How does the strength of the Fe-Solvent bond affect the formation of $^1Fe(CO)_4$(solvent)

A Cowan, P Portius, X-Z Sun, M W George

*School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

M Towrie, K L Ronayne

Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., OX11 0QX, UK

Main contact email address: *mike.george@nottingham.ac.uk*

Introduction

The photochemistry of $Fe(CO)_5$ has been studied as a model system for spin changes in organometallic systems[1]. It was shown over 30 years ago that photolysis of $Fe(CO)_5$ in cryogenic (12K) matrices generates the triplet intermediate, $^3Fe(CO)_4$, which could be converted to $^1Fe(CO)_4(CH_4)$ in CH_4 matrices[2]. Photolysis of $Fe(CO)_5$ in Ar matrices generates only $^3Fe(CO)_4$ without any evidence for $^1Fe(CO)_4Ar$, but doping the Ar matrices with either CH_4 or Xe allowed $^3Fe(CO)_4$ to be converted to $^1Fe(CO)_4(CH_4)$ or $^1Fe(CO)_4Xe$, Scheme 1.
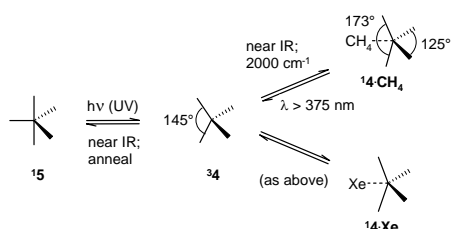
Scheme 1. Photochemistry of $Fe(CO)_5$ in CH_4 and Xe matrices, adapted from reference [1].

In condensed phase processes, interactions with the solvent play an important role in governing the reactivity of organometallic intermediates which may modify the behaviour of the system. Fast time-resolved infrared spectroscopy (TRIR), a combination of UV flash photolysis and fast IR detection, has proved to be a powerful tool in unraveling the photochemistry of metal carbonyl complexes. Grevels and coworkers were able to characterise the $^1Fe(CO)_4$(cyclohexane) intermediate on the microsecond timescale generated following irradiation of $Fe(CO)_5$ in cyclohexane at room temperature[3]. Harris *et al.* used ps-TRIR to characterise $^3Fe(CO)_4$ in hexane solution and to show that it is stable up to 660 ps[4]. We recently demonstrated that $^3Fe(CO)_4$ converts to $^3Fe(CO)_4$(heptane) on the nanosecond timescale ($\tau = 13$ ns) in *n*-heptane solution at room temperature[5]. We also performed the first ps-TRIR measurements in supercritical fluids and this enabled us to replicate the matrix experiments at room temperature and measure rate constants for steps that had merely been deduced from matrix experiments[2]. This allows a unique way to probe such reactions in solution since doping supercritical argon with more coordinating solvents allows the factors governing spin-change to be investigated. In this paper we wish to address two unanswered questions. Firstly, does $^3Fe(CO)_4$ react with Kr to form $^1Fe(CO)_4Kr$ and secondly how fast does $^3Fe(CO)_4$ react with H_2 in the condensed phase? The latter has important implications for quantum chemical calculations.

Results and Discussion

Figure 1(a) shows the FTIR spectrum of $Fe(CO)_5$ in supercritical Kr (*sc*Kr) (5500 psi) in the presence of CO (60 psi). Figure 1(b) shows the ps-TRIR spectra obtained at a range of time delays following 267 nm excitation of this solution. 2 ps after photolysis the two parent $Fe(CO)_5$ bands at

2006 and 2028 cm^{-1} are bleached and a broad featureless band is observed at lower energy. The transients produced immediately after the flash are formed in a vibrationally excited state which leads to the broad featureless bands. Within the first 50 ps these transients have relaxed and four new transient $\nu(CO)$ bands can be clearly observed at 1934, 1960, 1977 and 1996 cm^{-1}. The $\nu(CO)$ bands at 1977 and 1996 cm^{-1} can be readily assigned to the species $^3Fe(CO)_4$ in *sc*Kr by analogy to previous matrix isolation[2] and TRIR studies[5]. Similarly the band at 1934 cm^{-1} can be assigned to the species $Fe(CO)_3$[5].

A weak band is present at 1960 cm^{-1}. We have seen similar features in TRIR experiments in other solvents[5] and in these experiments the feature was tentatively assigned to rapid formation of a small amount of $^1Fe(CO)_4$(solvent). We tentatively assign the band at 1960 cm^{-1} to be due to $^1Fe(CO)_4Kr$ which is formed as a minor product, as the initially formed $^1Fe(CO)_4$ converts to $^3Fe(CO)_4$.

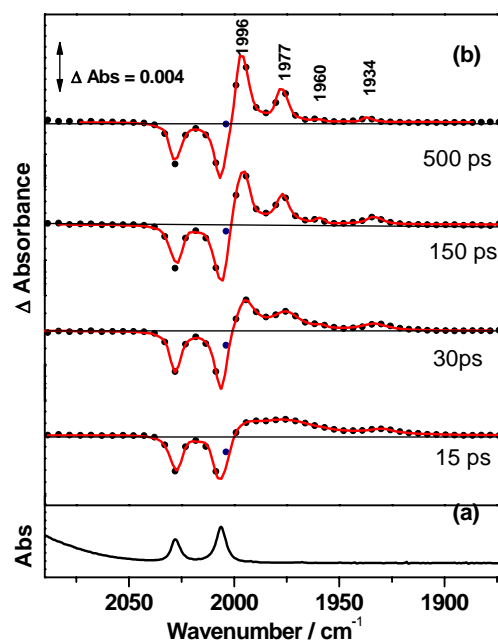**Figure 1. (a)** FTIR spectrum of $Fe(CO)_5$ in *sc*Kr (5500 psi) in the presence of CO (60 psi) at 296 K; **(b)** ps-TRIR spectra following 267nm excitation of the solution at selected pump-probe delay times.

Figure 2 shows the ns-TRIR spectra obtained following photolysis (267 nm) of $Fe(CO)_5$ in *sc*Kr (5500 psi) in the presence of CO (60 psi). The bands due to $^3Fe(CO)_4$ decay in the presence of CO to reform $Fe(CO)_5$. Thus it appears that there is some initial formation of $^1Fe(CO)_4Kr$ on the picosecond timescale but this complex is highly reactive and decays very rapidly. The lack of production of a long-lived $^1Fe(CO)_4$(solv) species in this reaction can be attributed to the poor coordinating ability of *sc*Kr. Similar results are also observed following photolysis in supercritical Ar (*sc*Ar). As stated

above, in the presence of the heptane, a more strongly coordinating solvent, the long-lived species $^1Fe(CO)_4$(n-heptane) is formed rapidly (13 ns) from $^3Fe(CO)_4$.

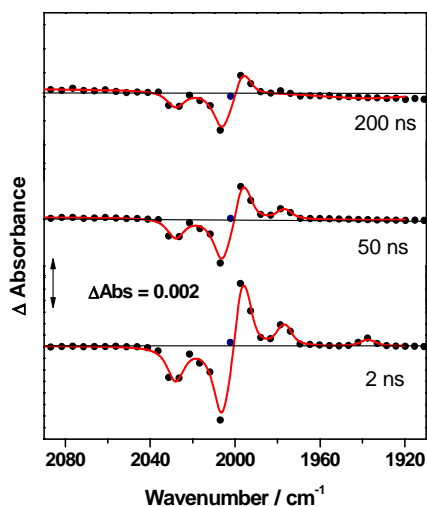**Figure 2.** ns-TRIR spectra of $Fe(CO)_5$ in scKr (5500 psi) in the presence of CO (60 psi) at 296 K following 267nm excitation of the solution at selected delay times.

We observe $^3Fe(CO)_4$ reacting with CO to form $Fe(CO)_5$. We have no evidence for the formation of $^1Fe(CO)_4$Kr from $^3Fe(CO)_4$ but it can not be ruled out that $^1Fe(CO)_4$Kr is formed on the pathway to regenerate $Fe(CO)_5$. We have also examined the reactivity of $Fe(CO)_3$ which has a lifetime of ca. 3.0 ± 0.5 ns in scKr. It is interesting to compare the lifetime of $Fe(CO)_3$ in different solvents. During photolysis of $Fe(CO)_5$ in scAr, scXe and heptane the tricarbonyl species were found to have lifetimes of 0.3, 18 and 117 ns respectively[5]. These results were interpreted to show that solvent coordination to $Fe(CO)_3$ led to a stabilization of this species with respect to the reaction with CO. The relative stability could then be explained by an increasing Fe-solvent bond strength, in the order Ar << Xe < heptane. By comparison to calculated diffusion controlled rates for the reaction of $Fe(CO)_3$ with CO, it was proposed that Ar was only very weakly coordinated to the $Fe(CO)_3$ fragment. The lifetime for the $Fe(CO)_3$ species in scKr is significantly longer than in scAr, but shorter than for $Fe(CO)_3$(heptane) which supports the assignment of a weakly bound $Fe(CO)_3$Kr species.

Photolysis of $Fe(CO)_5$ in scAr doped with H_2

Photolysis of $Fe(CO)_5$ in scAr (4500 psi) in the presence of H_2 (90psi) and CO (60 psi) initially produces broad featureless bands which evolve to produce four distinct bands at 1998, 1981, 1963 and 1940 cm^{-1} (figure 3). The former two bands are due to $^3Fe(CO)_4$. The later can be assigned to $Fe(CO)_3$ by comparison with TRIR data of $Fe(CO)_5$ in scAr. The band at 1963 cm^{-1} decays rapidly ($\tau = 29.6 \pm 0.9$ ns). A similar peak was observed in pure scAr but in the absence of H_2 this feature decayed much faster $\tau = 770 \pm 60$ ps and was tentatively assigned to $^1Fe(CO)_4$Ar. The extended lifetime in the presence of H_2 leads to the tentative assignment of this feature in these experiments to the dihydrogen species $^1Fe(CO)_4(\eta^2$-$H_2)$, which has been previously postulated[6].

$^3Fe(CO)_4$ decays with a lifetime of 280 ± 22 ns. A new feature at 2046 cm^{-1} grows in which can be readily assigned to cis-$Fe(CO)_4H_2$[6]. The growth of $Fe(CO)_4H_2$ can be fitted to a biexponential with a fast component (ca. 30 ns) and a second slower component of 247 ± 13 ns which matches the decay of the bands assigned to $Fe(CO)_4(H_2)$ and $^3Fe(CO)_4$.
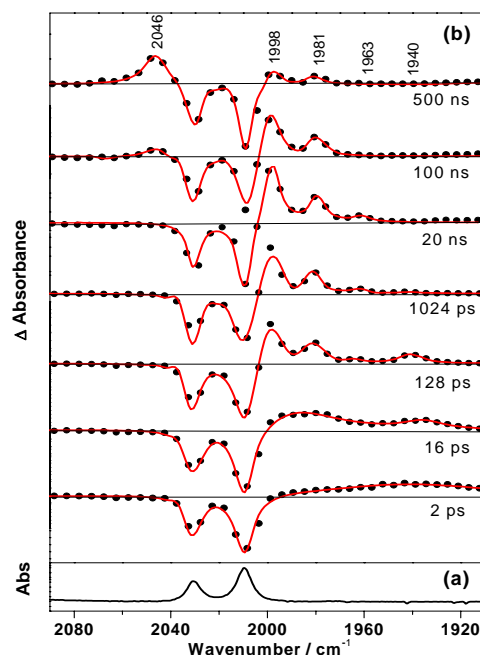

Figure 3. (a) FTIR spectrum of $Fe(CO)_5$ in scAr (4500 psi) in the presence of H_2 (90 psi) and CO (60 psi) at 298K; **(b)** TRIR spectra following 267 nm excitation of the solution at selected delay times.

Conclusions

TRIR studies on the picosecond and nanosecond timescale have shown that photolysis of $Fe(CO)_5$ in supercritical Kr generates $^3Fe(CO)_4$ and $Fe(CO)_3$ with evidence for rapid formation of $^1Fe(CO)_4$Kr. $^3Fe(CO)_4$ reacts with CO to reform $Fe(CO)_5$. $Fe(CO)_3$ decays very rapidly but slower than the expected diffusion controlled rate providing evidence that this species should be assigned to $Fe(CO)_3$Kr.

Following photolysis of $Fe(CO)_5$ in scAr doped with H_2, the species $^3Fe(CO)_4$ has been seen to decay slowly (ca. 280 ns) to eventually form $Fe(CO)_4H_2$. This slow rate is presumed to be as a result of the system crossing from the triplet to the singlet potential energy surface during the course of the reaction. A weak feature which is tentatively assigned to $^1Fe(CO)_4(H_2)$ is seen to decay rapidly (ca. 30 ns) apparently forming $^1Fe(CO)_4H_2$ in a spin allowed reaction.

References

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