



PHOTOREDUCTION OF MALACHITE GREEN USING BENZOPHENONE

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ABSTRACT

Photoreduction of malachite green was monitored spectrophotometrically in presence of benzophenone. The effects of various parameters like pH, concentration of dye, concentration of benzophenone etc. has been observed. The photoreduction of dye follow pseudo-first order kinetics. A tentative mechanism for photoreduction of malachite green has been proposed.

Key words : Photoreduction, Malachite green, Benzophenone

INTRODUCTION

Dyes are quite useful to humanity but are toxic and carcinogenic in nature also. An attempt is made to photoreduce these dyes by using benzophenone as a photosensitizer. Energy transfer plays a key role in photoreduction, 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. Jockusch et al.² reported the photoreduction of organic dyes in ketone amine system, whereas Jain et al³. used malachite green for photoreduction by sodium and potassium carbonate. Ameta et al⁴. reported the photoreduction of methylene blue by aqueous bicarbonate. Gupta et al.⁵ also investigated the photocatalytic degradation of a mixture of two dyes using untreated TiO₂ and silver ion doped TiO₂ under UV radiations. Triplet sensitized photobleaching of crystal violet was investigated by Naguib et al⁶., while Ohtani et al⁷. investigated the visible light induced reduction of methyl viologen in polyvinyl alcohol containing N-methyl-2-pyrrolidones. A detailed survey of literature reveals that no attention has been paid to the use of ultra violet light for photoreduction of malachite green by benzophenone as a photosensitizer. Therefore, the present work was undertaken.

EXPERIMENTAL

A stock solution of malachite green was prepared in ethanol. The photoreduction of dye was observed by taking dye solution and 0.15 g 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.

Rate constant was calculated using the relation- $k = 2.303 \cdot x \text{ slope}$

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

Table 1: A typical run

[Malachite green] = 4.00×10^{-5} M

pH = 5.0

[Benzophenone] = 1.65×10^{-2} M

Time (sec.)	O.D. (Optical Density)	1+ log (O.D.)
0	1.114	1.046
30	1.052	1.022
60	0.822	0.914
90	0.589	0.770
120	0.430	0.633
150	0.282	0.450
180	0.162	0.209
210	0.112	0.049

$k_1 = 6.14 \times 10^{-3} \text{ sec}^{-1}$; $k_2 = 1.42 \times 10^{-3} \text{ sec}^{-1}$

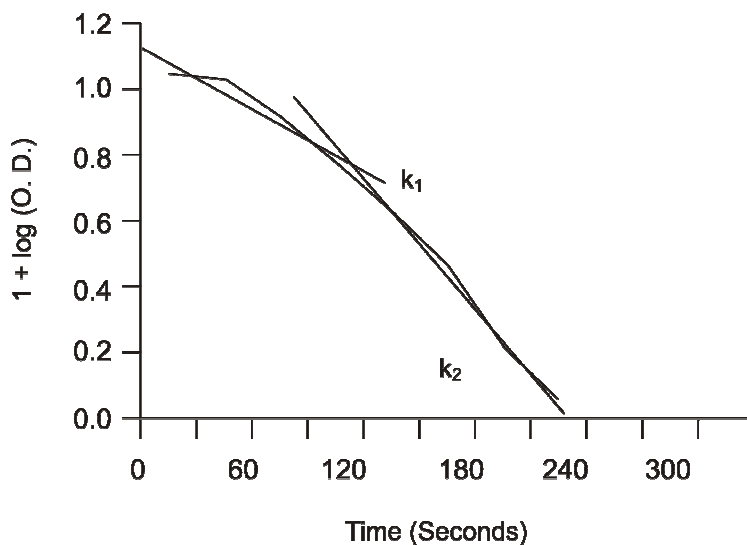


Fig. 1: A typical run

Effect of pH

The pH of the medium is expected to affect the rate of photoreduction of malachite green, and hence, photoreduction of malachite green was investigated at different pH values.

Table 2: Effect of pH

[Malachite green] = 4.00×10^{-5} M

[Benzophenone] = 1.65×10^{-2} M

pH	Rate constant (sec^{-1})	
	$k_1 \times 10^3$	$k_2 \times 10^3$
3.5	3.92	1.09
4.0	4.74	1.15
4.5	5.54	1.20
5.0	6.14	1.42
5.5	4.12	1.18
6.0	2.86	0.95

The effect of the change in pH on the rate of reaction may be explained on the basis that as the pH was increased above 5.0, the dye molecules may not remain in its positively charged state and, therefore, a corresponding decrease in the rate of reaction has been observed. On the other hand, again a decrease in the rate of the reaction has been observed on decreasing pH of the reaction. This may be attributed to the presence of more protons in the solution, which may interfere in the abstraction of hydrogen from the ketyl radical of the benzophenone by the dye molecules. Thus, resulting into a corresponding decrease in the rate of the photoreduction of malachite green.

Effect of malachite green concentration

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

Table 3. Effect of malachite green concentration

[Benzophenone] = 1.65×10^{-2} M		pH = 5.0	
[Malachite green] x 10^5 M	Rate constant (sec^{-1})		
	$k_1 \times 10^3$	$k_2 \times 10^3$	
2.50	2.95	0.36	
2.85	4.13	0.51	
3.33	5.78	1.15	
4.00	6.14	1.42	
5.00	2.36	1.21	
6.66	1.53	0.96	

It has been observed that the value of rate constant increases with increasing dye concentration but then the rate starts decreasing above its concentration 4.00×10^{-5} M. As the concentration of dye was increased, there was a corresponding increase in the number of dye molecules 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.,

[Malachite green] = 4.00×10^{-5} M, a decrease in the rate of the reaction was observed with the increase in the concentration of the dye. 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.

Table 4. Effect of benzophenone concentration

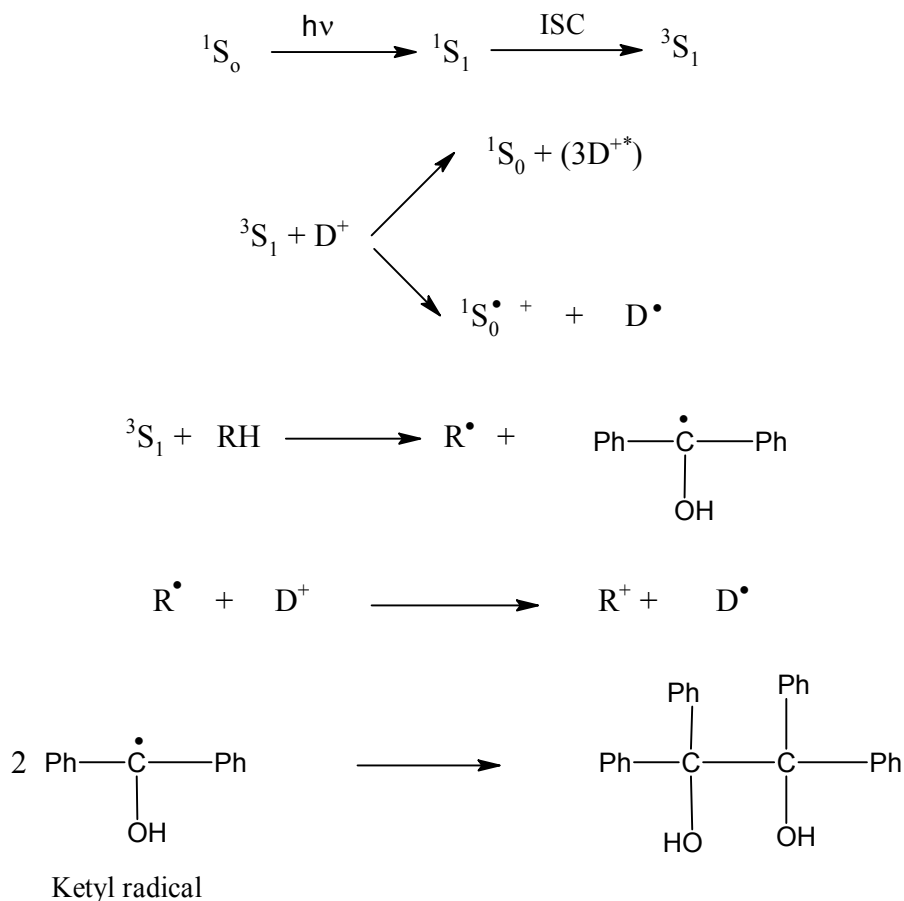
[Malachite green] = 4.00×10^{-5} M		pH = 5.0	
[Benzophenone] x 10^2 M	Rate constant (sec ⁻¹)		
	$k_1 \times 10^3$	$k_2 \times 10^3$	
0.55	2.32	1.82	
1.10	7.61	1.86	
1.65	6.14	1.42	
2.20	4.44	1.36	
2.75	3.62	1.19	
3.30	2.33	1.06	

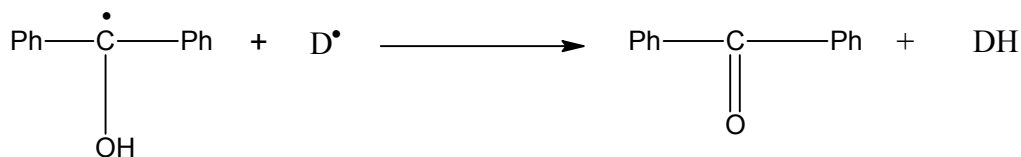
It has been observed that photoreduction of dye molecules in the presence of benzophenone as sensitizer, depends on the concentration of benzophenone. Initially, on increasing the concentration of benzophenone, the rate of photoreduction increases but after a certain value of concentration, the rate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

It leads to an increase in the rate of photoreduction. 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 photoreduction of malachite green was observed.

MECHANISM

On the basis of these observations, a tentative mechanism has been proposed for photoreduction of malachite green.





where S, D and RH represents sensitizer benzophenone, dye malachite green 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 ($^1S_0^{+}$).

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. This ethoxy radical (R) can donate its electron to the cationic dye to convert the dye into radical form (D). 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). This dye radical ultimately abstract hydrogen from ketyl radical to oxidise it into original benzophenone, the sensitizer. In this process, the dye is being reduced to DH.

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