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PHOTOCHEMICAL BLEACHING OF BASIC FUCHSIN BY BENZOPHENONE

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ABSTRACT

Photochemical bleaching of Basic fuchsinwas monitored spectrophotometrically in presence of benzophenone.The effects of various parameters like pH, concentration of dye, concentration of benzophenone etc. has been observed. The photochemical bleaching of dye follow pseudo-first order kinetics. A tentative mechanism forphotochemical bleaching of Basic fuchsin has been proposed.

Key Words: Photochemical bleaching, Basic fuchsin, Benzophenone

INTRODUCTION

Dyes are quite useful to humanity but are toxic and carcinogenic in nature also. An attempt is made to photochemical bleaching of these dyes by using benzophenone as a photosensitizer.Energy transfer plays a key role in photochemical bleaching, where the molecule absorbs light energy corresponding to a convenient wave length. Acridine dyes can be photoreduced with allyl thiourea, while EDTA was used for photoreduction of methylene blue by Millich and Oster1. Jockuschet al2. reported the photoreduction of organic dyes in ketone amine system,whereasJain et al3. used malachite green for photoreduction of sodium and potassium carbonate. Ametaet al4. reported the photoreduction of methylene blue by aqueous bicarbonate. Gupta et al5 also investigated the photocatalytic degradation of a mixture of two dyes using untreated TiO2 and silver ion doped TiO2 under UV radiations. Triplet sensitized photobleachingof crystal violet was investigated by Naguib et al6.,while Ohtani et al7. investigated the visible light induced reduction of methyl viologen in poly vinyl alcohol containing N-methyl-2–pyrrolidones. A detailed survey of literature reveals that little attention has been paid to the use of ultra violet light for photochemical bleaching of Basic Fuchsin by benzophenone as a photosensitizer. Therefore the present work was undertaken.

.EXPERIMENTAL

A stock solution of basic fuchsin was prepared in ethanol. The photochemical bleaching of dye was observed by taking dye solution and 0.15g benzophenone was added to it. A multi-lamp reactor was used for irradiation purpose, which contains eight ultra- violet lamps with wave length 530 nm. A quartz tube was used as reaction vessel which is, immersed in the center of these lamps. The progress of reaction was observed by taking optical density at regular intervals using spectrophotometer [JASCO Model ,7800].

RESULT AND DISCUSSION

A plot of log O.D. (Optical density) v/s time was linear but in two stages, the second stage being faster. Hence, both the stages of this reaction follow pseudo-first order kinetics.

Rate constant k = 2.303 x slope

A TYPICAL RUN

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

Table 1: A Typical Run

[Basic Fuchsin] = 5.00 x 10^{-5} M pH=8.0

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

Time (Seconds)	**O.D. (Optical Density)**	**1+ log (O.D.)**
0	1.596	1.20
30	1.458	1.16
60	1.307	1.11

90	1.098	1.04
120	0.845	0.92
150	0.585	0.76
180	0.339	0.53
210	0.211	0.32
240	0.131	0.11
270	0.109	0.03

k_1 = 3.80 x 10^{-3} sec^{-1}

k_2= 1.53 x $10^{-2}$$sec^{-1}$

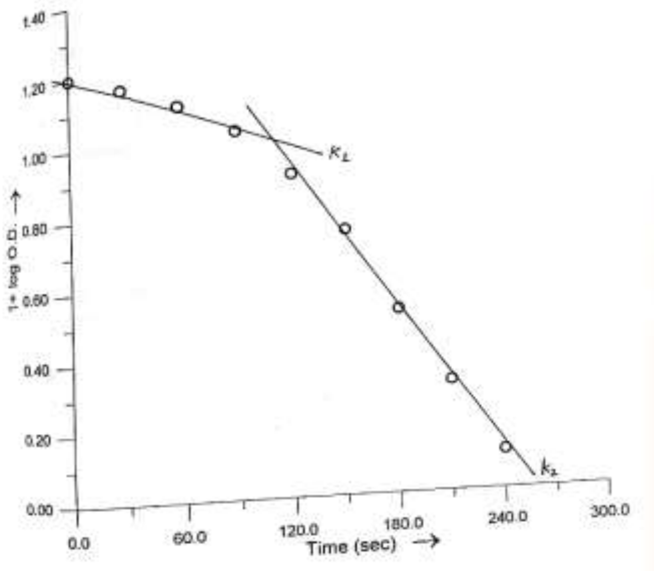

FIGURE1 : A TYPICAL RUN

EFFECT OF pH

The pH of the medium is expected to affect the rate of photochemical bleaching of Basic Fuchsin was investigated in thepH range 5.5 to 10.0. The experimental findings are reported in Table **2**and graphically presented in figure **2**.

TABLE 2: EFFECT OF pH

[Basic Fuchsin] = 5.00 x 10^{-5} M [Benzophenone] = 1.65 x 10^{-2} M

pH	**Rate Constant (sec^{-1})**	
	k_1 x 10^3	**k_2x 10^2**
5.5	2.62	0.36
6.0	2.84	0.42
6.5	2.94	0.64

7.0	3.12	0.83
7.5	3.54	0.93
8.0	3.8	1.53
8.5	3.42	0.87
9.0	2.75	0.71
9.5	2.56	0.60
10.0	2.42	0.50

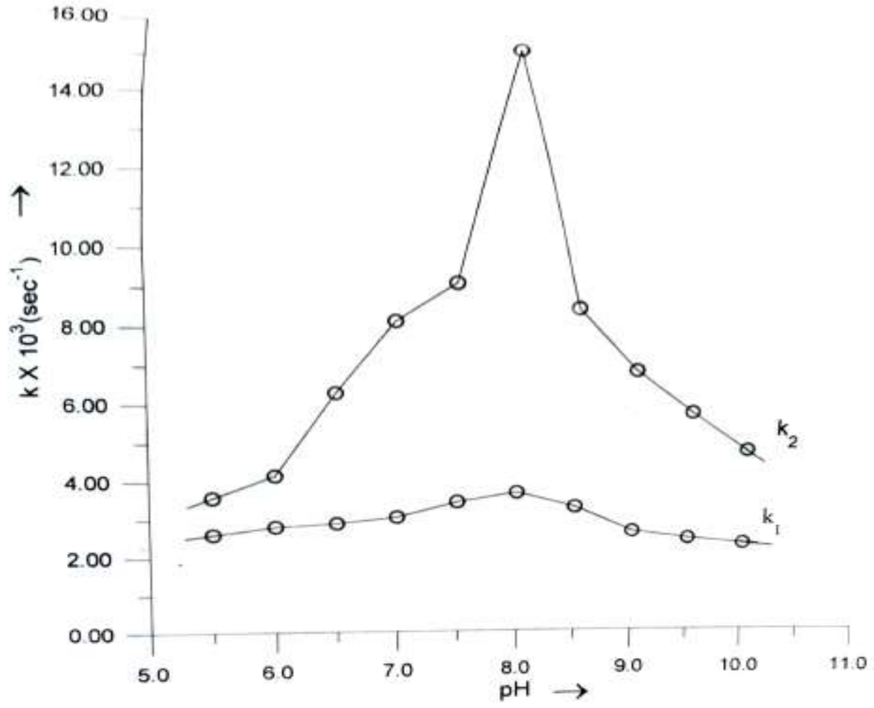

FIGURE 2: EFFECT OF pH

EFFECT OF BASIC FUCHSIN CONCENTRATION

Effect of variation of dye concentration was also studied by taking different concentration of basic fuchsin keeping all other factors constant. The experimental findings are reported in Table **3** and graphically presented in figure **3**.

TABLE 3:EFFECT OF BASIC FUCHSIN CONCENTRATION

[Benzophenone] = 1.65 x 10^{-2} M pH = 8.0

[Basic Fuchsin] x 10^5M	**Rate Constant (sec^{-1})**	
	k_1 x 10^3	**k_2x 10^2**
2.50	2.52	0.48
2.85	2.94	0.51

3.33	3.46	0.55
4.00	3.62	0.60
5.00	3.80	1.53
6.66	3.00	0.69

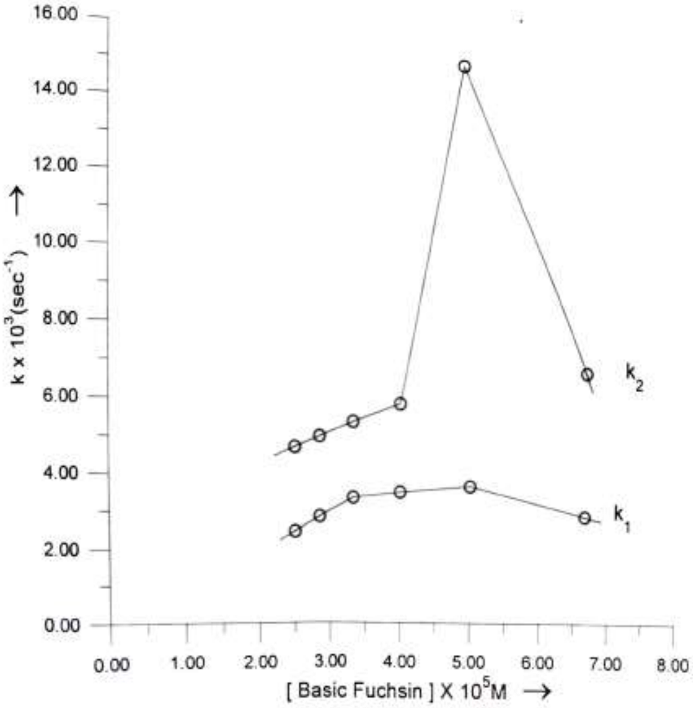

FIGURE 3: EFFECT OF EOSINE CONCENTRATION

EFFECT OF BENZOPHENONE CONCENTRATION

The concentration of benzophenone may also affect the rate of bleaching and therefore, different amounts of benzophenone were used. The results are reported in the table 4. The experimental findings are reported in Table**4**and graphically presented in figure **4**.

TABLE 4:EFFECT OF BENZOPHENONE CONCENTRATION

[Basic Fuchsin] = 5.00 x 10^{-5} M pH =8.0

[Benzophenone] x 10^2 M	**Rate Constant (sec^{-1})**	
	k_1 x 10^3	**k_2 x 10^3**
0.55	1.20	1.91
1.1	6.03	1.97
1.65	3.80	1.53
2.2	3.64	1.19

2.75	3.40	0.89
3.3	3.29	0.76

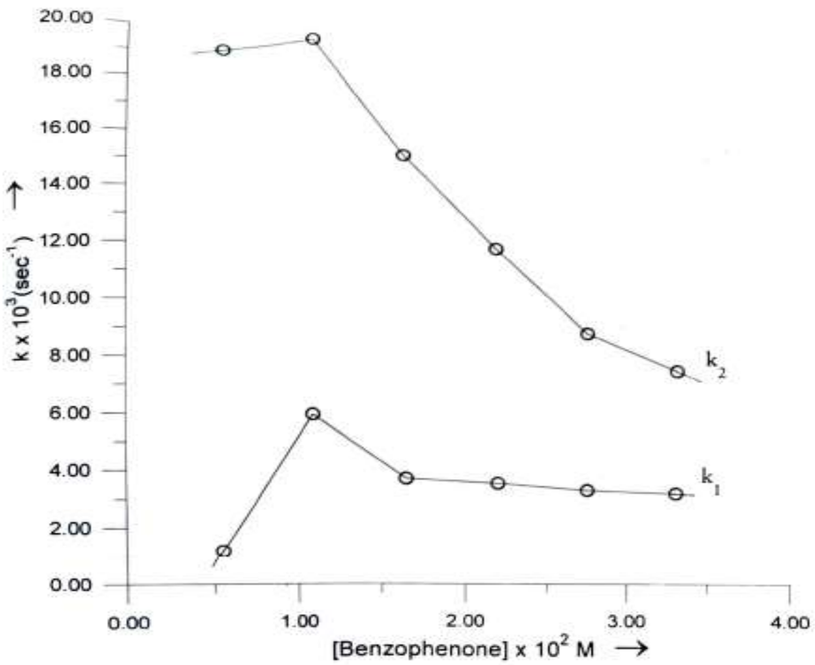

FIGURE 4: EFFECT OF BENZOPHENONE CONCENTRATION

MECHANISM

On the basis of these observations, a tentative mechanism has been proposed for photochemical bleachingofBasicFuchsin.

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

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

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

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

$$R^{\cdot} + D^+ \rightarrow R^+ + D^{\cdot} \qquad (4.0)$$

$$2\ Ph - \overset{\cdot}{C}(OH) - Ph \longrightarrow Ph - C(Ph)(OH) - C(Ph)(OH) - Ph \qquad (5.0)$$

Ketyl radical

$$Ph - \overset{\bullet}{\underset{OH}{C}} - Ph + D^{+} \longrightarrow Ph - \overset{+}{\underset{OH}{C}} - Ph + D^{\bullet} \quad (6.0)$$

$$Ph - \overset{\bullet}{\underset{OH}{C}} - Ph + D^{\bullet} \longrightarrow Ph - \underset{O}{\overset{\|}{C}} - Ph + DH \quad (7.0)$$

where S, D and RH represents sensitizer benzophenone, dye Basic Fuchsin and the solvent ethanol), respectively. The sensitizer benzophenone is excited to its singlet state ($^1S_1$) from its ground state ($^1S_0$), which on intersystem crossing yields triplet state of benzophenone ($^3S_1$). This triplet state may react with cationic dye (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 triplet state of sensitizer by the dye molecule to give the malachite green radical ($D^{\bullet}$) and cationic 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 solvents like ethanol (RH), to generate a pair of ketyl and ethoxy radical. Thisethoxy radical ($R^{\bullet}$) can donate its electron to the cationic dye to convert the dye into radical form ($D^{\bullet}$).Now, this ketyl radical may dimerize to give benzpinacol, however, it was detected by spot test only and that too after long exposure. On the other hand, the ketyl radical can convert cationic dye (D^+) into dye radical ($D^{\bullet}$). This dye radical ultimately abstract hydrogen from ketyl radical to oxidise it into original benzophenone, the sensitizer. In this process, the dye being reduce to DH.

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