

I.R.-monitored Flash Photolysis of $\text{Fe}(\text{CO})_5$ in Benzene Solution

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A transient species (k ca. 10 s^{-1}), formed from flash photolysis of $\text{Fe}(\text{CO})_5$ in C_6D_6 and assigned from its i.r. spectrum as $\text{Fe}(\text{CO})_4 \cdot (\text{C}_6\text{D}_6)$, reacts with CO to give $\text{Fe}(\text{CO})_5$ and with $\text{Fe}(\text{CO})_5$ to give a binuclear iron carbonyl compound, apparently in both cases *via* a highly reactive intermediate.

Pentacarbonyliron is well known to lose carbon monoxide in a very efficient photoprocess¹ which results in the formation of $\text{Fe}_2(\text{CO})_9$ or, in the presence of suitable ligands (L), of $\text{LFe}(\text{CO})_4$ and $\text{L}_2\text{Fe}(\text{CO})_3$ derivatives.² Alkene complexes of this type are involved in catalytic photoreactions such as hydrogenation and isomerisation of alkenes.^{3–5} Even though the structure and i.r. spectra of the photogenerated fragments $\text{Fe}(\text{CO})_n$ ($n = 2–4$) in low-temperature matrices^{6,7} and in the gas phase⁸ have been studied in detail, there are no published data on these species in solution. In contrast, transient species observed from $\text{Cr}(\text{CO})_6$ in solution have been extensively investigated^{9–11} and their structure explained by reference to matrix isolation data.⁷ A similar approach with $\text{Fe}(\text{CO})_5$ (in an earlier study¹²) was hindered by the featureless near-u.v. and visible absorptions of the transient species, so that the identity of the reactive compounds detected could not be assigned.

These problems have now been overcome using i.r.-monitored flash photolysis, and we report here the spectra of two transient iron carbonyl compounds formed from $\text{Fe}(\text{CO})_5$ in benzene solution and provide kinetic evidence for a third highly reactive species.

The flash photolysis equipment with i.r. detection has been described elsewhere.¹⁰ It has a xenon lamp as excitation source (pulse full width at half maximum $1.5 \mu\text{s}$) and a rapid i.r. detector which allow the study of species with lifetimes greater than $5 \mu\text{s}$. Samples of $\text{Fe}(\text{CO})_5$ (3×10^{-4} – $5 \times 10^{-3} \text{ M}$) in C_6H_6 and in C_6D_6 [†] were either degassed under

[†] C_6D_6 is transparent between 1800 and 2100 cm^{-1} (except at about 1880 cm^{-1}), whereas C_6H_6 absorbs strongly in the regions 1800 – 1830 and 1940 – 1970 cm^{-1} . C_6D_6 was therefore the preferred solvent for measurements over the entire spectral CO range (*e.g.*, Figure 1a).

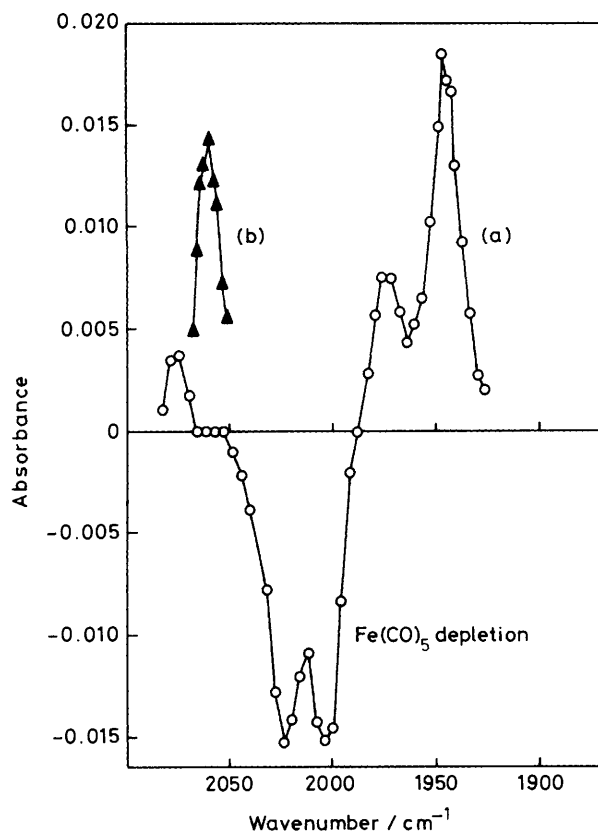
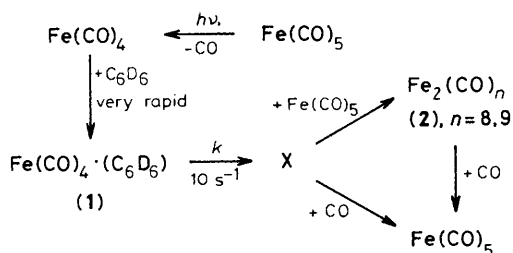


Figure 1. (a) (○) Initial transient i.r. difference spectrum produced by the flash photolysis of 6×10^{-4} M $\text{Fe}(\text{CO})_5$ in CO-saturated C_6D_6 solution, due to absorptions of $\text{Fe}(\text{CO})_4 \cdot (\text{C}_6\text{D}_6)$ (1) and depletion of $\text{Fe}(\text{CO})_5$ absorptions at 2024 and 2004 cm^{-1} . Note that the $\text{Fe}(\text{CO})_5$ depletion bands are not in the expected 2:3 ratio indicating the presence of an additional positive $\text{Fe}(\text{CO})_4 \cdot (\text{C}_6\text{D}_6)$ (1) absorption at ca. 2004 cm^{-1} . (b) (▲) Transient i.r. difference spectrum of $\text{Fe}_2(\text{CO})_n$ ($n = 8, 9$) in CO-saturated C_6H_6 solution, its appearance being concurrent with the decay of (1); $[\text{Fe}(\text{CO})_5] = 5 \times 10^{-3}$ M.



Scheme 1

vacuum or purged with argon or carbon monoxide.‡ The initial i.r. difference spectrum observed after flash excitation of $\text{Fe}(\text{CO})_5$ (6×10^{-4} M) in C_6D_6 solution is given in Figure 1a. Three distinct new bands at 2076, 1974, and 1946 cm^{-1} may be distinguished as well as depletion bands due to $\text{Fe}(\text{CO})_5$ at 2024 and 2004 cm^{-1} . However, these depletion bands do not occur in the expected 2:3 ratio, indicating that a

‡ In contrast to the behaviour upon flash photolysis of $\text{Cr}(\text{CO})_6$,⁹⁻¹¹ the decay kinetics of the transients reported here are not sensitive to sample preparation procedures.

fourth absorption band of the transient species overlaps with the 2004 cm^{-1} band. Such a four-band spectrum is expected for a mononuclear C_{2v} iron tetracarbonyl complex. [In dinuclear iron carbonyls, e.g. $\text{Fe}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$,¹³ all prominent CO stretching vibrations occur only above 2000 cm^{-1} .] Furthermore, the spectrum obtained does not resemble that of either 'naked' $\text{Fe}(\text{CO})_4$ or $\text{Fe}(\text{CO})_4 \cdot (\text{methane})$ observed in rare gas matrices,⁶ and we assign it to a complex $\text{Fe}(\text{CO})_4 \cdot (\text{C}_6\text{D}_6)$ (1). The nature of binding of the $\text{Fe}(\text{CO})_4$ with benzene is at present uncertain but it is probably similar to that in $\text{Fe}(\text{CO})_4 \cdot (\text{alkene})$ complexes.‡

Compound (1) decays with a first-order rate constant of ca. 10 s^{-1} in C_6H_6 and C_6D_6 solutions at room temperature. This rate is not affected by the concentration of $\text{Fe}(\text{CO})_5$ or by saturation of the solution under 1–1.3 atm of argon, carbon monoxide, or helium–carbon monoxide (4:1 v/v) mixture. In solutions saturated under 1.3 atm of CO and dilute in $\text{Fe}(\text{CO})_5$, the decay of (1) yields $\text{Fe}(\text{CO})_5$ almost exclusively. As the $\text{Fe}(\text{CO})_5$ concentration is increased, concurrent formation (i.e., k ca. 10 s^{-1}) of a new species (2) absorbing at 2060 cm^{-1} is observed (Figure 1b). The yield of (2) increases with $\text{Fe}(\text{CO})_5$ concentration and at about 5×10^{-3} M the strong signal at 2060 cm^{-1} indicates that a significant conversion of (1) into (2) must have taken place (as shown by the relative intensities of the 1946 and 2060 cm^{-1} bands in Figures 1a and 1b, respectively). These observations are consistent with competition for (1) by CO and $\text{Fe}(\text{CO})_5$. The fact that the rate of decay of (1) is independent of the concentrations of CO and $\text{Fe}(\text{CO})_5$ suggests that a further very reactive mononuclear species (X) must be formed initially from (1) (see Scheme 1).¶ The intermediate X is only implied by these considerations. Since they demand also a very short lifetime, we cannot expect to observe X under our conditions.

Species (2) is relatively long-lived, disappearing with a rate constant of ca. $2 \times 10^{-2} \text{ s}^{-1}$ in CO-saturated solution. As no further CO stretching absorptions are noted and as no permanent product other than $\text{Fe}(\text{CO})_5$ is found after this experiment, it is probable that (2) reforms $\text{Fe}(\text{CO})_5$. Only one band (at 2060 cm^{-1}) has so far been observed for (2). However, it is possible that additional bands are obscured by the $\text{Fe}(\text{CO})_5$ absorptions between 2000 and 2030 cm^{-1} . The high intensity of the 2060 cm^{-1} band and the absence of any terminal CO stretching vibrations in the 2000–1900 cm^{-1} region point to a binuclear iron carbonyl compound. No bridging CO vibrations were observed but these, if present, may be too weak to be seen under our conditions. We propose therefore that the binuclear species is either $\text{Fe}_2(\text{CO})_8$ or a soluble form of $\text{Fe}_2(\text{CO})_9$ (vide supra and ref. 13).

There remains the problem of the identity of the rapidly reacting intermediate X. An attractive possibility is that X is a

§ E.g., see the data for $\text{Fe}(\text{CO})_4 \cdot (\text{alkene})$ complexes.¹⁴ Attempts to generate $\text{Fe}(\text{CO})_4 \cdot (\text{C}_6\text{D}_6)$ in low-temperature matrices were made on a suggestion of a referee but so far have proved unsuccessful. In neat C_6D_6 and in moderately Ar-diluted C_6D_6 the bands in the spectrum were too broad as to allow any positive identification of products, whereas in C_6D_6 –argon mixtures [$\text{Fe}(\text{CO})_5$: C_6D_6 : Ar ca. 1:40:1000] only 'naked' $\text{Fe}(\text{CO})_4$ was observed.

¶ In very recent experiments we have observed that the rate of reaction of (1) with *trans*-cyclo-octene, yielding $\text{Fe}(\text{CO})_4 \cdot (\text{trans-cyclo-octene})$, depends on the concentration of *trans*-cyclo-octene. This implies that the reaction of (1) with alkenes is mechanistically different from that with CO or $\text{Fe}(\text{CO})_5$. It is conceivable that, e.g., factors such as different spin [singlet vs. triplet; we may recall in this context that $\text{Fe}(\text{CO})_4$ has a triplet ground state in low-temperature matrices⁶] and stereoselectivities (C_{3v} vs. C_{2v} geometry) play a role.

spin isomer of (1).§ In this case the intersystem crossing to X would have to be the rate-determining step in the decay of (1). Other possibilities for X, such as 'naked' Fe(CO)₄, Fe(CO)₃, Fe(CO)₃·(benzene), and a conformational isomer of Fe(CO)₄·(benzene), are more difficult to reconcile with the experimental observations.

In conclusion, this flash photolysis study has provided the first clear evidence for the nature and kinetic behaviour of the products formed from Fe(CO)₅ in solution and again^{10,11} demonstrates the usefulness of i.r. monitoring of transient species.

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