h} for a tricarbonyl). Unfortunately there are insufficient data (apart from d^{10} systems[8]) to show whether these results are generally valid for unsaturated carbonyls. If the predictions are correct, an explanation must be found for the distortion of $[Fe(CO)_3]$. Jahn–Teller effects do not seem likely since the distortion $D_{3h} \longrightarrow C_{3v}$ does not alter the degeneracy of the ground state. Other possible explanations involve the matrix itself, the distortion being caused either by crystal packing effects or by specific matrix–host interactions. Turner and Rest reported that the distortion of the fragment $[Ni(CO)_3]$ varied from one matrix to another.[9] However $[Ni(CO)_3]$ has since been shown to be planar[8] and their results appear to be a concentration effect.[10] Studies on $[Fe(CO)_4]$ suggest a specific matrix–carbonyl interaction with several matrices, notably CH_4, Xe, and N_2,[2] and such an interaction may well be responsible for the distortion of $[Fe(CO)_3]$. Unfortunately it is impossible to predict from these results which structure 'free' $[Fe(CO)_3]$ would adopt in the absence of a matrix.

TABLE 2

Wavenumbers and force constants of $[M(CO)_3]$ species in different matrices

Molecule	Matrix	Wavenumber/ cm^{-1}	Force constant/ mdyn $Å^{-1}$
$[Fe(CO)_3]$	Xe	2036	15·57
		1927	0·58
	CH_4	2040·1	15·627
		1930·4	0·586
	Kr	2044	15·67
		1933	0·60
	Ar	(2042 ± 2 cm^{-1})[a]	15·70
		1935·6	0·6
$[Fe(CO)_3N_2]$	N_2	2189, 2184	
		2045, 2043	15·83[b]
		1954, 1948	0·51[b]
$[Ni(CO)_3]$[c]		2017	
$[Ni(CO)_3N_2]$[d]	N_2	2266	
		2098	17·01[b]
		2031, 2027	0·38[b]

[a] Calculated using ^{13}CO substitution (see text). [b] Using average values of wavenumbers. [c] Ref. 8. [d] Ref. 6.

Prolonged photolysis of $[Fe(CO)_5]$ in a CH_4 matrix produced a C–O stretching band at **1876** cm^{-1}, a frequency lower than that of $[Fe(CO)_3]$. This band was presumably due to a lower carbonyl, $[Fe(CO)_x]$ ($x = 1$ or 2). Without data for the symmetric stretching modes of dicarbonyl species, isotopic substitution is less helpful for these fragments than with higher carbonyls since the force constant calculations are not over-determined. All the bands are required for the calculation and there are no bands left to use as a check of the assignment. In these circumstances the bands must be assigned using relative intensities, and in our experiments the results were inconclusive. Lower carbonyl bands were also observed in nitrogen (*ca.* **1916**, **1911** cm^{-1}) and argon matrices (*ca.* **1905** cm^{-1}). U.v. studies showed the formation of iron atoms under these conditions,[2] indicating that all the CO groups can be removed from $[Fe(CO)_5]$.

CONCLUSION

These experiments show that effect of u.v. photolysis on the complex $[Fe(CO)_5]$ is the stepwise loss of CO groups, and that the resulting fragments $[Fe(CO)_4]$ and $[Fe(CO)_3]$ do not adopt the most symmetrical structure. This distortion may be due to interaction with the matrix.*

EXPERIMENTAL

The apparatus used in these experiments has already been described.[1] The matrix gases (B.O.C. Grade X) and $[Fe(CO)_5]$ (redistilled commercial) were used without further purification. $[Fe(CO)_{5-x}(^{13}CO)_x]$ was prepared by gas phase exchange with ^{13}CO (Prochem 90%) using the method of Crichton and Rest.[11] The principal product was solid $[Fe_2(CO)_9]$, the formation of which unfortunately prevented the preparation of a truly statistical mixture of isotopically substituted molecules. Frequency measurements were made using DCl in the reference beam of the spectrometer, and were reproducible to 0·2 cm^{-1}.

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* *Note added in proof:* Recent molecular-orbital calculations (J. K. Burdett, unpublished work) indicate that $[M(CO)_x]$ fragments do not necessarily adopt the most symmetrical structures. In particular the calculations predict a bond angle in $[Fe(CO)_3]$ of 111° which is remarkably close to that observed in the matrix (108 ± 3°). This suggests that the C_{3v} structure of $[Fe(CO)_3]$ is not the result of matrix interactions.

[8] R. I. DeKock, *Inorg. Chem.*, 1971, **10**, 1205.
[9] A. J. Rest and J. J. Turner, *Chem. Comm.*, 1969, 1026.
[10] A. J. Rest, unpublished results.
[11] O. Crichton and A. J. Rest, *Inorg. Nuclear Chem. Letters*, 1972, **9**, 391.