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Preliminary communication

Metal carbonyl photolysis and its reversal; probable spurious nature of "trigonal bipyramidal $Mo(CO)_5$"

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Current interest in the photolysis of metal carbonyls[1-4] prompts us to report results that are relevant to the nature of the species described[1] as trigonal bipyramidal $Mo(CO)_5$, the nature of the "reverse photolysis" by which $W(CO)_6$ is regenerated from $W(CO)_5$ and CO in solid matrices[3], and the relationship between the species $Cr(CO)_5$, the electronic spectrum of which has been observed in solution by flash photolysis[4], and the species $M(CO)_5$ observed in low-temperature glasses[1,3].

We have achieved essentially quantitative conversion of the species $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ to square pyramidal pentacarbonyls, $M(CO)_5$, by irradiation with near UV light ($\nu < 35000$ cm^{-1}) in pentane-methylcyclohexane glasses at ca. 90 K; our data for these species agree well with those of Sheline *et al.*[1]. The parent hexacarbonyls are regenerated rapidly above the softening point of the glass (detectable by changes in the form of the weak solvent IR bands). The pentacarbonyls are stable for at least 24 hours, and possibly indefinitely, in the dark at 90 K, but in agreement with Turner *et al.* we find that irradiation with longer wavelength light ($\nu < 31000$ cm^{-1}) causes photoreversal, *i.e.* detectable regeneration of the parent hexacarbonyls.

If the photolysis is carried out at 90 K in 2-methyltetrahydrofuran (MeTHF) glass, different products are obtained to which we assign the structure $M(CO)_5$MeTHF on the basis of their IR spectra [*e.g.* for $Cr(CO)_5$MeTHF bands are observed at 2075 cm^{-1} vw (A_1), 1935 cm^{-1} vs (E), 1884 cm^{-1} ms (A_1)]. The lowering of frequencies from those found in $M(CO)_5$ [1,3] is due to the $\bar{\sigma}$-donor power of MeTHF as a ligand. No photoreversal could be observed, and the thermal regeneration of the parent hexacarbonyls was a slow process, requiring a day at room temperature under our conditions. The conversion[5] of $V(CO)_6^-$ to $V(CO)_5$MeTHF$^-$ could, however, be reversed by visible light at 90 K.

The UV spectra of the species $M(CO)_5$MeTHF and $M(CO)_5$ are extremely similar; thus all spectra show a long wavelength broad weak ($\epsilon \sim 3000$) maximum, which occurs at 20700 cm^{-1} (very broad), 24400 cm^{-1} and 24000 cm^{-1} in $Cr(CO)_5$, $Mo(CO)_5$ and $W(CO)_5$, and at 22700 cm^{-1}, 24400 cm^{-1} and 23800 cm^{-1} in $Cr(CO)_5$MeTHF, $Mo(CO)_5$MeTHF and $W(CO)_5$ MeTHF, respectively.

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McIntyre's $Cr(CO)_5$ generated in hydrocarbon solution at room temperature is described[5] as having a maximum around 22000 cm^{-1}, very similar to the corresponding band in $Cr(CO)_5OEt_2$; this strongly suggests that McIntyre's species and ours are identical The species $M(CO)_5$ are in every case capable of reacting with the molecules that form the solvent cage, $M(CO)_5$ being in no case detected in MeTHF. It follows that the failure of $M(CO)_5$ to recombine with lost CO in hydrocarbon matrices is not due to any energetic barrier (as some earlier work[3] appears to imply) but rather to some other cause, which presumably is escape of translationally 'hot' CO from the solvent cage during the primary photochemical cleavage. The simplest explanation of the phenomenon of photoreversal is that it is due to transitory local lattice softening on thermal degradation of the absorbed photon; thus photoreversal is shown by $M(CO)_5$ and also by $V(CO)_5MeTHF^-$, but not by the less labile $M(CO)_5MeTHF$ species.

At their softening point, glasses in which $Mo(CO)_5$ (C_{4v}) has been generated show the bands assigned by Sheline *et al.* to $Mo(CO)_5$ (D_{3h}), which was claimed as the more stable form[1]; the appearance of these bands is followed rapidly by a transient complexity in the spectrum which then changes to that of $Mo(CO)_6$. We reject the assignment of the bands to "$Mo(CO)_5$ (D_{3h})" for two reasons. Firstly, our work indicates that room temperature dissolved $Cr(CO)_5$ has C_{4v} symmetry; so dramatic a difference between Cr^0 and Mo^0 would be surprising. Secondly, the new species is formed neither in primary photolysis nor under photoreversal conditions, although both of these, on our interpretation, produce transient lattice softening. The new species requires bulk softening, and is therefore most likely polynuclear. "$Mo(CO)_5$ (D_{3h})" would have required a triplet ground state; its purported existence has a bearing on the assignment of other photochemical fragments[6] and its formation as the most stable isomer would have been relevant to the theory of Chatt and Shaw[7] on metal–carbon bond cleavage. Its probable non-existence as a stable species is thus of some interest.

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