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Preliminary communication

Intermediates in chromium carbonyl photochemistry

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We describe below experiments of relevance to the photochemistry of $M(CO)_6$ species (M = Cr, Mo and W) and the nature of the $M(CO)_5$ intermediates.

In previous work[1,2] we have shown that for $Cr(CO)_5$ (C_{4v}), generated by photolysis of $Cr(CO)_6$ in an argon matrix at 20 K, the visible absorption band occurs at 542 nm. In hydrocarbon glasses[3,4] at 77 K the corresponding band is at 485 nm although the infrared spectrum is very little changed[2,5]; on flash photolysis[3] of $Cr(CO)_6$ in cyclohexane at room temperature, the initial detectable product [assumed to be $Cr(CO)_5$ (C_{4v})] has an absorption at 483 nm. The discrepancy between the argon and hydrocarbon environments led us to investigate the behaviour of $Cr(CO)_6$ in a solid methane matrix at 20 K.

The UV/visible spectra of $Cr(CO)_6$ in methane and in argon at 20 K are virtually identical; on photolysis the product in methane has a band at 237 nm (*i.e.* the same as in argon[2]) and a band at 492 nm (*cf.* 542 nm in argon[2]). We suggest that this shift of the visible band is due to an interaction between methane and the 'hole' in C_{4v} $Cr(CO)_5$, assuming, as seems reasonable, that the interaction with argon is zero**. There is growing evidence for such direct interaction between a coordinately unsaturated transition metal complex and a saturated hydrocarbon *e.g.* the observations of Hodges *et al.*[7] on Pt^{II} activation of simple alkanes. Thus we suggest that the species observed in 77 K glasses and the first observable flash photolysis product, are both C_{4v} $Cr(CO)_5S$ (S=hydrocarbon solvent), not C_{4v} $Cr(CO)_5$.

The only real evidence for D_{3h} $M(CO)_5$ has come from Sheline and co-workers[5] who observed that on melting a glass containing $Mo(CO)_5$ the IR spectral changes were consistent with $C_{4v} \longrightarrow D_{3h}$ (the C_{4v} form was assumed to be frozen in the solid glass). Braterman and co-workers[4] have very recently argued that this spectral change is due to polymer formation and that there is no evidence for the D_{3h} structure.

Experiments in this laboratory support these conclusions:

Firstly IR bands similar to those assigned by Sheline to D_{3h} $Mo(CO)_5$ can be generated by photolysis of $M(CO)_6$ (M = Cr, Mo, W) in argon at 20 K but they are much weaker than the bands due to $M(CO)_5$ (C_{4v}), $M(CO)_4$ etc. Moreover the intensities of

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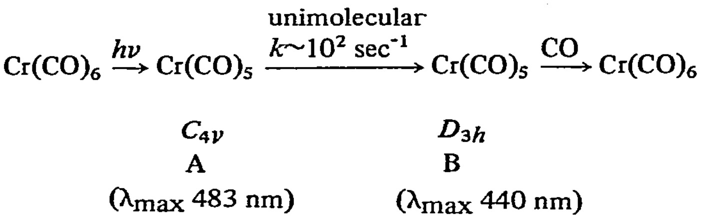
**The effect of change in L on the visible absorption band of $Cr(CO)_5L$ has been discussed elsewhere[6].

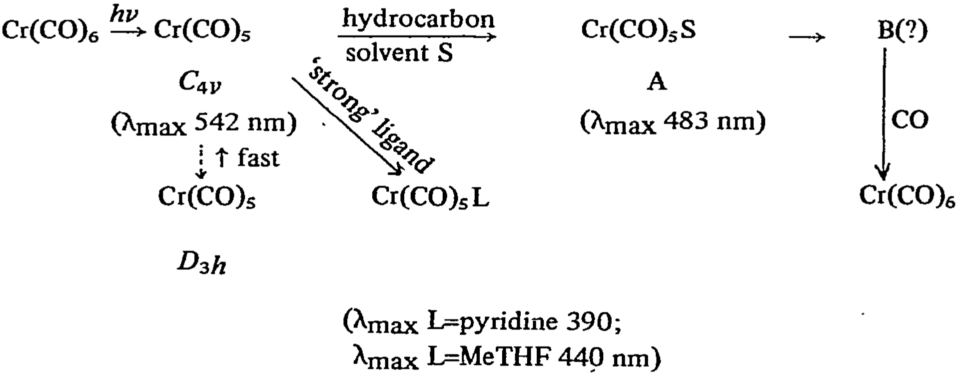
these 'Sheline' bands are dilution dependent[8] (at a dilution of $M(CO)_6$ in argon of 1 in 40,000 they do not appear at all). Thus we conclude they must be polymer bands probably due to reaction of $M(CO)_6$ with $M(CO)_5$.

Secondly $M(CO)_x$ ($M = Cr, Mo, W; x = 1$–4) can be prepared either by prolonged photolysis of very dilute $M(CO)_6$ in argon at 20 K or by cocondensing a stream of M atoms with carbon monoxide/argon at 20 K. IR spectra show that these species adopt a symmetrical, and presumably lowest energy, configuration. For example $M(CO)_3$ fragments show only one C—O stretching band and must therefore be planar (D_{3h}). Thus, in argon at least, the matrix does not force the fragments to adopt a structure derived simply by removing CO's from $M(CO)_6$. Hence since there is no IR evidence for a D_{3h} structure for $M(CO)_5$ on photolysis in dilute matrices or on atom synthesis, it is very unlikely that this form is more stable than the C_{4v} form.

These results are of considerable relevance to the solution photochemistry of $Cr(CO)_6$. Below are compared Nasielski's Scheme (1) and our suggestion (2).



$$Cr(CO)_6 \xrightarrow{h\nu} \underset{\substack{C_{4v}\\ \text{A}\\ (\lambda_{max}\ 483\ \text{nm})}}{Cr(CO)_5} \xrightarrow[\;]{\substack{\text{unimolecular}\\ k\sim 10^2\ \text{sec}^{-1}}} \underset{\substack{D_{3h}\\ \text{B}\\ (\lambda_{max}\ 440\ \text{nm})}}{Cr(CO)_5} \xrightarrow{CO} Cr(CO)_6 \qquad (1)$$



(2)

As Brown[9] has pointed out, Scheme 1 contains two surprises: the lack of observable reaction of A with CO, and the slow $C_{4v} \rightarrow D_{3h}$ interconversion rate. The lack of reaction of A with CO is certainly surprising since $M(CO)_5$ C_{4v} fragments react with excess CO in argon matrices at about 40 K[2]. In (2) we suggest a rapid $C_{4v} \rightarrow D_{3h}$ equilibrium lying towards C_{4v}. This would be consistent with the observations of Darensbourg *et al.*[10] on ^{13}CO exchange. It is probable that the reverse reaction of $Cr(CO)_5$ (C_{4v}) with CO is largely suppressed by the overwhelming concentration of solvent giving $Cr(CO)_5S$.

The argument for the transition A ⟶ B being $C_{4v} \longrightarrow D_{3h}$ depends on Sheline's experiment and the fact that the visible band of $Cr(CO)_5$ shifts to 440 nm on melting[3]. If Braterman[4] and we are correct there is no evidence for D_{3h} and in fact the implication is that B is polymeric. This however has pointed kinetic consequences; for A ⟶ B to be unimolecular or pseudounimolecular: either (a) A and B must both contain *one* Cr atom, or (b) A and B must both be polymeric with the same number of Cr atoms, or (c) A ⟶ B must be *e.g.* $Cr(CO)_5S + Cr(CO)_6 \longrightarrow Cr_2(CO)_{11}$ with $Cr(CO)_6$ in large excess.

There are clear objections to each of these alternatives but no doubt more detailed kinetic and spectroscopic work will resolve the problem.

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