Photoexcitation of Potassium Octacyano-Tungstate (IV)-1,10-Phenanthroline System: Kinetics and Mechanism of the Reaction

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The kinetics of the reactions of photochemically generated $[W(CN)_7OH]^{4-}$ in basic and $[HW(CN)_7(H_2O)]^{2-}$ in acidic medium with 1,10-phenanthroline have been studied in buffer solutions of pH 4.2—10.6, ionic strength 7.5×10^{-2} mol kg^{-1} at 20 °C. Quantum yield for formation of photoproduct was calculated and it was found to depend on pH, ligand and, $[W(CN)_8]^{4-}$ concentrations. The pseudo-first-order rate constant and quantum yield values in acidic medium are higher than in basic medium and the mechanisms of the photochemical substitution reactions are different in two mediums.

The photochemical behavior of $[M(CN)_8]^{n-}$ (where M=Mo or W and n=3 or 4) has been reviewed.[1,2] In the case of $[M(CN)_8]^{4-}$ ions, irradiation leads to an intermediate red compound with an increase in pH. Prolonged hydrolysis leads to a violet final product in the case of $K_4W(CN)_8$ and a blue product in the case of $K_4Mo(CN)_8$. The first stage is reversible in the dark which represents the mechanism of photochemical cyanide exchange[3,4] while the second is not reversible and represents the formation of the final product.

$$[M(CN)_8]^{4-} + 2H_2O \xrightarrow{h\nu} [M(CN)_7(H_2O)]^{3-} + HCN + OH^- \quad (1)$$

Photoaquation mechanism was interpreted by Adamson[2,5,6] and Carassiti[7-10] to be photolysis in ligand field band represented by the photoaquation reaction (1). The anion has been isolated[11,12] as the red product $Ag_3M(CN)_7(H_2O)$.

There is general agreement that the final blue or violet product in the case of $K_4Mo(CN)_8$ and $K_4W(CN)_8$ respectively is a tetracyano complex.

$$[M(CN)_7(H_2O)]^{3-} + OH^- \xrightarrow{h\nu} [M(CN)_4O(OH)]^{3-} + 2HCN + CN^- \quad (2)$$

The final product was originally thought to be eight-coordinate but it now seems likely to be $[MO(OH)(CN)_4]^{3-}$ in solutions and $[MO_2(CN)_4]^{4-}$ in solid.[13,14]

In this paper the kinetics of the reactions of photochemically generated species from potassium octacyanotungstate(IV) with 1,10-phenanthroline have been reported. Quantum yield has been calculated and its variation with respect to complex, ligand, and hydrogen ion concentrations investigated. Mechanism of the reaction in acidic as well as basic medium has been proposed and a rate equation has been derived.

Experimental

Reagents and General Procedure: $K_4W(CN)_8$ was prepared by the method of Leipoldt et al.[15] 1,10-Phenanthroline used was of BDH A. R. grade. Potassium trisoxalatoferrate(III) used as chemical actinometer was prepared by the method of Parker.[16] It has quantum yield of 1.21 at 370 nm. Buffer solutions in the pH range 4—6.5 were prepared from potassium hydrogen phthalate and hydrochloric acid and in the pH range 7—10 from borax and sodium hydroxide. Ionic strength was maintained at 7.5×10^{-2} mol kg^{-1} using potassium perchlorate. The temperature was maintained at 20±0.2 °C.

Photophysics immersion well quartz reactor cat. 3210 model RQ 125 was used for irradiation at around 365 nm. The absorbance was recorded on spectoromom 361 spectrophotometer using quartz cell. The pH of the solutions were recorded on Elico pH meter type APX 175 E/X S. No. 138.

Light intensity was calculated by the method given by Murov.[17] Rate measurements were carried out under pseudo-first-order conditions. The stoichiometry of the photolysis reaction between $K_4W(CN)_8$ and 1,10-phenanthroline was determined by Job's method of continuous variation and mole ratio method. These solutions were exposed to 365 nm light for different intervals of time under the atmosphere of nitrogen. The color of the solution changed from yellow to green and the absorbance of the green solution was measured at 450 nm, the wavelength of absorbance maximum. The pseudo-first-order rate constants for the reaction were obtained by plotting $\ln(A_\infty - A_0)/(A_\infty - A_t)$ against time, where A_∞, A_t, and A_0 are the absorbances at the end, time t and at the start of the reaction respectively. The quantum yield was calculated by the method given by Pitts and Calverts.[18]

Results and Discussion

The stoichiometry of the substitution reaction of potassium octacyanotungstate(IV) with 1,10-phenanthroline was found to be 1:1. Variation of rate constant and quantum yield values with respect to ionic strength, pH, complex and ligand concentrations was studied in basic and acidic medium. In basic medium it has been found that the rate constant and quantum yield values decrease with increase of complex concentration and pH but no marked change in them is observed by varying the ligand concentration and ionic strength. Pseudo-first-order rate constants along with quantum yield values in basic medium are listed in Table 1.

In acidic medium the rate of the reaction and quan-

tum yield values are found to increase with increase in ligand and hydrogen ion concentrations and decrease with increase of complex concentration. The reaction-rate and quantum yields are unaffected by change of ionic strength. Pseudo-first-order rate constants along with quantum yield values are listed in Table 2.

The mechanism proposed to explain these observations in basic medium is given in Scheme 1.

$$[W(CN)_8]^{4-} \overset{h\nu}{\rightleftharpoons} [W(CN)_8]^{4-*} \quad Ia \tag{3}$$

$$[W(CN)_8]^{4-*} + [W(CN)_8]^{4-} \xrightarrow{k_1} 2[W(CN)_8)]^{4-} \tag{4}$$

$$[W(CN)_8]^{4-*} + OH^- \xrightarrow{k_2} [W(CN)_7(OH)]^{4-} + CN^- \tag{5}$$

$$[W(CN)_7(OH)]^{4-} + \text{phen} \xrightarrow{\text{fast}} [W(CN)_6(\text{phen})]^{2-} + CN^- + OH^- \tag{6}$$

Scheme 1.

The complex $[W(CN)_8]^{4-}$ absorbs light and gets excited, this excited species either gets deactivated by collision with $[W(CN)_8]^{4-}$ or undergoes cyanide exchange with OH^- forming $[W(CN)_7(OH)]^{4-}$ which reacts with the added ligand, 1,10-phenanthroline to give the product $[W(CN)_6(\text{phen})]^{2-}$. The rate equation is derived as follows:

$$dp/dt = k_2[W(CN)_8]^{4-*}, \tag{7}$$

$[W(CN)_8]^{4-}$ is obtained by applying steady state approximation,

$$[W(CN)_8]^{4-*} = Ia/(k_2+k_1[W(CN)_8]^{4-}),$$
$$dp/dt = Ia \cdot k_2/(k_2+k_1[W(CN)_8]^{4-}). \tag{8}$$

Quantum yield

$$\Phi = dp/dt/Ia = k_2/(k_2+k_1[W(CN)_8]^{4-}),$$
$$1/\Phi = 1 + k_1/k_2[W(CN)_8]^{4-}. \tag{9}$$

Table 1. Rate Constant and Quantum Yield for Reaction between $K_4W(CN)_8$ and 1,10-Phenanthroline in Alkaline Medium[a)]

$[W(CN)_8]^{4-}\times10^4$ / mol l^{-1}	pH	$k\times10^4\pm0.5$ / s^{-1}	$\Phi\times10^2$ / mol/einstein
7.0	8.0	15.0	6.4±0.2
8.0	8.0	13.0	4.9±0.6
9.0	8.0	8.0	4.7±0.5
10.0	8.0	5.0	4.3±0.5
11.0	8.0	4.0	4.0±0.6
6.0	8.5	12.0	5.6±0.3
6.0	8.7	9.0	5.1±0.4
6.0	9.1	6.0	4.2±0.1
6.0	10.0	4.0	3.5±0.3
6.0	10.6	2.0	2.0±0.1

a) Irradiation wavelength=365 nm, Absorbance measured at 450 nm. Temperature=20±0.2 °C, $I_0=2.736\times10^{-4}$ einstein cm^{-3}, Ionic strength=7.5×10^{-2} mol kg^{-1}. [1,10-phen]=8×10^{-3} mol l^{-1}.

The plot of $1/\Phi$ versus $[W(CN)_8]^{4-}$ (Fig. 1) gave a straight line with slope $(k_1/k_2)=1.1\times10^4$ and with intercept equal to one. This also confirms the mechanism proposed in Scheme 1.

Photochemical reaction between $K_4W(CN)_8$ and 1,10-phenanthroline in acidic medium was found to show different mechanism from that of basic medium.

$$[W(CN)_8]^{4-*} + H_3O^+ \xrightarrow{k_3,\ \text{fast}} [HW(CN)_7(H_2O)]^{2-} + CN^- \tag{10}$$

$$[HW(CN)_7(H_2O)]^{2-} + \text{phen} \xrightarrow{k_4} [W(CN)_6(\text{phen})]^{2-} + HCN + H_2O \tag{11}$$

Scheme 2.

Table 2. Rate Constant and Quantum Yield for Reaction between $K_4W(CN)_8$ and 1,10-Phenanthroline in Acidic Medium[a)]

$[W(CN)_8]^{4-}\times10^4$ / mol l^{-1}	pH	$[1,10\text{-phen}]\times10^3$ / mol l^{-1}	$k\times10^3\pm0.6$ / s^{-1}	Φ / mol/einstein
8.0	4.2	2.0	4.0	0.12
8.0	4.2	4.0	4.1	0.13
8.0	4.2	6.0	4.3	0.14
8.0	4.2	10.0	5.1	0.15
8.0	4.2	12.0	5.4	0.19
2.0	4.2	8.0	8.0	0.48
4.0	4.2	8.0	7.3	0.44
6.0	4.2	8.0	6.7	0.36
8.0	4.2	8.0	5.3	0.32
12.0	4.2	8.0	4.4	0.28
6.0	4.6	8.0	6.3	0.30
6.0	5.0	8.0	5.6	0.25
6.0	5.5	8.0	4.7	0.22
6.0	6.0	8.0	4.0	0.17
6.0	6.5	8.0	3.5	0.11

a) Irradiation wavelength=365 nm. Absorbance measured at 450 nm. Temperature=20±0.2 °C, $I_0=2.736\times10^{-4}$ einstein cm^{-3}, Ionic strength=7.5×10^{-2} mol kg^{-1}.

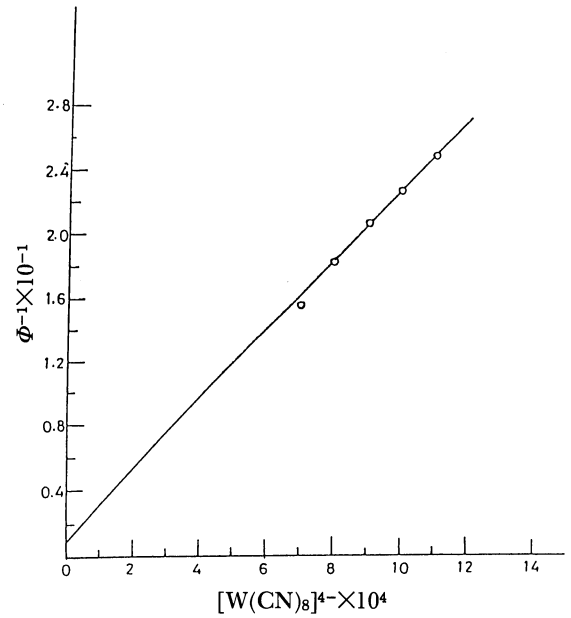

Fig. 1. Plot of $1/\Phi$ against $[W(CN)_8]^{4-}$ for the reaction between $K_4W(CN)_8$ and 1,10-phenanthroline in basic medium.

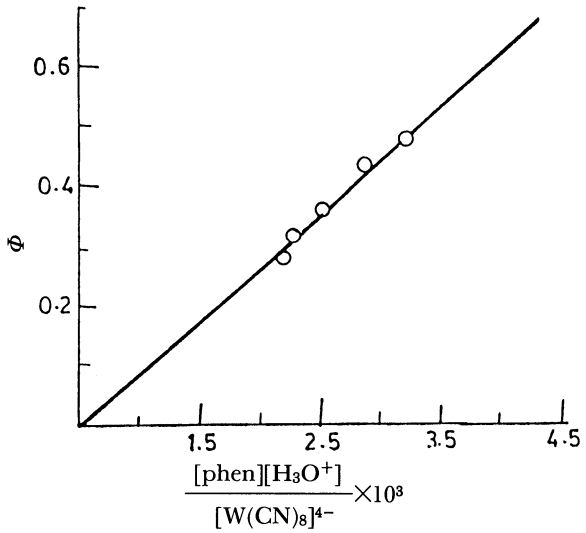

Fig. 2. Plot of Φ against $[Phen][H_3O^+]/[W(CN)_8]^{4-}$ for reaction between $K_4W(CN)_8$ and 1,10-phenanthroline in acidic medium.

The complex $[W(CN)_8]^{4-*}$ formed in equation (3) undergoes fast cyanide exchange with water in acidic medium to give $[HW(CN)_7(H_2O)]^{2-}$ [19] which reacts with 1,10-phenanthroline to give the product $[W(CN)_6(phen)]^{2-}$. This is represented in Scheme 2.

The rate equation for the formation of $[W(CN)_6(phen)]^{2-}$ from Scheme 2 is derived as follows:

$$dp/dt = k_4[phen][HW(CN)_7(H_2O)]^{2-}. \quad (12)$$

$[HW(CN)_7H_2O]^{2-}$ is obtained by applying steady state approximation

$$[HW(CN)_7(H_2O)]^{2-} = k_3Ia\,[H_3O^+]/k_1[W(CN)_8]^{4-}$$
$$dp/dt = k_3k_4[phen][H_3O^+]\,Ia/k_1[W(CN)_8]^{4-} \quad (13)$$

Quantum yield

$$\Phi = dp/dt/Ia = k_4k_3/k_1[phen][H_3O^+]/[W(CN)_8]^{4-} \quad (14)$$

Plot of Φ against $[phen][H_3O^+]/[W(CN)_8]^{4-}$ gave a straight line (Fig. 2) passing through the origin with a slope$=k_3k_4/k_1=3.5\times10^2$. This also confirms the proposed mechanism in Scheme 2. Reaction (11) consists of two steps, the first step which is slow involves the loss of water[20] by donor nitrogen of 1,10-phenanthroline and the second step, which is quite faster than the first, is closing of the chelate ring, accompanied by the loss of HCN. The higher rate of the reaction and large quantum yield obtained at lower pH is due to the formation of protonated species $[HW(CN)_7H_2O]^{2-}$ which reacts rapidly with 1,10-phenanthroline. The latter is a weak base, 1,10-phenanthroline cation, $C_{12}H_9N_2^+$ has a pK value of 4.96.[21] In acidic medium the excited species, $[W(CN)_8]^{4-*}$ gets protonated at cyano group which causes electron density to shift from W-CN bond axis towards cyano group. The bond in W-CN can be described as a combination of σ and π interactions. An M←C σ bond forms by donation of the unshared electron pair on the carbon atom into a metal orbital of σ symmetry directed to the center of the π system of the ligand; simultaneously a filled d_π or hybrid $d_{p\pi}$ orbital of the metal atom overlaps with an empty $2_{p\pi}$* (antibonding) orbital of the carbon atom. On protonation π bond which is weaker and σ bond which is stronger behave oppositely, i.e. the former becomes stronger and the latter becomes weaker leading to elongation and consequent weakening of W-CN bond. Hence, there is an increase in the reaction rate and the quantum yield. Since ionic strength does not affect the rate of the reaction and the quantum yield implying that the reaction mechanism is not a dissociative one.

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