

Photobleaching of Eosin-Y and Erythrosine using Hexacyanoferrate(II)

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The photobleaching of dyes [Eosine – Y and Erythrosine] were carried in the presence of potassium hexacyanoferrate (II) and progress of the reaction was observed spectrophotometrically. The effects of various operating variables like pH, concentration of dyes and potassium hexacyanoferrate (II) and light intensity on the rate of the reaction was also observed. It was observed that photobleaching of dyes follows pseudo-first order kinetics. A tentative mechanism has also been proposed for the photobleaching of dyes in presence of potassium hexacyanoferrate (II).

Key words: Photobleaching, Eosine–Y and Erythrosine potassium hexacyanoferrate (II)

INTRODUCTION

Water essential for the life of living organism may become polluted as a result of numerous human activities. Chemical, food and beverage, textile, pesticides and insecticide, dyeing and printing industries are among those causing water pollution. Polluted water can have detrimental effects on living biota and ecosystem as well. Principle source of water pollution is dye based industries where water is colored due to dye component. This polluted colored water is of no use, neither for irrigation nor for domestic purpose. The removal of these toxic substances seems necessary. A number of attempts have been made to remove these dyes from polluted water like adsorption by charcoal, thermal dehydration, chemical transformation, etc. but photocatalytic reactions seem to be most promising.

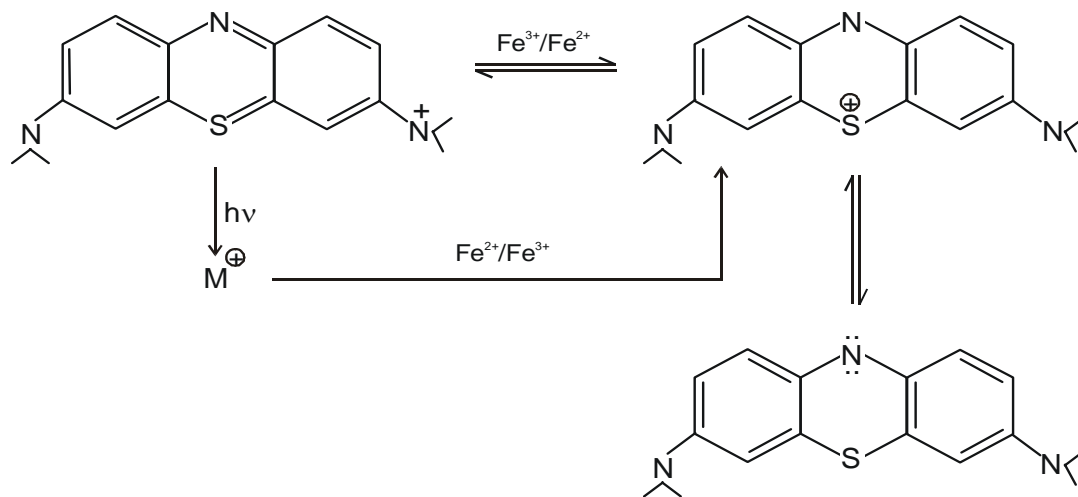
Iron has a rich coordination chemistry and many of its complexes have found use in [practical

application. Iron complexes are widely used as a basis of convenient analytical methods for the detection and estimation of iron up to part per million. The field of photocatalysis has been intensively reviewed by Scheavello¹ and Ameta et al.². Photodegradation of dye pollutants on silica gel supported TiO₂ particles under the visible light has been studied by Chen et al.³. Punjabi et al.⁴ studied the photoreduction of Congo red by ascorbic acid and EDTA as reductants and cadmium sulphide as a photocatalyst.

The photochemistry of transition metals has been a matter of interest for a chemist due to their exclusive redox properties. Among these complexes Fe (II), Fe (III), Mn (II), Cr (II), Pt (II), Pt (IV), Hg (II), Au (II) and Au (IV) have been studied by different workers. Photochemistry of number of metal complexes like Cr, Fe, Co, Pt, Mo and W has been studied by Wu et al.⁵. The glycinate complex of Fe(III) undergoes

photodecomposition yielding Fe (II) and oxidation products of glycine⁶.
Photochromic electron transfer

reaction of methylene blue system has been investigated by Parker⁷.



The photochemistry of Fe^{3+} - amino acid system was also investigated and it was observed that α -amino acids undergo deamination reactions, whereas β -amino acids are transformed into amino aldehydes⁸. Vineze et al.⁹ reported the quantum yields of the energy transfer in the $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system.

$[\text{Fe}(\text{CN})_6]^{4-}$ is an extremely stable compound in acid solution, where it is extensively protonated. The photosensitivity of $[\text{Fe}(\text{CN})_6]^{4-}$ was extensively studied in the nineteenth century by Porret¹⁰, Schonebein¹¹ and Kassner¹².

Photo-oxidation of various carboxylic acids has been investigated by irradiating their solutions containing Fe^{3+} ions with visible or U.V. light. This photochemical process gives Fe^{2+} , carbon monoxide and the oxidised products of acids, as reported by Baxendala and Bridge¹³, Gilbert¹⁴, Benrath¹⁵ and Ghosh and Mitra¹⁶. The kinetics of the photochemical

decomposition of $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2+}$ and the activation parameters are reported by Ronco and Aymonino¹⁷

From the above literature survey, it is evident that lot of attention has been paid on the role of iron complexes in number of chemical and photochemical reactions, but negligible attention has been paid on the use of potassium hexacyanoferrate (II) as a homogeneous photocatalyst for the degradation of dyes. This gave us an impulse to investigate the photobleaching of dyes eosine – Y and erythrosine in presence of potassium hexacyanoferrate (II).

EXPERIMENTAL DETAILS

Stock solutions of eosine – Y and erythrosine were prepared by dissolving their 0.0692 gm and 0.0880 gm, respectively in 100 mL doubly distilled water, so that the concentration of dyes solutions were 1.0×10^{-3} M. A stock solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ was prepared by

dissolving 0.4220 g in 100 mL doubly distilled water, so that the concentration of stock solution was 0.01 M. In case of eosine – Y, 1.6 mL of 0.01 M solution of $K_4 [Fe(CN)_6]$ was taken in a beaker and 22.2 mL doubly distilled water and 1.2 mL solution of eosine – Y was added. Similarly, for dye erythrosine 0.8 mL of 0.01 M solution of $K_4 [Fe(CN)_6]$ was taken in a beaker and 23.9 mL doubly distilled water and 0.3 mL solution of rose bengal was added to it dropwise.

Then the reaction mixture was exposed to light. A 200 W tungsten lamp (Philips) was used for irradiation purpose. The absorbance of the solution was measured at $\lambda_{max} = 510$ for both; eosine – Y and erythrosine at regular time intervals using UV-visible spectrophotometer (Systronics Model 106). The pH of the solution was

measured by a digital pH meter (Systronics Model 335). The desired pH of solution was adjusted by the addition of previously standardised 0.1 N sulphuric acid and 1 N sodium hydroxide solution.

RESULTS AND DISCUSSION

An aliquot of 3.0 mL was taken out from the reaction mixture at regular time intervals and the absorbance was measured. The results for typical run is given in Table 1. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of eosine – Y and erythrosine decrease with increasing time of exposure. A plot of $1 + \log A$ versus time was linear and follows pseudo first order kinetics. The rate constant was measured using following expression : $k = 2.303 \times \text{Slope}$

TABLE – 1: A TYPICAL RUN

[Eosin-Y] = 4.8×10^{-5} M; [Pot.Hexacyanoferrate(II)]= 6.4×10^{-4} M; Ph=5.5; Intensity of light =60 mW cm ⁻²		[Erythrosine] = 1.2×10^{-5} M; [Pot. Hexa Cyanoferrate]= 3.2×10^{-4} ;p=5; light intensity=60mW cm ⁻²	
Time(Min)	1 + log A	Time (Min)	1 + log A
0.0	0.950	0.0	0.945
15.0	0.896	15.0	0.865
30.0	0.804	30.0	0.795
45.0	0.763	45.0	0.729
60.0	0.699	60.0	0.649
75.0	0.633	75.0	0.580
90.0	0.574	90.0	0.494
105.0	0.546	105.0	0.436
$k = 8.85 \times 10^{-4} \text{ sec}^{-1}$		$k = 7.67 \times 10^{-4} \text{ sec}^{-1}$	

Effect of pH

The photochemical reaction between potassium ferrocyanide and dyes may be affected by pH and therefore, the effect of the pH on the photochemical reaction has been investigated in the pH range 4.5 to 7.0 and 4.0 to 7.0 for eosine – Y and erythrosine, respectively keeping all other factors identical.

It was observed that initially rate of reaction increases with increasing pH up to 5.5 and 5.0 for eosine – Y and erythrosine, respectively. After these pH values a further increase in pH decreases the reaction rate. It may be attributed to the fact that on decreasing pH below 5.5 and 5.0, the dye molecules remain

in their protonated form and the ferrocyanide ions does not exist in its anionic form i.e. it exists as a weak acid $H_4 [Fe(CN)_6]$. This acid will not provide free ferrocyanide ions and will lose its photolabile nature and as a consequence, no photoelectron will be produced, which is responsible for the bleaching of dye. On the other hand, when, pH is increased towards neutral side i.e., above 5.5 and 5.0 for eosine – Y and erythrosine, respectively, potassium hexacyanoferrate does not exist in its protonated form and dye also remains in its almost neutral form. Therefore, there is no electrostatic attraction between dye and $K_4 [Fe(CN)_6]$ molecules. This results in a slight decrease in rate of reaction.

TABLE – 2 : EFFECT OF pH

[Eosin-Y] = 4.8×10^{-5} M [Pot. Hexacyanoferrate (II)] = 6.4×10^{-4} M Intensity of light = 60.0 mWcm^{-2}		[Erythrosine] = 1.2×10^{-5} M [Pot. Hexacyanoferrate (II)] = 3.2×10^{-4} M Intensity of light = 60.0 mWcm^{-2}	
pH	$k \times 10^4 (\text{sec}^{-1})$	pH	$k \times 10^4 (\text{sec}^{-1})$
4.5	3.01	4.0	1.35
5.0	4.12	4.5	5.01
5.5	8.85	5.0	7.67
6.0	4.00	5.5	6.25
6.5	1.65	6.0	5.00
7.0	1.50	6.5	3.25
–	–	7.0	1.21

TABLE – 3 : EFFECT OF CONCENTRATION OF DYE

[Pot. Hexacyanoferrate (II)] = 6.4×10^{-4} M pH = 5.5 ; intensity of light = 60.0 mWcm^{-2}		[Pot. Hexacyanoferrate (II)] = 3.2×10^{-4} M pH = 5.0 ; Intensity of light = 60.0 mWcm^{-2}	
[Eosin-Y] $\times 10^5$ M	$k \times 10^4$ (sec $^{-1}$)	[Erythrosine] $\times 10^5$ M	$k \times 10^4$ (sec $^{-1}$)
4.0	2.01	0.4	2.50
4.4	3.05	0.8	5.45
4.8	8.85	1.2	7.67
5.2	6.27	1.6	6.00
5.6	5.23	2.0	3.55
6.0	1.25	2.4	2.72
6.4	1.20	–	–

Effect of dye concentration

The effect of concentration of eosine – Y and erythrosine on the rate of reaction was observed and the results are reported in Table 3.

It is clear from the table that as the concentration of dyes were increased, the reaction rate also increases due to increase in number of molecules participating in the reaction. But the retardation in the rate of reaction above concentration 4.8×10^{-5} M and 1.2×10^{-5} M for eosine – Y and erythrosine, respectively may be explained on the basis that the dyes will start acting as internal filter and does not allow light to reach on the K_4 $[\text{Fe}(\text{CN})_6]$ molecules. This results in decrease of the reaction rate.

Effect of potassium hexacyanoferrate (II) concentration

The effect of concentration of potassium hexacyanoferrate (II) on the rate of reaction was also observed and the results are given in Table 4.

It was observed that the rate of reaction increases on increasing the concentration of K_4 $[\text{Fe}(\text{CN})_6]$ as more molecules of K_4 $[\text{Fe}(\text{CN})_6]$ are available for ejection of photoelectron. But the decrease in the rate of reaction was observed on increasing the concentration of potassium hexacyanoferrate (II) above a particular concentration i.e., 6.4×10^{-4} M and 3.2×10^{-4} M for eosine – Y and erythrosine, respectively. It may be explained on the basis that K_4 $[\text{Fe}(\text{CN})_6]$ solution is pale yellow in colour and its larger concentration will decrease the intensity of light in the bulk of the solution by acting as an internal filter, which in turn, will result in retardation of the reaction rate.

TABLE – 4: EFFECT OF POTASSIUM HEXACYANOFERRATE (II) CONCENTRATION

[Eosin-Y] = 4.8×10^{-5} M pH = 5.5 ; Intensity of light = 60.0 mWcm^{-2}		[Erythrosine] = 1.2×10^{-5} M pH = 5.0 ; Intensity of light = 60.0 mWcm^{-2}	
$K_4[\text{Fe}(\text{CN})_6] \times 10^4 \text{ M}$	$k \times 10^4 (\text{sec}^{-1})$	$K_4[\text{Fe}(\text{CN})_6] \times 10^4 \text{ M}$	$k \times 10^4 (\text{sec}^{-1})$
6.0	1.01	2.4	3.51
6.2	1.23	2.8	4.05
6.4	8.85	3.2	7.67
6.6	6.72	3.6	6.01
7.8	5.40	4.0	5.00
7.0	5.45	4.4	4.07
–	–	4.8	3.05

Effect of light intensity

The effect of intensity of light was also observed on this photochemical reaction. The results are tabulated in Table 5.

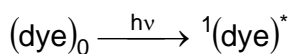
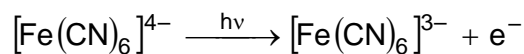
It was observed that the rate of reaction increases on increasing the intensity of light upto 60.0 mWcm^{-2} and thereafter, a decrease was observed on increasing the intensity further. It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increased, resulting into a higher rate. The decrease in the rate beyond 60.0 mWcm^{-2} may be due to the thermal effects caused by increase in intensity.

MECHANISM

On the basis of the experimental observations and corroborating the existing literature a tentative mechanism has been proposed for the degradation of eosine – Y and erythrosine in presence of $K_4[\text{Fe}(\text{CN})_6]$ and light.

In the primary photochemical reaction, $[\text{Fe}(\text{CN})_6]^{4-}$ ions absorb light and eject an electron, which is used in the reduction of dyes. The dyes molecules also absorb light and gets excited to their singlet state. The singlet dye undergoes intersystem crossing to triplet dye molecules.

The electron, which is ejected from the $[\text{Fe}(\text{CN})_6]^{4-}$ will reduce dyes to their leuco forms.



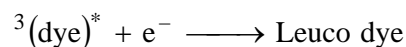


TABLE – 5: EFFECT OF LIGHT INTENSITY

[Eosin-Y] = 4.8 x 10 ⁻⁵ M [Pot. Hexacyanoferrate (II)] = 6.4 x 10 ⁻⁴ M pH = 5.5		[Erythrosine] = 1.2 x 10 ⁻⁵ M [Pot. Hexacyanoferrate (II)] = 3.2 x 10 ⁻⁴ M pH = 5.0	
Intensity	k x 10 ⁴ (sec ⁻¹)	Intensity	k x 10 ⁴ (sec ⁻¹)
20.0	1.73	20.0	2.50
30.0	1.98	30.0	3.15
40.0	2.45	40.0	3.27
50.0	2.50	50.0	4.05
60.0	8.85	60.0	7.67
70.0	3.03	70.0	5.45

Potassium ferrocyanide is a photolabile species and it ejects an electron on exposure to light. This electron can be successfully used to reduce a number of dyes like eosine – Y and erythrosine into their leuco counterparts. Thus it is a newer technique to carry out photobleaching of dyes in the effluents of printing, textile and dyeing industries.

CONCLUSION

The hexacyanoferrate (II) complexes are effective alternative for the photobleaching of dyes eosine – Y and erythrosine.

ACKNOWLEDGEMENT

We are thankful to Prof. Suresh C. Ameta for critical valuable suggestion from time to time.

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