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Preliminary communication

Ultraviolet/visible absorption spectrum and photochromism of pentacarbonyl tungsten, ($W(CO)_5$)

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In 1962–'63 Sheline and co-workers[1] obtained convincing infrared evidence for the existence of $M(CO)_5$ (M = Cr, Mo, W) by photolysis of $M(CO)_6$ in frozen 1/4 isopentane/methylcyclohexane solutions at 77°K, and commented on the yellow colour of the irradiated glass containing $W(CO)_5$. In 1964, El-Sayed[2] claimed to have obtained the UV/visible absorption spectrum of $Mo(CO)_5$ by photolysis of $Mo(CO)_6$ in 1/1 ether/isopentane at room temperature but Dobson[3] suggested that the absorptions were due to $M(CO)_5$(ether).

In this laboratory the photolytic behaviour of carbonyls in inert matrices at 20°K has been investigated (the lower temperature stabilises species that recombine at higher temperatures) and we have previously described the reverse photolysis whereby irradiation with light of longer wavelength than the fragment-producing (*e.g.* $HMn(CO)_4$ + CO or $M(CO)_5$ (M = Cr, Mo, W) + CO) light reverses the reaction (*e.g.* to give $HMn(CO)_5$ or $M(CO)_6$)[4]. Here we present preliminary UV/visible spectral data on $W(CO)_5$ which in turn explains the reversal step.

Figure 1 shows six spectra taken during one experiment with the same sample of $W(CO)_6$ in argon. The following points should be noted:

(*i*) The t_{1u} C–O stretching vibration of the O_h $W(CO)_6$ molecule should be a single band (ν = 1987 cm^{-1} (1)); the high-frequency component (ν = 1992 cm^{-1}) is probably due to a slight distortion in the matrix and will be discussed elsewhere[5].

(*ii*) The UV/visible spectra were obtained with a simple instrument with some attenuation of the reference beam; the high extinction coefficients of $W(CO)_6$ absorptions mean that very little sample is required, and the pulsed matrix isolation technique[6] produces a very clear solid compared with highly scattering matrices more frequently observed. The bands at 224 (2) and 286 nm (3) (~ 44700 and ~ 34900 cm^{-1}) show very little shift from the gas phase and are assigned[7] to $^1A_{1g} \rightarrow {}^1T_{1u}$ metal to ligand charge transfer bands.

(*iii*) Following Sheline *et al.*[1] the bands (4) (1964 cm^{-1}) and (5) (1932 cm^{-1}) are assigned to the E and A_1 (CO(5)) C–O stretching vibrations of square-pyramidal (C_{4v}) $W(CO)_5$ (CO groups 1, 2, 3, 4 in the plane, CO group 5 perpendicular to the plane); the band due to molecular CO (2138 cm^{-1}) and the high-frequency band at 2098 cm^{-1} (A_1 CO(1–4)) are only observed in those experiments where much more CO and $W(CO)_5$ are produced; the low intensity of the 2098 cm^{-1} band indicates an essentially planar

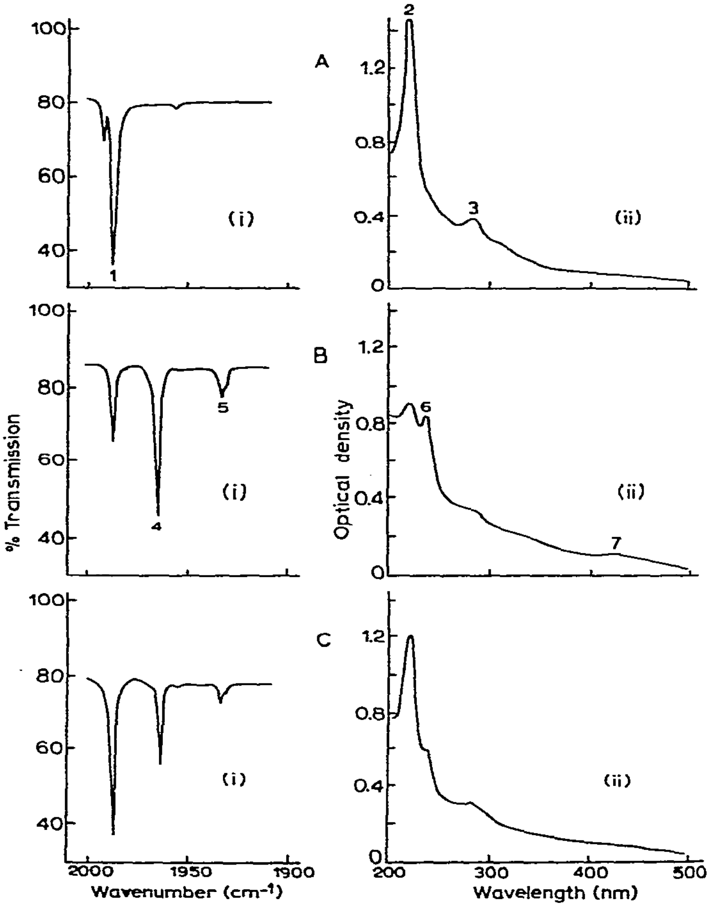

Fig.1. A. (*i*) IR (Perkin–Elmer 521) and (*ii*) UV/visible (Perkin–Elmer UV137) spectra of $W(CO)_6$ in argon (1/250) after pulsing on to KBr window at 20°K; B. (*i*) IR and (*ii*) UV/visible spectra after 30 seconds photolysis through a quartz window with an unfiltered medium pressure mercury arc; C. (*i*) IR and (*ii*) UV/visible spectra after 1½ minutes irradiation with soda glass-filtered mercury arc (*i.e.* no radiation $\lambda < 330$ nm).

TABLE 1

Band number (see Fig.1)	(1) 1987 cm^{-1}	(2) 224 nm	(3) 286 nm	(4) 1964 cm^{-1}	(5) 1932 cm^{-1}	(6) 239 nm	(7) 436 nm
Optical density before photolysis *i.e.* spectra A	0.39[a]	0.88	0.08				
Optical density after photolysis *i.e.* spectra B	0.12	0.29	0.03	0.26	0.04	0.31	0.03
Optical density after reversing radiation *i.e.* spectra C	0.34	0.63	0.05	0.14	0.02(5)	0.13	0.01
		$W(CO)_6$			$W(CO)_5$		

[a] This does not include the high frequency component at 1992 cm^{-1}.

$W(CO)_4$ group[★]. Following Cotton and Kraihanzel[8] force constants for $W(CO)_5$ are $k_1 = 15.25$, $k_2 = 16.25$, $k_i = 0.34$ mdynes/Å compared with $W(CO)_6$, $k_2 = 16.41$, $k_i = 0.29$ mdynes/Å.

(*iv*) Table 1 gives approximate optical density values for IR and UV/visible bands (1) to (7). It is clear that bands (6) (239 nm–41800 cm^{-1}) and (7) (436 nm–23900 cm^{-1}) belong to $W(CO)_5$ and are presumably related to the charge-transfer bands in $M(CO)_5L$ (M = Cr, Mo, W; L = donor) and $XMn(CO)_5$ (X = H, halogen, CH_3, etc.), for example $W(CO)_5$ (piperidine), 247 and 405 nm.

The assignment of the charge-transfer bands in $M(CO)_5L$ and $XMn(CO)_5$ in not certain, *e.g.* Gray *et al.*[9] assigned the long wavelength band in $XMn(CO)_5$ to b_2 $(3d_{xy}) \rightarrow e(\pi^*, CO(5))$ $(^1A_1 \rightarrow {}^1E)$ whereas Braterman and Walker[10] place the essentially metal e orbital higher than b_2 and assign the band to $e(3d_{xz}, d_{yz}) \rightarrow a_1$ $(\pi^*, CO(1\text{–}5))$ $(^1A_1 \rightarrow {}^1E)$. The similarity of k_2 in $W(CO)_5$ and $W(CO)_6$, the low value of k_1 in $W(CO)_5$ and the long wavelength of the low energy charge-transfer band in $W(CO)_5$ suggest that this band depends largely on participation of π^* CO(5) in the appropriate molecular orbitals. If this is the case then the reversal mechanism depends on irradiation of $W(CO)_5$ to produce an excited state involving mostly W and π^* CO(5) which allows requisition of the CO molecule; the four other CO ligands are virtually uninvolved. Loss of CO from $W(CO)_6$ and $W(CO)_5$ (for which we have evidence[5]) is suppressed since this depends on irradiation in the 2–300 nm region. Experiments are in progress to investigate the photochemistry in more detail using monochromatic irradiation.

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[★] In a footnote, Dobson[3] wondered whether the IR bands[1] should be assigned to a complex of $W(CO)_5$ with a very weak donor, possibly N_2. We have independent evidence[5] that, with N_2 in the matrix, IR bands are produced which are unrelated to $W(CO)_5$, and also it is difficult to imagine argon acting as a ligand.