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Photochemistry of iron pentacarbonyl in poly(vinyl chloride), polytetrafluoroethylene and low-density polyethylene films at 12–298 K: infrared spectroscopic evidence for the reversible formation of the carbon monoxide loss products iron tetracarbonyl and tricarbonyl, and their reactions with species in the films

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Infrared spectroscopic evidence (C—O stretching region) is presented to show that near-UV irradiation ($280 < \lambda < 350$ nm) of $Fe(CO)_5$ in low-density polyethylene (LDPE), poly(vinyl chloride) (PVC) and polytetrafluoroethylene (PTFE) films at *ca* 12 K affords the coordinatively unsaturated species $Fe(CO)_4$ and $Fe(CO)_3$. The species $Fe(CO)_3$ recombines with CO at *ca* 60 K whilst $Fe(CO)_4$ recombines at *ca* 80 K. The species also react with the polymeric medium and with residual solvent molecules [hexane, dichloroethane, tetrahydrofuran (THF)] in the films. The species $Fe(CO)_4$...(PVC) and $Fe(CO)_4$...(dichloroethane), in which the $Fe(CO)_4$ fragments are probably coordinated by chlorine atoms in the PVC or solvent molecules, are less thermally stable than $Fe(CO)_4$(THF) and are converted to $Fe(CO)_5$ on warming the films to above *ca* 140 K. Similarly, the species $Fe(CO)_4$(LDPE) and $Fe(CO)_4$(hexane), arising from interaction of $Fe(CO)_4$ with hydrogen atoms in the polymer or solvent molecules, are converted to $Fe(CO)_5$ on warming the films from *ca* 100 K to *ca* 130 K. The major product formed in LDPE films at 298 K is probably $Fe(CO)_4$(olefin) arising from olefin impurities in the poly(ethylene), whilst in the PVC films in the presence or absence of THF the major product resembles $(\eta^3-C_3H_5)Fe(CO)_3Cl$, i.e. $Fe(CO)_4$ and $Fe(CO)_3$ fragments bound to allyl chloride impurities in the PVC. The potential of polymer films for trapping and characterizing unstable species is discussed.

Keywords: Photochemistry, $Fe(CO)_5$, low temperature studies, polymer films, infrared spectroscopy, $Fe(CO)_4$, $Fe(CO)_3$

INTRODUCTION

It is well known that $Fe(CO)_5$ undergoes photochemical substitution of CO ligands by other ligands in solution to form derivatives of the type $Fe(CO)_4L$ (e.g. L = phosphine, amine or olefin).[1–4] These reactions have been proposed[1] to proceed by a dissociative mechanism involving the 16-electron species $Fe(CO)_4$.

In an early study, Sheline and co-workers[5] obtained infrared (IR) spectroscopic evidence for an unstable CO-loss product generated on near-ultra-violet (UV) irradiation of $Fe(CO)_5$ in methylcyclohexane/isopentane glasses at 77 K. The product, which was thermally converted to the parent pentacarbonyl on subsequently softening the glasses, was proposed to be the species $Fe(CO)_4$. Poliakoff and Turner[6] later studied in detail the infrared spectra of $Fe(CO)_5$ photolysis products in frozen gas matrices at 12 K. The fragments were found to be highly reactive and to recombine thermally with photoejected CO on annealing the matrices to *ca* 30 K. On irradiation of $Fe(CO)_5$ in methane matrices at 12 K, both the

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species $Fe(CO)_4$ and $Fe(CO)_4CH_4$ were shown to form.[6] The infrared spectrum of the latter species, in which the $Fe(CO)_4$ fragment interacts with a matrix molecule, was found to be similar to that obtained[5,6] on irradiation of $Fe(CO)_5$ in hydrocarbon glasses. This indicated that the product observed in the glasses was probably the species $Fe(CO)_4$...(glass) rather than the naked coordinately unsaturated fragment $Fe(CO)_4$.

Galembeck has reported[7] that irradiation ($\lambda > 300$ nm) of $Fe(CO)_5$ in polytetrafluoroethylene (PTFE) films at room temperature results in the formation of the dimer $Fe_2(CO)_9$, by analogy with the reaction of $Fe(CO)_5$ observed in pure hydrocarbon solvents.[8] Recently, De Paoli and co-workers[9] have discussed infrared spectra obtained on photolysis of $Fe(CO)_5$ in thick low-density polyethylene (LDPE) films at room temperature. The new bands observed in the spectra were assigned to the species $Fe(CO)_4$ and $Fe(CO)_3$. This assignment seems surprising in view of the high reactivity of these species observed previously[6] in frozen gas matrices at temperatures as low as 30 K. Accordingly, the photochemistry of $Fe(CO)_5$ in LDPE films has been reinvestigated* as part of a study of rigid media which can be used as alternatives to frozen gas matrices and which are of interest in relation to chemical reactions in natural and man-made membranes.[11]

EXPERIMENTAL

(a) Equipment

The detailed use of the closed-cycle helium refrigerator and cryostat (Air Products and Chemicals Model CSW 202), spectrometers (Nicolet 7199 Fourier transform infrared spectrometer; Pye-Unicam SP1800B UV/visible spectrometer), and the photolysis source (Philips HPK 125 W) have been described elsewhere.[12] The glass cryostat for use at 77 K has been described elsewhere[13] and is commercially available (Applied Photophysics Ltd).

(b) Preparation of polymer films

(i) Poly(vinyl chloride) (PVC) films

Suspension-polymerized PVC in a powdered form, which contains no photostabilizers or any other additives (Corvic D60/11, ICI Ltd; 500 mg), was dissolved in either sodium-dried tetrahydrofuran (THF) ('AnalaR' grade, BDH Ltd; 20 cm^3) at 25 °C or in 1,2-dichloroethane ('AnalaR' grade, BDH Ltd; 50 cm^3) at 40 °C in a 200-cm^3 beaker, while stirring with a magnetic stirrer. A sample (2–4 mg) of the metal carbonyl compound under study was then added to the solution at 25 °C. The beaker was covered with aluminium foil to prevent the solution from being exposed to room lighting or sunlight. The solution was then poured into a Petri dish (10 cm diameter) placed on a flat surface obtained by levelling a supported glass plate. In this way the dish was kept horizontal and it was covered with aluminium foil with sufficient ventilation to allow the solvent to evaporate. This procedure, which is based on the technique described by Oster *et al.*,[14] gave films of uniform thickness (*ca* 100 μm). When preparing films containing air-sensitive compound, the film-casting solution was made up in a three-necked round-bottomed flask purged with nitrogen. The solution was then transferred, using a syringe, to the Petri dish within a nitrogen-purged desiccator placed on a levelled surface. The desiccator was covered with aluminium foil and the solvent allowed to evaporate (*ca* 20 h, THF solutions; *ca* 48 h, dichloroethane solutions) by maintaining a steady nitrogen purge (*ca* 1 psi, 6.9 kPa). When a film (thickness *ca* 100 μm) had been cast, a sharp-bladed microspatula was used to detach it from the walls of the Petri dish. The dish was then filled with cold distilled water, which enabled the film to be peeled away easily from the base of the dish. The film was subsequently dried between filter papers and wrapped in aluminium foil. Films containing air-sensitive compounds were immediately stored under nitrogen (in a desiccator) on being extracted from the Petri dish. The amount of $Fe(CO)_5$ (solute) used in preparing films was generally kept low such that the mole ratio, (—CH_2CHCl—) units:solute in the polymeric medium was approximately 1000:1. In some room-temperature experiments, where bimolecular reactions were studied, the concentration of $Fe(CO)_5$ in the films was increased, e.g. 10 mg of $Fe(CO)_5$ in 500 mg of PVC, where a (—CH_2CHCl—):solute ratio of *ca* 200:1 was obtained.[15] The films contained approximately 4% by weight of residual casting solvent.[13]

The infrared spectra of all PVC films showed a weak band at *ca* 1730 cm^{-1}. This band, which has been observed previously in spectra of PVC films cast from solutions,[16] has been assigned to impurity carbonyl

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*A preliminary report of this work has been published elsewhere.[10]

groups in the PVC, arising from thermal and/or photochemical degradation of the polymer.[17] PVC cast into films from dichloroethane solutions which had been heated to 70 °C in air contained a higher concentration of carbonyl groups than that cast into films from solutions at 25 °C, under nitrogen. The electronic absorption spectra of PVC films showed a weak band at *ca* 280 nm and other weak absorptions in the region 300–350 nm. These bands have been assigned, respectively, to impurity carbonyl and olefinic groups in the PVC, by analogy with spectra recorded previously.[16,18]

(ii) Low-density polyethylene (LDPE) and polytetrafluoroethylene (PTFE) films

LDPE and PTFE film media containing the complex $Fe(CO)_5$ were prepared using the sorption technique described by De Paoli and co-workers.[19] Thick films of LDPE (WVG 23, ICI Ltd) (25 mm diameter, 0.5 mm thick) were soaked for 5–10 min in solutions of $Fe(CO)_5$ (1 cm^3) in hexane (10 cm^3) in beakers placed inside a nitrogen-filled desiccator. Films of PTFE (Fluon, ICI Ltd) (25 mm diameter, 0.1 mm thick), which allow a much lower degree of sorption of $Fe(CO)_5$ due to the high crystallinity of the polymer, were soaked in similar solutions for about 8 h. The films were wrapped in aluminium foil and stored under nitrogen.

(c) Mounting of films

The polymer film samples were clamped between two calcium fluoride (CaF_2) discs (25 mm diameter) in the copper holder using brass screws. Indium gaskets were placed between the discs and holder to ensure a good thermal contact. Films of the same diameter as the discs were used so that they could be clamped as tightly as possible, again to ensure a good thermal contact. The glass cryostat was evacuated (10^{-4} torr, 133×10^{-4} Pa) prior to filling the refrigerant vessel with liquid nitrogen. It was allowed to cool down for 20 min before the sample was irradiated. A similar procedure was followed for the liquid-helium cryostat (vacuum 10^{-7} torr, 133×10^{-7} Pa; cooling time *ca* 45 min). Temperatures of the CaF_2 disc holder were monitored using a gold-chromel thermocouple. Thermal reactions of photoproducts generated in films at 12 K were monitored by switching off the compressor unit and allowing the films to warm up slowly to room temperature over a period of *ca* 5 h.

Polymer films were also mounted in the glass cryostat during photolysis experiments at room temperature. The cryostat was evacuated before irradiation in order to remove any possible oxygen contamination of the films.

(d) Infrared spectral subtractions

Infrared spectral subtractions were obtained in cases where the absorptions for a product, formed in a film on irradiation, were overlapped by the absorptions for unreacted parent molecules. The subtractions were performed by subtracting the absorbance spectrum of the parent complex, multiplied by a 'scaling factor', from the absorbance spectrum obtained after irradiation. In some cases, it was not possible to 'subtract out' parent bands completely from a spectrum recorded after irradiation of a film. This arose when the baseline in a spectrum obtained after irradiation differed slightly from that in the spectrum recorded before irradiation – a problem encountered when repositioning the film sample in the beam of the spectrometer. Spectral subtractions (absorbance mode) were also performed in cases where the absorptions for a product, thermally generated in a film warmed after irradiation at 12 K (or at 77 K), were overlapped by those for the parent complex. Films warmed to above *ca* 90 K were recooled prior to subtracting parent bands in spectra recorded at 12 K (or at 77 K). This allowed for any changes in the positions and/or widths of bands in spectra occurring with changes in temperature, which could give rise to spurious features in subtracted spectra. All subtracted spectra were subsequently converted to percentage transmittance form.

RESULTS

(a) Photolysis of $Fe(CO)_5$ in low-density polyethylene (LDPE)

Figure 1(a) shows the infrered spectrum of $Fe(CO)_5$ in a thick LDPE film* at 12 K. The spectrum is analogous to that recorded for $Fe(CO)_5$ in cyclohexane solutions.[20] The two bands seen at 2020 and 1998 cm^{-1} have been assigned, respectively, to A_2'' and E' carbonyl stretching vibrations of the

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*The film was immersed in a 10% solution of $Fe(CO)_5$ in hexane at 293 K for 3 min.

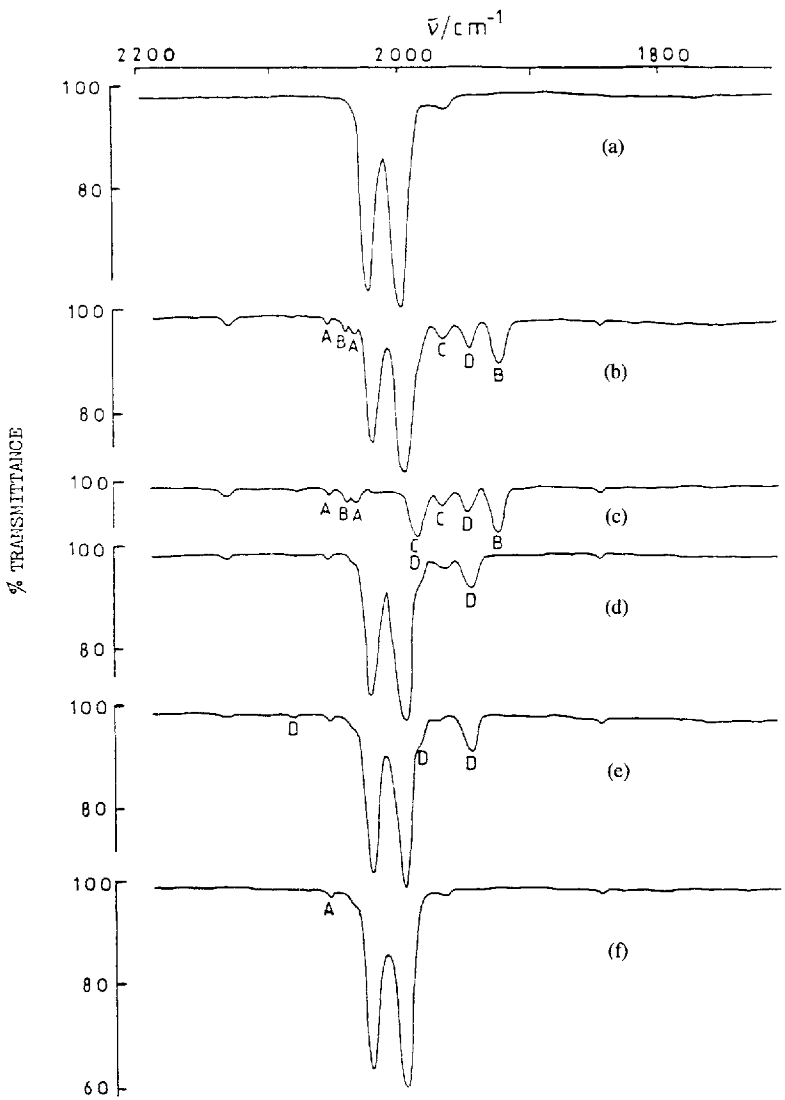

Figure 1 Infrared spectra from an experiment with $Fe(CO)_5$ in an LDPE film at 12 K: (a) before irradiation; (b) after 20 min irradiation ($280 < \lambda < 350$ nm); (c) spectral subtraction, (b) $- N$(a) where N is a scaling factor; (d) after warming the film to *ca* 60 K; (e) warming to *ca* 80 K; (f) warming to *ca* 130 K. Bands marked A–D are for products (see text).

complex,[20] which has a trigonal bipyramidal (D_{3h}) structure.[21] The weak absorption observed at 1961 cm^{-1} is assigned as a satellite band arising from the natural occurrence of ^{13}C. Irradiation of the film at 12 K with near-UV light ($280 < \lambda < 350$ nm)† produced new bands [labelled A–D; Fig. 1(b)] in the spectrum at 2055, 2038, 2030, *ca* 1987, 1962, 1946 and 1924 cm^{-1}, together with a band for free carbon monoxide (CO) at 2136 cm^{-1}, whilst the bands at *ca* 1987 cm^{-1} (labelled C and D), which appeared as a shoulder on the parent band at 1998 cm^{-1}, was revealed on substracting the parent bands from the spectrum [Fig. 1(c)]. On subsequently warming the film to *ca* 60 K, the product bands (B) at 2038 and 1924 cm^{-1} increased in intensity. At the same time, the band for free CO and the new bands (C) at 1987 and 1962 cm^{-1} decreased in intensity [Fig. 1(d)]. Further warming the film to *ca* 80 K led to the disappearance of the new bands (C) whilst the other

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†Combination filter: Pyrex glass disc (thickness 2 mm) + quartz gas cell (pathlength 25 mm) containing bromine gas (300 torr, 40 kPa).

product bands (D) and the parent bands further increased in intensity. At this stage [Fig. 1(e)], another new very weak band (D) was observed in the spectrum at *ca* 2080 cm^{-1}. The new bands (D) disappeared on subsequently warming the film to *ca* 130 K, which led to further regeneration of the parent compound $Fe(CO)_5$ [Fig. 1(f)]. It is evident from the changes observed in the spectrum on warming the film from 12 K that the new bands A–D arise from different products. The weak product bands (A) at 2055 and 2030 cm^{-1}, which persisted in the spectrum on warming the film to *ca* 130 K, were also observed in spectra on irradiation of $Fe(CO)_5$ in LDPE films at room temperature (discussed below). The new bands B, C and D occur at similar wavenumbers to those observed[6] on irradiation of $Fe(CO)_5$ in methane (CH_4) matrices. The bands B and C, which disappeared on warming the film to *ca* 80 K [Fig. 1(e)] are assigned to the coordinatively unsaturated species $Fe(CO)_3$ and $Fe(CO)_4$, respectively (Table 1). The intensity pattern and positions of the other new bands (D) at *ca* 2090, 1987 and 1946 cm^{-1} [Fig. 1(e)] are similar to those observed[6] for the species $Fe(CO)_4\ldots(CH_4)$ in CH_4 matrices (Table 1). The fact that the bands D increased in intensity on warming the film to *ca* 80 K suggests that these bands may possibly arise from the species $Fe(CO)_4$ interacting with hydrogen atoms in the LDPE (see Discussion).

Table 1 Comparison of infrared band positions[a] (cm^{-1}) for $Fe(CO)_5$ and its photoproducts in LDPE, PVC and PTFE films[b] (*ca* 12 K) with those in CH_4 matrices[c] (*ca* 12 K) and SF_6 matrices[c] (*ca* 35 K).

Complex	LDPE	CH_4	PVC	PTFE	SF_6
$Fe(CO)_5$	2020s	2022s	2019s	2024s	2030s
	1998s	2000s	1996s	2005s	2006s
			1985s		
$Fe(CO)_4$	1987s	1993s	1984s	1998s	1999s
	1982sh	1985m	1980sh	1993m	1994m
	1962s	1966s	1961s	1974s	1973s
$Fe(CO)_4(L)$[d]	2080w	2088w	2072w	–[g]	–[h]
	1987s	1994s	1984[f]	1995w	
	1980sh	1982w	1980sh	–[g]	
	1946vs	1950vs	1944vs	1950w	
$Fe(CO)_4(THF)$[e]	–[h]	–[h]	2060m	–[h]	–[h]
			1959s		
			1945vs		
$Fe(CO)_3$	2038w	2040w	2030[i]	–[g]	2042w
	1924s	1930s	1927s	1933s	1935s

L = polymer, solvent[d,e] or CH_4. [a]s, strong; m, medium; w, weak; sh, shoulder. [b]This work. [c]Data from Ref. 6. [d]Hexane in LDPE and PTFE films; dichloroethane in PVC films. [e]Product formed on warming films to *ca* 80 K. [f] Band overlapped by band for $Fe(CO)_4$. [g]Band too weak to be observed. [h]Species not observed to form. [i]Band overlapped by band for $Fe(CO)_5$.

Figure 2(a) shows the infrared spectrum of $Fe(CO)_5$ in an LDPE film at room temperature (298 K). This film contained a higher concentration of the pentacarbonyl* than the film used in the experiment at 12 K. On irradiating the film at room temperature with near-UV light ($280 < \lambda < 350$ nm), new bands (A, E and F) grew in the spectrum at 2074, 2055, 2040, 2030, *ca* 1992, 1973 and 1950 cm^{-1} along with a weak band (A) in the bridging carbonyl stretching region at 1840 cm^{-1}. At the same time, the parent bands decreased in intensity [Fig. 2(b)]. The new band (E) at 1992 cm^{-1}, which was overlapped by the parent band at 1998 cm^{-1}, was revealed on subtracting the parent bands from the spectrum [Fig. 2(c)]. The new bands B were all seen to increase at the same rate indicating that they arose from a single photoproduct. This product was observed to be quite thermally stable and persisted in the film at 298 K over a period of 48 h. Furthermore, the decomposition of this product in a film exposed to air was seen to proceed more slowly than that of residual $Fe(CO)_5$ in the same film. The other new bands (A and F) [Fig. 2(c)] are attributed to other photoproducts which are also thermally stable in films at 298 K. The yield of the product A was observed to increase, relative to the yields of the products A and F, as the concentration of the parent complex $Fe(CO)_5$ in the films was increased. The product A, which shows infrared absorptions (ν_{CO} 2055, 2030 and 1840 cm^{-1}) at similar wavenumbers to those observed following irradiation of $Fe(CO)_5$ in PTFE films at 298 K (Table 2), is proposed to be the dimer $Fe_2(CO)_9$.† The other photoproducts (E and F) formed in the LDPE film at 298 K are most probably mononuclear species (see Discussion). Separate experiments showed that free CO is produced along with the products E and F on irradiation of $Fe(CO)_5$

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*The film was immersed in a 10% solution of $Fe(CO)_5$ in hexane for 5 min, as in the experiments described by De Paoli and co-workers.[9]

†It was not possible to obtain an authentic sample of $Fe_2(CO)_9$ sorbed into LDPE films owing to the insolubility of this compound. The infrared absorptions A [Fig. 2(c)] do, however, occur at similar wavenumbers to those observed for $Fe_2(CO)_9$ (ν_{CO} 2060, 2035 and 1847 cm^{-1}) in argon matrices[22] at 12 K.

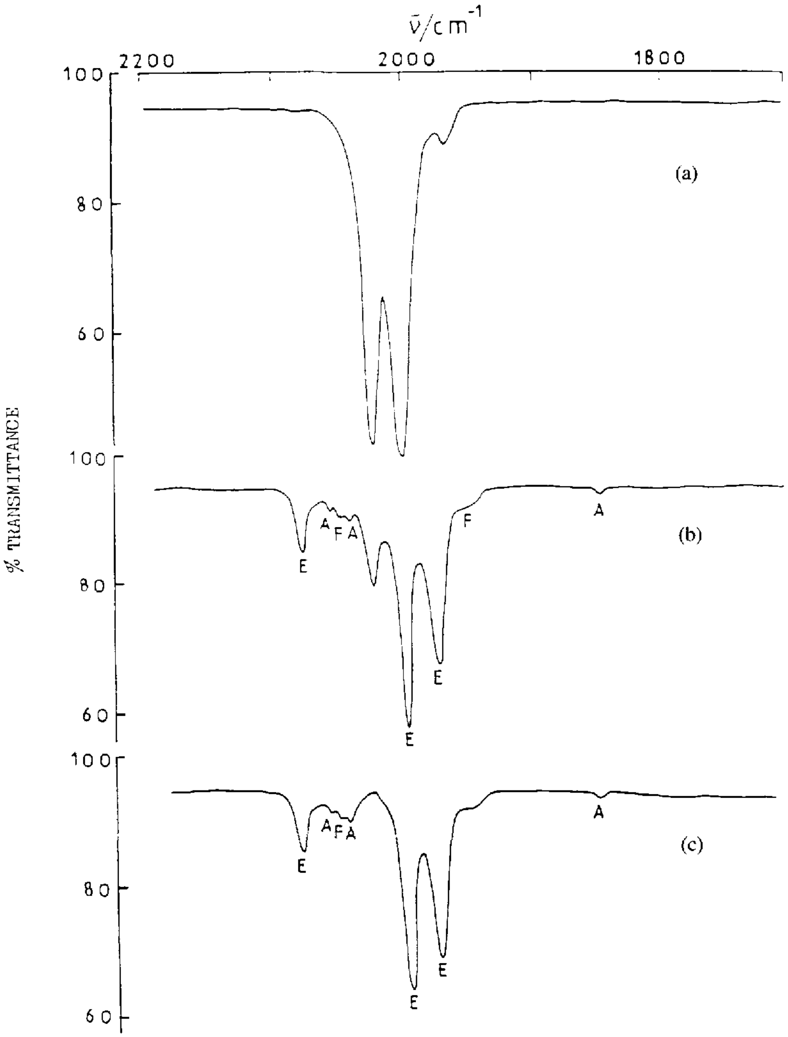

Figure 2 Infrared spectra from an experiment with $Fe(CO)_5$ in an LDPE film at 298 K; (a) before irradiation: (b) after 20 min irradiation ($280 < \lambda < 350$ nm); (c) spectral subtraction, (b) $-N$(a), where N is a scaling factor. Bands marks A, E and F are for products (see text).

in LDPE films at 298 K. The free CO was not observed in the films at room temperature but was detected (ν_{CO} 2136 cm^{-1}) on subsequently cooling the films to 77 K after irradiation.

(b) Photolysis of $Fe(CO)_5$ in poly (vinyl chloride) films

Figure 3(a) shows the infrared spectrum of $Fe(CO)_5$ at 12 K in a PVC film (2 mg/500 mg) cast from a dichloroethane solultion (298 K). The spectrum shows broader bands than those seen for the pentacarbonyl in LDPE films. The lower-wavenumber (E') carbonyl stretching band is split into two components at 1996 and 1985 cm^{-1} whilst the higher wavenumber (A_2'') band at 2019 cm^{-1} is overlapped by another band at *ca* 2030 cm^{-1}. The observed splitting and broadening of the bands may possibly be due to a lowering of the effective symmetry of the pentacarbonyl molecules by the sites occupied in the PVC medium and may also arise form solute–polymer interactions. The electronic absorption spectrum of $Fe(CO)_5$ in the film at 12 K [Fig. 4, curve (a)] showed a band at *ca* 290 nm which occurred as a shoulder on a much more intense band at *ca* 250 nm. The spectrum is analogous to that obtained[23] for $Fe(CO)_5$ in hydrocarbon solvents. The

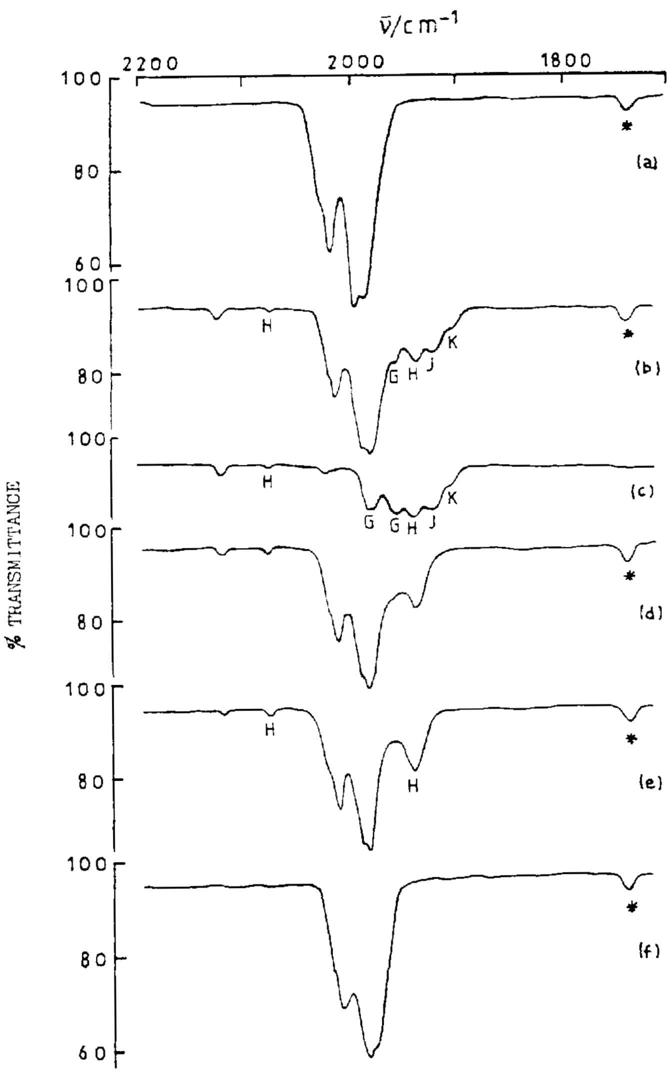

Figure 3 Infrared spectra from an experiment with $Fe(CO)_5$ in PVC films (cast from a dichloroethane solution) at 12 K; (a) before irradiation; (b) after 20 min irradiation (280 < λ 350 nm); (c) spectral subtraction, (b) − *S*(a), where *S* is a scaling factor; (d) after warming film to *ca* 60 K; (e) after warming to *ca* 80 K; (f) after warming to *ca* 180 K. Bands marked G–K are for products (see text) and that marked * is for ketone groups in PVC.

band at 285 nm has been assigned[24] to a ligand field transition $(d_{xy}, d_{x^2-y^2} \rightarrow d_{z^2})$ which is thought to be responsible for the photochemistry of $Fe(CO)_5$ observed in solution.[25] Irradiation of the film with light corresponding to the ligand field band produced new weak bands in the electronic absorption spectrum in the region 340–420 nm [Fig. 4, curve (b)]. At the same time, several new bands (labelled G–K) appeared in the infrared spectrum, along with the band for free CO, whilst the bands for $Fe(CO)_5$ decreased in intensity [Fig. 3(b)]. Other new bands (G and H), which grew underneath the parent band at 1985 cm^{-1}, were revealed on subtracting the parent bands from the spectrum [Fig. 3(c)]. On subsequently warming the film to *ca* 60 K, the new bands J and K at 1927 and 1906 cm^{-1}, respectively, disappeared whilst the bands (H) at 2072 and 1944 cm^{-1} and those for $Fe(CO)_5$ increased in intensity. At the same, the other new band (G) at 1961 cm^{-1} and the band for free CO decreased [Fig. 3(d)]. The new band G disappeared on further warming the film to *ca* 80 K which led to further increases in the bands H and the parent bands

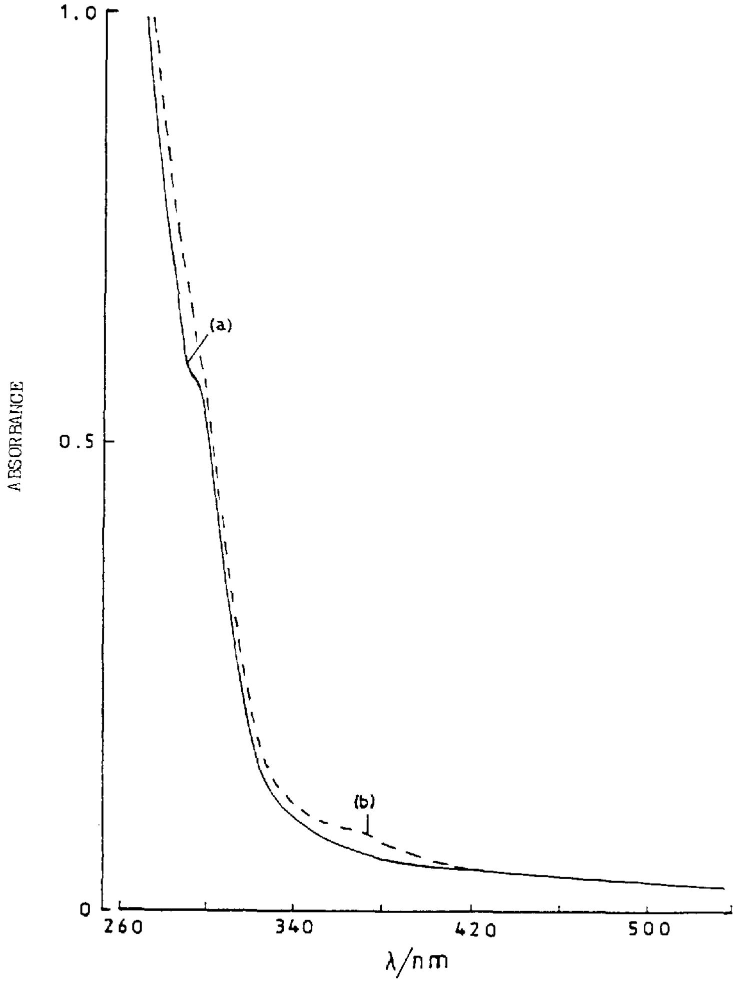

Figure 4 Ultraviolet–visible spectra from an experiment with $Fe(CO)_5$ in a PVC film (cast from a dichloroethane solution) at 12 K; (a) before irradiation; (b) after 20 min irradiation ($280 < \lambda < 350$ nm).

[Fig. 3(e)]. Complete conversion of the product H to the parent compound occurred on subsequently warming the film from *ca* 140 K to *ca* 180 K [Fig. 3(f)]. The photoproduct bands (G, J and K) which disappeared on warming the film to *ca* 80 K [Fig. 3(b)–(e)] are evidently associated with unstable CO-loss products. The bands (G) at *ca* 1984 and 1961 cm^{-1} and the band (J) at 1927 cm^{-1} are assigned to the species $Fe(CO)_4$ and $Fe(CO)_3$, respectively, by analogy with the bands observed for these species LDPE films and in CH_4 matrices at 12 K (Table 1). The product (H) which persists in PVC films at temperatures above 140 K shows bands (ν_{CO} 2072 and 1944 cm^{-1}) of similar relative intensities as the bands seen at 2088 and 1950 cm^{-1} for the species $Fe(CO)_4 \ldots (CH_4)$ in CH_4 matrices (Table 1). This suggests that the product may be the species $Fe(CO)_4 \ldots$(PVC) in which the $Fe(CO)_4$ fragment interacts with a hydrogen or chlorine atom in the PVC. The other photoproduct (K) (ν_{CO} 1906 cm^{-1}), which was observed to form in LDPE films at 12 K but which disappeared on warming the PVC film to *ca* 60 K [Fig. 3(d)], may possibly be the species $Fe(CO)_3$(PVC) (see Discussion).

The species $Fe(CO)_4$ and $Fe(CO)_3$ were also observed to form on irradiation of $Fe(CO)_5$ at 12 K in PVC films cast from THF solutions. Warming these films to *ca* 80 K led to some regeneration of the pentacarbonyl and the formation of another product (ν_{CO} 2060, 1959 and 1945 cm^{-1}). This product is proposed to be the complex $Fe(CO)_4$(THF), arising from a reaction of $Fe(CO)_4$ or $Fe(CO)_3$ with residual

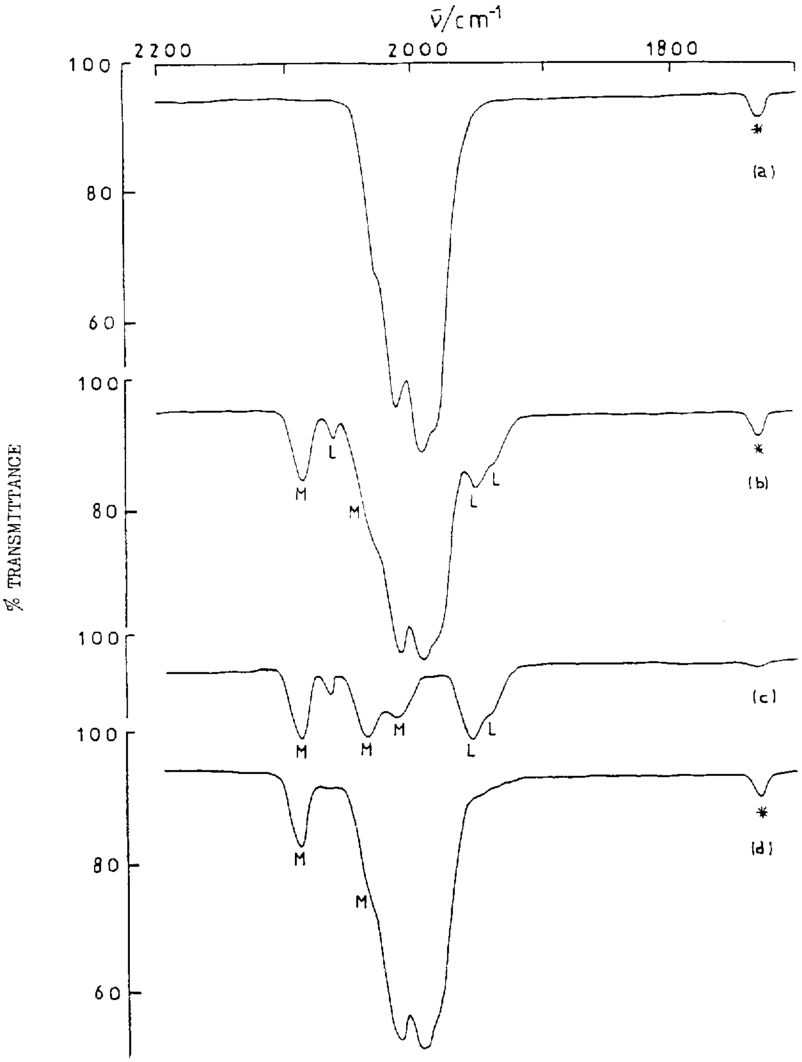

Figure 5 Infrared spectra from an experiment with $Fe(CO)_5$ in a PVC film (cast from a THF solution) at 298 K; (a) before irradiation; (b) after 15 min irradiation ($280 < \lambda < 350$ nm); (c) spectral subtraction, (b) − T(a), where T is a scaling factor; (d) after leaving the film in the dark for 20 h. Bands marked L and M are for products (see text) and that marked * is for ketone groups in PVC.

THF in the films. The infrared adsorptions for the product occur at very similar wavenumbers to those reported[26] for the complex $Fe(CO)_4(MeTHF)$ (ν_{CO} 2062, 1963 and 1946 cm^{-1}) formed on irradiation ($\lambda < 300$ nm) of $Fe(CO)_5$ in methyltetrahydrofuran (MeTHF) glasses at 77 K.

The infrared spectrum of $Fe(CO)_5$ at room temperature (298 K) in a PVC film (3 mg/500 mg) cast from a THF solution is shown in Fig. 5(a). Irradiation of the film with near-UV light ($280 < \lambda < 350$ nm) led to the formation of the complex $Fe(CO)_4(THF)$ (L) and another product (M) with infrared absorptions at 2090, 2040 and *ca* 2015 cm^{-1} [Fig. 5(b)]. The new band at 2105 cm^{-1} was revealed on subtracting the parent bands from the spectrum [Fig. 5(c)]. Thermal conversion of $Fe(CO)_4(THF)$ to $Fe(CO)_5$ was observed on subsequently leaving the film at 298 K in the dark [Fig. 5(d)]. The other product (M) was, however, seen to be thermally stable at room temperature and persisted in the film over a period of several days.* The product (M) was also observed to form on irradiation of $Fe(CO)_5$ at 298 K in PVC films (3 mg/500 mg) cast from dichloroethane solutions and does not, therefore, arise from a reaction involving

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*The film was not exposed to air.

THF (see Discussion). No infrared absorptions attributable to the dimer $Fe_2(CO)_9$ were observed following irradiation of $Fe(CO)_5$ in the PVC films at 298 K; cf. the absorptions (A) seen after photolysis of $Fe(CO)_5$ in LDPE films at 298 K (Fig. 3) and at 12 K (Fig. 1).

(c) Photolysis of $Fe(CO)_5$ in polytetrafluoroethylene (PTFE) films

Figure 6(a) shows the infrared spectrum of $Fe(CO)_5$ in a PTFE film cooled to 12 K. The film was immersed in a 10% solution of the pentacarbonyl in hexane for 3 h at 298 K, prior to cooling. The spectrum is very similar to that recorded previously for $Fe(CO)_5$ in SF_6 matrices[6] at 35 K and shows terminal carbonyl stretching bands at 2024 (A_2'') and 2005 cm^{-1} (E'). Irradiation ($280 < \lambda < 350$ nm) of the film produced new bands (N, P and Q) in the spectrum at 2062, 2032, 1998, 1993, 1973, 1933 and 1829 cm^{-1}, together with a band for free CO, whilst the parent bands decreased in intensity [Fig. 6(b)]. On subsequently warming the film to *ca* 90 K, the new bands P and Q disappeared whilst the parent bands increased. At the same time,

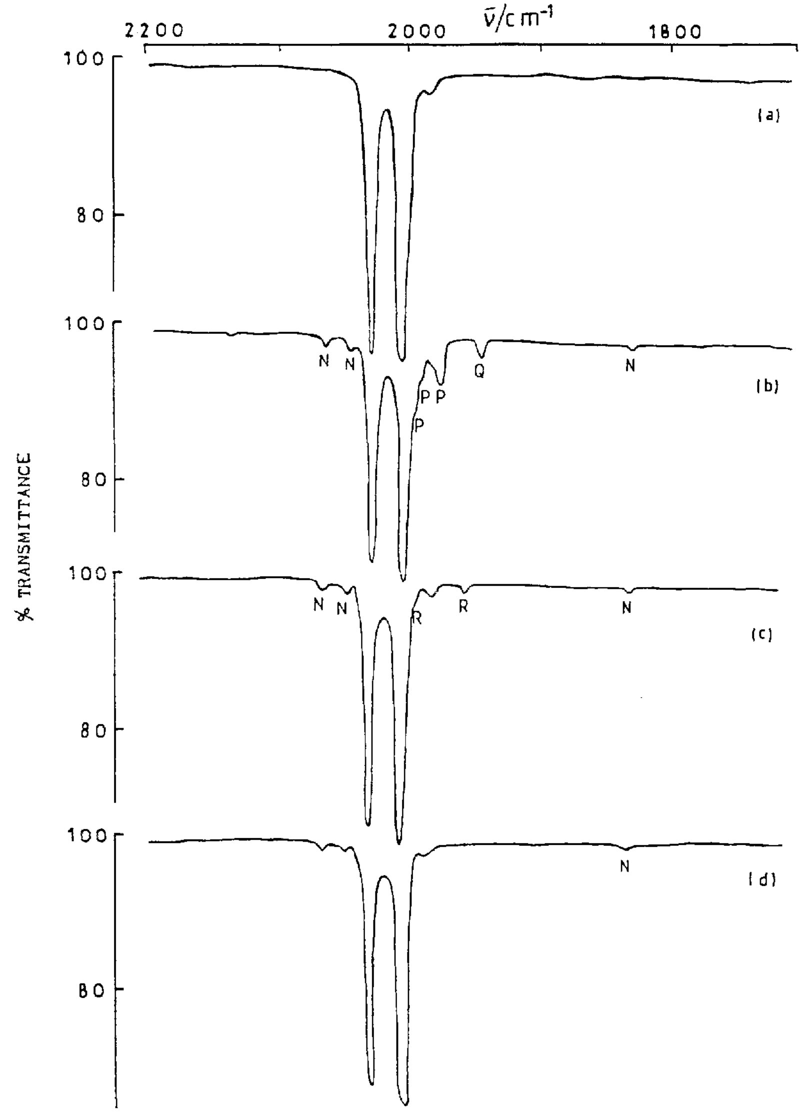

Figure 6 Infrared spectra from an experiment with $Fe(CO)_5$ in a PTFE film at 12 K; (a) before irradiation; (b) after 120 min irradiation ($280 < \lambda < 350$ nm); (c) after warming the film to *ca* 90 K; (d) after warming to *ca* 130 K. Bands marked N, P, Q and R are for products (see text).

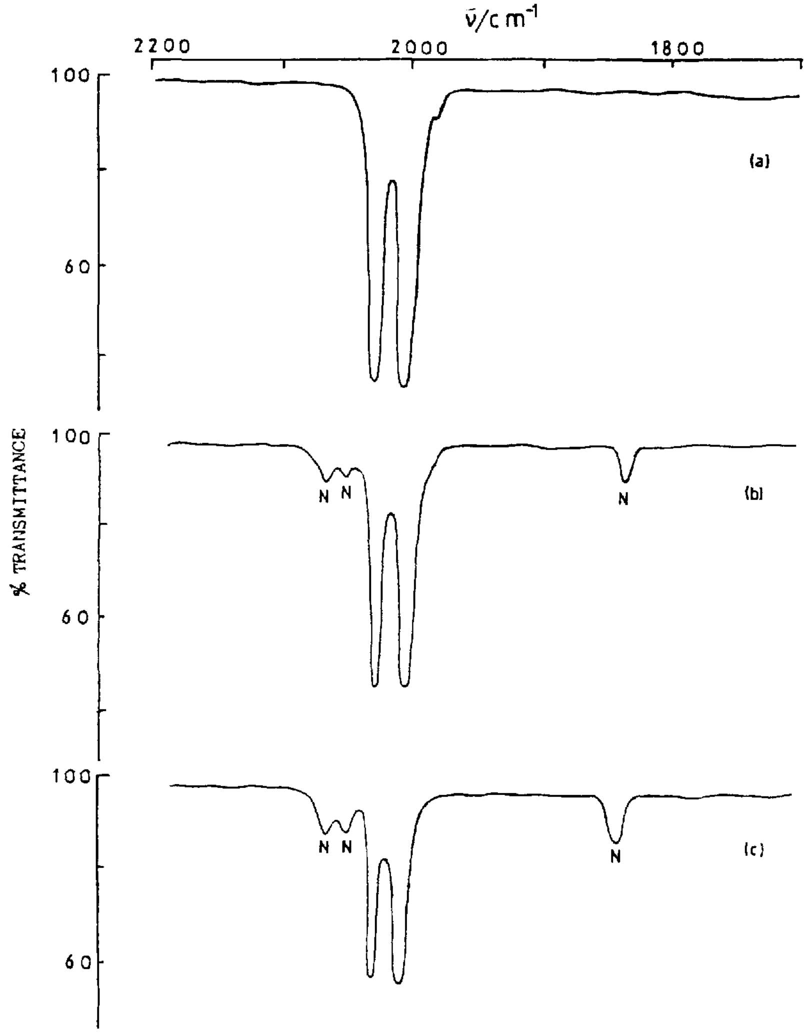

Figure 7 Infrared spectra from an experiment with $Fe(CO)_5$ in a PTFE film at 298 K; (a) before irradiation; (b) after 50 min irradiation ($280 < \lambda < 350$ nm); (c) after a further 100 min irradiation. Bands marked N are for product (see text).

weak new bands (R) grew in the spectrum at *ca* 1995 and 1950 cm^{-1} [Fig. 6(c)]. These bands disappeared on further warming the film to *ca* 130 K [Fig. 6(d)]. The weak product bands (N) at 2062, 2032 and 1829 cm^{-1}, which persisted in the spectrum on warming the film, are assigned to the dimer $Fe_2(CO)_9$, previously observed to form (ν_{CO} 2062, 2030 and 1829 cm^{-1}) on irradiation of $Fe(CO)_5$ in PTFE films at room temperature.[7] The product bands (P) at 1998, 1993 and 1973 cm^{-1}, observed on irradiation of the film at 12 K, are assigned to the species $Fe(CO)_4$ by analogy with the bands observed for this species in SF_6 matrices (Table 1). The other photoproduct band (Q) at 1933 cm^{-1} is assigned to the fragment $Fe(CO)_3$ by analogy with infrared data obtained for this species in matrices[6] and in LDPE and PVC films at 12 K (Table 1). The weak new bands (R) which appeared on warming the film may possibly arise from the species $Fe(CO)_4$ interacting with hexane solvent molecules sorbed into the films (see Discussion). The photolysis of $Fe(CO)_5$ in the film at 12 K was seen to proceed at a much slower rate than that in PVC or LDPE films, under the same irradiation conditions, owing to the lower transparency of the PTFE film to the near-UV light.

Irradiation ($280 < \lambda < 350$ nm) of $Fe(CO)_5$ in a PTFE film* at room temperature (298 K) [Fig. 7(a)–

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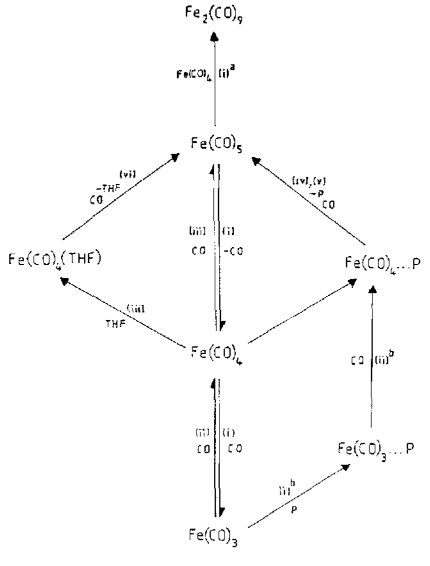
*The film was immersed in a 10% solution of $Fe(CO)_5$ in hexane at 298 K for 8 h.

(c)] resulted in the formation of the dimer $Fe_2(CO)_9$ (N). No other products were observed to form in the film.

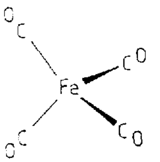
DISCUSSION

Scheme 1 summarizes the photochemistry of the complex $Fe(CO)_5$ observed in LDPE, PVC and PTFE films at 12 K and the thermal reactions proposed to occur on warming the films after irradiation. Photolysis of $Fe(CO)_5$ in the films at 12 K is seen to lead to the formation of the species $Fe(CO)_4$ and $Fe(CO)_3$, by analogy with the reactions observed previously in frozen gas matrices.[6] The $Fe(CO)_3$ fragment could possibly arise from secondary photolysis of $Fe(CO)_4$. Alternatively, the fragments $Fe(CO)_4$ and $Fe(CO)_3$ could be formed via a single-photon absorption process where $Fe(CO)_4$ is produced from $Fe(CO)_5$ in a vibrationally or electronically excited state and undergoes loss of CO to form $Fe(CO)_3$ The infrared spectra of the species $Fe(CO)_4$ and $Fe(CO)_3$, formed in the films at 12 K, correspond with those of the fragments generated in frozen gas matrices (Table 1) which were shown[6] to have C_{2v} and C_{3v} geometries (structures **I** and **II**).

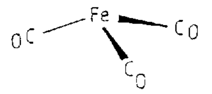


Scheme 1 P = hydrogen atom in LDPE or hexane solvent molecule, or chlorine atom in PVC or dichloroethane solvent molecule.

(i) $h\nu$ ($280 < \lambda < 350$ nm) at 12 K; (ii) warming the film from 12 K to *ca* 60 K; (iii) warming film from 12 K to *ca* 80 K; (iv) warming LDPE or PTFE film from *ca* 100 K to *ca* 130 K; (v) warming PVC film from *ca* 140 K to *ca* 180 K; (vi) thermal reaction at 298 K. [a]Only observed in LDPE and PTFE films. Product formed in low yield. [b]Observed in PVC films.

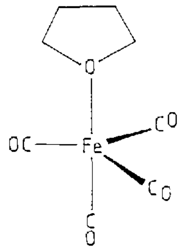


I



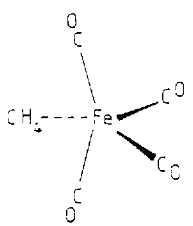
II

The observation that the species $Fe(CO)_4$ and $Fe(CO)_3$ recombine with photoejected CO in polymer films at temperatures below 80 K indicates that these species are very reactive. The infrared spectrum of the complex $Fe(CO)_4(THF)$, observed to form on warming PVC films containing THF (Table 1), is analogous to the spectra observed for CO photosubstitution products of the type $Fe(CO)_4L$ (C_{3v} symmetry) (e.g. $Fe(CO)_4PPh_3$, ν_{CO} 2052 (*w*, A_1), 1975 (s, A_1) and 1946 (vs, E) cm^{-1}, in hexane[2]) formed on irradiation of $Fe(CO)_5$ in solution and indicates that the complex has the structure **III** shown below.

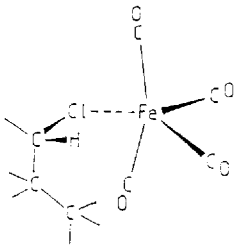


III

Irradiation ($280 < \lambda < 350$ nm) of $Fe(CO)_5$ in LDPE films at 12 K is seen to lead to the formation of a product (D), besides the species $Fe(CO)_4$ and $Fe(CO)_3$, which shows infrared absorptions (ν_{CO} 2080, 1987, 1980 and 1946 cm^{-1}) similar to those of the species $Fe(CO)_4...(CH_4)$ (structure **IV**; C_{2v} symmetry) produced on irradiation of $Fe(CO)_5$ in CH_4 matrices[6] (Table 1). An analogous product (H) is formed on irradiation of $Fe(CO)_5$ in PVC films at 12 K. The same products (D) and (H) are thermally generated from the species $Fe(CO)_4$ and $Fe(CO)_3$ on warming films from 12 K to *ca* 80 K. These products are not the same as those seen to form on irradiation of $Fe(CO)_5$ in LDPE or PVC films at 298 K (discussed below). The product (D) formed in the LDPE films may be the photogenerated species $Fe(CO)_4$ interacting with hydrogen atoms in the polymer (cf. structure **IV**).



IV



V

The $Fe(CO)_4$ fragments could possibly also interact with hexane solvent molecules present in the films.* Similarly, the product (H) generated in the PVC films could arise from the species $Fe(CO)_4$ interacting with a chlorine atom in the PVC or in a residual dichloroethane solvent molecule in the films cast from dichloroethane solutions (cf. structure V). Any interaction which exists between $Fe(CO)_4$ and the polymer or hexane solvent molecules in the LDPE films, after irradiation at 12 K, must be weak since the parent compound $Fe(CO)_5$ is regenerated on warming the films to *ca* 120 K. Complete regeneration of $Fe(CO)_5$ in the PVC films was only observed after warming the films to *ca* 180 K, which suggests that stronger interactions may occur between the $Fe(CO)_4$ fragments and the PVC or dichloroethane solvent.

The other product (K) observed to form on irradiation of $Fe(CO)_5$ in PVC films at 12 K [Fig. 3(c)] may possibly be the species $Fe(CO)_3$...(PVC). Consistent with this is the observation that the product (K) disappears along with the species $Fe(CO)_3$ on warming films to *ca* 60 K at the same time as the tetracarbonyl species (D) (proposed structure V) is generated. The possibility that the product (K) (ν_{CO} 1906 cm^{-1}) is the species $Fe(CO)_2$, generated from $Fe(CO)_3$, seems unlikely since the product was not observed to form in LDPE or PTFE films at 12 K.†

The observation that the species $Fe(CO)_4$ recombines with CO or interacts with the polymer (or solvent molecules) in the LDPE films at temperatures below *ca* 60 K is consistent with the fact that only the species $Fe(CO)_4$...(glass) was observed[5,6] on photolysis of $Fe(CO)_5$ in hydrocarbon glasses at 77 K.

The $Fe(CO)_4$ fragments generated on irradiation of $Fe(CO)_5$ in PTFE films at 12 K show infrared absorptions very similar to those observed[6] for the fragments in SF_6 matrices at 35 K (Table 1). Warming the films to *ca* 90 K [Fig. 6(c)] is seen to lead to the formation of a product (R) with infrared absorptions (ν_{CO} *ca* 1994 and 1950 cm^{-1}) similar to those seen for $Fe(CO)_4$...(CH_4) and which disappears on further warming the film to *ca* 130 K. This product could possibly be the species $Fe(CO)_4$ interacting with a fluorine atom in the PTFE. However, the product is formed in a much lower yield than the products (D and H) generated from $Fe(CO)_4$ in the LDPE and PVC films. This suggests that the product R may arise from interaction of the $Fe(CO)_4$ fragment with hexane solvent molecules sorbed into the PTFE films rather than from interaction with the polymer itself. Interestingly, no infrared spectroscopic evidence for the species $Fe(CO)_4$...(SF_6) was obtained in photolysis of $Fe(CO)_5$ in the SF_6 matrices.[6]

No spectroscopic evidence was obtained for the formation of the dimer $Fe_2(CO)_9$ on photolysis of $Fe(CO)_5$ in the PVC films at 12.–298 K. The dimer was, however, observed to form as a minor product on irradiation ($280 < \lambda < 350$ nm) of $Fe(CO)_5$ in the LDPE and PTFE films at 12 K and at 298 K. The photoconversion of $Fe(CO)_5$ to $Fe_2(CO)_9$ observed in solution[8] has been proposed[25] to involve a reaction of the photogenerated species $Fe(CO)_4$ with an unreacted molecule of $Fe(CO)_5$. The fact that the dimer is seen to form in the LDPE and PTFE films even at 12 K implies that the parent $Fe(CO)_5$ molecules are not isolated in these films. The observation that the dimer is only produced in a low yield suggests, in fact, that this complex is only generated in the surface layers of the films where aggregates of the sorbed $Fe(CO)_5$ molecules may be formed. In the solvent-cast PVC films the $Fe(CO)_5$ molecules are uniformly dispersed and remain isolated in the films at low temperatures, thus preventing the formation of the dimer.

Irradiation ($280 < \lambda < 350$ nm) of $Fe(CO)_5$ in LDPE and PVC films at 298 K leads to the formation of products which are not formed in PTFE films. The infrared bands (E and F) observed for the products generated in the LDPE films [Fig. 2(c)] are identical with those reported[9] by De Paoli and co-workers. The bands (E) seen at 2074, 1993 and 1973 cm^{-1} were

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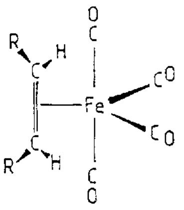
*Hexane solvent sorbed into the LDPE films during the preparation of the samples [see Experimental, Subsection (b(ii))] could not be detected by weighing the films. However, similar films which were immersed in pure hexane solutions for 6 h were found to contain approximately 1% by weight of hexane.

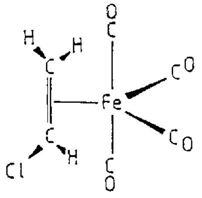
†Prolonged UV irradiation of $Fe(CO)_5$ in an argon matrix at 12 K led to the formation of a product (ν_{CO} 1906 cm^{-1}) which was suggested[6] to be the species $Fe(CO)_2$.

assigned to the species $Fe(CO)_4$ whilst the weaker bands (F) at 2040 and 1950 cm^{-1} were assigned[9] to the species $Fe(CO)_3$.* The intensity patterns and positions of the bands (E and F) are, however, in poor agreement with those observed for $Fe(CO)_4$ and $Fe(CO)_3$ in LDPE films at 12 K and in frozen gas matrices[6] (Table 1). Additionally, the thermal stability of the room-temperature photoproducts in LDPE films containing CO (detected on cooling the films) is inconsistent with the high reactivity of the species $Fe(CO)_4$ and $Fe(CO)_3$ towards CO seen in films even at temperatures below 60 K (Scheme 1). The positions and relative intensities of the product bands E [Fig. 2(c)] are, in fact, similar to those observed for known olefin complexes of the type $Fe(CO)_4(RCR{=}CHR)$ (e.g. $Fe(CO)_4$(*cis*-2-pentene), ν_{CO} 2079 (m, A_1), 1995 (s, B_2) and 1972 (s, B_1) cm^{-1} in hexane[27]) which, unlike the $Fe(CO)_4L$ complexes ($L = \sigma$ donor ligand) described above, e.g. $Fe(CO)_4(PPh_3)$, have C_{2v} symmetry (structure **VI**). This suggests that the product E, which is only seen to form in LDPE and not in PTFE films, may possibly arise from bonding of the photogenerated species $Fe(CO)_4$ to the LDPE at some site of unsaturation. Infrared spectra of the LDPE films indeed showed weak absorptions at 888, 903 and 960 cm^{-1} which have been assigned[28] to impurity vinylidene, vinyl and vinylene groups, respectively, in the polymer. The product E formed in the LDPE films at 298 K (Table 2) could be a complex of the type $Fe(CO)_4$(olefin) in which the $Fe(CO)_4$ fragment is coordinated by an olefinic group in a polymer chain (cf. structure **VI**).† It might be expected that, in the LDPE films at room temperature, the polymer chains and photogenerated $Fe(CO)_4$ fragments would have sufficient mobility to enable any impurity olefinic groups in the LDPE to coordinate to the fragments before the photoejected CO diffused back to the metal centres.

The photoproduct (M) observed to form on irradiation of $Fe(CO)_5$ in the PVC films at 298 K (Fig. 5) could similarly arise from the species $Fe(CO)_4$ bonding to some site of unsaturation in the PVC polymer. The infrared absorptions for this product (ν_{CO} 2090, 2040, and *ca* 2015 cm^{-1}) do, in fact, occur at significantly higher wavenumbers than those observed for the product E formed in the LDPE films at room temperature. The product M could be the fragment $Fe(CO)_4$ coordinated by an impurity chloroethylene group in the PVC (cf. structure **VII**). The intensity pattern of the product bands M [Fig. 5(c)] is not, however, consistent with a complex of the type $Fe(CO)_4$(olefin) with either C_{2v} symmetry, e.g. the known complex $Fe(CO)_4(H_2C{=}CHCl)$ (structure **VII**) (ν_{CO} 2098 (m, A_1), 2031 (m, A_1), 2018 (s, B_2) and 1999 (s, B_1) cm^{-1}, in hexane[29]) or with C_{3v} symmetry, e.g. (η^2-butadiene)$Fe(CO)_4$ (ν_{CO} 2084 (w, A_1), 2004 (m, A_1) and 1981 (s, E) cm^{-1}, in tetrachloroethylene (C_2Cl_4).[30] It is interesting to note that the bands are similar to those observed for the η^3-allyl complex (η^3-C_3H_5)$Fe(CO)_3Cl$ [ν_{CO} 2096 (s), 2050 (s) and 2012 (s) cm^{-1})] generated on irradiation



VI



VII

Table 2 Positions of infrared bands (cm^{-1}) for photoproducts formed on near-UV irradiation of $Fe(CO)_5$ in LDPE, PVC and PTFE films at 298 K

Film	Product (proposed formula)	ν_{CO}
LDPE	$Fe(CO)_4(CH_2{=}CR_2)$[a] or $Fe(CO)_4(RCH{=}CHR')$[a]	[b] 2074m
		1994vs
		1973s
	$Fe_2(CO)_9$	2055
		2030
		1840
PVC	$Fe(CO)_3(RCH\underset{\cdot}{-}CH\underset{\cdot}{-}CHR)Cl$[d,e]	2090s
		2040s
		2015s
PTFE	$Fe_2(CO)_9$[c]	2062
		2032
		1829

[a] R = —CH_2—; R′ = H or —CH_2— in LDPE. [b] Bands assigned to the species $Fe(CO)_4$ in Ref. 9. [c] Minor product. Complex also formed in a low yield in films irradiated at 12 K. [d] R = —CH_2CHCl— in PVC. [e] Complex $Fe(CO)_4$(THF) also formed in films containing THF.

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*Other weak bands attributable to the dimer $Fe_2(CO)_9$ (*cf.* bands marked A in figure 2(c)) were observed in the spectra.[9]

†Only three carbonyl infrared bands are actually observed for the product E. However, the bands corresponding to the B_2 and lower-frequency A_1 CO stretching modes (which for $Fe(CO)_4$(*cis*-2-pentene) occur at similar wavenumbers) may overlap giving rise to the intense band at *ca* 1994 cm^{-1} [Fig. 2(c)].

($\lambda > 290$ nm) of $Fe(CO)_5$ in the presence of allyl chloride in hexane solution.[31] This complex is thought to form via the coordinatively unsaturated species $Fe(CO)_3(H_2C{=}CHCH_2Cl)$, in which the chlorine atom is transferred from the allyl chloride ligand to the metal (Eqns [1]–[3]).[31]

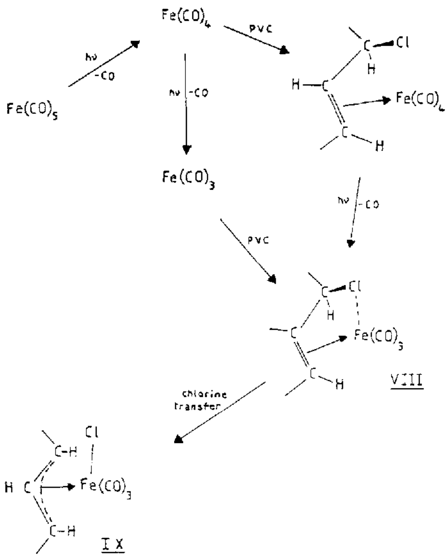
$$Fe(CO)_5 \xrightarrow[H_2C=CHCH_2Cl]{h\nu} (CO)_4Fe(H_2C{=}CHCH_2Cl) + CO \qquad [1]$$

$$(CO)_4Fe(H_2C{=}CHCH_2Cl) \xrightarrow[-CO]{h\nu} (CO)_3Fe(H_2C{=}CHCH_2Cl) \qquad [2]$$

$$(CO)_3Fe(H_2C{=}CHCH_2Cl) \longrightarrow (CO)_3Fe(H_2C\cdots CH\cdots CH_2)Cl \qquad [3]$$

The product (M) generated in the PVC films at 298 K could also be a complex of the type $Fe(CO)_3(\eta^3\text{-allyl})Cl$, which could form following the coordination of $Fe(CO)_4$ or $Fe(CO)_3$ by an impurity 'allyl chloride' group in the PVC. This is illustrated in Scheme 2, which shows a possible reaction mechanism based on that proposed[31] for the conversion of $Fe(CO)_5$ to $(\eta^3\text{-}C_3H_5)Fe(CO)_3Cl$ in solution (Eqns [1]–[3]).

It is interesting to note that whilst an allylic chlorine atom in the PVC could be transferred to the metal in the coordinated $Fe(CO)_3$ fragment (species **VIII**, Scheme 2), an allylic hydrogen atom could also be transferred from the polymer to the metal, leading to the formation of an η^3-allyl hydride complex (i.e. the hydride analogue of species **IX**, Scheme 2). Complexes of the type $Fe(CO)_3(\eta^2\text{-olefin})$ and $Fe(CO)_3(\eta^3\text{-allyl})H$ have been proposed[27] to be intermediates in some photocatalysed reactions in which $Fe(CO)_5$ is used as the catalyst precursor. An allyl hydride complex could be formed on irradiation of $Fe(CO)_5$ in LDPE films, following the coordination of $Fe(CO)_4$ or $Fe(CO)_3$ by an olefinic group in the polymer. The minor product F observed to form in films irradiated at 298 K (Fig. 2) could possibly be such a complex.



Scheme 2 Proposed mechanism for photoconversion of $Fe(CO)_5$ to η^3-allyl chloro complex in PVC films.

CONCLUSIONS

It is apparent from the above results that polymer films can mimic gas matrices at *ca* 12 K for trapping and characterizing unstable species. Indeed, polymer films have a major advantage over gas matrices, which require that substrates are volatile, in that involatile molecules and ones which decompose on heating can be dispersed in polymer films.

It is important to recognize the potential of groups within the polymer films to coordinate to the highly reactive species produced by X-ray irradiation and photolysis, especially if the films are used near ambient temperatures. Failure to do this leads to incorrect assignments, e.g. by De Paoli *et al.*[9]

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