

Photolysis of Octacyanomolybdate(IV) and Diethylenetriamine System: Kinetics and Mechanism of the Reaction

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The ligand field (LF) excitation of $[\text{Mo}(\text{CN})_8]^{4-}$ produces $[\text{Mo}(\text{CN})_7\text{OH}]^{4-}$ which reacts with diethylenetriamine (dien) in 5:2 stoichiometry. Rate constants and quantum yields for the formation of the photoproduct were calculated and found to be dependent on pH, ligand and $[\text{Mo}(\text{CN})_8]^{4-}$ concentrations. A reaction mechanism for the photochemical reaction of $[\text{Mo}(\text{CN})_8]^{4-}$ and dien is proposed. Rate constants and quantum yields are maximum at pH 7.4 and pH > 7.4, the reverse reaction generating octacyanocomplex from heptacyano species, is faster, at low pH the ligand is protonated which is less reactive and hence rate of reaction and quantum yield values decrease. At higher concentrations of $[\text{Mo}(\text{CN})_8]^{4-}$ to give eventually a second-order rate constant. The ionic strength does not affect the reaction rate, implying that the mechanism is not dissociative.

INTRODUCTION

The irradiation into the ligand field (LF) bands of octacyano complexes of molybdenum(IV) and tungsten(IV) in alkaline solutions lead primarily to substitution of one cyanide ligand by water.¹ The photochemical primary reaction is followed by a number of secondary thermal steps, resulting in the loss of further 3 cyanide ligands with the formation of the final product, $[\text{M}(\text{CN})_4\text{O}(\text{OH})]^{3-}$ (M = Mo or W)^{2,3}. Thomas *et al.*^{4,5} have proposed a photocatalytic system based on the photochemical generation of free cyanide from octacyanomolybdate(IV) and octacyanotungstate(IV) ions and have photochemically synthesized $[\text{Mo}(\text{CN})_4(\text{phen})_2]$ (phen = 1,10-phenanthroline).⁶ The kinetics of reversible photoaquation of $\text{K}_4\text{Mo}(\text{CN})_8$ in aqueous solution using an ion-selective electrode have been reported by Gaspar and Beck.⁷ Leipoldt *et al.*⁸ have performed a kinetic study of the reaction between *trans*-dioxotetracyanomolybdate(IV) ions and 1, 10-phenanthroline; the photo-reactivity of octacyanotungstate(V) ion has been reported by Kemp *et al.*⁹ in aqueous and by Sieklucka¹⁰ in nonaqueous media. Ali *et al.*¹¹ have reported the kinetics and mechanism of the photoreactions of $[\text{W}(\text{CN})_8]^{4-}$ with 1,10 phenanthroline, $[\text{M}(\text{CN})_8]^{4-}$ (M = Mo or W) with ethylenediamine.

More recently, kinetics and mechanism of oxidation of hydrogen peroxide by $[\text{W}(\text{CN})_8]^{3-}$ in alkaline aqueous media¹² and kinetics and mechanism of com-

plexation between hydroxopentaaquochromium¹³ and $[\text{Mo}(\text{CN})_8]^{4-}$ in acidic medium have been reported.

The present work deals with the findings of the reaction between octacyanomolybdate(IV) and diethylenetriamine (dien) in aqueous medium in presence of UV light. Rate constants and quantum yields has been determined and the mechanism of the reaction proposed.

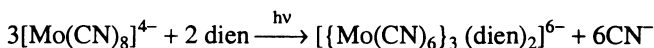
EXPERIMENTAL

$\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ was prepared by the method of Leipoldt *et al.*¹⁴ Dien was of A.R. grade. $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ used as a chemical actinometer with quantum yield of 1.21 at 370 nm was prepared by Parker method.¹⁵ Buffer solutions used in the study were prepared according to Bates¹⁶ as follows: pH 4.1–5.9 $\text{KHC}_8\text{H}_4\text{O}_4 + \text{KOH}$; 5.8–8.0 $\text{KH}_2\text{PO}_4 + \text{KOH}$; 8.0–9.1 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{HCl}$; 9.2–10.8 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{KOH}$. The ionic strength was maintained at $9.0 \times 10^{-2} \text{ m}$ with aqueous NaClO_4 . A photophysics immersion well quartz reactor (Cat. 3210, model RQ 125) was used for irradiation at *ca.* 365 nm. The temperature of the reactor was kept at $25 \pm 0.2^\circ\text{C}$ by circulating cold water through it. The absorbance was recorded on a Perkin-Elmer Lambda 3B spectrophotometer using 1 cm quartz cells. The pH values of the solutions were recorded on an Elico pH meter (type APX E/X S.No. 138). The light intensity was calculated by Murov's method¹⁷ and the quantum yield was determined by the technique of Calvery and Pitts.¹⁸ The stoichiometry of the reaction was determined by Job's method¹⁹ using continuous variation and mole ratio technique.²⁰ Kinetic measurements were performed under pseudo first-order conditions on solutions exposed to UV light of *ca.* 365 nm for different time intervals.

RESULTS AND DISCUSSION

The electronic absorption spectra of aqueous $\text{K}_4\text{Mo}(\text{CN})_8$ yellow solution consists of a band at 365 nm with a shoulder at 410 nm. On continued irradiation in the LF band both the peak and the shoulder gradually decrease with the simultaneous appearance of a maximum at 610 nm, the solution turns blue. The aqueous solution of $[\text{Mo}(\text{CN})_8]^{4-}$ and dien on exposure to UV light of *ca.* 365 nm turns red and the electronic absorption spectra show a maximum at 490 nm (Fig. 1). The intensity initially increases with exposure time and then starts to decrease due to the decomposition of the photoproduct formed (Fig. 2).

The stoichiometry of the photolysed mixture of $\text{K}_4\text{Mo}(\text{CN})_8$ and dien was found to be 3 : 2 as determined by Job's method using continuous variation and mole ratio technique. The reaction may be represented as



The pseudo first-order rate constant for the reaction was obtained by plotting $\ln(A_\infty - A_0)/(A_\infty - A_t)$ vs. time, where A_∞ , A_t and A_0 are the absorbances at the end, at time t and at the start of the reaction respectively. The kinetics of the photolysis were studied by irradiation of the system at approximately 365 nm;

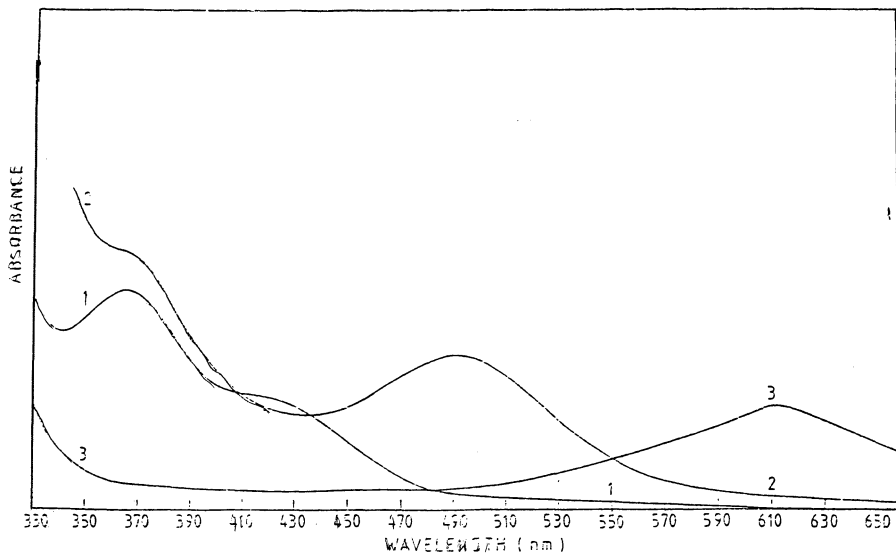


Fig. 1 Electronic absorption spectra of aqueous solutions of (1) unirradiated $K_4Mo(CN)_8$ (2) irradiated $K_4Mo(CN)_8$ and diethylenetriamine. (3) irradiated $K_4Mo(CN)_8$

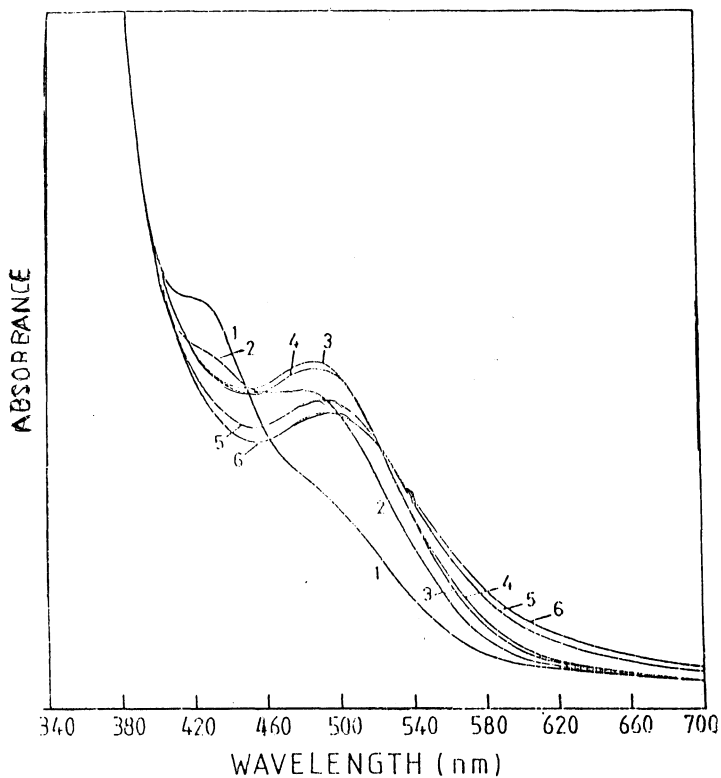


Fig. 2 Time-resolved spectra of $K_4Mo(CN)_8$ + dien system on exposure to UV light. (1)–(6) after 2, 4, 8, 10, 16 and 20 minutes of irradiation.

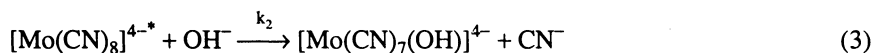
the temperature and ionic strength were maintained at $25 \pm 0.2^\circ\text{C}$ and 9.0×10^{-2} M respectively. The absorbances of the resulting solutions were measured at 490 nm. Pseudo first-order rate constants, together with quantum yield values, are listed in Table 1 for the $\text{K}_4\text{Mo}(\text{CN})_8$ -dien system.

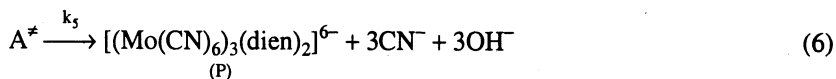
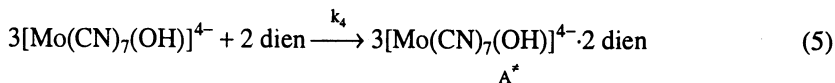
TABLE-I
RATE CONSTANTS AND QUANTUM YIELDS OF PHOTOCHEMICAL REACTION
BETWEEN $\text{K}_4\text{Mo}(\text{CN})_8$ AND DIETHYLENETRIAMINE (dien)

$10^4 \times [\text{Mo}(\text{CN})_8^{4-}]$ (mol)	$10^3 \times [\text{dien}]$ (mol)	pH	$10^2 \times k$ (s^{-1}) obsd	ϕ (mol einstein $^{-1}$)
5.0	5.0	7.4	4.1	0.78
6.0	5.0	7.4	3.9	0.67
7.0	5.0	7.4	3.7	0.59
9.0	5.0	7.4	3.4	0.46
11.0	5.0	7.4	2.7	0.37
13.0	5.0	7.4	2.1	0.31
10.0	3.0	7.4	2.5	0.10
10.0	4.0	7.4	2.8	0.17
10.0	6.0	7.4	3.3	0.39
10.0	7.0	7.4	3.5	0.52
10.0	8.0	7.4	3.8	0.67
10.0	5.0	5.4	2.2	0.27
10.0	5.0	6.5	2.5	0.31
10.0	5.0	7.0	2.6	0.35
10.0	5.0	7.4	3.1	0.38
10.0	5.0	8.0	2.7	0.34
10.0	5.0	8.6	1.9	0.31
10.0	5.0	9.1	1.3	0.21
10.0	5.0	10.0	1.2	0.18

Ionic strength, 9.0×10^{-2} M; Irradiation wavelength, 365 nm; absorbance measured at 490 nm; $I_0 = 7.446 \times 10^{-4}$ einstein min^{-1} ; temperature, $25 \pm 0.2^\circ\text{C}$.

The reaction rates and quantum yields increase with an increase in pH up to 7.4 and then again decrease. The reaction rates and quantum yields increase with an increase in ligand concentration and decrease with an increase in $[\text{Mo}(\text{CN})_8^{4-}]$ concentrations is given in Scheme 1 (eqns 1-6).





Scheme-1

From Scheme-1, the rate equation for the formation of the final product is given by the rate law

$$d[P]/dt = K_5[A^*] \quad (7)$$

Applying the steady state hypothesis for species $[A]^*$, $[\text{Mo}(\text{CN})_7(\text{OH})]^{4-}$ and $[\text{Mo}(\text{CN})_8]^{4-}$, we obtain:

$$[A^*] = K_4[\text{Mo}(\text{CN})_7(\text{OH})]^{4-}{}^3[\text{dien}]^2/k_5 \quad (8)$$

$$[\text{Mo}(\text{CN})_7(\text{OH})]^{4-} = K_2[\text{OH}^-][\text{Mo}(\text{CN})_8]^{4-}*/k_3[\text{CN}^-] + K_4[\text{Mo}(\text{CN})_7(\text{OH})]^{4-}{}^2[\text{dien}]^2 \quad (9)$$

$$[\text{Mo}(\text{CN})_8]^{4-}*/k_1 = I_a/k_1[\text{Mo}(\text{CN})_8]^{4-} + k_2[\text{OH}^-] \quad (10)$$

Here I_a represents the concentration of the absorbed photons.

$$\begin{aligned} \longrightarrow [\text{Mo}(\text{CN})_7(\text{OH})]^{4-} &= I_a k_2 [\text{OH}^-] / \{ (k_3 [\text{CN}^-] \\ &+ k_4 [[\text{Mo}(\text{CN})_7(\text{OH})]^{4-}]^2 [\text{dien}]^2) (k_1 [[\text{Mo}(\text{CN})_8]^{4-}] + k_2 [\text{OH}^-]) \} \end{aligned} \quad (11)$$

If $k_3 \gg k_4$,

$$[\text{Mo}(\text{CN})_7(\text{OH})]^{4-} = k_2 [\text{OH}^-] I_a / \{ (k_3 [\text{CN}^-]) (k_1 [[\text{Mo}(\text{CN})_8]^{4-}] + k_2 [\text{OH}^-]) \} \quad (12)$$

$$d[P]/dt = I_a k_2 k_4 [\text{dien}]^2 [\text{OH}^-] / \{ (k_3 [\text{CN}^-]) (k_1 [[\text{Mo}(\text{CN})_8]^{4-}] + k_2 [\text{OH}^-]) \} \quad (13)$$

$$\text{Thus, } \phi = dp/dt/I_a = k_2 k_4 [\text{OH}^-] [\text{dien}]^2 / \{ (k_3 [\text{CN}^-]) (k_1 [[\text{Mo}(\text{CN})_8]^{4-}] + k_2 [\text{OH}^-]) \}$$

$$\text{At pH} \leq 7.4, k_1 [[\text{Mo}(\text{CN})_8]^{4-}] \gg k_2 [\text{OH}^-]$$

$$\text{Hence, } \phi = k_2 k_4 [\text{OH}^-] [\text{dien}]^2 / k_1 k_3 [\text{CN}^-] [[\text{Mo}(\text{CN})_8]^{4-}] \quad (14)$$

In terms of Eq. (14), an increase is expected in the rate of formation production (P) and in the quantum yield with an increase in pH and ligand concentration and a decrease is expected with an increase in the concentration of $[\text{Mo}(\text{CN})_8]^{4-}$. This is observed to be so at $\text{pH} \leq 7.4$. However, at $\text{pH} > 7.4$, when $[\text{OH}^-]$ becomes comparable to $[\text{Mo}(\text{CN})_8]^{4-}$ the reaction rate should decrease according to Eq.(13). This is experimentally observed and recorded in Table-1. In acidic medium, the reverse reaction to form $[\text{Mo}(\text{CN})_8]^{4-}$ from $[\text{Mo}(\text{CN})_7(\text{OH})]^{4-}$ becomes slow, but the ligand gets protonated and is less reactive (experimentally it was seen that the solution gets turbid). Hence, at $\text{pH} < 7.4$ or $\text{pH} > 7.4$, the reaction rate and quantum yields are found to decrease. The plot of ϕ vs. $[\text{OH}^-] [\text{dien}]^2 / [\text{Mo}(\text{CN})_8]^{4-}$ in Fig. 3 gives a straight line passing through the origin confirming the proposed mechanism in Scheme-1.

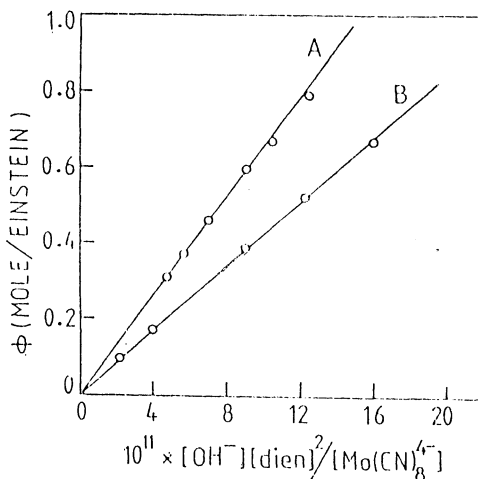


Fig. 3 Plot of ϕ vs. $10^{11} \times [\text{OH}^-][\text{dien}]^2/\text{Mo}(\text{CN})_8^{4-}$ for reaction between $\text{K}_4\text{Mo}(\text{CN})_8$ and dien: (a) variation in $[\text{Mo}(\text{CN})_8^{4-}]$ (b) variation in $[\text{dien}]$.

The rate of product formation and the quantum yield increase with a decrease in $[\text{Mo}(\text{CN})_8]^{4-}$ concentration; hence, it appears that at infinitely small $[\text{Mo}(\text{CN})_8]^{4-}$ concentration, the reaction rate should be infinitely fast. However, this is not so as can be seen in the limiting rate law Eq. (15) obtained from Scheme-1, assuming that at very low concentrations of $[\text{Mo}(\text{CN})_8]^{4-}$ deactivating collisions between $[\text{Mo}(\text{CN})_8]^{4-}$ and $[\text{Mo}(\text{CN})_8]^{4-*}$ become negligible and thus $k_1[\text{Mo}(\text{CN})_8]^{4-}$ can be neglected in Eq. (13) to obtain

$$\begin{aligned} \phi &= k_2k_4[\text{OH}^-][\text{dien}]^2/(k_2k_3[\text{OH}^-][\text{CN}^-]) \\ &= k_4[\text{dien}]^2/k_3[\text{CN}^-] \end{aligned} \quad (15)$$

The limiting rate law Eq. (15) contains $[\text{CN}^-]$ in the denominator suggesting that the reaction rate decreases when $[\text{Mo}(\text{CN})_7(\text{OH})]^{4-}$ is formed from $[\text{Mo}(\text{CN})_8]^{4-}$ releasing CN^- . At high concentrations of $[\text{Mo}(\text{CN})_8]^{4-}$ a first-order rate law is obeyed, but at low concentrations this is no longer followed. The first order rate law at higher concentrations of $[\text{Mo}(\text{CN})_8]^{4-}$ should fall off at low concentrations to reach, eventually, a second-order rate constant. Furthermore, since the rate constants and quantum yields are almost constant during variation of the ionic strength, the reaction mechanism cannot be dissociative.

A comparison of $\text{K}_4[\text{Mo}(\text{CN})_8]$ -en in UV light^{11b} and that of $\text{K}_4[\text{Mo}(\text{CN})_8]$ -dien systems reveals that the latter system has higher rate constant and quantum yield, probably because of increased denticity of dien and due to the large ring size (seven membered) of the chelate formed. The other end of the chelate molecule will contact complex ion²¹ as is evident by the 3 : 2 stoichiometry of the reaction.

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