Inorganica Chimica Acta, *156* (1989) 7–8

Photochemical Reactivity in Molybdenum Clusters: Competition between Photosubstitution and Phosphorescence in $Mo_6Cl_{14}^{2-}$

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(Received August 9, 1988)

The phosphoresence of $Mo_6Cl_{14}^{2-}$ has been associated with the presence of three closely spaced electronic levels, T_{1u}, E_u and T_{2u}, with intrinsic lifetimes; see eqns. (1)–(3) [1–3].

This mixture of states in thermal equilibrium, namely with relative Boltzman populations of 65.2% T_{2u}, 28.9% E_u and 5.9% T_{1u} at 298 K, gives rise to a long-lived phosphorescence, e.g. *ca.* 180 μs at 298 K in acetonitrile, which can be quenched by electron acceptors [3, 4]. In quenching experiments, observation of the reduced quenchers by flash photolysis has clearly demonstrated that the excited states behave as reducing species.

In this work, the use of scavengers and time-resolved techniques led to the detection of previously unreported photosubstitution reactions which compete with the generation of the emissive states.

Results and Discussion

Although continuous wave photolysis ($\lambda_{excit} = 366$ nm, $I_0 = 6.7 \times 10^{-6}$ Einstein L^{-1} s^{-1}) of $Mo_6Cl_{14}^{2-}$ in deaerated acetonitrile failed to induce spectral changes which one could relate to photochemical reactions, these changes were clearly observed (Fig. 1) when photolyses were carried out in solutions containing various concentrations of either Br^- or I^-, *i.e.* 10^{-2} M Br^- or 10^{-2}–10^{-1} M I^-. These observations are in accord with a photoexchange of chloride ligand by bromide or iodide, as shown in eqn. (4)

$$Mo_6Cl_{14}^{2-} + X^- \xrightarrow{h\nu} Mo_6Cl_{13}X^{2-} + Cl^- \qquad (4)$$

(X = Br, I)

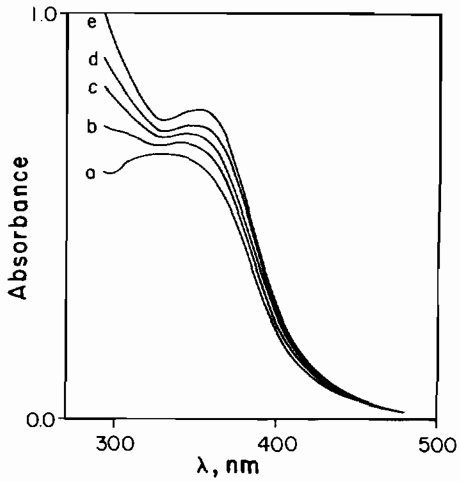

Fig. 1. Spectral changes recorded in 366 nm photolyses (I_0 = 6.7 × 10^{-6} Einstein L^{-1} s^{-1}) of 10^{-3} M $Mo_6Cl_{14}^{2-}$ in deaerated acetonitrile containing 0.1 M I^-. The spectra were recorded at (a) 0 min, (b) 60 min, (c) 120 min, (d) 180 min and (e) 270 min with a 0.2-cm optical path.

A further verification of the nature of the photoreaction was carried out by following the incorpora- of labeled I^- in the cluster, eqn. (5), according to a procedure described by Sheldon [5].

$$Mo_6Cl_{14}^{2-} + {}^*I^- \xrightarrow{h\nu} Mo_6Cl_{13}{}^*I^{2-} + Cl^- \qquad (5)$$

In 366 nm irradiations of $Mo_6Cl_{14}^{2-}$ in deaerated solutions of isotopically enriched I^-, we have observed the incorporation of I^- with a quantum yield that depends on the I^- concentration, *i.e.* $0.2 \times 10^{-3} < \theta < 2.0 \times 10^{-3}$ for $0.2 > [I^-] > 2.0 \times 10^{-2}$ M.

Flash photolysis and flash fluorescence experiments were carried out in apparatus described elsewhere with sample solutions which were previously deaerated by bubbling with (O_2-free) nitrogen [6, 7]. A comparison of the kinetics of the phosphorescent emission and of the transient spectra reveals that the spectral changes observed in flash photolysis are not unequivocally related to the decay of the photoemissive states. Indeed, flash irradiations ($\lambda_{excit} >$ 400 nm and 250 J/pulse) of $Mo_6Cl_{14}^{2-}$ in deaerated acetonitrile induce transient spectra (Fig. 2) which disappear with almost the same half-life (180 μs) as determined for the phosphorescence under the same experimental conditions. Such an observation

$$\begin{tikzcd} & (T_{1u})Mo_6Cl_{14}^{2-} \arrow[r, "13\ \mu s"] & Mo_6Cl_{14}^{2-} + h\nu \quad (1) \\ Mo_6Cl_{14}^{2-} \arrow[ur] \arrow[r] \arrow[dr] & (E_u)Mo_6Cl_{14}^{2-} \arrow[r, "185\ \mu s"] & Mo_6Cl_{14}^{2-} + h\nu \quad (2) \\ & (T_{2u})Mo_6Cl_{14}^{2-} \arrow[r, "370\ \mu s"] & Mo_6Cl_{14}^{2-} + h\nu \quad (3) \end{tikzcd}$$

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0020-1693/89/$3.50
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$$\begin{tikzcd} Mo_6Cl_{14}^{2-} \arrow[r, "-h\nu"] & {}^*Mo_6Cl_{14}^{2-} \arrow[r] \arrow[dr, "-Cl^-"'] & (T_{1u},E_u,T_{2u})Mo_6Cl_{14}^{2-} \arrow[r, "-h\nu"] & Mo_6Cl_{14}^{2-} & (6) \\ & & Mo_6Cl_{13}^{2-} \arrow[r, dashed, "+Cl^-"'] & Mo_6Cl_{14}^{2-} & (7) \end{tikzcd}$$

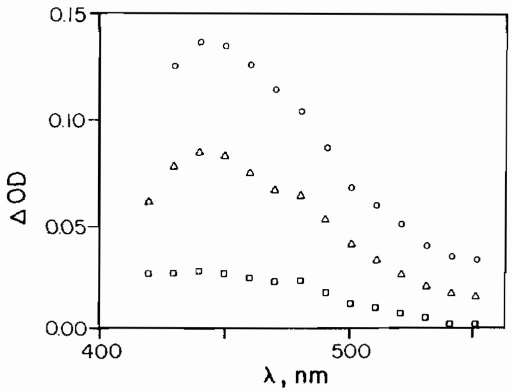

Fig. 2. Transient spectra recorded in flash photolyses (λ_{excit} > 400 nm) of 2.0 × 10^{-4} M $Mo_6Cl_{14}^{2-}$ in deaerated acetonitrile with delays after the flash of (○) 30 μs, (△) 150 μs and (□) 450 μs.

TABLE 1. Dependence of the Emission and Transient Spectra Half-life on the $Mo_6Cl_{14}^{2-}$ Concentration

$[Mo_6Cl_{14}^{2-}]$ (M)[a]	T (μs)	
	Emission[b]	Absorption[c]
10^{-4}	170	~200
10^{-3}	170	75.0
10^{-2}	170	12.5
10^{-2} [d]	170	16.6

[a] Experiments carried out with low intensity (440 nm) excitations in deaerated CH_3CN. Ionic strength adjusted with 2 × 10^{-2} M $LiClO_4$ unless otherwise stated. [b] Emissions followed at λ_m = 780 nm. [c] Optical density change followed at λ_m = 490 nm. [d] Ionic strength adjusted with 2 × 10^{-2} M LiCl.

is in good agreement with literature reports about the phosphorescence of the molybdenum cluster in dilute solutions but does not account for the photochemical behavior of the complex under a broader range of experimental conditions (Table 1) [1, 3].

The results given in Table 1 show that the rate of decay of the transient spectra, associated with the fate of the excited states and reaction intermediates, depends on the concentration of complex and electrolyte while the emission lifetime remains constant under similar experimental conditions. These observations about the kinetics of the phosphorescence and transient absorption spectra indicate that intermediates are generated simultaneously with the emissive states and that such intermediates and the excited states undergo transformations by parallel paths, eqns. (6) and (7).

In eqns. (6) and (7) it is possible that the intermediate $Mo_6Cl_{13}^-$ has coordinated solvent despite the fact that acetonitrile is a poor ligand and that the excited state, $^*Mo_6Cl_{14}^{2-}$, is one of the charge-transfer states placed in the vicinity of the emissive states. Moreover, reactions of such intermediates with excess $Mo_6Cl_{14}^{2-}$ account for the dependence of the transient spectra half-life on the molybdenum concentration.

Acknowledgements

The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-3096 from the Notre Dame Radiation Laboratory.

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