Infrared Spectra and Photochemistry of the Complex Pentacarbonyliron in Solid Matrices at 4 and 20 K: Evidence for Formation of the Complex Tetracarbonyliron

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The i.r. spectrum of the complex pentacarbonyliron, $[Fe(CO)_5]$, has been recorded in a number of different low-temperature matrices. U.v. photolysis produces new bands in the C–O stretching region; these bands disappear on exposure to longer-wavelength light and are assigned to the tetracarbonyl fragment $[Fe(CO)_4]$ plus carbon monoxide. The fragment probably adopts a C_{3v} structure due to Jahn–Teller distortion of the tetrahedron. In an argon matrix the formation of $[Fe(CO)_4]$ becomes irreversible after prolonged photolysis; this is due to diffusion through the solid argon of CO molecules.

THERE has been considerable argument as to whether the complex pentacarbonyliron, $[Fe(CO)_5]$, reacts photochemically *via* a tetracarbonyl fragment $[Fe(CO)_4]$ or an excited state of the pentacarbonyl molecule, $[Fe(CO)_5]^*$. Keeley and Johnson[1] proposed the mechanism in equations (1) and (2) for the gas-phase formation of the

$$[Fe(CO)_5] \xrightarrow{h\nu} [Fe(CO)_5]^* \qquad (1)$$

$$[Fe(CO)_5]^* + [Fe(CO)_5] \longrightarrow [Fe_2(CO)_9] + CO \qquad (2)$$

complex $[Fe_2(CO)_9]$. This mechanism, which was based on the rate of incorporation of ^{14}CO into the $[Fe_2(CO)_9]$ complex, is now somewhat discredited.[2] By studying the photochemical exchange between the complex $[Fe(CO)_5]$ and $C^{18}O$ in solution and the scrambling of CO ligands between the complexes $[Fe(CO)_5]$ and $[Fe(C^{18}O)_5]$, Noack and Ruch[3] produced strong evidence for an $[Fe(CO)_4]$ intermediate [equation (3)]. Similarly flash-

$$[Fe(CO)_5] \rightleftharpoons [Fe(CO)_4] + CO \qquad (3)$$

photolysis experiments on the complex $[Fe(CO)_5]$ in solution[4] can be interpreted on the basis of initial formation of $[Fe(CO)_4]$, and the latter complex has been extensively postulated as an intermediate derived from the complex $[Fe_2(CO)_9]$.[5] Attempts to identify an $[Fe(CO)_4]$ species, by flash photolysis in the gas phase[6] or in solution,‡ have so far been unsuccessful.

Sheline and his co-workers[7] isolated the complex $[Fe(CO)_5]$ in hydrocarbon glasses at 77 K. Photolysis produced new i.r. bands which were attributed to $[Fe(CO)_x]$ species but not definitely assigned. On melting the glass a new band was observed at 1834 cm^{-1}, which may have been due to formation of the complex $[Fe_2(CO)_9]$. More recently, Newlands and Ogilvie[8] photolysed the complex $[Fe(CO)_5]$ with acetylene and ethylene in argon matrices and observed bands due to $[Fe(CO)_4(olefin)]$ complexes.

In this laboratory, the photolysis of metal carbonyl complexes in inert matrices at 15 or 20 K has provided spectroscopic evidence for carbonyl fragments and also given information concerning the mechanism of CO loss.[9] In preliminary experiments with the complex $[Fe(CO)_5]$ in an argon matrix at 20 K, Rest[10] showed that new i.r. bands appeared on photolysis. The spectra were difficult to interpret because (*a*) the spectrum of the $[Fe(CO)_5]$ complex in a matrix was exceedingly complicated and (*b*) the intensities of the bands which appeared on photolysis were low and only a small fraction of the parent pentacarbonyl complex reacted.

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‡ von Gustorf and Grevels[2] observed a transient spectrum on flash photolysing the complex $[Fe(CO)_5]$ in benzene; this is however almost certainly due to a carbonyl benzene complex, not $[Fe(CO)_4]$.[4]

[1] D. F. Keeley and R. E. Johnson, *J. Inorg. Nuclear Chem.*, 1959, **11**, 33.

[2] E. Koerner von Gustorf and F.-W. Grevels, *Fortschr. Chem. Forsch.*, 1969, **13**, 336.

[3] K. Noack and M. Ruch, *J. Organometallic Chem.*, 1969, **17**, 309.

[4] E. Koerner von Gustorf and F.-W. Grevels, unpublished work.

[5] P. S. Braterman and W. J. Wallace, *J. Organometallic Chem.*, 1971, **30**, C17.

[6] A. B. Callear and R. J. Oldman, *Trans. Faraday Soc.*, 1967, **63**, 2888.

[7] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, 1963, **84**, 3589; 1964, **85**, 1013.

[8] M. J. Newlands and J. F. Ogilvie, *Canad. J. Chem.*, 1971, **49**, 343.

[9] M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2939.

[10] A. J. Rest and J. J. Turner, *Proc. 4th Internat. Conf. Organometallic Chem.*, Bristol, 1969.

We have previously reported the reaction between the complex $[Fe(CO)_5]$ and $C^{18}O$ in an argon matrix,[11] and here we describe a series of experiments with this complex in a variety of matrices, which provide strong evidence for the reversible formation of the complex $[Fe(CO)_4]$, the i.r. spectrum of which is most easily interpreted in terms of a tetrahedron distorted to a C_{3v} structure. This distortion is *probably* a consequence of Jahn–Teller distortion of the d^8 system. The experiments also give some indication as to the fate of the photochemically produced carbon monoxide.

RESULTS AND DISCUSSION

Short Photolysis in Various Matrices.—Figure 1(*a*) shows the i.r. spectrum of the complex $[Fe(CO)_5]$ in the C–O stretching region in a neon matrix (1 : 2000) at 4 K. In solution and in the gas phase, the complex $[Fe(CO)_5]$ shows two i.r. bands which are assigned to A_2'' and E' modes of a D_{3h} molecule, the A_2'' band being at higher frequency. In the neon matrix not only are both the strong bands split, the A_2'' more than the E', but there are also two weak bands at 2043 and 2004 cm^{-1}. We have found more than two bands in the spectra of the $[Fe(CO)_5]$ complex in a variety of different matrices and discuss the origins of these extra bands below, but it should be noted here that the bands are due to distortion and different sites for the complex.

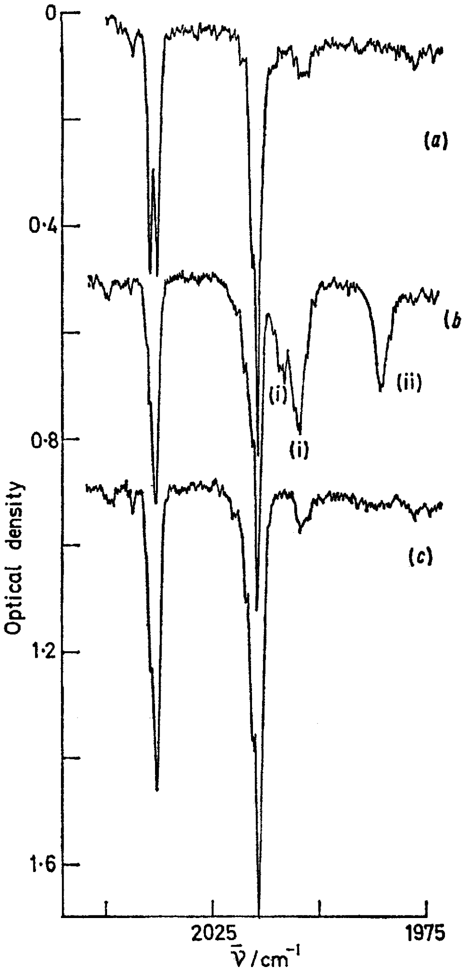

FIGURE 1 I.r. spectrum of the complex $[Fe(CO)_5]$ in a neon matrix (1 : 2000) at 4 K after (*a*) spray-on, (*b*) u.v. photolysis (1 min), and (*c*) photolysis with the Nernst glower (3 min)

After photolysis (1 min) with a medium-pressure mercury arc [Figure 1(*b*)], the strong bands of the $[Fe(CO)_5]$ complex were considerably reduced in intensity and the splitting of the A_2'' band disappeared. At the same time three new bands were formed [two of these, close together, are labelled (i) and the lower-frequency band (ii)]. Both these spectra were recorded using a filter to remove the visible and u.v. light from the i.r. spectrometer beam. Figure 1(*c*) shows the result of exposing the matrix to the unfiltered Nernst glower for 3 min. The new bands [(i) and (ii)] totally disappeared and the $[Fe(CO)_5]$ bands grew in intensity, and, apart from changes in splittings, were exactly the same as those in Figure 1(*a*). This experiment showed that the reaction occurring on u.v. photolysis was completely reversible [equation (4)].

$$[Fe(CO)_5] \underset{\text{Nernst}}{\overset{\text{u.v.}}{\rightleftharpoons}} \text{Products} \qquad (4)$$

The possible consequences of photochemical excitation of a matrix-isolated $[Fe(CO)_5]$ molecule, assuming that any product will be in its electronic ground state, are as in equations (5)—(9). On the basis of this initial

$$[Fe(CO_5] \rightleftharpoons [Fe(CO)_5]^* \text{ (excited state)} \qquad (5)$$

$$[Fe(CO)_5](D_{3h}) \longrightarrow [Fe(CO)_5]\text{, with another structure, } e.g.\ C_{4v} \qquad (6)$$

$$[Fe(CO)_5] \longrightarrow [Fe(CO)_{5-x}] + x\text{CO} \qquad (7)$$

$$[Fe(CO)_5] + \text{matrix molecule} \longrightarrow [Fe(CO)_4\text{ (matrix)}] + \text{CO, } etc. \qquad (8)$$

$$2[Fe(CO)_5] \longrightarrow e.g.,\ [Fe_2(CO)_9],\ [Fe_2(CO)_8]\text{, and CO} \qquad (9)$$

experiment, reactions (8) and (9) seem improbable. It seems extremely unlikely that the species $[Fe(CO)_x]$ could be a sufficiently strong Lewis acid to react with neon. (We shall in a later paper describe experiments which *do* indicate interactions with a number of other matrix materials.) Since the same results were obtained at very high dilutions of the complex $[Fe(CO)_5]$ in the matrix, the formation of dimeric carbonyl complexes is also unlikely. The bands (i) and (ii) do not correspond to those of either $[Fe_2(CO)_8]$ or $[Fe_2(CO)_9]$.[11]

Figure 2(*a*) shows the spectrum obtained on condensing a larger quantity of $[Fe(CO)_5]$–neon mixture on to a cold window. The spectrum was the same as that in Figure 1(*a*), except that weak bands could be observed due to $[Fe(CO)_{5-x}(^{13}CO)_x]$ species in natural abundance. On photolysis not only did the (i) and (ii) bands appear as before, but also a very weak band grew at 2144 cm^{-1} [Figure 2(*b*)]. The position of this band corresponds very closely to that reported by previous authors for matrix-

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[11] M. Poliakoff and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2403.

isolated CO.[12,13] Photolysis with the Nernst glower caused the CO band to disappear together with the bands (i) and (ii) [Figure 2(*c*)]. In all these experiments the bands (i) and (ii) always had the same relative intensities and must have been due to the same carbonyl fragment. These results show that photolysis of the complex [$Fe(CO)_5$] produces CO and consequently a lower iron carbonyl complex. Thus both an excited state of [$Fe(CO)_5$] and a different isomer of [$Fe(CO)_5$] [reactions (5) and (6)] can be eliminated as the stable photochemical products. Thus the most plausible interpretation of the reaction is the formation of a lower carbonyl complex as in (7).

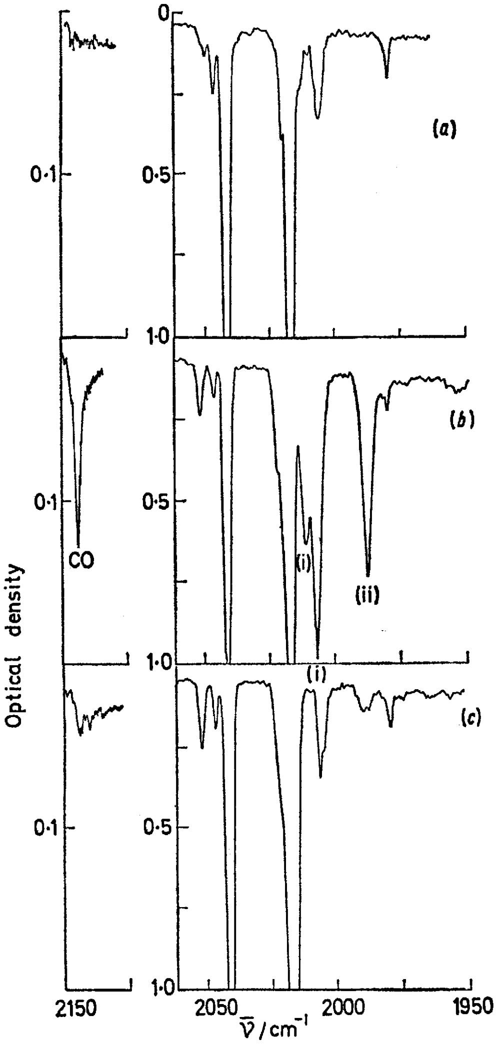

FIGURE 2 I.r. spectrum of the complex [$Fe(CO)_5$] in a neon matrix (1 : 2000) at 4 K after (*a*) spray-on, (*b*) u.v. photolysis (10 min), and (*c*) photolysis with the Nernst glower (5 min). The expanded optical-density scale between 2150 and 2125 cm^{-1} is to be noted

It has been shown that the primary step in the photolysis of other metal carbonyl complexes is loss of a single CO group,[2,9] and it seems most probable that in the present case the product was [$Fe(CO)_4$]. We shall show below that the spectra can be successfully interpreted in terms of this species, and in a later paper we will present evidence for the species [$Fe(CO)_3$]. A [$Fe(CO)_4$] fragment would initially be expected to adopt a tetrahedral or square-planar structure, but the presence of more than one band in the i.r. spectrum implies a distorted structure. In order to see whether this distortion was merely an effect of the neon matrix, we generated this intermediate in a variety of different matrices.

Figure 3(*b*) summarises the frequencies of bands in the regions (i) and (ii), produced on photolysis of the complex [$Fe(CO)_5$] in a variety of matrices at 20 K. In all cases reversal occurred on irradiation with the unfiltered Nernst glower of the spectrometer. In SF_6 and CF_4 matrices the process was not totally reversible and there was some overall loss of the [$Fe(CO)_5$] complex, perhaps due to some carbonyl complex–matrix reaction.* The reversal was somewhat slower than that in argon (*i.e.* 15 min rather than 30 s), but this may have been a consequence of the scattering nature of these matrices. Small amounts of photolysis could even be observed in pure CO matrices! In addition reversal could be achieved by warming many of the matrices and then recooling to 20 K (annealing).

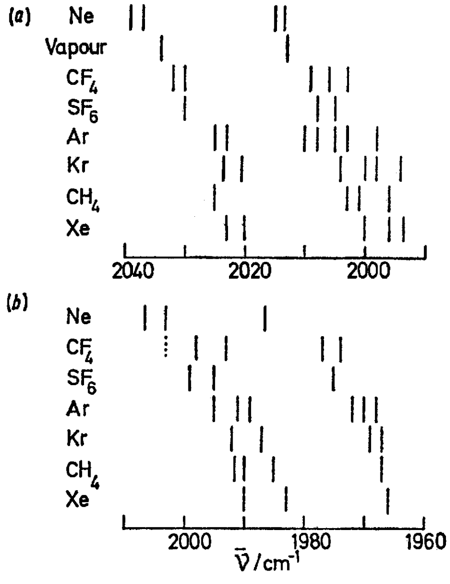

FIGURE 3 Schematic representation of the frequencies of the C–O stretching bands in various matrices for (*a*) the complex [$Fe(CO)_5$] (some of the weaker bands have been omitted), data for the vapour phase from D. M. Adams, 'Metal–ligand and Related Vibrations,' Arnold, 1966, p. 121, (*b*) bands appearing on photolysis of [$Fe(CO)_5$] {the band shown with a broken line was partially obscured by a parent [$Fe(CO)_5$] band}

It is clear from Figure 3 that there was an overall

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* Gas-phase flash photolysis of $Fe(CO)_5$–SF_6 mixtures results in rapid formation of FeF.[14] Such a reaction could have occurred in this case, but the i.r. absorptions of the matrix material would have obscured any product band.

[12] G. E. Leroi, G. E. Ewing, and G. C. Pimentel, *J. Chem. Phys.*, 1964, **40**, 2298.

[13] J. B. Davies and H. E. Hallam, *J.C.S. Faraday II*, 1972, **68**, 509.

[14] A. B. Callear, personal communication.

'solvent shift' to low frequency for both the complexes $[Fe(CO)_5]$ and $[Fe(CO)_4]$ as the matrix was changed from neon to xenon. It is also clear that the small splittings do not disguise the A_2'' and E' bands of the $[Fe(CO)_5]$ complex. Consequently, from a comparison of the $[Fe(CO)_4]$ and $[Fe(CO)_5]$ spectra, it seems reasonable to assign the bands (i) and (ii) to two different modes of the complex $[Fe(CO)_4]$. We suggest that the small splittings in these bands are 'matrix effects,' similar to those for the complex $[Fe(CO)_5]$, while the 'bands' themselves represent fundamental vibrations of the complex $[Fe(CO)_4]$ which would be observed in the absence of the matrix.

U.v. spectra of $[Fe(CO)_5]$–$[Fe(CO)_4]$ were not as informative as one might have hoped, owing to the overlap of bands and the incomplete conversion. However in the matrices that were studied (Ne, SF_6, Ar, and CH_4), a broad band due to the complex $[Fe(CO)_4]$ was detected at 320 ± 10 nm. Unlike the absorptions of the complex $[Cr(CO)_5]$,[15,16] the position of this band did not appear to change much from one matrix to another. The regeneration of the complex $[Fe(CO)_5]$ from $[Fe(CO)_4]$, by the Nernst glower, could be shown (by use of filters) to be due to absorption in the 'tail' of this 320 nm band. The fact that the reversal could also be achieved by annealing supports our original theory[9] that the mechanism of these photochemical reversals in matrices is essentially thermal in nature.

Further evidence that the bands (i) and (ii) are due to the complex $[Fe(CO)_4]$ comes from two observations. First, it is to be expected that simple removal of CO from a carbonyl complex will lower the average C–O stretching frequencies. This effect has been observed for $[Ni(CO)_x]$ ($x = 1$—4),[17] $[Cr(CO)_x]$ ($x = 1$—6),[18] and other carbonyl complexes, and obviously applies in this case. Secondly, in a number of experiments using very high dilution and long photolysis, bands, assignable to $[Fe(CO)_x]$ species ($x < 4$), were observed at frequencies lower than those of (i) and (ii). It is interesting that bands produced during photolysis of the complex $[Fe_2(CO)_9]$, isolated in various matrices,[11] were different from those of $[Fe(CO)_4]$. This confirms the conclusion that, in these experiments, no $[Fe(CO)_4]$ was generated from the complex $[Fe_2(CO)_9]$.

Structure of $Fe(CO)_4$.—Assuming that unperturbed $[Fe(CO)_4]$ has two bands in the C–O stretching region, what structures are consistent with such a spectrum? Tetrahedral and square-planar structures can be eliminated as these should only have one i.r. band. The other possibilities are D_{2d} and D_{2h} (two bands), C_{3v} (three bands), and C_{2v} and lower symmetries (four bands). In the absence of further evidence, none of these structures can be totally excluded. However, a D_{2h} structure seems chemically rather improbable. The pair of bands (i) and (ii) are remarkably similar in relative position and intensity to those observed in solid complex $[Ni(CO)_4]$ and for $[Co(CO)_4]^-$ in tetrahydrofuran (THF) solution. Solid $[Ni(CO)_4]$ is known to have C_3 site symmetry, and its i.r. spectrum has been examined by Jones,[19] who assigned the bands as follows:

2123vvw	A_1	
2038vvs	E	$\left.\begin{matrix}\\ \\ \end{matrix}\right\}$ splitting of the T_2 mode
2022vs	A_1	

(Two bands, at 2116vvw and 2045sh cm^{-1}, were assigned to combination bands.)

In many solvents, the complex $[Co(CO)_4]^-$ has only a single band (consistent with T_d symmetry), but in THF more bands are observed due to ion-pair formation. Edgell and his co-workers[20] have assigned bands in the spectrum of the complex $[Co(CO)_4]^-$ in THF to the C_{3v} distorted anion:

2003vw	A_1
1899	E
1855	A_1

Further evidence for a C_{3v} structure is our observation that an exceedingly weak band was observed at 2089 cm^{-1} (in an argon matrix) when a large amount of the complex $[Fe(CO)_4]$ was present. The band had an intensity approximately 1/100th of that of the band (ii), but unfortunately could not be conclusively shown to be due to the complex $[Fe(CO)_4]$. A C_{3v} structure would be expected to have its third band at about this frequency. The evidence appears to favour a C_{3v} structure although we have been unable to disprove the D_{2d} alternative. The matrix splittings of the $[Fe(CO)_4]$ bands may be due to a small C_{2v} distortion of the C_{3v} (or D_{2d}) structure, but it is unfortunately not possible to confirm this. Attempts to 'prove' the C_{3v} structure by generating the complex $[Fe(CO)_4]$ in an argon matrix doped with $C^{18}O$ and producing axial $[Fe(CO)_4(C^{18}O)]$ were foiled by the broadness of the carbonyl bands in the doped matrices.

If we are correct in assuming that the complex $[Fe(CO)_4]$, in either the 'gas-phase' or inert fluid solvent, would have the C_{3v} structure, it is interesting to consider the reasons for this. First it is worth noting that the molecule $[Co(CO)_4]$, generated by photolysis of the complex $[Co(CO)_3NO]$ in a CO matrix, has been proved by isotopic substitution to have a C_{3v} structure[21] substantially distorted from T_d. The electronic states of a tetrahedral $[Fe(CO)_4]$ d^8 molecule are $^1A_1$, ^1E, $^1T_2$, and $^3T_1$. The latter is likely to be the ground state. Since this state is orbitally degenerate, the molecule would be expected to undergo Jahn–Teller distortion. It is not possible to predict the magnitude of this distortion, but, as the degeneracy in the $[Fe(CO)_4]$ complex arises from unfilled antibonding orbitals, the distortion will probably be larger than that in $[V(CO)_6]$, where the degeneracy is

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[15] M. A. Graham, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Organometallic Chem.*, 1972, **34**, C34.

[16] R. N. Perutz and J. J. Turner, unpublished work.

[17] R. L. DeKock, *Inorg. Chem.*, 1971, **10**, 1205.

[18] M. A. Graham, Ph.D. Thesis, University of Cambridge, 1971.

[19] L. H. Jones, *Spectrochim. Acta*, 1963, **19**, 1899.

[20] W. F. Edgell, M. T. Yand, and N. Koizumi, *J. Amer. Chem. Soc.*, 1965, **87**, 2563; W. F. Edgell and J. Lyford, *ibid.*, 1971, **93**, 6407.

[21] O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J.C.S. Dalton*, 1973, 1321.

in non-bonding orbitals. Haas and Sheline[22] have obtained *some* spectroscopic evidence for dynamic Jahn–Teller distortion in the complex [V(CO)$_6$] in the gas phase, and so one would expect that the distortion of the [Fe(CO)$_4$] complex would be easily detectable in a matrix, where the i.r. bands are much sharper.

The Jahn–Teller active modes for a T_d molecule in T electronic state are E and T_2; an E distortion would result in a D_{2d} molecule and a T_2 distortion in a C_{3v} molecule. The ion [NiCl$_4$]$^{2-}$, iso-electronic with [Fe(CO)$_4$], has D_{2d} symmetry in some salts,[23] but the adoption of this structure rather than that of C_{3v} might be due to crystal-packing effects.

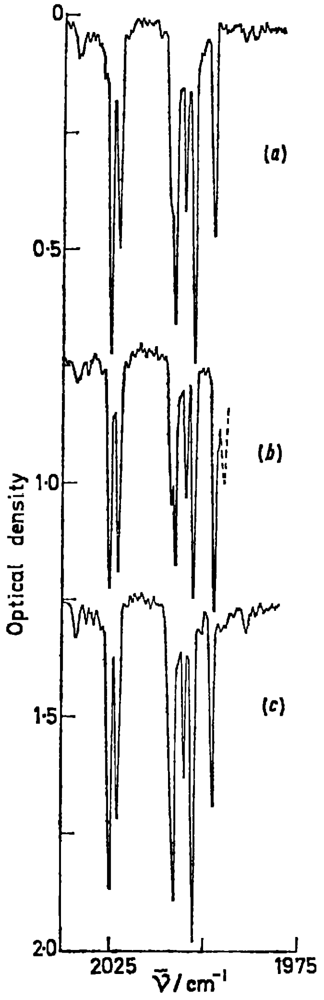

FIGURE 4 I.r. spectrum of the complex [Fe(CO)$_5$] in an argon matrix (1 : 10 000) at 20 K after (*a*) spray-on, (*b*) u.v. photolysis (7 min) {the band drawn as a broken line was due to the complex [Fe(CO)$_4$], lower-frequency [Fe(CO)$_4$] bands have been omitted}, and (*c*) photolysis with the Nernst glower (8 min)

Prolonged Photolysis in Argon Matrices.—The results obtained on prolonged photolysis of the complex [Fe(CO)$_5$] in argon matrices were significantly different from those on short photolysis. Before interpreting these results, it is important to examine the intensity changes of the bands in the spectrum of the [Fe(CO)$_5$] complex itself. Figure 4(*a*) shows the spectrum of the [Fe(CO)$_5$] complex in an argon matrix. Since this complex has only five carbonyl groups and at least eight bands were observed, there must have been more than one 'type' of [Fe(CO)$_5$] or polymeric species present. The latter can be ruled out as the splittings became better resolved with increasing dilution of the [Fe(CO)$_5$] complex. The splittings were not due to particular orientations of the [Fe(CO)$_5$] molecules relative to the cold window of the cryostat, since neither rotating the window relative to the spectrometer beam, nor rotating the polarisation of the beam, had any effect on the spectrum. The effect was not due to impurities as samples of the [Fe(CO)$_5$] complex from different sources (and directly synthesised from Fe + CO) gave identical patterns. The spectra in Figures 4(*a*) and 5(*a*) were obtained using the Pulsed Matrix Isolation (PMI) technique as developed by Rochkind.[24] Identical splittings were obtained with matrices deposited using slow spray-on methods. Small variations in relative intensities were noticed between different experiments and annealing of the matrices could change these intensities slightly. On brief u.v. photolysis [Figure 4(*b*)], some [Fe(CO)$_5$] bands decreased substantially in intensity while others barely changed. The bands returned to their original intensities after photolysis with the Nernst glower [Figure 4(*c*)].

Figure 5(*a*) again shows the spectrum of the complex [Fe(CO)$_5$] in an argon matrix. Note that in this experiment, although the splittings of the bands were identical to those in Figure 4, the relative intensities of the bands were different. On prolonged u.v. photolysis [Figure 5(*b*)], several of the [Fe(CO)$_5$] bands disappeared, and there were changes in relative intensities among those that remained. *The bands which disappeared were those that were unaffected by brief photolysis.* Annealing the matrix to 38 K regenerated these bands [Figure 5(*c*)]. [The spectra in Figure 5 were in fact taken from two different experiments. However, we feel justified in presenting them as a single Figure because spectra corresponding to Figure 5(*b*) were exactly superimposable. The reappearance of bands on annealing occurred in all argon-matrix experiments and not just in this case.] *

This behaviour is consistent with isolation of the complex [Fe(CO)$_5$] in different sites in the matrix, the relative concentrations of sites and hence the intensity pattern being determined by the 'spray-on' conditions of the particular experiment. The changes in intensity pattern can then be interpreted; we shall illustrate the argument by reference to *two* unspecified sites A and B. Although

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* *Note added in proof:* A similar complicated pattern in i.r. spectra of the complex [Fe(CO)$_5$] in argon and xenon matrices has been reported (B. I. Swanson, L. H. Jones, and R. R. Ryan, *J. Mol. Spectroscopy*, 1973, **45**, 324). The spectra appear to be less well resolved than those reported here, perhaps because of the higher complex to matrix gas ratio used.

[22] H. Haas and R. K. Sheline, *J. Amer. Chem. Soc.*, 1966, **88**, 3219.

[23] G. D. Stucky, J. B. Folkers, and J. J. Listenmacher, *Acta Cryst.*, 1960, **13**, 807.

[24] M. M. Rochkind, *Spectrochim. Acta*, 1971, **27A**, 547.

there may be more sites we do not feel there is sufficient evidence to be more specific. The complexes [Fe(CO)$_5$] and [Fe(CO)$_4$] and CO are in rapid equilibrium. Since the u.v. absorption coefficients are large, the net effect of the reactions is substantial local heating of the matrix. This *local* heating converts sites B to A, but the ratio of A to B is restored by *overall* annealing of the matrix. This behaviour is very similar to that observed for the photolysis of the complexes [W(CO)$_6$][9] and [Mn(CO)$_4$NO] [25,26] in argon matrices. If we assume that reversal {*i.e.* [Fe(CO)$_4$ + CO $\longrightarrow$ [Fe(CO)$_5$]} is slower in A than B sites, perhaps for steric reasons, then *short* photolysis, before localised heating has had much effect, will show decrease of the complex [Fe(CO)$_5$] in A but little change in B, whereas *long* photolysis, accompanied by considerable local heating, will show [Fe(CO)$_5$] in B sites decreasing relative to A.

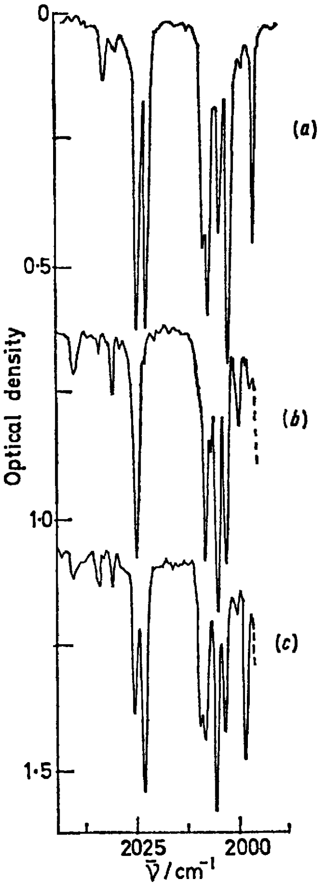

FIGURE 5 I.r. spectrum of the complex [Fe(CO)$_5$ in an argon matrix (1 : 10 000) at 20 K after (*a*) spray-on, (*b*) u.v. photolysis (225 min), and (*c*) annealing the matrix to 38 K and then recooling to 20 K {bands due to the complex [Fe(CO)$_4$] have been omitted}

Figure 6 demonstrates the effects of long photolysis on the bands of the complex [Fe(CO)$_4$] and CO produced from [Fe(CO)$_5$] in an argon matrix. Although presented as a single Figure, the [Fe(CO)$_4$] and CO bands were recorded in different experiments because of their very different intensities (*cf.* Figure 2). On short u.v. photolysis, bands (i) and (ii) appeared together with a band due to CO at 2142 cm^{-1} [Figure 6(*a*)]. When the matrix was photolysed with the Nernst glower, all the bands totally disappeared, again as before. After prolonged u.v. photolysis [Figure 6(*b*)], the CO band became broader and a peak appeared at 2138 cm^{-1}. At the same time *extra* (i) bands appeared and the relative intensities of the (ii) bands changed. On photolysis with the Nernst glower, the high-frequency part of the CO band and the original bands (i) and (ii) disappeared as before, but the new bands were unaffected [Figure 6(*c*)]. Annealing of the matrix had no effect, apart from a slight overall sharpening of the bands. The new bands could not therefore have been due to the same effects as those that changed the [Fe(CO)$_5$] spectrum, because if they had, annealing should have regenerated the 'missing' bands. Thus prolonged photolysis generated irreversible [Fe(CO)$_4$] and CO.

The frequencies of the CO band provide an explanation for this irreversibility. The band of irreversible CO was at 2138 cm^{-1}, which is identical in frequency to that assigned by Dubost and Abouaf-Marguin to monomeric CO molecules in an argon matrix.[27] The reversible CO band (2142 cm^{-1}) is close in frequency to that attributed to CO dimers, 2143 cm^{-1}.[13] Similarly there is a difference between the frequencies of reversible and irreversible [Fe(CO)$_4$]. It seems very improbable that dimeric CO could be formed at these dilutions (1 : 10 000), and a more plausible explanation of these frequency shifts is

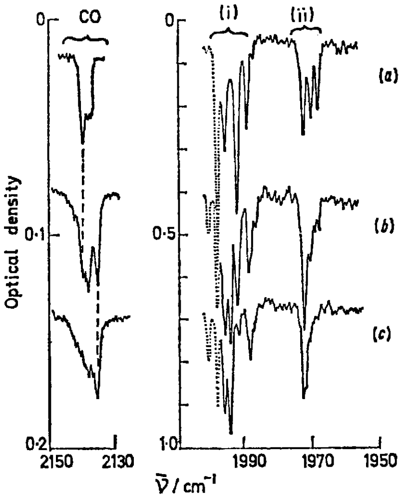

FIGURE 6 I.r. spectra of the complex [Fe(CO)$_4$] and CO produced on u.v. photolysis of [Fe(CO)$_5$] in an argon matrix (1 : 10 000) at 20 K. (The expanded optical-density scale between 2150 and 2130 cm^{-1} is to be noted.) The bands shown as broken lines are due to the complex [Fe(CO)$_5$]. {Higher-frequency bands of [Fe(CO)$_5$] have been omitted}. After photolysis for (*a*) 7 min, (*b*) 225 min, and (*c*) 5 min with the Nernst glower

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[25] A. J. Rest, *Chem. Comm.*, 1970, 345.

[26] M. Poliakoff, Ph.D. Thesis, University of Cambridge, 1972.

[27] H. Dubost and L. Abouaf-Marguin, *Chem. Phys. Letters*, 1972, **17**, 269.

that there is a weak interaction between the complex $[Fe(CO)_4]$ and CO produced by initial photolysis. Prolonged photolysis causes sufficient local melting to allow the CO molecule to diffuse away from the $[Fe(CO)_4]$ complex, preventing regeneration of $[Fe(CO)_5]$. Since the band pattern of both forms of the $[Fe(CO)_4]$ complex are so similar, one must conclude that any interaction with photochemically produced CO is insufficient to affect the shape of the $[Fe(CO)_4]$ fragment.

CONCLUSION

We have shown that u.v. photolysis of the complex $[Fe(CO)_5]$ in a wide variety of matrices results in formation of the complex $[Fe(CO)_4]$. This species apparently has a C_{3v} structure. In a separate paper we will report the reaction of this species with a variety of reactive matrices to form $[Fe(CO)_4L]$ molecules, and relate the results reported here to those obtained by Stolz *et al.* using hydrocarbon glasses at 77 K.[7]

EXPERIMENTAL

All experiments were performed using an Air Products AC-3L Cryo-Tip Joule–Thomson refrigerator using hydrogen and helium gas. I.r. spectra were recorded using a Grubb–Parsons 'Spectromajor' spectrometer, modified so as to operate in the region of 2000 cm^{-1} without a grating change, and calibrated with DCl. U.v. spectra were recorded with a Perkin-Elmer 356 spectrometer. The photolysis source was a Phillips HPK 125 W medium-pressure arc. The i.r. filter was No. L-03400/0g produced by Ocli Optical Coatings Ltd. All gases were of grade 'X' purity (B.O.C.), except SF_6 and CF_4 which were supplied by Cambrian Gases Ltd. The complex $[Fe(CO)_5]$ was either redistilled commercial grade, or prepared by reaction of Fe and CO.

We thank the S.R.C. for support, King's College, Cambridge, for a maintenance grant (to M. P.), and Drs. J. K. Burdett, J. S. Ogden, and A. J. Rest, and Messrs. O. Crichton and R. N. Perutz for helpful discussions.

[2/2722 *Received, 4th December,* 1972]