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PHOTO REDUCTION OF EOSINUSING BENZOPHENONE

Dr. Bindu Kataria (Associate Professor)

Department of Chemistry, Government Meera Girls College,Udaipur[Rajasthan, India

ABSTRACT

In the presence of benzophenon the reaction of eosin Photoreduction parameters were observedspectrophotometrically i.e the effects of pH, dye concentration , benzophenone concentration etc,observations on this reaction indicated that dye photoreduction is apseudo-first order kinetics. An approximate mechanism forphotoreduction of eosin has been presented in this paper.

Key Words: Benzophenone,EosinPhotoreduction

INTRODUCTION

The current transition in the world of fashion has put revolution in the textile industry. Today industry is inventing new colorizedclothing, households etcwith frequent changes which can cater needs of young generationwho are fond of fabulous and attractive outlook. Dyes are playing vital role in this textile revolution. The waste water from textile industry is quite toxic and carcinogenic in nature due to presence of these dyes. Presence of dye in waste water poses environmental problems. Since dyes are non biodegradable and stable hence poses major problems in treatment. Using benzophenone as photosensitizer, dye (eosin) photoreduction attempt is made to study more.In photoreduction enrgy transfer is the key phenomena in which molecules absorbs light energy according to convenient wave length. F Millich , G Oster[1] studies EDTA for photoreduction of methylene blue as well as Acridine dyes photoreduction with allyl thiorea. In ketone amine system the organic dyes were photoreduced and reported by Jockusch et al[2]. In other studyJain et al[3]investegatedsodium and potassium carbonate photoreduction using eosin. Similarly by using aqueous bicarbonatephotoreduction of methylene blue was reported by S. Jain, J. Vardia, R. Ameta, S.C.Ameta[4]. H. Mallesha at al[5]studied photoreduction of benzophenone analoguesby

Alcohol and Ether. Untreated TiO2 and silver ion doped TiO2 under UV radiations used to photocatalytic degradation of a mixture of two dyes investigated Gupta et al[6].Triplet sensitized photobleaching of crystal violet was investigated by Naguib et al[7].Visible light induced reduction of methyl viologen in poly vinyl alcohol containing N-methyl-2–pyrrolidonesreported by Ohtani et al[8]. To enhance the photodegradation of organic pollutants in water on graphitic carbon nitride (GCNO) under visible light irradiation using employed oxygen doping investigated by Liu et al[9].Four organic dyes (Eosin-Y, Perylene , Nile red, and Coumarin) were used by them to dye sensitize the GCNO photocatalyst. Molla et al[10]. evaluated use of dye –sensitizes TiO2 and observed that itb is one of the most promising methods for the visible –light induced detoxification of pollutants. Eman at al[11]reportedphotodegradation of Eosin Y Using Silver-Doped Magnetic Nanoparticles. A detailed literature survey indicated the it is prudent to use ultra violet light for photoreduction of eosin by benzophenone as a photosensitizer, therefore the present study work was undertaken.

BRIEFEXPERIMENTAL

Eosin, ethanol stock solution was preparedand 0.15g benzophenon solution is added to dye to study photoreduction. Awave length of 366nm with eight ultra –voilet lamps were used for radiation purpose as a multi-lamp reactor. At the centre of these lamps a quarts tube was used as reaction vessel. Optical density was measured at a regular interval with help of spectrophotometer [JASCO Model ,7800].

RESULT AND EXPLAINATIONS

A Graph between log (Optical density) v/s time was plotted and it was found linear but in two stages. Slope of first stage reaction curve indicated slow but second stage was much faster.

In this process pseudo-first order kinetics was observed in both of the stages of reaction.

Rate constant k = 2.303 x slope

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A TYPICAL RUN

A typical run is given in Table **1** and Figure **1.**

Table 1: A Typical Run

[Eosin] = 6.66 x 10^{-5} M pH=5.5

[Benzophenone] = 1.65 x 10^{-2} M

Time (Seconds)	**Optical Density (O.D)**	**1+ log (O.D.)**
0	1.709	1.23
30	1.663	1.22
60	1.608	1.20
90	1.455	1.16
120	1.269	1.10
150	1.052	1.02
180	0.880	0.94
210	0.753	0.87
240	0.659	0.81
270	0.552	0.74

k_1 = 2.17 x 10^{-3} sec^{-1}

k_2= 5.48 x 10^{-3} sec^{-1}

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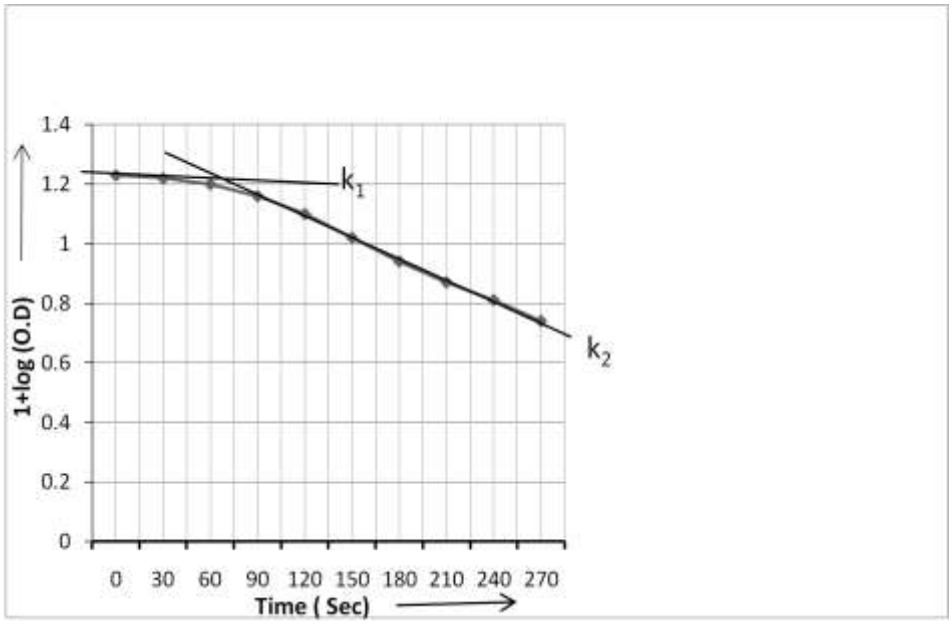

Figure 1: Plot between Optical density v/s time for photoreduction of eosin

STUDY ON EFFECT OF pH

The pH of the medium is expected to affect the rate of photoreduction of eosin was investigated in thepH range 4.0 to 7.0. The experimental findings are reported in Table **2**and graphically presented in figure **2**.

Table 2: EFFECT OF pH

[Eeosin] = 6.66 x 10^{-5} M [Benzophenone] = 1.65 x 10^{-2} M

pH	**Rate Constant (sec^{-1})**

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	$k_1 \times 10^3$	$k_2 \times 10^3$
4.0	1.08	2.18
4.5	1.36	3.31
5.0	2.06	4.62
5.5	2.17	5.48
6.0	1.62	5.14
6.5	1.36	1.83
7.0	0.81	1.51

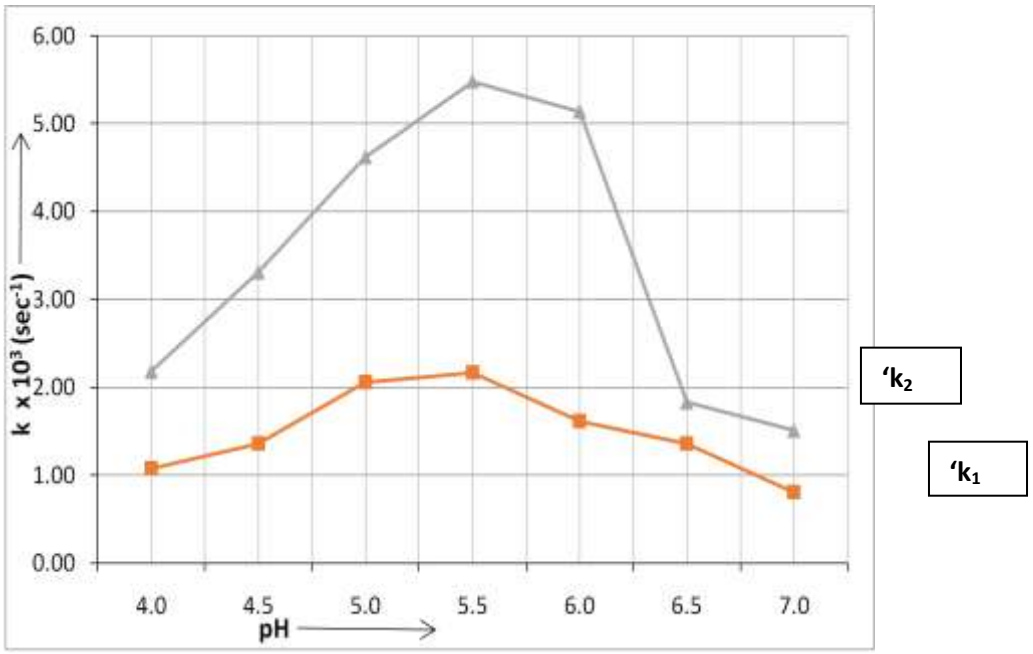

Figure 2: Effect of pH on photoreductionn of eosin

During this process it was noticed that increase in pH increases rate of photoredcution of eosin, upto the point where it obtain optimum value at pH = 5.5. Beyond this limit of pH a decrease in pattern was observed.

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The pH effect on the reaction rate can be explained that as the pH was decreased lower than 7.0, then the dye molecule may directly combine with proton to get itself in reduced form (bleached form). It reaches on optimum rate at pH =5.5.

Similarly a decrease in the photobleaching of dye has been investigated on decreasing pH of the reaction below 5.5.

Such phenomena may be attributed to the fact that there is a possibility of competitive reaction of proton with that of ethoxy or dye anion.

Thedecreased rate indicated that protonation of ethoxy ion dominates over reduction of the dye,resulted the rate of photo bleaching as retarded.

EFFECT OF EOSIN CONCENTRATION

Effect of variation of dye concentration studied with different concentration of eosinretaining other parametersas constant. Findings of experiments reported in Table **3** and presented graphically in figure **3**.

TABLE 3:EFFECT OF EOSIN CONCENTRATION

[Benzophenone] = 1.65×10^{-2} M pH = 5.5

[Eosin] x 10^5 M	**Reaction Rate Constant (sec^{-1})**	
	$k_1 \times 10^3$	**$k_2 \times 10^3$**
5.00	0.53	3.70
5.50	0.99	4.19
6.00	1.41	4.72
6.66	2.17	5.48
8.00	1.70	5.26
10.00	0.72	4.94

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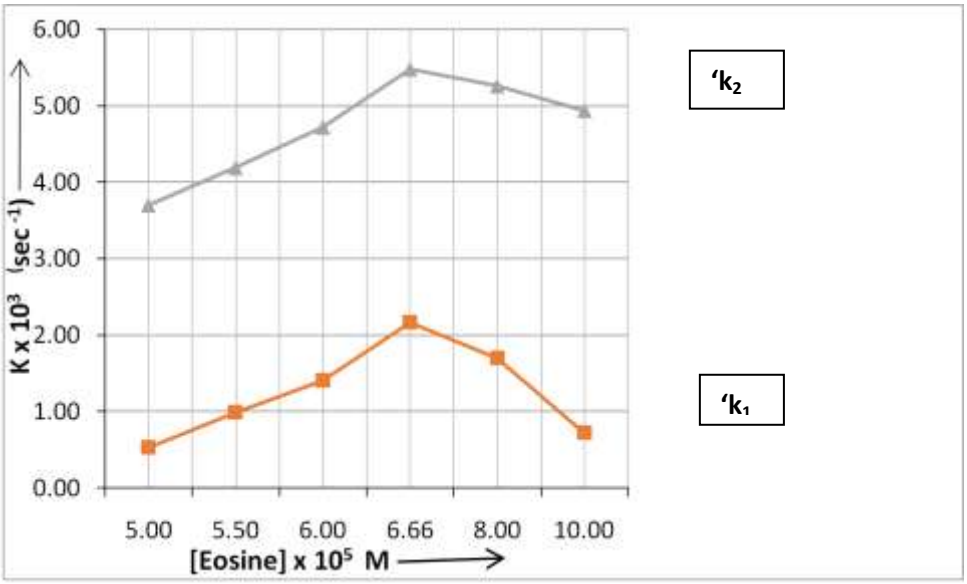

Figure 3: Effect of eosin concentration

An increase in rate constant observed with increase in dye concentration, but rate decreased beyond eosin concentration of 6.66 x 10^{-5} M.

Increase in dye concentration,increases the number of dye molecules for participation in thephotochemical redox reaction, an increase in the rate of photobleaching of dye has been investigated. Beyond concentration of limit i.e., [eosin] = 6.66 x 10^{-5} M, a decrease in reaction rate was observed with the increase the dye concentration solution

It is explained as, an increase in the dye concentration beyond a limit will not permit the desired light intensity to reach the dye molecules in the bulk of the solution within a limited time domain or in other wordsthe dye itself acts as a filter, hence decreased rate of the reaction has been observed.

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EFFECT OF BENZOPHENONE CONCENTRATION

Benzophenoneconcentration may affect the rate of bleaching therefore, different concentrations of benzophenone were used and results reported in the table 4. The experimental findings are provided below in Table**4**as well as presentedgraphically in figure **4**.

TABLE 4:EFFECT OF BENZOPHENONE CONCENTRATION

[Eosin] = 6.66 x 10^{-5} M pH = 5.5

[Benzophenone] x 10^2 M	**Rate Constant (sec^{-1})**	
	k_1 x 10^3	**k_2 x 10^3**
0.55	2.04	4.00
1.10	3.61	6.12
1.65	2.17	5.48
2.20	1.84	4.84
2.75	1.20	3.02
3.30	0.62	1.92

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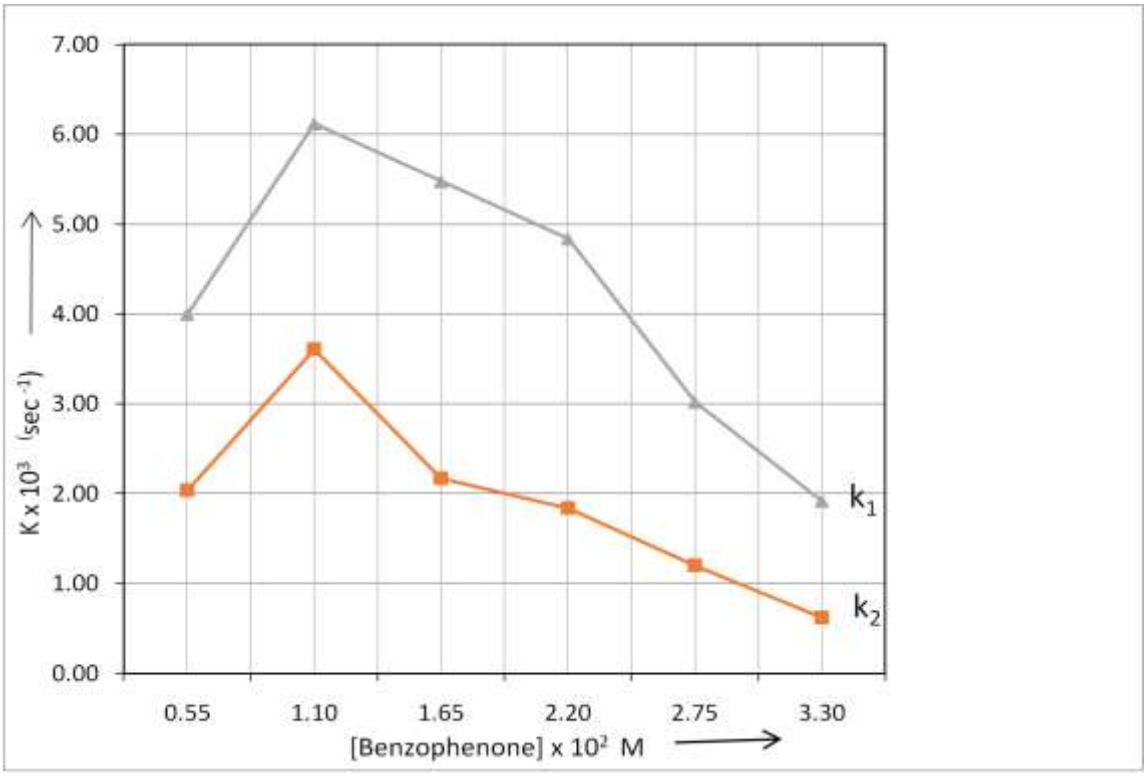

Figure 4: Effect of benzophenon concentration

Benzophenone as sensitizer during photoreduction of dye molecules has been observed and it is found that concentration of benzophenone affects the reaction. In the beginning rate of photoreduction increases with increase in concentration of benzophenoneupto certain value of concentration, beyond this rate of photoreduction decreases.

This phenomena may be explained as low concentration of benzophenone, provides free movement of sensitizer molecules can react easily with dye molecule in excited state, which leads increase in the rate of photoreduction. Similarly further increase in the molecules of sensitizer concentration , theirs movement in the excited state to the dye molecule is hindered by themselves, so that they are deactivated before they reach the dye molecules to have any interaction in the desired time limit. Therefore, a decrease in the photoreduction of eosin was observed.

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MECHANISM

Based on the observations a tentative mechanism has been proposed for photoreduction ofEosin.

$$^1S_0 \xrightarrow{h\upsilon} {}^1S_1 \xrightarrow{ISC} {}^3S_1 \qquad (1.0)$$

$$^3S_1 + D^- \rightarrow {}^1S_0 + (^3D^-)^* \qquad (2.1)$$

$$^3S_1 + D^- \rightarrow {}^1S_0^{\cdot -} + D^{\cdot} \qquad (2.2)$$

$$^3S_1 + RH \longrightarrow R^{\cdot} + Ph - \underset{\displaystyle OH}{\overset{\displaystyle Ph}{\overset{|}{C^{\cdot}}}} - Ph \qquad (3.0)$$

$$2\ Ph - \underset{\displaystyle OH}{\overset{\displaystyle Ph}{\overset{|}{C^{\cdot}}}} - Ph \longrightarrow Ph - \underset{\displaystyle OH}{\overset{\displaystyle Ph}{\overset{|}{C}}} - \underset{\displaystyle OH}{\overset{\displaystyle Ph}{\overset{|}{C}}} - Ph \qquad (4.0)$$

Ketyl radical

$$D^- + RH \rightarrow DH + R^- \qquad (5.0)$$

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$$R^- + H^+ \longrightarrow RH \quad (6.0)$$

$$D^- + H^+ \longrightarrow DH \quad (7.0)$$

$$Ph - \underset{\underset{OH}{|}}{C^{\cdot}} - Ph + \underset{\underset{O}{||}}{D^{\cdot}} \longrightarrow Ph - \underset{\underset{O}{||}}{C} - Ph + DH \quad (8.0)$$

$$Ph - \underset{\underset{OH}{|}}{C^{\cdot}} - Ph + \underset{\underset{O}{||}}{R^{\cdot}} \longrightarrow Ph - \underset{\underset{O}{||}}{C} - Ph + RH \quad (9.0)$$

where S, D and RH represents sensitizer benzophenone, dye eosin and the solvent ethanol C_2H_5OH), respectively

The sensitizer benzophenone is excited to its singlet state ($^1S_1$) from its ground ($^1S_0$), which on inter system crossing yields triplet state of benzophenone ($^3S_1$). This triplet state reacts with anaioncdye (D^-) in two manners.

i) Transferring the energy to the dye molecule to excite it into its triplet state ($^3D^-$)* and reverting the sensitizer to its singlet ground state ($^1S_0$) and

ii) Abstraction of an electron from dye molecule by the triplet state of sensitizer to give the radical ($D^{\cdot}$) and anionic radical of singlet ground state of the sensitizer ($^1S_0^{\cdot -}$)

The triplet excited state of sensitizer can easily abstract hydrogen radical from the hydrogen donor solvent like ethanol (RH), to generate a pair of Ketylradical ($Ph - \underset{\underset{OH}{|}}{C^{\cdot}} - Ph$) and ethoxy radical ($R^{\cdot}$).

This Ketyl radical may dimerize to give benzpinacol , however, it was detected by spot test only, and that too after long exposure.

The anionic dye eosin (D^-) may abstract a hydrogen from ethanol (RH) and in turn the dye is reduced to its leuco form (DH).

The ethoxy ion reacts with proton reverting back to the solvent molecule.

Dye molecule may also accept protons for self reduction. The ethoxy radical

($R^{\bullet}$) and dye radical ($D^{\bullet}$) will complete the reduction by abstracting a hydrogen from Ketyl radical of benzophenon ; Thus regenerating the solvent ethanol and sensitizer benzophenon.

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