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Preliminary communication

INFRARED SPECTROSCOPIC EVIDENCE FOR CARBON MONOXIDE DISSOCIATION AND RADICAL PATHWAYS IN THE PHOTOCHEMICAL REACTIONS OF (η-CYCLOPENTADIENYL)(METHYL)TRICARBONYLMOLYBDENUM

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Summary

Infrared spectroscopy of organometallic complexes in polymer films at 12—293 K has been used to investigate reactive species; in the photoreactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)$ both CO dissociation and Mo—CH_3 bond homolysis reactions were observed.

Photosubstitution reactions of mononuclear complexes of the type $CpM(CO)_3(CH_3)$ (Cp = $\eta^5\text{-}C_5H_5$; M = Cr, Mo, W) have been examined by several workers and involve primarily the dissociative loss of CO. For example, irradiation of the complexes in hydrocarbon solutions in the presence of PPh_3 leads to the formation of $CpM(CO)_2(PPh_3)(CH_3)$ [1,2]. However, in the absence of ligands, the complexes form CH_4 and the dimeric complexes $[CpM(CO)_3]_2$ and $[CpM(CO)_2]_2$ [2,3], which suggests that M—CH_3 bond homolysis, giving rise to radicals, is an important primary photoprocess. In the case of $CpW(CO)_3(CH_3)$, the reaction to form the dimer was greatly suppressed when the irradiation was carried out under a CO atmosphere compared to that under Ar [4]. This indicates that CO dissociation could be the primary photochemical event rather than the cleavage of M—CH_3 bond. ESR studies on these complexes have shown that the species responsible for the signal is a photo-generated metal-centred radical in which the M—CH_3 bond is retained, i.e. $CpM(CO)_2(CH_3)^{-\cdot}$ [5]. The formation of the 17 electron radical $CpM(CO)_3^{\cdot}$ has been suggested in steady-state [6] and flash photolysis [7] studies to account for the formation of $CpM(CO)_3Cl$ from $[CpM(CO)_3]_2$ in CCl_4 solution. Similarly a pathway involving radicals has been proposed to account for the photochemical formation of the dimer $[CpFe(CO)_2]_2$ from $CpFe(CO)_2R$ complexes [8].

The nature of intermediates in the photochemical reactions of organometallic compounds, especially metal carbonyls, has been established by the IR and UV-visible spectra of such species trapped in frozen matrices of the rare gases, CH_4, N_2 and CO [9]. Such studies have often been criticised [10] as bearing little relation to photochemical mechanisms in solution because of the rather special nature of the materials and the very low temperatures (10—30 K). As part of our investigation of alternatives to gas matrix isolation studies especially for involatile ionic compounds [11] and those which decompose on sublimation, we report here the photochemical reactions of $CpMo(CO)_3(CH_3)$ in a polyvinyl chloride (PVC) polymer matrix at temperatures in the range 10—293 K. One previous report has appeared describing the use of PVC films at 77 K but this study deliberately doped the film with THF in order to observe $Cr(CO)_5(THF)$ and no details of the experimental procedure were given [12].

Irradiation of $CpMo(CO)_3CH_3$ (Fig. 1(a)) in PVC (5 mg/500 mg) at 12 K* using a medium-pressure mercury lamp (HPK 125 W) with wavelength $300 < \lambda < 370$ nm** produced three new IR bands in the terminal CO stretching region at 2130 cm^{-1} (free CO), 1851 and 1822 cm^{-1} along with broadening of the parent peak at 1950 cm^{-1} (Fig. 1(b)). Further irradiation caused increases in the bands at 2130, 1950 and 1851 cm^{-1}, and a decrease in the band at 1822 cm^{-1} (Fig. 1(c)). This decrease was associated with the appearance of two new bands at 2048 and 1969 cm^{-1}. On warming the polymer matrix to 40 and 100 K (Fig. 1(d) and 1(e), which was identical to the spectrum produced on photolysis of the films at 77 K) the bands at 1950 and 1851 cm^{-1} decreased together with that of free CO and the parent $CpMo(CO)_3(CH_3)$ bands grew as did the band at 1822 cm^{-1}. Further warming to 293 K caused the disappearance of all the above product bands and the growth of a new pair of bands at 2048 and 1969 cm^{-1} (Fig. 1(f), which was identical to the spectrum produced on photolysis at 293 K).

In making assignments of the various new bands it should be noted that at no time were bands observed which could be attributed to the dimer $[CpMo(CO)_3]_2$ (see below and Table 1), i.e. the $CpMo(CO)_3(CH_3)$ molecules are "isolated" in the polymer film, or to THF remaining in the film. The forward photolysis and 40 K reversal of the pair of bands at 1950 and 1851 cm^{-1} together with CO is analogous to the behaviour of $CpMo(CO)_3(CH_3)$ in a CH_4 matrix at 12 K, where ^{13}CO labelling identified the primary photoproduct as $CpMo(CO)_2(CH_3)$ [13]. An alternative explanation is that the bands arise from $CpMo(CO)_2(CH_3)(THF)$, cf. $Cr(CO)_5(THF)$ [12]. This explanation can probably be ruled out because: (i) the films in this experiment were pumped at high

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*PVC films were prepared by dissolving the complex and PVC (Corvic D60/11) in THF (25 ml) and then pouring the solution in to a petri-dish (10 cm radius), supported on Hg, to evaporate overnight. The resulting film was mounted between LiF plates and cooled using a Displex CSA-202 closed-cycle refrigerator (Air Products and Chemical Inc). IR spectra were recorded on a Grubb—Parsons Spectromajor spectrometer.

**Combination of quartz gas cell (path length 25 mm) containing Br_2 gas (300 Torr) and pyrex glass disc (thickness 18 mm).

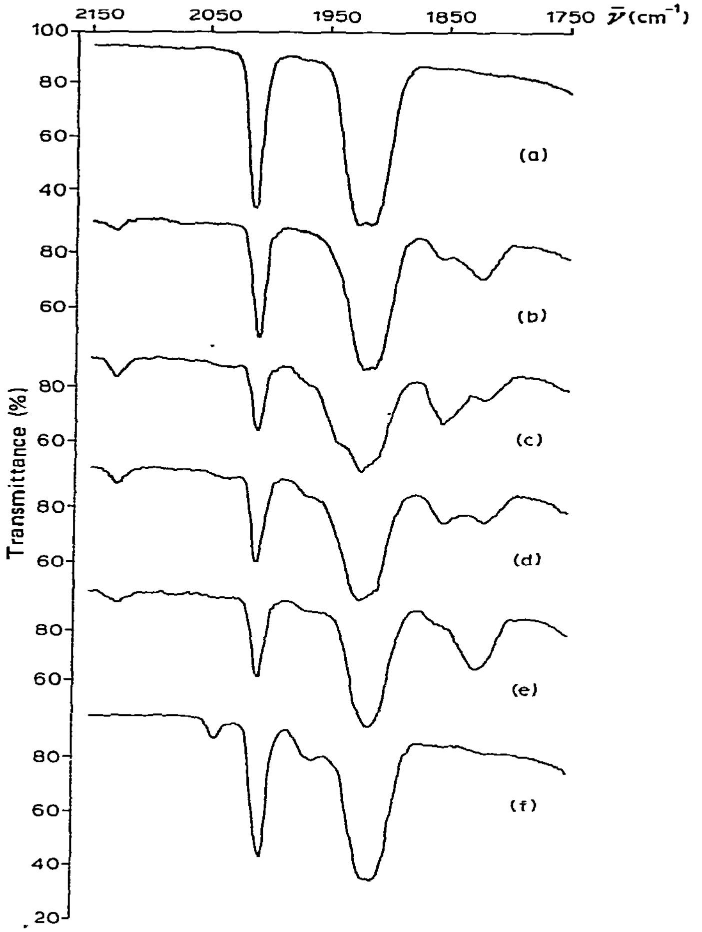

Fig. 1. IR spectra from an experiment with $CpMo(CO)_3(CH_3)$ in a PVC film at 12 K: (a) before irradiation, (b) after irradiation with $300 < \lambda < 370$ nm for 30 minutes, (c) after irradiation with $300 < \lambda < 370$ nm for further 105 minutes, (d) after warming to 40 K and recooling to 12 K, (e) after warming to 100 K and recooling to 12 K, and (f) after warming to 293 K.

TABLE 1

BAND POSITIONS (cm^{-1}) FOR $CpMo(CO)_3(CH_3)$ AND $[CpMo(CO)_3]_2$ AND THEIR PHOTOPRODUCTS IN CH_4 AND PVC POLYMER MATRICES AT 12 K AND IN CCl_4 SOLUTION AT 293 K

Complex	PVC	CH_4	CCl_4
$CpMo(CO)_3(CH_3)$	2015	2023.9	2020
	1922	1937.9	1935
$CpMo(CO)_2(CH_3)$	1950	1966.0	—
	1851	1880.1	
$CpMo(CO)_3Cl$	2048	—	2057
	1969		1985
$[CpMo(CO)_3]_2$	2008 1955 1909	1969.7 1925.1	1960 1914
$CpMo(CO)_3^{\bullet}$	1930[a] 1822	—	—

[a] Band obscured by the broad 1922 cm^{-1} band of $CpMo(CO)_3(CH_3)$ in experiments when the radical was generated from this compound.

vacuum and showed no IR bands for residual THF, (ii) the initial species formed in the $Cr(CO)_6$/PVC film experiment was $Cr(CO)_5$ and $Cr(CO)_5(THF)$ was only formed on annealing to 120 K [12] (iii) the bands for $Cr(CO)_5(THF)$ occur at lower wavenumbers than those for $Cr(CO)_5$ whereas in this work the same band shift from CH_4 to PVC is observed for the product bands as for the bands of the parent compound, $CpMo(CO)_3CH_3$ (Table). The band at 1822 cm^{-1} together with a band at 1930 cm^{-1} also appeared when $[CpMo(CO)_3]_2$ was photolysed in a PVC film at 77 K. It seems likely therefore, that the second primary photoproduct of $CpMo(CO)_3CH_3$ is $CpMo(CO)_3^{\bullet}$ (Table 1). This assignment is supported by the known solution photochemistry [6] and the fact that the final pair of product bands at 2048 and 1969 cm^{-1} can be assigned to $CpMo(CO)_3Cl$ by comparison with CCl_4 solution data (Table 1).

$$[CpMo(CO)_3]_2 \xrightleftharpoons{h\nu,\ CCl_4} 2\ CpMo(CO)_3^{\bullet} \rightarrow 2\ CpMo(CO)_3Cl$$

The studies of $CpMo(CO)_3CH_3$ in the PVC film (Scheme 1) support the previously proposed mechanisms of decarbonylation and radical formation providing the first evidence for $CpMo(CO)_3^{\bullet}$. Other studies in PVC films at 12—293 K

$$\begin{tikzcd}
CpMo(CO)_3CH_3 \arrow[r, "(i)"] \arrow[d, shift right, "(i)"'] & CpMo(CO)_3^{\bullet} + CH_3^{\bullet} \arrow[d, "{(i),(ii),(iii)}"] \\
CpMo(CO)_2CH_3 + CO \arrow[u, shift right, "(ii)"'] & CpMo(CO)_3Cl
\end{tikzcd}$$

SCHEME 1. (i) $h\nu$; $300 < \lambda < 370$ nm, (ii) warming up, (iii) Cl radicals in PVC.

of the photoreactions of $CpMo(CO)_2(PPh_3)(CH_3)$, which is not amenable to gas matrix isolation studies because of thermal decomposition and $CpFe(CO)_2(CH_3)$ indicated the formation of $CpMo(CO)_2(PPh_3)Cl$ and $CpFe(CO)_2Cl$ respectively, i.e. further examples of radical pathways [14].

These results clearly demonstrate the potential of polymer films for investigating the photoreactions of organometallic compounds. Additionally the variety of photoreaction observed at different temperatures 10—293, 77 and 293 K emphasises the importance of studies at a variety of temperatures. This is in contrast to other reports of photoreactions of transition metal carbonyl complexes in polymer films [15,16], where it was specifically emphasised [16] that a polymer film at 293 K was a possible replacement for elaborate gas matrix isolation studies requiring expensive cryogenic equipment. Further work is in progress in our laboratories to extend our studies of radical pathway in PVC films, to investigate the temperature dependent photoreactions of organometallic complexes in unsaturated polymers, e.g. polybutadiene, and of ionic compounds in water soluble polymers, e.g. polyvinylalcohol. Such studies have potential applications in polymer chemistry where "photocuring" of polymers doped with metal complexes could lead to important changes in polymer structure.

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