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PHOTOCHEMISTRY OF THE GROUP VI METAL HEXACARBONYLS IN POLYVINYL-CHLORIDE FILM MATRICES AT 12–298 K. THE REACTIVITY OF THE SPECIES $M(CO)_5$ AND $M(CO)_5(THF)$*

RICHARD H. HOOKER and ANTONY J. REST *

Department of Chemistry, The University, Southampton, S09 5NH (Great Britain)

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Summary

The photochemistry of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) in polyvinyl chloride (PVC) film matrices over a wide temperature range (12–298 K) has been studied. Infrared spectroscopic evidence for the formation of the species $M(CO)_5$ and $M(CO)_5(THF)$ is presented. The effect of temperature and the influence of the polymeric medium on the observed photoreactions is discussed and the results are compared with those obtained using the following matrix materials: paraffin wax discs, frozen gases and hydrocarbon glasses.

Introduction

Polymer or plastic films have provided organic photochemists with a very convenient matrix for trapping luminescent intermediates and free radicals at temperatures between 80 and 350 K [1–5]. In an early study, Massey and Orgel [6] found that a methylmethacrylate polymer containing a small amount of $M(CO)_6$ (M = Cr, Mo or W) assumed a yellow colour when irradiated at room temperature with UV light. They proposed that the $M(CO)_5$ fragment had been formed. On leaving the irradiated matrix in the dark the parent hexacarbonyl slowly reformed, although when the polymer was cooled by liquid nitrogen the pentacarbonyl remained trapped in the matrix. McIntyre [7] later reported that the thermal back reaction (eq. 1) following flash photolysis of $Cr(CO)_6$ in a polystyrene film occurred

$$Cr(CO)_5 + CO \rightarrow Cr(CO)_6 \qquad (1)$$

at a much slower rate than in solution.

More recently, metal carbonyl fragments have been generated extensively by in

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday, this work, which originates from the studies (AJR, Cambridge, 1968–73) into the use of gas matrices at 20 K to trap unstable species and to which Professor Emeléus contributed stimulating advice and unstinting encouragement, affirms the usefulness of polymer films as matrices; polymer films were first used for organometallic species by Massey and Orgel at Cambridge (1961), but this work has not been followed up, and has lain fallow in the literature since then.

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situ photolysis of parent molecules in frozen gas matrices at $\leqslant 20$ K and fully characterised by IR spectroscopy [8,9]. In order to relate unstable species observed in a rigid matrix to possible photochemical mechanisms in solution it is very useful to be able to study reactions in a variety of matrix media and at different temperatures. Sheline and his co-workers [10] studied the photochemistry of metal hexacarbonyls in hydrocarbon glasses at ca. 80 K. An advantage in using these matrices is that thermal reactions of photogenerated fragments can be monitored as the glass is slowly warmed and the products subsequently observed in solution [11–13]. Since McIntyre's experiment, the use of polymer matrices for studying metal carbonyl photochemistry has been limited, probably because solute IR bands are generally much broader than those exhibited by the frozen gas matrices [8]. It is surprising, though, that virtually no IR spectroscopic data has appeared in the literature for the fragment $M(CO)_5$ (M = Cr, Mo or W) generated in a polymer matrix. De Paoli and his co-workers [14–16], who have monitored the photoreactions of $Fe(CO)_5$ with olefins in inert polymers, recently suggested that polymer films at room temperature provide a possible alternative to frozen gas matrices which require expensive cryogenic equipment. Having established [17], however, that a polyvinyl chloride (PVC) matrix is suitable for use over the whole temperature range 12–298 K we report here a study of the photochemistry of the Group VI metal hexacarbonyls in PVC films.

Experimental

Polymer films

Metal carbonyls have been introduced into polymer films by soaking the latter in solutions of the carbonyl for a period depending on the degree of crystallinity of the polymer [8,15]. In attempting to obtain a polymer matrix in which the concentration of carbonyl was uniform throughout, the films in this study were prepared using a solvent-casting technique [4,17]. 500 mg of PVC (Corvic D60/11, obtained from ICI) were dissolved in either 20 ml of freshly distilled THF (tetrahydrofuran) at 25°C or 50 ml of 1,2-dichloroethane at 40°C with rapid stirring. A 4 mg sample of hexacarbonyl was then added and the resulting solution poured into a petridish (10 cm diameter) which was kept horizontal on a mercury bath. The bath was kept in the dark and the solvent allowed to evaporate overnight. The polymer film (thickness ca. 40 μ) was then extracted from the dish by filling the latter with distilled water and cutting round the edge of the film which floated to the surface.

Paraffin wax discs

Thin discs were prepared from a solution of 4 mg of hexacarbonyl in 500 mg of melted paraffin wax. Since wax discs are liable to fall off single spectroscopic windows in cryostats at low temperatures the discs were cast between two CaF_2 windows (25 mm diameter). A portion of hot wax was poured onto a warmed window, kept horizontal, and a second window carefully placed onto the wax surface. It was generally difficult to obtain a wax disc of as uniform a thickness as the polymer films.

Apparatus

Cryogenic temperatures (ca. 12 K) were obtained using a Displex CSA-202 closed cycle helium refrigerator system (Air Products and Chemical Inc.). A piece of polymer film was evenly clamped between two CaF_2 windows (diameter 25 mm) at the cryotip. It was important that the diameter of the film was the same as that of the windows so that the former could be clamped as flat * and as tightly as possible to ensure a good thermal contact. Wax discs cast between two windows were also attached to the cryotip which was cooled within a vacuum shroud (10^{-7} Torr) containing outer CaF_2 windows. The polymer or wax matrix could then be irradiated at 12 K and subsequently warmed up slowly to room temperature by switching off the refrigerator. Temperatures were monitored using an Air Products Displex control gauge. In experiments at room temperature polymer films and wax discs were held between windows in a Nujol-mull plate holder.

Photolysis and spectroscopy

A water cooled mercury arc lamp (Philips HPK 125W) was used as the photolysis source at a distance of ca. 12 cm from the matrix. Irradiation into specific wavelength bands was achieved using the following filters: filter A, $\lambda < 350$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 gas (300 Torr): filter B, $\lambda > 400$ nm, quartz gas cell (pathlength 25 mm) containing Cl_2 (2 atm) + pyrex disc (thickness 3 mm).

IR spectra were recorded using a Nicolet 7199 Fourier Transform Infrared (FTIR) spectrometer (resolution 0.5 cm^{-1}). An advantage in using this instrument was that the computer availability enabled spectra to be stored and subsequently ratioed so that reactions occurring in the matrices could be followed easily. UV-visible spectra of polymer films were recorded on a Pye-Unicam SP 1800 UV spectrophotometer with a blank film in the reference beam.

Results

Spectra of polymer films

No IR absorptions due to the PVC matrix were observed in the region of interest (2200–1800 cm^{-1}) in this study. Evidence for residual THF in films cast from this solvent was found when polymer bands in the region 1500–900 cm^{-1} were subtracted out of spectra. These films also exhibited broad IR bands at ca. 1775 and 1740 cm^{-1} which have been assigned to the oxidised THF residues butyrolactone and α-hydroxytetrahydrofuran, respectively, by other workers [18]. Another absorption, probably due to chloroketone groups in the polymer [19], was seen at 1735 cm^{-1}. Films cast from 1,2-dichloroethane solution only showed a band at ca. 1728 cm^{-1} for ketones. No change in intensity of the above bands was seen during irradiation of the polymer films in this study. UV-visible spectra of blank PVC films showed no absorptions at wavelengths greater than 240 nm.

Photochemistry at room temperature

The IR spectra of chromium, molybdenum and tungsten hexacarbonyls in PVC films show a broad $\nu(CO)$ T_{1u} band at 1978, 1980 and 1974 cm^{-1}, respectively, and a broad but well resolved $\nu(CO)$ E_g band at higher wavenumbers (see Table 1). The

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* Interference fringes were obtained in spectra of polymer films which were not perfectly flat.

bands are broad even when only 0.2% by weight (1/500 mg) of carbonyl is present in the polymer matrix, suggesting that significant polymer–solute interactions exist. The ν(CO) E_g band, which has been observed for metal hexacarbonyls in various hydrocarbon glasses at 77 K [13] probably results from site symmetry effects or from some distortion of the carbonyl molecules trapped in amorphous sites of the polymer matrix. IR and UV-visible spectra of $W(CO)_6$ in a PVC film cast from THF solution are shown in Fig. 1(a) and 2(a). On UV irradiation (filter A) of the film at room temperature new IR bands appeared at 2074w, 1929 and 1887 cm^{-1} with a reduction in the parent bands (Fig. 1(b)). The film, which had turned yellow in

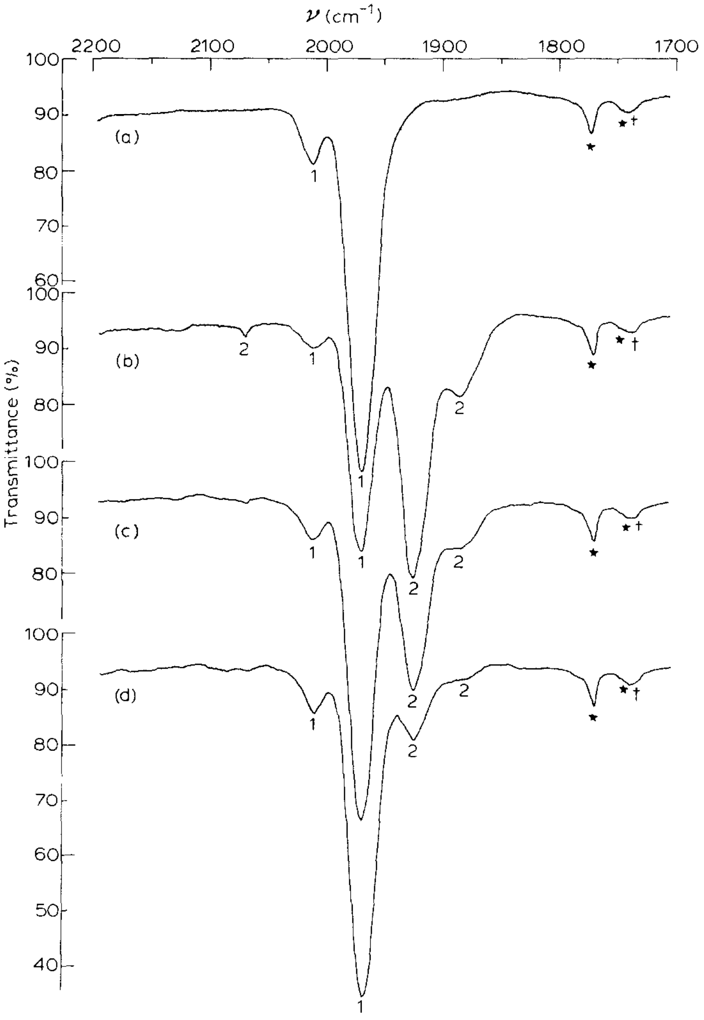


Fig. 1. Infrared spectra from an experiment with $W(CO)_6$ in a PVC film (cast from THF solution) at 298 K: (a) before photolysis; (b) after 5 min photolysis using filter A; (c) as (b) then leaving film in dark for 8 h and (d) as (b) then leaving film in dark for 6 days. Bands marked 1 and 2 are for the species $W(CO)_6$ and $W(CO)_5(THF)$, respectively. Bands marked (★) and (†) are for oxidised THF residues and chloro ketones, respectively.

TABLE 1

POSITIONS OF IR BANDS (cm^{-1}) IN TERMINAL CARBONYL STRETCHING REGION FOR METAL HEXACARBONYLS AND THEIR PHOTOPRODUCTS IN PVC FILMS AND PARAFFIN WAX DISCS

Complex	Assignment	Cr	Mo	W	
$M(CO)_6$[a]	E_g	2021	2022	2016	
	T_{1u}	1978	1980	1974	
$M(CO)_6$[b]	T_{1u}	1983	1985	1980	
$M(CO)_5$[c]	A_1	2080w	2086w	2084w	(2080w)[d]
	E	1949	1956	1946	(1932)[d]
	A_1	1922[e]	1921[e]	1918[e]	(1888)[d]
		–	–	–	(24390)[f]
$M(CO)_5$[g]	A_1	[h]	2092	2090	
	E	[h]	1965	1956	
	A_1	[h]	1929	1929	
$M(CO)_5(THF)$[a]	A_1	2078w	2078w	2074w	
	E	1936	1940	1929	
	A_1	1892	1892	1887	
		22470[f]	24510[f]	23810[f]	

[a] In PVC film. [b] In wax disc. [c] In PVC film, 12–200 K. [d] $W(CO)_5$ in PVC film, 298 K. [e] Band occurs as shoulder. [f] Electronic absorption ($e(xz,yz) \rightarrow a_1$) in PVC film, 298 K. [g] In wax disc, 12–100 K. [h] Species not studied in wax.

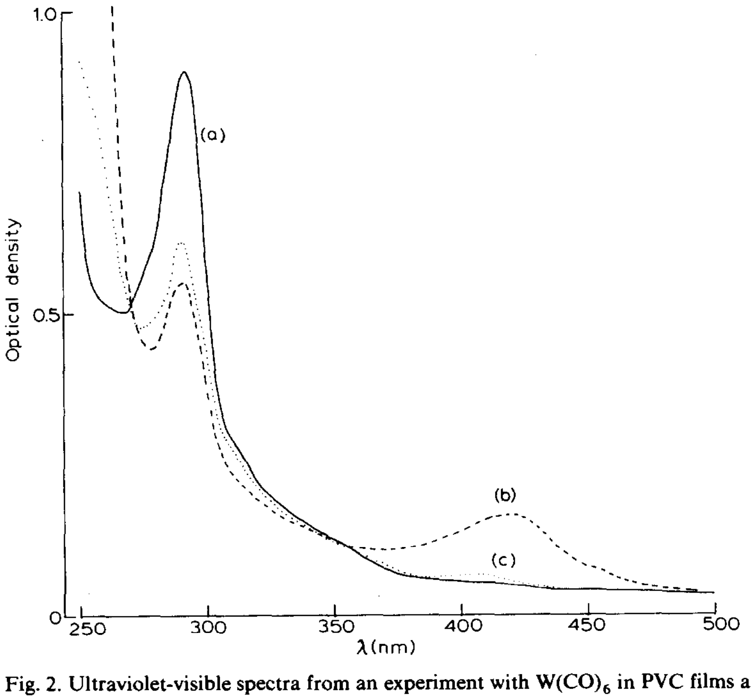


Fig. 2. Ultraviolet-visible spectra from an experiment with $W(CO)_6$ in PVC films at 298 K: (a) $W(CO)_6$ in film, cast from THF, before photolysis; (b) after 5 min photolysis using filter A and (c) after similar photolysis of $W(CO)_6$ in film cast from 1,2-dichloroethane solution.

colour, also exhibited a new absorption at 420 nm (Fig. 2(b)). A very slow reversal of the reaction occurred on leaving the polymer in the dark for several days (Fig. 1(c)–1(d)). Irradiation of $W(CO)_6$ under the same conditions in a PVC film cast from 1,2-dichloroethane solution also produced three new IR bands but at higher wave-numbers (2080w, 1932 and 1888 cm^{-1}) and a broad absorption at ca. 410 nm (Fig. 2(c)). In contrast, thermal reversal of the reaction in this film occurred after only a few minutes. The bands at 2074, 1929 and 1887 cm^{-1} are at slightly lower wave-numbers than those for $W(CO)_5(THF)$, formed on irradiation of $W(CO)_6$ in hexane solution containing THF [20], and can be assigned to this complex formed in the polymer films in which THF is present. UV irradiation of $Cr(CO)_6$ and

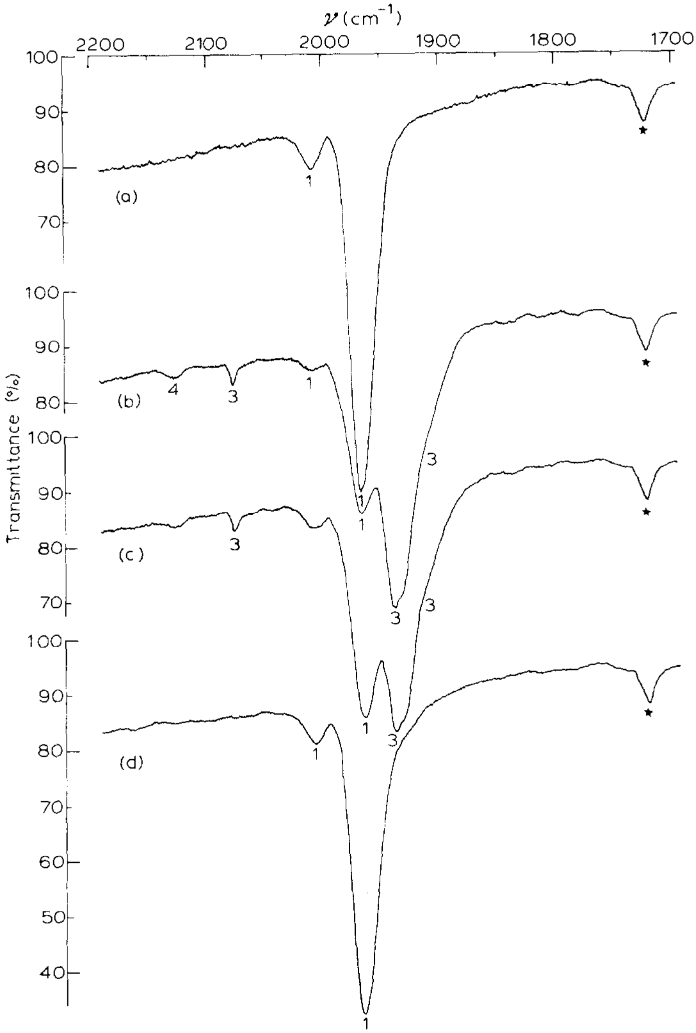


Fig. 3. Infrared spectra from an experiment with $W(CO)_6$ in a PVC film (cast from 1,2-dichloroethane): (a) before photolysis, at 12 K; (b) after 15 mins photolysis using filter A; (c) as (b) then warming to 120 K and (d) as (c) then further warming to room temperature. Bands marked 1, 3 and 4 are for $W(CO)_6$, $W(CO)_5$ and free CO, respectively. Band marked (★) is for ketones in polymer.

$Mo(CO)_6$ in these films resulted in the formation of the species $Cr(CO)_5(THF)$ and $Mo(CO)_5(THF)$, respectively, although the hexacarbonyls were regenerated in the dark more quickly than the tungsten analogue. When $Cr(CO)_6$ and $Mo(CO)_6$ were photolysed at room temperature in PVC films free of THF no evidence for a new carbonyl species was seen, even on obtaining IR spectra immediately and prolonged irradiation lead to decomposition of the hexacarbonyls. No photoproducts were observed when all three hexacarbonyls were irradiated in paraffin wax discs at the same temperature.

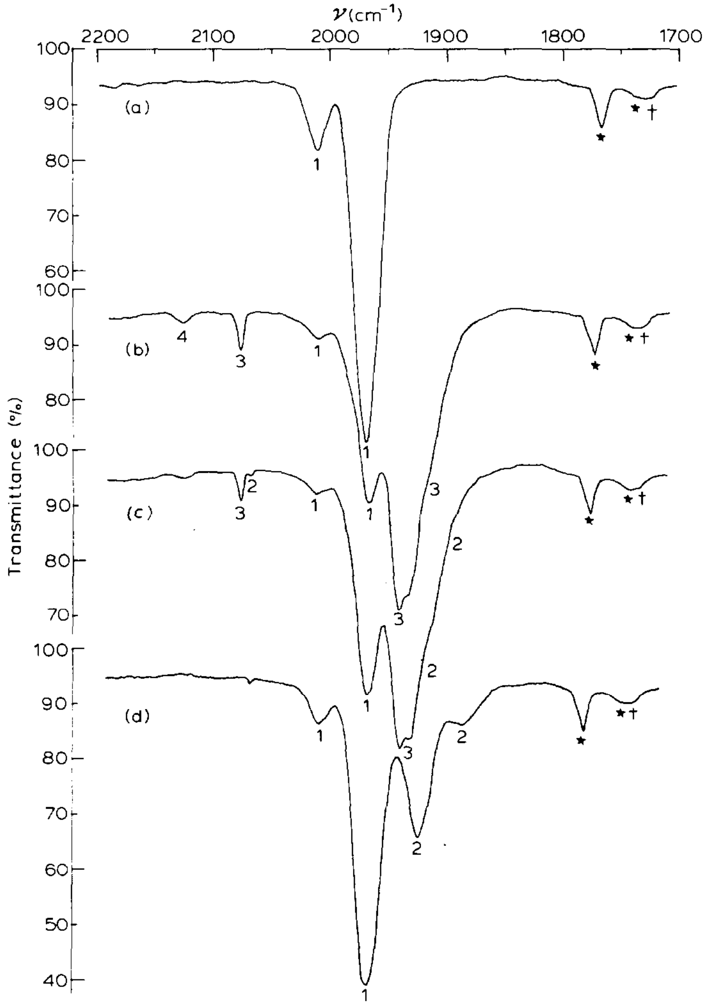


Fig. 4. Infrared spectra from an experiment with $W(CO)_6$ in a PVC film (cast from THF): (a) before photolysis, at 12 K; (b) after 15 mins photolysis using filter A; (c) as (b) then warming to 120 K and (d) as (c) then further warming to room temperature. Bands marked 1, 2, 3 and 4 are for $W(CO)_6$, $W(CO)_5(THF)$, $W(CO)_5$ and free CO, respectively. Bands marked (★) and (†) are for oxidised THF residues and chloro ketones, respectively.

Photochemistry at 12 K and reactions on warming

On lowering the temperature of the polymer films the IR spectra of the hexacarbonyls become slightly sharper (T_{1u}, full width at half-maximum (fwhm) 25 cm^{-1}) but with no significant shift in band positions (Figures 3(a) and 4(a)). On UV irradiation (filter A) of $W(CO)_6$ in films at 12 K new IR bands appeared at 2084w, 1946 and 1918(sh) cm^{-1}, together with a band for free CO at 2135 cm^{-1}, at the expense of the parent bands (Fig. 3(b) and 4(b)). The photoreaction can be reversed at 12 K by irradiation of the polymer matrix with visible light (filter B). On slowly warming the films the above product bands decreased with regeneration of the hexacarbonyl. When films cast from THF solution were used, however, the IR bands for $W(CO)_5(THF)$ were also seen in the spectra as the temperature of the polymer approached 120 K (Fig. 4(c)). This species continued to form, together with the hexacarbonyl, on further warming to ca. 200 K at which point the bands for the

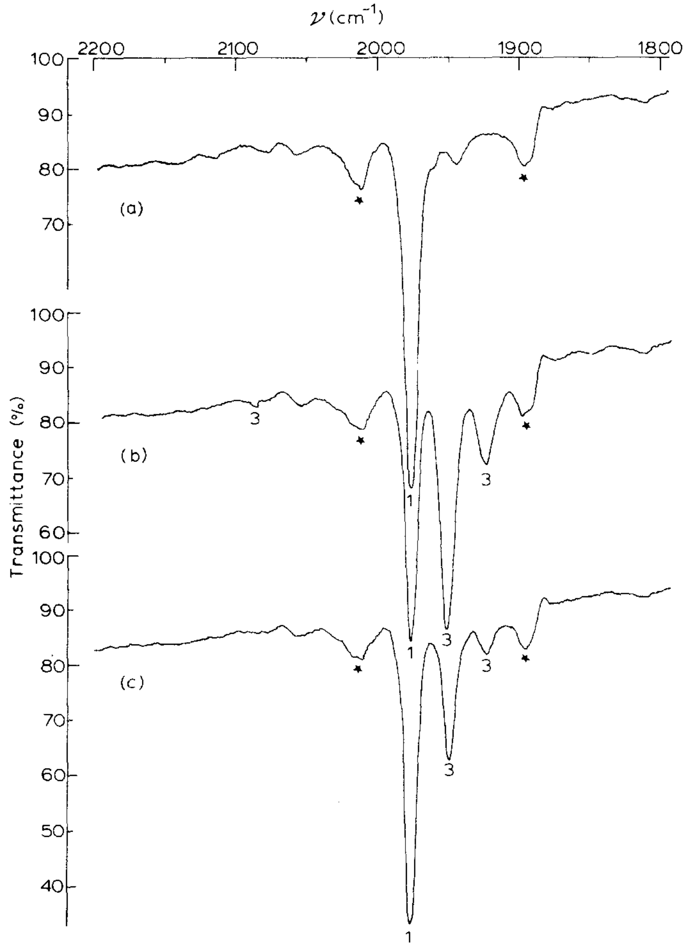


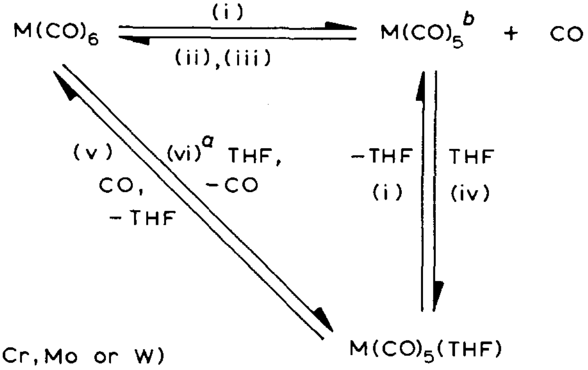
Fig. 5. Infrared spectra from an experiment with $W(CO)_6$ in a paraffin wax disc: (a) before photolysis, at 12 K.; (b) after 15 min photolysis using filter A and (c) as (b) then warming to 100 K. Bands marked 1 and 3 are for $W(CO)_6$ and $W(CO)_5$, respectively. Bands for impurities in the wax are marked (★).

primary photoproduct disappeared. Subsequent warming to room temperature resulted in some conversion of $W(CO)_5(THF)$ to $W(CO)_6$. Reactions analogous to those seen in PVC films free of THF were observed in paraffin wax matrices. Figure 5(a) shows the IR spectrum of $W(CO)_6$ in paraffin wax at 12 K. Unlike the polymer films, the waxes exhibited IR absorptions in the carbonyl region, probably due to impurities. However, the spectra of the metal carbonyls are considerably sharper ($\nu(CO)$ T_{1u}, fwhm 12 cm^{-1}) than those obtained using polymer film matrices. Irradiation of $W(CO)_6$ in the wax at 12 K produced new IR bands at 2136w, 2090w, 1956 and 1929 cm^{-1}. Thermal reversal of the reaction occurred on warming the disc to 100 K. Unfortunately, however, the disc developed cracks on subsequent warming to ca. 150 K and no further reaction could be monitored. By comparison with the data obtained from other matrix studies [13,21] and the thermal reactions observed, the product IR bands at 2084, 1946 and 1918 cm^{-1} for the PVC matrices can be assigned to the fragment $W(CO)_5$. It was possible to regenerate this fragment from the complex $W(CO)_5(THF)$ by UV irradiation (filter A) of a PVC film which had been recooled from 200 to 12 K.

In other experiments, reversible formation of the unstable species $Cr(CO)_5$ and $Mo(CO)_5$ from the hexacarbonyls was observed in PVC films irradiated at 12 K (see Table 1) and the thermal reactions seen on warming to room temperature were analogous to those seen for the tungsten pentacarbonyl fragment.

Discussion

The photoreactions of the Group VI metal hexacarbonyls observed in PVC films in this study are summarised in Scheme 1.



SCHEME 1. (i) $h\nu$ (filter A) at 12 K; (ii) $h\nu$ (filter B) at 12 K; (iii) Warming to 200 K; (iv) Warming between 100 and 200 K; (v) Thermal reaction above 200 K; (vi) $h\nu$ (filter A) at 298 K. [a] Reaction observed in solution (ref. 20). [b] Unstable species observed in other low temperature matrices.

The generation of the pentacarbonyl fragment * and the photoreversal at 12 K are analogous to the reactions observed in hydrocarbon glasses [13] and frozen gas

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* Turner and his co-workers [22] have generated $Cr(CO)_5$ by photolysis of $Cr(CO)_6$ at 77 K in a PVC film doped with THF and observed the formation of $Cr(CO)_5(THF)$ and $Cr(CO)_6$ on warming to 120 K. However, no experimental details or spectroscopic data were presented.

matrices [21]. Since polymer matrices are thought to be rather cavernous [8] compared with the frozen gases it is interesting that the photoreversal is seen as it suggests that the photoejected CO molecules do not necessarily diffuse far away from the photolysis sites at very low temperatures. The fact that no IR bands for polymeric species (e.g. $(OC)_5M$–(CO)–$M(CO)_5$) are seen even on warming to room temperature indicates that the hexacarbonyl molecules are isolated in our solvent-cast PVC films. In contrast, the bimolecular photoreactions which have been observed in other polymer film matrices [15], prepared by soaking films in solutions of the reagents, probably result from the relatively high local concentration of species and the presence of aggregates in these films. Braterman and his co-workers [11], while studying the thermal reactions of $M(CO)_5$ fragments generated in hydrocarbon glasses, have found that IR spectra may become complicated around the glass softening temperature due to formation of aggregates and shifts in the solvent baseline. Further, changes in solvent absorptions in the frequency region of interest when varying the temperature of these glassy matrices can cause some difficulty in monitoring reactions. Similarly, the cracking of wax discs in our experiments presents a problem in attempting to follow thermal reactions of photolysis fragments on warming a wax matrix. The PVC films, however, do not undergo any macroscopic change and these matrices retain some degree of rigidity over the whole temperature range covered in this study. Motion of the polymer chains probably ceases at the very low temperatures and bimolecular interactions between, for example, $W(CO)_5$ and neighbouring THF ligands are prevented. However, the polymer matrix does not become too rigid to prevent photoejection of this bulky ligand from the species $M(CO)_5(THF)$ (M = Cr, Mo or W) at 12 K. Similar ejection of methyl-THF and pyridine from the $M(CO)_5$ fragment in hydrocarbon glasses [11] and solid argon [23], respectively, has been observed.

The suggestion by Massey and Orgel [6] that the $M(CO)_5$ fragments (M = Cr, Mo or W) observed in their polymethylmethacrylate matrices were possibly stabilised by oxygen donating groups in the polymer itself seems likely in view of the fact that the "naked" pentacarbonyl intermediates, except for $W(CO)_5$, were not observed at room temperature in the PVC films. In fact, the reported [6] carbonyl band shift of 40 cm^{-1} to lower energy for the pentacarbonyls in polymethylmethacrylate relative to the hexacarbonyl band positions can be compared with the shift in band positions for $M(CO)_5(THF)$ relative to $M(CO)_6$ in the PVC films (see Table). The IR bands at 2080, 1932 and 1888 cm^{-1} observed on photolysis of $W(CO)_6$ in PVC films free of residual THF may be associated with the species $W(CO)_5$ interacting strongly with the polymer matrix (possibly stabilised by neighbouring ketone groups) before the photoejected CO, which remains in the polymer films, returns to the metal. In contrast, it appears that none of the above pentacarbonyls can be stabilised in paraffin wax at room temperature. The observation that $W(CO)_5$ is apparently more stable than $Cr(CO)_5$ or $Mo(CO)_5$ in the room temperature PVC matrices is interesting in view of the photochemistry of the Group VI metal hexacarbonyls observed in hydrocarbon solutions [21]. Since the IR bands seen for $W(CO)_5$ in the polymer films at 12 K are at higher wave numbers (2084, 1946 and 1918 cm^{-1}) it is likely that there is less interaction between the carbonyl fragment and the polymer matrix, the former being thermally stable at the very low temperature.

Conclusion

The results of this study demonstrate that solvent-cast polymer film matrices may be used to study organometallic photochemistry at a variety of different temperatures and have some advantages over hydrocarbon glass and paraffin wax matrices. The main attraction of such a polymer matrix is that it enables photochemists (i) to isolate, at cryogenic temperatures, unstable species which may also be studied in frozen gas matrices, (ii) to monitor subsequent thermal reactions of such species over a wide temperature range and (iii) to relate these species to mechanisms of reactions in solution which are also observed in the polymer films at room temperature.

Although the IR bands exhibited by metal carbonyls in these matrices are relatively broader we have found that it is possible to overcome this problem using spectral subtraction facilities on our FTIR spectrometer and we are at present investigating the photoreactions of a range of these complexes in polymer films.

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