Int. J. Chem. Sci.: 13(1), 2015, 309-316
ISSN 0972-768X
www.sadgurupublications.com

USE OF HEXACYANOFERRATE (II) IN PHOTOBLEACHING OF ROSE BENGAL

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ABSTRACT

The photobleaching of dye rose Bengal was 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 of rose Bengal, Potassium hexacyanoferrate (II).

INTRODUCTION

The photocatalysis has emerged as a probable solution to number of the problems like energy crisis, environmental pollution, waste water treatment etc. The field of photocatalysis has been intensively reviewed by M. Scheavello[1] and Ameta et al.[2] Photodegradation of dye pollutants on silica gel supported TiO_2 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]

Iron has a rich coordination chemistry and many of its complexes find use in practical

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applications. Iron complexes are widely used as a basis of convenient analytical methods for the detection and estimation of iron up to parts per million.

The formation of ferric ions and hydrogen on irradiation of acidic solution of Fe^{2+} was reported by Jortner and Stein[6]. The photogalvanic effect has been observed in Fe^{2+} thionine system for solar energy conversion by Rabinowitch[7] and Ameta et al.[8].

$[Fe(CN)_6]^{4-}$ is an extremely stable compound in acid solution, where it is extensively protonated. The photosensitivity of $[Fe(CN)_6]^{4-}$ was extensively studied in the nineteenth century by Porret[9], Schonebein[10] and Kassner[11]. There are conflicting opinions regarding photocatalytic exchange between $[Fe(CN)_6]^{4-}$ and CN^-.[12,13]

Photoelectron production for transition metal complexes serves to illustrate intermolecular photoredox reaction where the central metal undergoes oxidation. Studies of photoelectron production have almost centered on aqueous photochemical reaction of solution of cyanide complexes, in particular, ferrocyanide $[Fe(CN)_6]^{4-}$ complexes.

$$[Fe(CN)_6]^{4-} \xrightarrow{h\nu} [Fe(CN)_6]^{3-} + e^-(aq.)$$

The photolysis of $[Fe(CN)_6]^{4-}$ leads to production of a photoelectron and thus provides a useful system for studying reaction chemistry of hydrated electrons.

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 like rose Bengal in presence of potassium hexacyanoferrate (II).

EXPERIMENTAL

Stock solution of rose Bengal was prepared by dissolving their 0.1049 g in 100 mL doubly distilled water, so that the concentration of dye solution was 1.0×10^{-3} M. A stock solution of $K_4 [Fe(CN)_6]$ was prepared by dissolving 0.4220 g in 100 mL doubly distilled water, so that the concentration of stock solution was 1.0×10^{-2} M. 0.9 mL of 0.01 M solution of $K_4 [Fe(CN)_6]$ was taken in a beaker and 23.4 mL doubly distilled water and 0.7 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 λ_{max} 545 nm, respectively, for rose Bengal 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 0.1 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 rose Bengal decreases 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 × Slope

Table 1: Typical run

Time (min)	[Rose Bengal] = 2.8×10^{-5} M [Pot. hexacyanoferrate (II)] = 3.6×10^{-4} M pH = 5.5 Intensity of light = 60.0 $mWcm^{-2}$	
	Absorbance (A)	**1 + log A**
0.0	0.869	0.939
15.0	0.712	0.852
30.0	0.572	0.757
45.0	0.465	0.667
60.0	0.374	0.573
75.0	0.321	0.506
90.0	0.258	0.411
105.0	0.196	0.293
		k = 2.47×10^{-4} 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 4.0 to 6.5 for rose Bengal, respectively keeping all other factors identical. Results are given in Table 2.

Table 2: Effect of pH

pH	[Rose Bengal] = 2.8×10^{-5} M [Pot. hexacyanoferrate (II)] = 3.6×10^{-4} M Intensity of light = 60.0 mWcm^{-2}
	k × 10^4 (s^{-1})
4.0	1.30
4.5	1.55
5.0	2.10
5.5	**2.47**
6.0	2.01
6.5	1.87

It was observed that initially rate of reaction increases with increasing pH upto 5.5. 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, 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 week 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, 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.

Effect of dye concentration

The effect of concentration of rose Bengal on the rate of reaction was observed and the results are reported in Table 3.

Table 3: Effect of dye concentration

Dye × 10^5 M	[Pot. hexacyanoferrate (II)] = 3.6 × 10^{-4} M pH = 5.5 Intensity of light = 60.0 $mWcm^{-2}$
	k × 10^4 (s^{-1})
1.0	0.96
1.2	1.02
1.5	1.41
2.0	1.72
2.5	1.08
2.8	**2.47**
3.0	2.41
3.5	2.36
3.6	2.30
4.0	2.18
4.4	2.00
4.5	1.92
5.0	1.80
5.2	1.65
6.0	1.01

It is clear from the above 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 2.8 × 10^{-5} M for rose Bengal may be explained on the basis that the dyes will start acting as internal filter above this concentration and does not allow light to reach on the K_4 $[Fe(CN)_6]$ 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.

Table 4: Effect of potassium hexacyanoferrate (II) concentration

[Pot. hexacyanoferrate (II)] × 10^4 M	[Rose bengal] = 2.8×10^{-5} M pH = 5.5 Intensity of light = 60.0 $\mathrm{mWcm^{-2}}$
	k × 10^4 (s^{-1})
1.2	1.05
2.0	1.52
2.8	2.01
3.6	**2.47**
4.0	2.19
4.4	1.95
5.2	1.77
6.0	1.53
8.0	1.48
10.0	1.41
12.0	1.36

It was observed that the rate of reaction increases on increasing the concentration of K_4 $[Fe(CN)_6]$ as more molecules of K_4 $[Fe(CN)_6]$ 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., 3.6×10^{-4} M. It may be explained on the basis that K_4 $[Fe(CN)_6]$ solution is pale yellow in color 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.

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 $\mathrm{mWcm^{-2}}$ 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 light intensity.

Table 5: Effect of light intensity

Light intensity (mWcm^{-2})	[Rose bengal] = 2.8×10^{-5} M [Pot. hexacyanoferrate (II)] = 3.6×10^{-4} M pH = 5.5
	k × 10^{4} (s^{-1})
20.0	1.03
30.0	1.52
40.0	1.95
50.0	2.20
60.0	**2.47**
70.0	2.00
80. 0	1.94

Mechanism

On the basis of the experimental observations and corroborating the existing literature a tentative mechanism has been proposed for the degradation of rose bengal in presence of $K_4[Fe(CN)_6]$ and light.

In the primary photochemical reaction, $[Fe(CN)_6]^{4-}$ 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 $[Fe(CN)_6]^{4-}$ will reduce dyes to their leuco forms.

$$[Fe(CN)_6]^{4-} \xrightarrow{h\nu} [Fe(CN)_6]^{3-} + e^-$$

$$(Dye)_0 \xrightarrow{h\nu} {}^1(Dye)^*$$

$$^1(Dye)^* \xrightarrow{ISC} {}^3(Dye)^*$$

$$^{3}(\text{Dye})^{*} + e^{-} \longrightarrow \text{Leuco dye}$$

$$\text{Leuco dye} \longrightarrow \text{Products}$$

Potassium ferrocyanide is a photo labile species and it ejects an electron on exposure to light. This electron can be successfully used to reduce a number of dye like rose Bengal into its leuco counterparts. Thus, it is a newer technique to carry out photobleaching of dye in the effluents of printing, textile and dyeing industries.

REFERENCES

1. M. Scheavello, Heterogeneous Catalysis, Wiley, New York (1997).
2. S. C. Ameta, R. Chaudhary, R. Ameta and J. Vardia. J. Ind. Chem. Soc., **80**, 257 (2003).
3. Y. X. Chen, K. Wany and J. Lovep, Photochem. Photobiol., **163A**, 281 (2004).
4. P. B. Punjabi, Rakshit Ameta, Ritu Vyas and Shilpa Kothari, Ind. J. Chem., **44A,** 2266 (2005).
5. Q. H. Wu, B. W. Zhang, Y. Cao, J. W. Bai and J. R., J. Photochem. Photobiol., **106**, 170 (1999).
6. J. Jortner and G. Stein, J. Phys. Chem., **66**, 1264 (1962).
7. E. Rabinowitch, J. Chem. Phys., **8**, 560 (1940).
8. S. C. Ameta, S. Khamesra, S. Seth and R. Ameta, J. Photochem. Photobiol., **48**, 81 (1989).
9. R. Porret, Schw. J., **17**, 263 (1816).
10. C. F. Schonebein, Pogg. Ann., **67**, 87 (1846).
11. G. Kassner, Arch. Pharm., **234**, 330 (1896).
12. A. W. Adamson, A. J. P. Welker and M. Volpe, J. Am. Chem. Soc., **72**, 4030 (1950).
13. N. F. Hall and A. G. Macdiarmid, J. Am. Chem. Soc., **76**, 4222 (1954).

Accepted : 19.01.2015