Photocatalytic Systems.
L.* Sequential Two-Photon Photoredox Reaction of Copper(II) Octacyanomolybdate(IV) Ion Pairs

D. REHOREK, A. REHOREK, P. THOMAS and
H. HENNIG

Sektion Chemie der Karl-Marx-Universität, DDR-7010 Leipzig, Liebigstrasse 18, G.D.R.

Received December 11, 1981

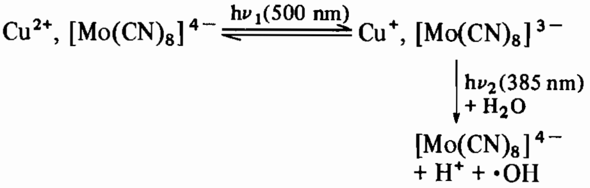
Sequential two-photon reactions induced by conventional light sources are of considerable interest, especially with respect to solar energy conversion processes [1]. We report here our observation that irradiation of aqueous solutions of copper(II) octacyanomolybdate(IV) ion pairs, which exhibit a strong intervalence charge transfer band at about 500 nm [2], leads to sequential two-photon photoredox reactions.

Although the efficiency of intervalence charge transfer excitation, eqn. (1), is expected to be very high, continuous monochromatic irradiation with a 200 W high-pressure mercury lamp led to only traces of Cu(I) and Mo(V):

$$\mathrm{Cu^{2+}, [Mo(CN)_8]^{4-}} \xrightleftharpoons{h\nu\ (500\ \mathrm{nm})} \mathrm{Cu^{+}, [Mo(CN)_8]^{3-}} \qquad (1)$$

Obviously, fast thermal back electron transfer competes with the escape of Cu(I) and Mo(V) from the primary cage. During polychromatic irradiation, however, hydroxyl radicals could be detected by the spin trapping technique using 5,5-dimethyl pyrroline-1-oxide as a spin trap [3] ($a_N = a_H = 1.49 \pm 0.02$ mT). Hydroxyl radicals are known to be the primary product of the photolysis of $[Mo(CN)_8]^{3-}$ in aqueous solution [4]. In order to avoid direct photooxidation of $[Mo(CN)_8]^{4-}$ by short-wavelength UV irradiation [5], light of $\lambda < 320$ nm was filtered by cut-off glass filters.

Control experiments with exclusively $Cu(NO_3)_2 \cdot 3H_2O$ and $K_4[Mo(CN)_8] \cdot 2H_2O$, respectively, did not give any evidence for the formation of hydroxyl radicals. No •OH radicals could be detected during the monochromatic irradiation of $Cu^{2+}/[Mo(CN)_8]^{4-}$ solution with light of either 365 nm or 492 nm. Since thermal reactions of $[Mo(CN)_8]^{3-}$, which has been prepared by oxidation of $[Mo(CN)_8]^{4-}$ with Ce(IV), did not give significant amounts of hydroxy spin adducts, it is very likely that the hydroxyl radicals which have been detected during polychromatic irradiation stem from secondary photolytic reactions of short-lived $[Mo(CN)_8]^{3-}$. Further evidence for •OH formation by a two-photonic process comes from bleaching of 4-N,N-dimethylamino nitrosobenzene, which is known to be an excellent scavenger for hydroxyl radicals [6]. Photoreactions leading to the formation of hydroxyl radicals are given in Scheme I.



$$\begin{aligned}&\mathrm{Cu^{2+}, [Mo(CN)_8]^{4-}} \xrightleftharpoons{h\nu_1(500\ \mathrm{nm})} \mathrm{Cu^{+}, [Mo(CN)_8]^{3-}}\\ &\qquad\qquad\qquad\qquad \Big\downarrow h\nu_2(385\ \mathrm{nm}) + \mathrm{H_2O}\\ &\qquad\qquad\qquad\qquad \mathrm{[Mo(CN)_8]^{4-} + H^+ + {\cdot}OH}\end{aligned}$$

Scheme I

However, at the present stage of investigation no information is available on whether ion-paired or free $[Mo(CN)_8]^{3-}$ ions are responsible for the formation of hydroxyl radicals.

References

1 G. Calzaferri, *Chimia, 32* (1978) 241.
2 H. Hennig, A. Rehorek, M. Ackermann, D. Rehorek and Ph. Thomas, *Z. Anorg. Allg. Chem.*, in press.
3 E. G. Janzen and J. I. P. Liu, *J. Magn. Reson., 9* (1973) 510, 513.
4 D. Rehorek, E. G. Janzen and H. J. Stronks, *Z. Chem.*, in press.
5 W. L. Waltz and A. W. Adamson, *J. Phys. Chem., 73* (1969) 4250.
6 D. Kraljic and C. N. Trumbore, *J. Amer. Chem. Soc., 87* (1965) 2547.

---

[*] Part XLIX, see ref. [4].

0020-1693/82/0000-0000/$02.75