



# **PHOTOCHEMICAL REACTION BETWEEN ROSE BENGAL AND BENZOPHENONE**

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## **ABSTRACT**

Photochemical reaction between rose bengal and benzophenone was monitored spectrophotometrically in the presence of benzophenone. The effect of various parameters like pH, Concentration of dye, concentration of benzophenone etc. has been observed. The photochemical reaction of dye follows pseudo-first order kinetics. A tentative mechanism for photochemical reaction between rose bengal and benzophenone has been proposed.

**Key Words:** Photochemical reaction, Rose bengal, Benzophenone.

## **INTRODUCTION**

Nature, now a days, is suffering from a serious problem of environmental pollution. A large amount of chemicals are produced in different industries, some of which are toxic to human life also. These pollutants are sometimes released into the environment either accidentally or in the form of industrial effluent. Coloured solution containing dyes, forms a part of industrial effluents from dyeing, textile and printing industries, which may cause serious global problems like skin cancer. Some processes have been extensively investigated to convert organic non-polar impurities into polar materials, which can be easily removed by ion exchange resin. Photochemistry of textile azo dyes with spectral characterization of excited state was studied by Vinodgopal and Karat; whereas Hatsui and Takeshita et al.<sup>2</sup> reported methylene blue sensitized photoreduction of quadricyclane. Sharma et al.<sup>3</sup> and Gulati et al.<sup>4</sup> used zinc oxide particulate system as a photocatalyst for the photobleaching of toulidine and rose bengal, respectively.

Photochemical reaction involving nitrosyl pentacyanoferrate (II) system was studied by Salvi et al.<sup>5</sup> Zhao et al.<sup>6</sup> observed the photochemical degradation of dimethylphthalate by Fenton reagent, whereas Yadav and Bhardwaj<sup>7</sup> reported use of PbS as semiconductor in degradation of rose bengal from effluents. Solar photocatalytic degradation of azo-dye, acid orange 24, by photo-Fenton process was investigated by Chacon et al.<sup>8</sup>

A detailed survey of literature reveals that little attention has been paid to the use of ultra-violet light for photochemical reaction of rose bengal. Benzophenone was selected as a photosensitizer, to carry out this reaction in a desired direction. Therefore, the present work was undertaken.

## EXPERIMENTAL

A stock solution of rose bengal was prepared in ethanol. The photochemical reaction between dye and benzophenone was observed by taking dye solution and 0.15 g was benzophenone was added to it. A multi-lamp reactor was used for irradiation purpose, which contains eight ultra-violet lamps with wave length 366 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].

## RESULTS AND DISCUSSION

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

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

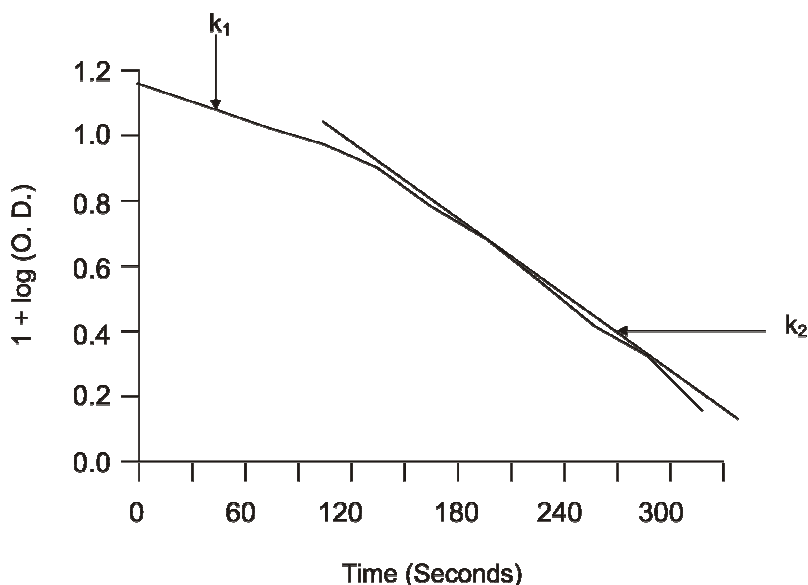
**Table 1. A typical run**

[Rose bengal ] = $4.00 \times 10^{-5}$ M		pH = 8.0
[Benzophenone] = $1.65 \times 10^{-2}$ M		
Time (Seconds)	O.D. ( Optical Density)	1+ log (O. D.)
0	1.380	1.13
30	1.226	1.08
60	1.083	1.03
90	0.918	0.96
120	0.818	0.91

Cont...

Time (Seconds)	O.D. ( Optical Density)	1+ log (O. D.)
150	0.609	0.78
180	0.495	0.69
210	0.371	0.56
240	0.263	0.41
270	0.213	0.32
300	0.154	0.18

$k_1 = 3.90 \times 10^{-3} \text{ (sec}^{-1}\text{)}; k_2 = 9.11 \times 10^{-3} \text{ (sec}^{-1}\text{)}$



**Figure 1: A typical run**

### Effect of pH

The pH of the solution is expected to affect the photochemical reaction of rose bengal, and hence, photochemical reaction of rose bengal was investigated at different pH values.

**Table 2: Effect of pH**[Rose bengal ] =  $4.00 \times 10^{-5}$  M[Benzophenone] =  $1.65 \times 10^{-2}$  M

pH	Rate constant ( sec <sup>-1</sup> )	
	k <sub>1</sub> x 10 <sup>3</sup>	k <sub>2</sub> x 10 <sup>3</sup>
6.5	0.80	5.20
7.0	1.25	6.12
7.5	2.04	6.94
8.0	3.90	9.11
8.5	1.11	5.72
9.0	1.02	5.65
9.5	0.46	5.54
10.0	0.38	5.40

The rate of photobleaching of rose bengal increases on increasing pH of the reaction medium. Now there are two competitive reactions i.e,[i] The abstraction of hydrogen radical form OH group of ketyl radical, and [ii] the abstraction of hydrogen radical form OH<sup>-</sup> ions.

The reaction [ii] is more preferable than the [i] because of the higher concentration of OH<sup>-</sup> ions. On increasing pH, an enhancement in the reaction rate has been observed. On increasing pH further above pH = 8.0, the abundance of OH<sup>-</sup> ions will not permit the rose bengal molecules (anionic dye) to pull the hydrogen radical due to electrostatic repulsion. As a consequence, the rate of photobleaching of rose bengal is retarded in higher alkaline range.

### Effect of rose bengal concentration

Effect of variation of dye concentration was also studied by taking different concentrations of rose bengal keeping all other factors constant. The results are summarized in Table 3.

**Table 3: Effect of rose bengal concentration**[Benzophenone] =  $1.65 \times 10^{-2}$  M ; pH = 8.0

[Rose bengal] x $10^5$ M	Rate constant ( sec <sup>-1</sup> )	
	$k_1 \times 10^3$	$k_2 \times 10^3$
2.50	3.27	5.00
2.85	3.58	5.21
3.33	3.74	6.04
4.00	3.90	9.11
5.00	1.17	6.34
6.66	0.62	4.02

It has been observed that the value of rate constant increases with increasing dye concentration but the rate starts decreasing above concentration  $4.00 \times 10^{-5}$  M. As the concentration of dye was increased, there was a corresponding increase in the number of dye molecule for participation in this photochemical redox reaction and thus, an increase in the rate of photobleaching of dye has been observed. After a certain limit i.e., [rose bengal] =  $4.0 \times 10^{-5}$  M, a decrease in the rate of the reaction was observed with the increase in the concentration of the dye solution. It may be explained on the basis that 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 in a limited time domain or in other words, one can say that the dye itself acts as a filter. Hence, a decrease in the rate of the reaction has been observed.

### 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.

It has been observed that photoreduction of dye molecules in the presence of benzophenone as sensitizer, depends on the concentration of benzophenone. Initially on increasing the concentration of benzophenone, the rate of photobleaching increases but after a certain value of concentration, the rate of photobleaching starts decreasing, on further increasing the concentration of benzophenone.

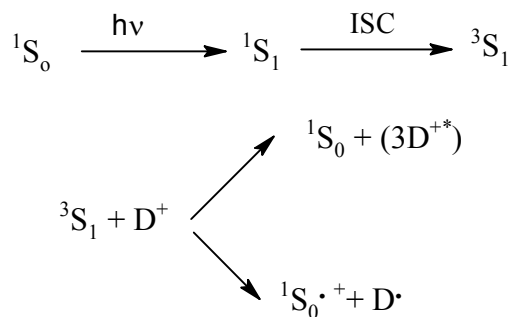
**Table 4. Effect of benzophenone concentration**[Rose bengal ] =  $4.00 \times 10^{-5}$  M ; pH = 8.0

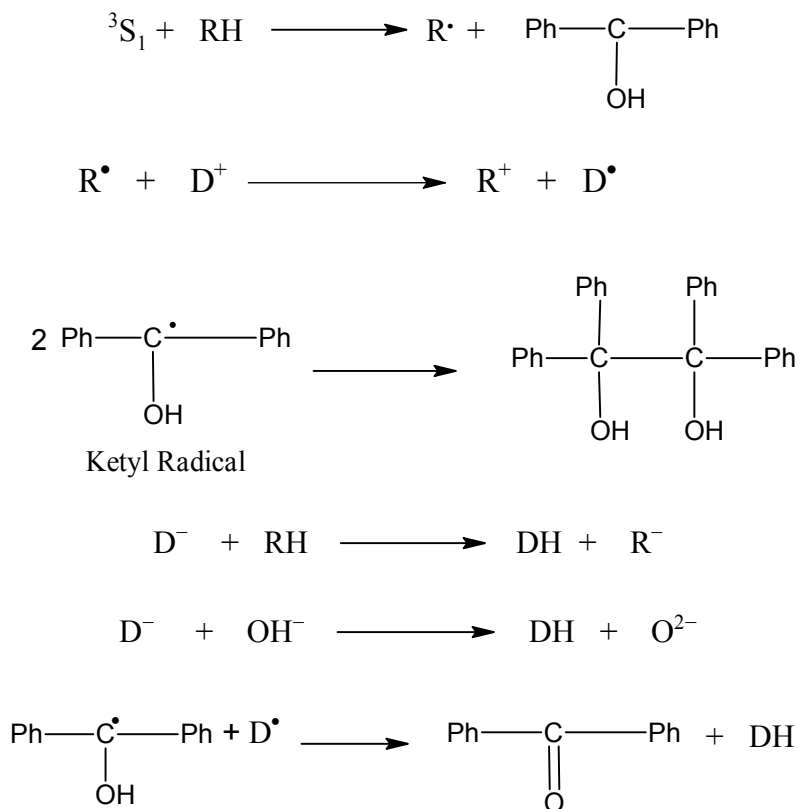
[Benzophenone] x $10^2$ M	Rate constant ( $\text{sec}^{-1}$ )	
	$k_1 \times 10^3$	$k_2 \times 10^3$
0.55	1.65	0.76
1.10	4.48	1.91
1.65	3.90	0.91
2.20	3.31	0.65
2.75	3.02	0.63
3.30	2.34	0.59

This may be explained on the basis that when the concentration of benzophenone is low, the movement of sensitizer molecules are relatively free, so that these can easily react with the dye molecules in their excited state. It leads to an increase in the rate of photoreduction of dye molecules. But when the concentration of sensitizer molecule was increased further, then their 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 photochemical bleaching of rose bengal was observed.

### MECHANISM

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





where S, D and RH represents sensitizer benzophenone, dye rose bengal and the solvent ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), 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 reacts 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 dye molecule by the triplet state of sensitizer to give the rose bengal radical ( $D^\bullet$ ) and anionic radical of singlet ground state of the sensitizer ( ${}^1S_0$ ).

The triplet excited state of sensitizer can easily abstract hydrogen radical from the hydrogen donor solvent like ethanol (RH), to generate a pair of ketyl and ethoxy radical

(R<sup>•</sup>). 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 (D<sup>-</sup>) abstract a hydrogen from ethanol (RH) or it may abstract H from OH<sup>-</sup> ions and in turn, the dye is reduced to its leuco form (DH). The ethoxy radical (R<sup>•</sup>) will complete the reduction by abstracting a hydrogen from ketyl radical of benzophenone. Thus, regenerating the solvent ethanol and sensitizer benzophenone.

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