Photoreversal of Secondary Photolysis in d⁶ Metal Carbonyls, and some Comments on Photoisomerisation and Photorotation
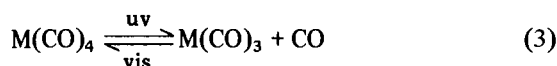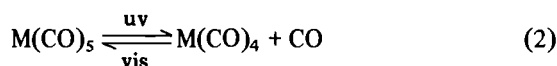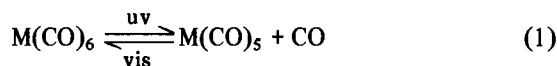
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It is well known that the primary photolysis of the Group VI metal hexacarbonyls is reversed by visible light (eqn. 1) [1], and this process has been convincingly assigned by J. J. Turner *et al.* to a reverse Berry photorotation rotation in an electronically excited, Jahn–Teller unstable, state of $M(CO)_5$ [2]. This state is also thought to be involved in the primary photolysis itself [3], as well as in the photoisomerisation processes of fragments of type $M(CO)_4$-CS [4] and, presumably, $M(CO)_4PR_3$ [5].

Turner and Perutz have reported that in CH_4 matrices at 20 K secondary and tertiary photolyses (eqns. 2, 3) show photoreversal [6]. Here we report the same phenomena in hydrocarbon glass at 77 K; we suggest that a wide-reaching extension of Turner's theory is required to explain these observations; and we present two challenges to experimentalists.

$$M(CO)_6 \underset{\text{vis}}{\overset{\text{uv}}{\rightleftharpoons}} M(CO)_5 + CO \qquad (1)$$

$$M(CO)_5 \underset{\text{vis}}{\overset{\text{uv}}{\rightleftharpoons}} M(CO)_4 + CO \qquad (2)$$

$$M(CO)_4 \underset{\text{vis}}{\overset{\text{uv}}{\rightleftharpoons}} M(CO)_3 + CO \qquad (3)$$

We find (Fig. 1) that when mixtures of $Mo(CO)_n^†$ (n = 3–6), formed at 77 K in hydrocarbon glass by UV irradiation [7], are irradiated at longer wavelength, the peak for $Mo(CO)_6$ gains in intensity at the expense of those for $Mo(CO)_5$, $Mo(CO)_4$ and CO, while those for $Mo(CO)_3$ are unaltered (Fig. 1). Presumably $Mo(CO)_5$ is being regenerated from $Mo(CO)_4 + CO$, as is $Mo(CO)_6$ from $Mo(CO)_5 + CO$, although direct regeneration of $Mo(CO)_6$ from $Mo(CO)_4 + 2CO$ is also consistent with our observations. The carbonyls of Cr and W behave similarly. In extensively photolysed mixtures photoreversal of tertiary photolysis (eqn. 3) also occurs (Fig. 2).

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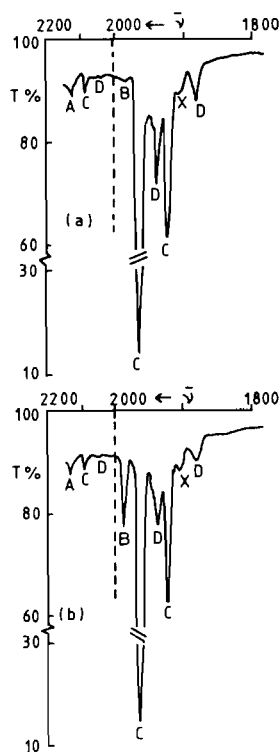
†More correctly, $M(CO)_n$(glass).

Fig. 1. Photolysis and photoreversal reactions in $Mo(CO)_6$ (hydrocarbon glass, 77 K, medium pressure Hg lamp). a) After 45 minutes irradiation, Pyrex filter; b) after a further 120 minutes, soda glass filter ($\lambda > 320$ nm): A = CO, B = $Mo(CO)_6$, C = $Mo(CO)_5$, D = $Mo(CO)_4$, E = $Mo(CO)_3$, X = incomplete solvent compensation.
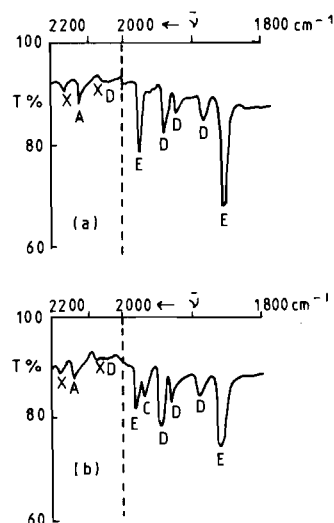

Fig. 2. Tertiary photoreversal reaction in $Mo(CO)_6$ (conditions as above). a) After 45 minutes irradiation, no filter; b) after 30 minutes irradiation, band pass filter ($\lambda > 335$ nm).

Accepting Turner's suggestion [3] that primary photolysis generates $M(CO)_5$ in its first excited configuration $b_1^2 e^3 a_1$, we infer that this configuration is not in itself dissociative, since primary photolysis takes place with loss of only one CO group. Secondary photolysis presumably takes place from the configuration $b_1^2 e^3 b_2$ of $M(CO)_5$, with loss of an equatorial CO group, the distinction is very similar to that between lower energy loss of amine and higher energy loss of equatorial CO in the photolysis of $Mo(CO)_5$ amine [8, 9].

Loss of CO from $M(CO)_5$ in an excited configuration will, irrespective of details, leave $M(CO)_4$ itself in an excited state until a separate decay step occurs (the ground state of the lowest, C_{2v}, form of $M(CO)_4$ is [10] of type $\psi_1^2\ \psi_2^2\ \psi_3^2$, while singly excited $M(CO)_5$ must correlate with a configuration of type $\psi_1^2\psi_2^2\psi_3\psi_4$). Now if $M(CO)_4$ collapses to its ground state *without* reorientation it should simply recapture CO to form $M(CO)_5$, and the secondary photolysis will be frustrated, just as frustrated primary photolysis is held responsible [3] for the failure [11] of the quantum yield in the primary photolysis of $M(CO)_6$ in fluids to reach unity. Photoreversal could then be attributed to the reverse photorotation. Unless we invoke such photorotation, unfrustrated secondary photolysis and its photoreversal remain mysterious processes, both in themselves and in their differences from those of primary photochemistry.

In a very wide range of cases, simple ligand loss from a complex is an excited state will lead directly to a fragment also in an excited state, which may well undergo facile photorotation and (if its ligands are distinguishable) photoisomerisation. The occurrence of these processes in C_{2v} $Mo(CO)_4$ (which is not capable of an orbital degeneracy) shows that Jahn–Teller instability is not a necessary condition. The general neglect of such processes may be justified simply because so much work is carried out in

water, where solvation of the fragment can presumably compete with isomerisation.

Two predictions follow. Species $M(CO)_4$ should when treated with polarised light show photorotation and, in the presence of CO, the related orientational effects of 'dichroic photodepletion without dichroic photoproduction' [3]. And asymmetrically substituted species, especially in weakly coordinating media, should show many cases of isomerisation directly accompanying photolytic ligand loss.

Our argument is closely related to the theory of the xi [12] states, but relates to distortions from ground state geometry after, rather than before, primary ligand loss. For steric reasons, especially in initially octahedral complexes, such post-dissociative distortions should be far larger and more sensitive to environment than those in the pre-dissociation states.

References

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