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Photolytic and photosensitised reactions of methylene blue with some cyclic ketones

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Abstract

Photolytic and photosensitised reactions of methylene blue with cyclohexanone and cyclopentanone were studied at 25°C under aerobic and anaerobic conditions using VIS and UV/VIS radiation. Photolytic reactions followed first order kinetics under aerobic and anaerobic conditions. Photosensitised reactions followed zero order kinetics under aerobic conditions with very slow rates. Photosensitised reactions reversed in the dark under anaerobic conditions after photolysis with VIS radiation. These reactions followed first-order kinetics in general. The photosensitised reactions of the dye with pre-irradiated cyclohexanone or cyclopentanone with UV/VIS radiation followed second-order kinetics and the reaction rate increased with increasing irradiation time. Some mechanistic possibilities are suggested. © 1998 Elsevier Science S.A.

Keywords: Photolytic reaction; Photosensitised reaction; Cyclohexanone; Cyclopentanone

1. Introduction

Methylene blue is a basic dye of the thiazine group. It is used as an oxidation–reduction indicator in chemistry and biology [1], as sensitizer in photo-oxygenation [2,3] and as electron exchanger with photogalvanic effect [4]. The photoredox behavior of methylene blue depends on the reaction medium [5].

It was found from the previous work on photosensitised reactions of neutral red with cyclohexanone that leucocarbinol neutral red was formed as a result of the formation of cyclohexanol, and leuconeutral red was formed by hydrogen transfer from the solvent to the dye [7].

The aim of the present work is to study the kinetic behavior of photolytic and photosensitised reactions of methylene blue with both cyclohexanone and cyclopentanone.

2. Experimental

Methylene blue, cyclohexanone and cyclopentanone were BDH grade. The solvents cyclohexanone and cyclopentanone were distilled under nitrogen before use.

About 10^{-4} M dye solution was prepared and left to stabilize for 45 min at room temperature in the dark. Dilutions with the same solvent cyclohexanone or cyclopentanone were carried out to obtain the required initial absorbance in the region 300–700 nm using SHIMADZU (160A-UV) UV–VIS spectrophotometer. Reaction kinetics were studied by measuring the changes of absorbance with time directly after the termination of irradiation.

The irradiation of samples was carried out by 200-W mercury–xenon lamp (ordered from Ealing electro optics) as the source of UV/VIS radiation. A 300-W xenon arc lamp type LX 300 F (ordered from ILC Technology was used as a source of VIS radiation, Ealing band pass interference filter, catalogue No. 35-4019) of 660 nm wave length center was used to ensure having radiation band in the area of dye absorbance. The filter was placed between the sample and the lamp. The quartz cell carriage was mounted on an optical bench 15 cm from the light source.

To study the reactions under anaerobic conditions, the air was replaced by passing nitrogen gas through the sample cell for 40 min before irradiation.

3. Results

(1) Spectra measurements showed that the absorbance maximum peaks of methylene blue in cyclohexanone and cyclopentanone were at 663.5 and 662.5 nm positions respectively.

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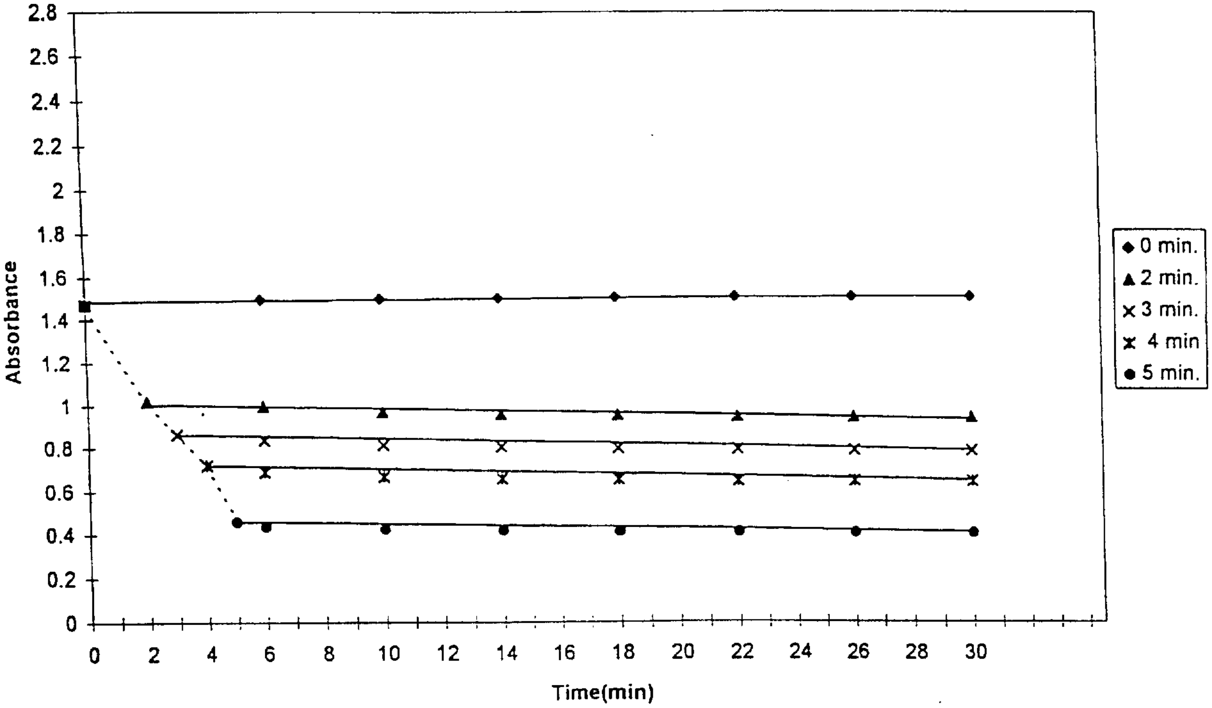


Fig. 1. Photolytic and photosensitized reactions of methylene blue with cyclohexanone under aerobic conditions. Changes in absorbance at 663.5 of methylene blue–cyclohexanone solutions following irradiation for 0, 2, 3, 4 and 5 min with VIS radiation.

(2) Photolytic and photosensitised reactions of the dye were studied by irradiating 2×10^{-5} M of dye solution with VIS radiation for different time intervals under aerobic and anaerobic conditions (Figs. 1–4). It was found that the photolytic reactions followed first-order kinetics with the following rates.

Solvent	Aerobic (min^{-1})	Anaerobic (min^{-1})	Figures
cyclohexanone	0.007	0.276	Figs. 1 and 2
cyclopentanone	0.0047	0.155	Figs. 3 and 4

The first parts of Figs. 1–4 with dotted lines represent the photolytic reactions and the continuous lines represent the photosensitised dark reactions.

The rates of the photolytic reactions under anaerobic conditions were 39.4 and 32.98 times faster than the ones under aerobic conditions in the case of cyclohexanone and cyclopentanone respectively, and the rates in cyclohexanone were 1.78 times faster than in cyclopentanone under anaerobic conditions and 1.49 times faster in the case of aerobic conditions.

(3) Photosensitised reactions reversed in the dark under anaerobic conditions after photolysis with VIS radiation. These reactions followed first-order kinetics in general (Figs. 2 and 4) and the rates increased with increasing irradiation time (Table 1).

(4) Photosensitised reactions in the dark under aerobic conditions after photolysis with VIS radiation followed zero-order kinetics with very slow rates (Figs. 1 and 3).

Table 1

Pre-irradiation time (min)	Rate of photosensitised reaction ($\mathrm{mol}^{-1}\ \mathrm{min}^{-1}$)	
	in cyclohexanone	in cyclopentanone
1	0.00510	0.00130
2	0.00670	0.00195
3	0.00720	0.00250
4	0.01580	0.00460

(5) A 1.5 ml solution of dye–cyclohexanone or dye–cyclopentanone of 3.0 absorbance was added in each case to 1.5 ml solvent pre-irradiated with UV/VIS radiation at different time intervals under aerobic conditions. It was found that the photosensitised dark reactions followed second-order kinetics and the rate increased with increasing time of pre-irradiation as shown by Fig. 5 in the case of cyclohexanone and Fig. 6 in the case of cyclopentanone.

Table 2 shows the time of pre-irradiation and the rates of the photosensitised reactions.

4. Discussion

The dye excitation states and radical formation and the reversibility of the dark reactions is explained by the following reaction sequence:

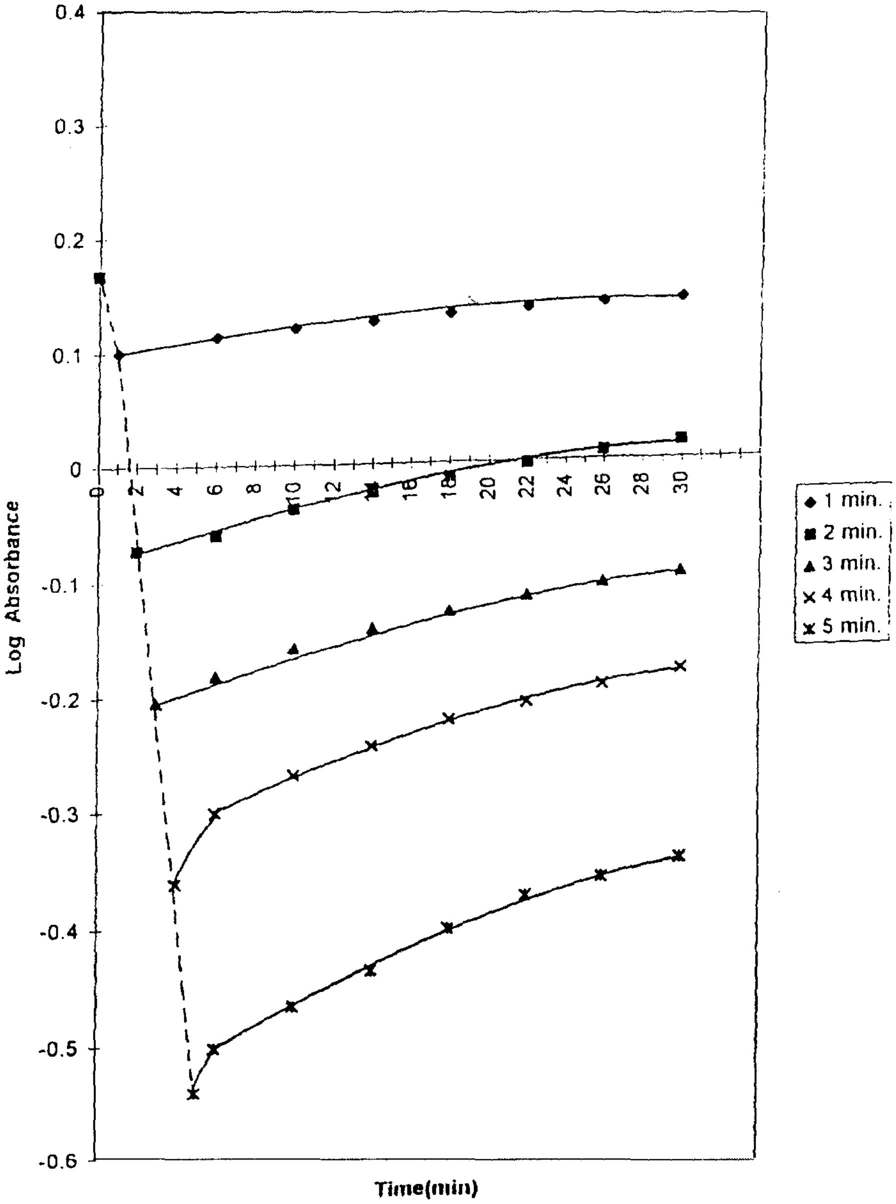
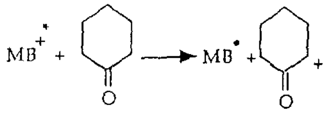


Fig. 2. Photolytic and photosensitized reactions of methylene blue with cyclohexanone under anaerobic conditions. Relation between log absorbance and time for the reverse dark reactions of methylene blue–cyclohexanone solutions following irradiation for 1, 2, 3, 4 and 5 min with VIS radiation.

$$\mathrm{MB^{+}} + h\nu \xrightarrow{\mathrm{VIS}} \mathrm{MB^{+\bullet}} \qquad (1)$$


(2)

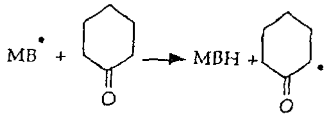

(3)

Table 2

Pre-irradiation time (min)	Rate of photosensitised reaction (mol^{-1} min^{-1})	
	in cyclohexanone	in cyclopentanone
1	0.00510	0.00130
2	0.00670	0.00195
3	0.00720	0.00250
4	0.01580	0.00460

$$\mathrm{MBH + MB^{+} \longrightarrow 2MB^{+} + H^{+} + e} \qquad (4)$$

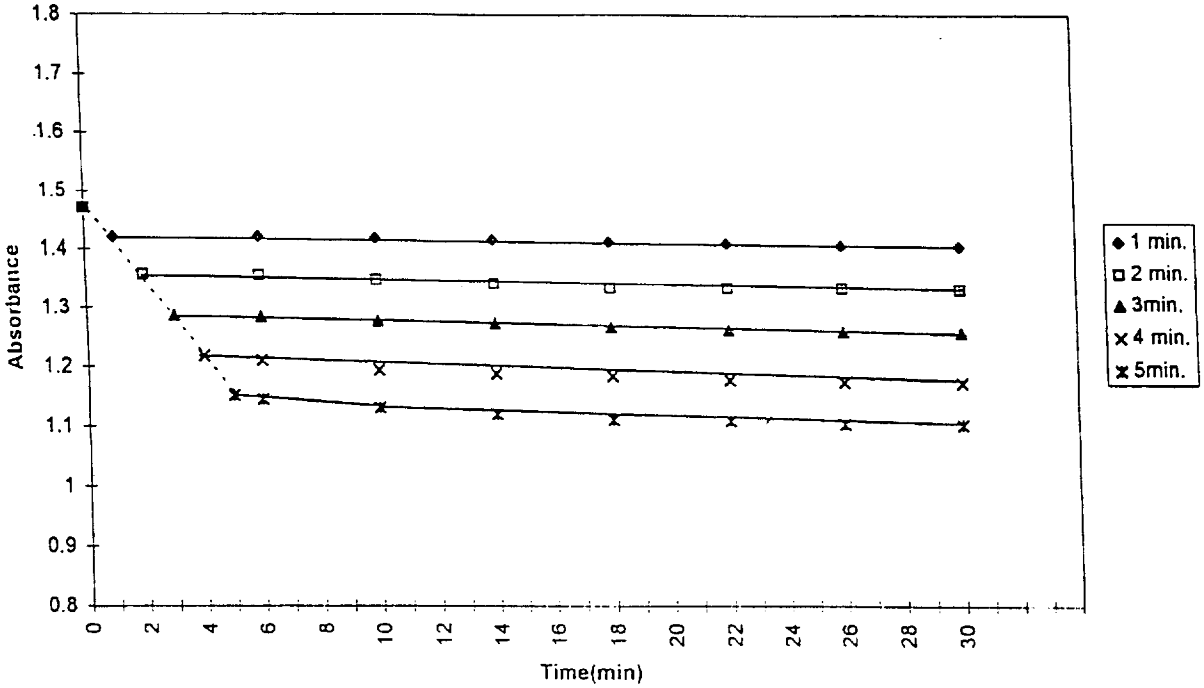
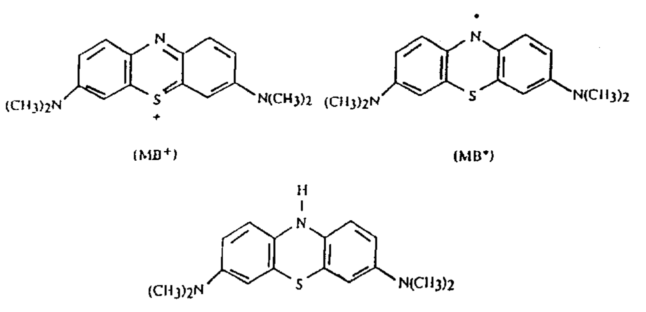


Fig. 3. Photolytic and photosensitized reactions of methylene blue with cyclopentanone under aerobic conditions. Changes in absorbance at 662.5 of methylene blue–cyclopentanone solution following irradiation for 1, 2, 3, 4 and 5 min with VIS radiation.

Methylene blue monomer exists in three oxidation states separated by a single electron. The three structural forms are shown below [6].



The bleaching of methylene blue (MB) alone in water is well-documented and is known to result from electron transfer D–D mechanism [8,9].

$MB^+ + {}^3MB^{+*} \rightarrow MB^{\cdot 2+}$ (half-oxidized dye)

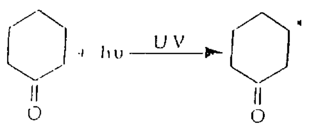
$+ MB$ (half-reduced dye)

$\rightarrow$ Products (leuco dye and demethylated products).

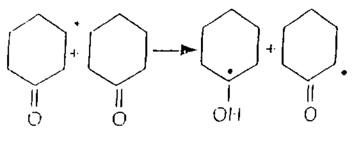
Hay et al. [5] studied the dependence on the reaction medium of the kinetics of three ground state elementary reactions occurring in an iron methylene blue photoredox system by investigating the relaxation of the photostationary state by flash photolysis. The rate constants which have been evaluated include the oxidation of leucomethylene blue (MBH) by methylene blue cation (MB^+) [5]. Eqs. (1)–(4) are in agreement with these findings.

The occurrence of the photosensitised dark reactions following the addition of the dye solution to the pre-irradiated solvent indicate that long-lived species were formed through photolysis of the solvent with UV/VS radiation.

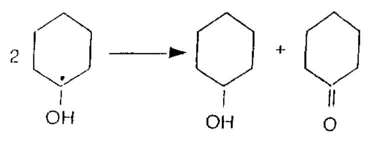
This behavior resembles that of the photosensitised dark reactions of neutral red with pre-irradiated cyclohexanone [10] validating the suggested mechanism as follows:



(5)



(6)



(7)

Cyclohexanol (or cyclopentanol) produced (as in Eq. (7)) then reacts with the dye cation MB^+ after the addition

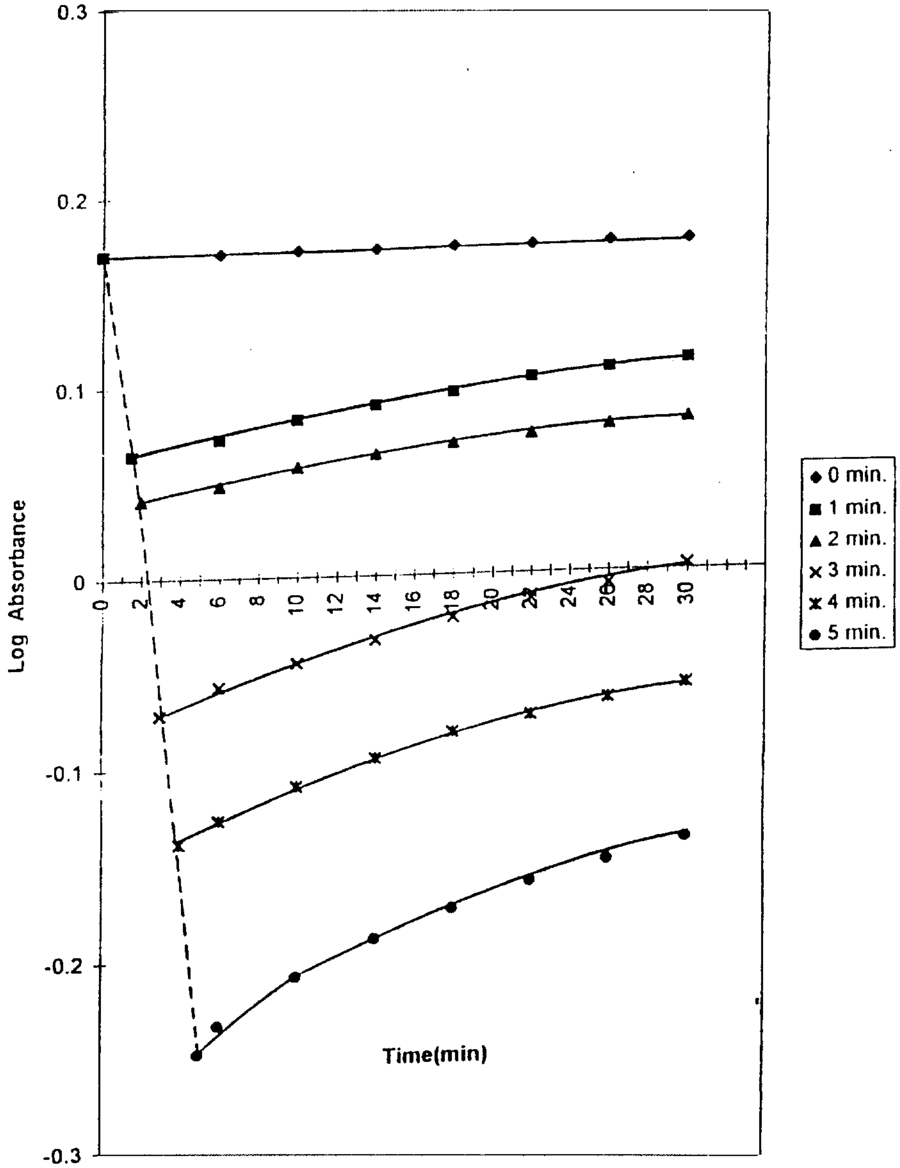
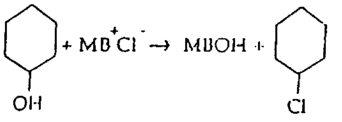


Fig. 4. Photolytic and photosensitized reactions of methylene blue with cyclopentanone under anaerobic conditions. Relation between log absorbance and time for the reverse dark reactions of methylene blue–cyclopentanone solutions following irradiation for 0, 1, 2, 3, 4 and 5 min with VIS radiation.

of the unirradiated dye solution to irradiated solvent as follows [7].



(8)

Spectra measurements showed that λ max at 663.5 nm and λ max at 662.5 nm positions for the dye absorbance in cyclohexanone and cyclopentanone decreased in height as the time of photolytic and photosensitised reactions proceed. When 0.1 N HCl was added after the termination of the reactions, the original peaks increased in height and the original colour reappeared indicating that the dye chromophore did not decompose by the action of radiation.

Photolytic reactions were slower under aerobic conditions possibly due to the reverse reaction as follows:

$$MB^* + O_2 \rightarrow MB^+ + \bar{O}_2 \qquad (9)$$

This mechanism resembles that suggested by Resch et al. [11] who studied the reduction of methylene blue by sulphide in the presence and in the absence of oxygen. The major dynamic feature of the mechanism is competition for MB by

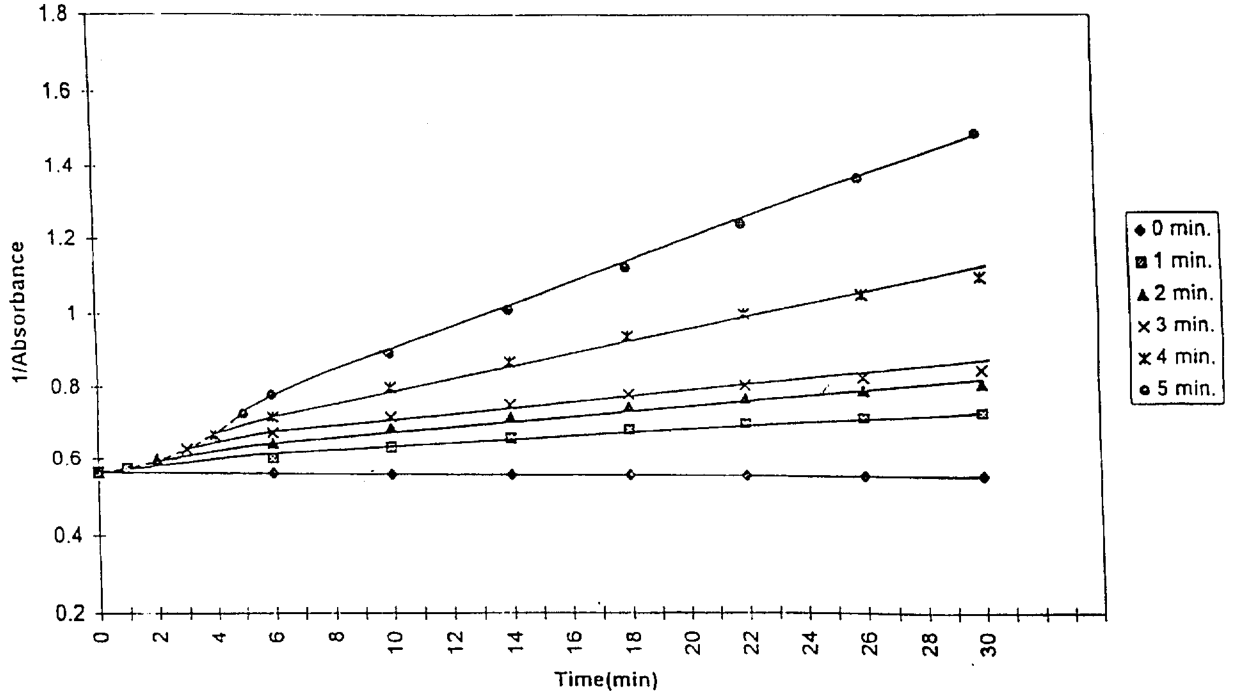


Fig. 5. Photolytic and photosensitized reactions of methylene blue with pre-irradiated cyclohexanone under aerobic conditions. Relation between 1/absorbance and time for methylene blue–cyclohexanone solutions added to irradiated solvent for 0, 1, 2, 3, 4 and 5 min with UV/VIS radiation.

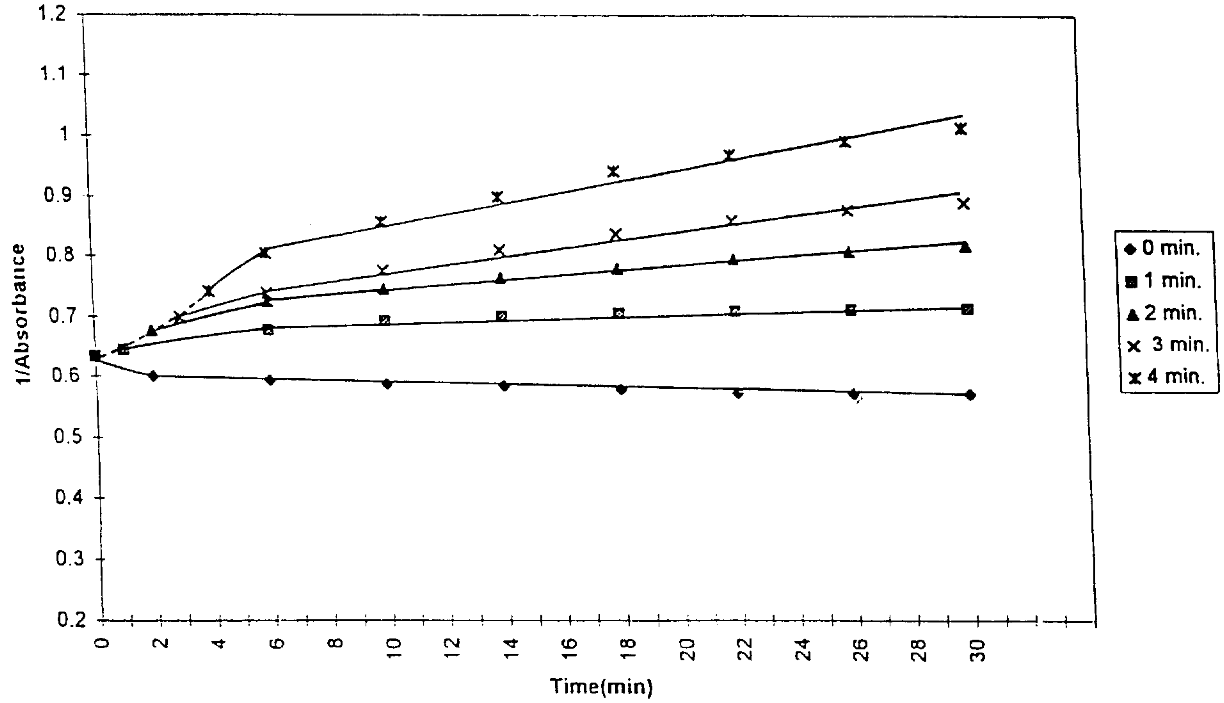


Fig. 6. Photolytic and photosensitized reactions of methylene blue with pre-irradiated cyclopentanone under aerobic conditions. Relation between 1/absorbance and time for methylene blue–cyclopentanone solutions added to irradiated solvent for 0, 1, 2, 3, 4 min with UV/VIS radiation.

oxidizing agents O_2 and H_2O_2 and the reducing agents HS^- and HS.

Photolytic reactions and photosensitised reactions were faster in the case of cyclohexanone due to the higher reactivity of cyclohexanone [12].

5. Conclusions

It was concluded from this work that leucomethylene blue (MBH) was formed as a result of VIS photolysis. A dark reaction occurred after photolysis stopped involving simultaneous oxidation and reduction as in Eq. (4). The rate of this reversed dark reaction increased with increasing irradiation time indicating that the rate-determining step depends on the concentration of MBH produced through photolysis under anaerobic conditions.

The behavior of photosensitised dark reactions following the addition of dye–ketone solution to solvent pre-irradiated with UV/VIS radiation resembles that of the photosensitised reactions of neutral red with pre-irradiated cyclohexanone [10] validating the suggested mechanisms Eqs. (5)–(8). Leucocarbinol methylene blue (MBOH) was produced as a result of the dark reaction between the dye and cyclohexanol or cyclopentanol produced through the action of UV-radiation on the corresponding cyclic ketones.

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