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Photolytic and photosensitised reduction of neutral red under VIS radiation

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Abstract

Spectral measurements for photolytic and photosensitised reactions of neutral red in cyclohexanone and cyclopentanone were studied at 25°C, using only VIS radiation. The photolysed reactions followed first order kinetics. The photosensitised reactions followed second order kinetics. It was concluded that leuconeutral red (NeH) was formed by abstracting a hydrogen atom from the cyclic ketones by the dye radical formed in both cases. The photolytic and photosensitised reactions were faster in cyclohexanone for all cases. Mixed UV/VIS radiation was used for the purpose of comparison. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Neutral red; Cyclohexanone; Cyclopentanone; Photolysed reactions; Photosensitised reactions

1. Introduction

Neutral red is a dye of the azine structure which has been used as both an acid base indicator and biological stain [1]. It was deduced from previous studies [2] that photosensitised reaction occurred following the addition of pre-irradiated cyclohexanone (with UV/VIS radiation) to nonirradiated dye solutions in cyclohexanone, due to the following:

1. Long-lived species were formed through photolysis of cyclohexanone before the addition of the dye solution. This species appeared to be the cyclohexanol formed as a result of UV absorption by cyclohexanone [3–5]. Cyclohexanol reacted with the cation to form leucocarbinol neutral red (NeOH) [3–5].
2. Electron transfer occurred from cyclohexanone to the excited dye cation by VIS radiation to form the dye radical. The dye radical abstracted hydrogen from cyclohexanone to form leuconeutral red (NeH) under anaerobic conditions [5].

In the present work only VIS radiation is used and UV radiation was excluded in order to validate the mechanism and to further investigate the kinetics of the reactions under VIS radiation only. Mixed UV/VIS was also used for comparison.

2. Experimental

Neutral red was BDH grade; cyclohexanone and cyclopentanone were supplied by Aldrich, and 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 were carried out to obtain required initial absorbance in the region 300–800 nm using Shumatzo (160A-UV) UV–VIS spectrophotometer.

Reaction kinetics were studied by measuring the changes of absorbance with time directly after termination of irradiation.

The irradiation of samples with VIS radiation was carried out by 300 W xenon arc lamp type LX 300F (ordered from ILC Technology). Quartz cells carriage was mounted on an optical bench 15 cm from the light source. Eealing edge interference filter (catalogue No. 35-6865, 70% transmission) was used to insure having visible radiation only and exclude any UV radiation to pass through. The filter was placed between the sample and the lamp.

The irradiation with UV/VIS radiation was carried out by osram ME/D box type, 250 W medium pressure mercury lamp fitted with a quartz window.

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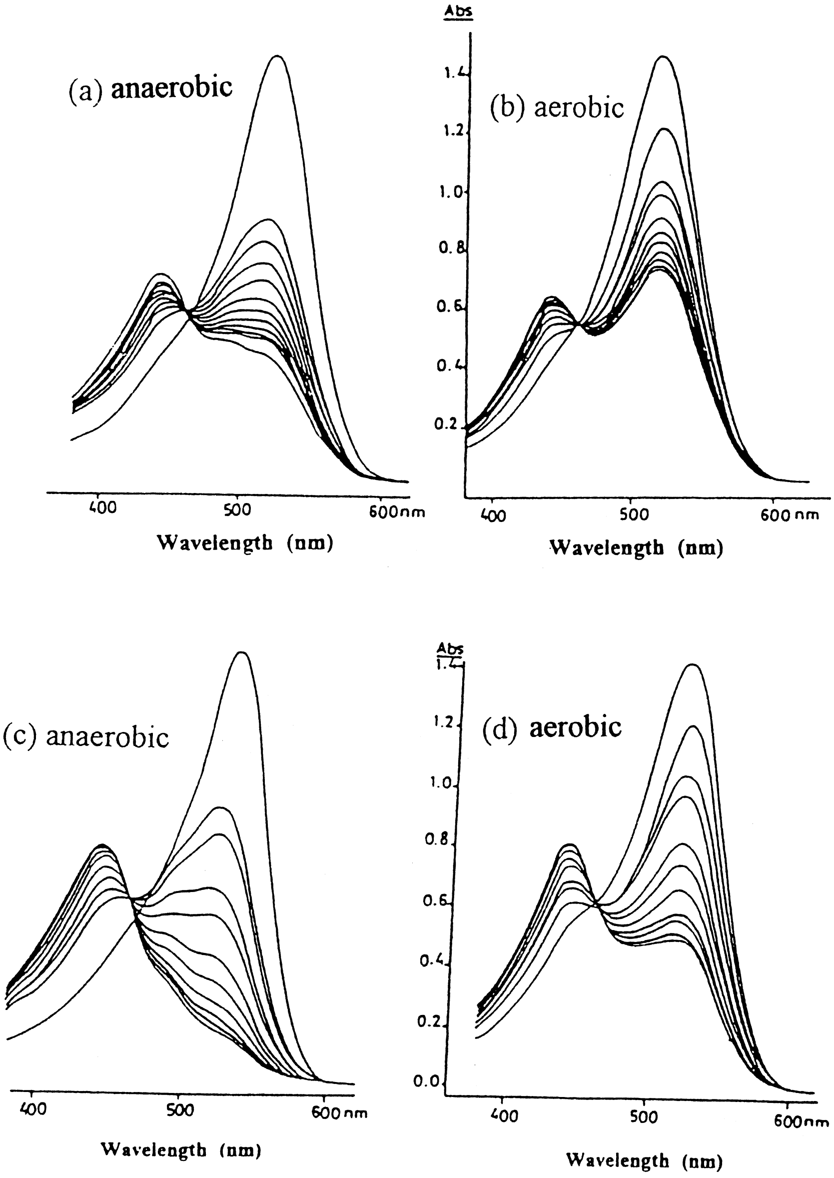


Fig. 1. Photosensitised reactions of neutral red after 4 min irradiation with UV/VIS. (a) and (b) in cyclopentanone, (c) and (d) in cyclohexanone.

Air replacement by nitrogen was carried out by passing nitrogen gas through sample cell for 40 min.

3. Results

Spectral measurements for repetitive scans after 4 min irradiation of 2×10^{-5} M dye solution with UV/VIS radiation under aerobic conditions, showed a decrease in the dye absorbance at λ_{max} 527 nm (in the case of cyclohexanone) or λ_{max} 522 nm (in the case of cyclopentanone) and appearance of a leucocarbinol neutral red peak at λ_{max} 444 nm. Fig. 1(a) and (b) illustrates the cases of cyclohexanone and cyclopentanone, respectively.

The last measurements were repeated under anaerobic conditions by irradiating the sample:

1. With UV/VIS radiation (Fig. 1(c)) in the case of cyclohexanone and (Fig. 1(a)) in the case of cyclopentanone.
2. With VIS radiation only (Fig. 2(a)) in the case of cyclohexanone and (Fig. 2(b)) in the case of cyclopentanone.

These measurements showed the appearance of another peak at λ_{max} 492 nm. This peak was more pronounced in the case of photolysis with VIS radiation (Fig. 2(a) and (b)) than in the case of photolysis with mixed UV/VIS irradiation (Fig. 1(a) and (c)).

The peak at λ_{max} 444 nm is less pronounced in the case of photolysis with VIS than with UV/VIS.

Photolytic and photosensitised reactions were studied by irradiating 1×10^{-5} M of dye solution under aerobic and anaerobic conditions for different time intervals with VIS radiation (Figs. 3–6, where the dotted lines represent the

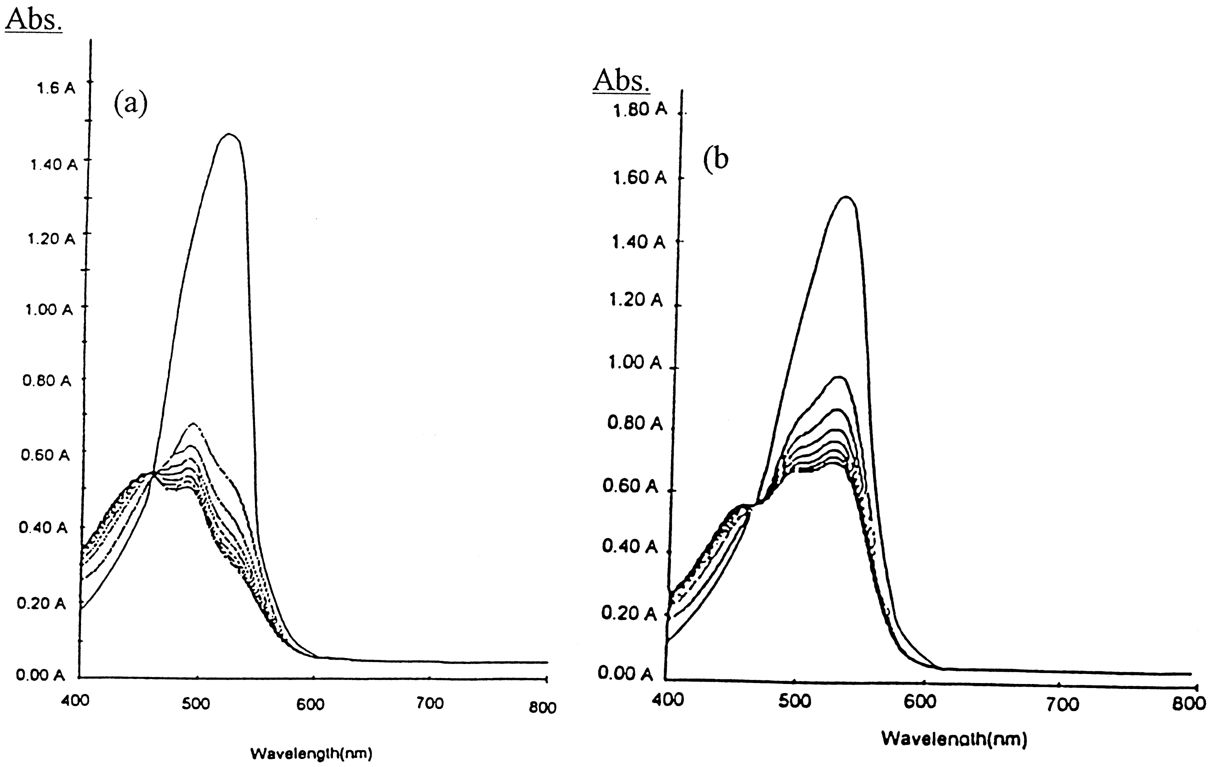


Fig. 2. Photosensitised reactions of neutral red, under anaerobic conditions, 4 min after irradiation with VIS radiation. (a) in cyclohexanone (b) in cyclopentanone.

photolytic reactions and continuous lines represent the photosensitised reactions).

1. Photolytic reactions in all cases followed first order kinetics with rates recorded in Table 1. These rates were higher in the case of cyclohexanone 1.627 times than in the case of cyclopentanone under aerobic condition and 2.75 times under anaerobic conditions.

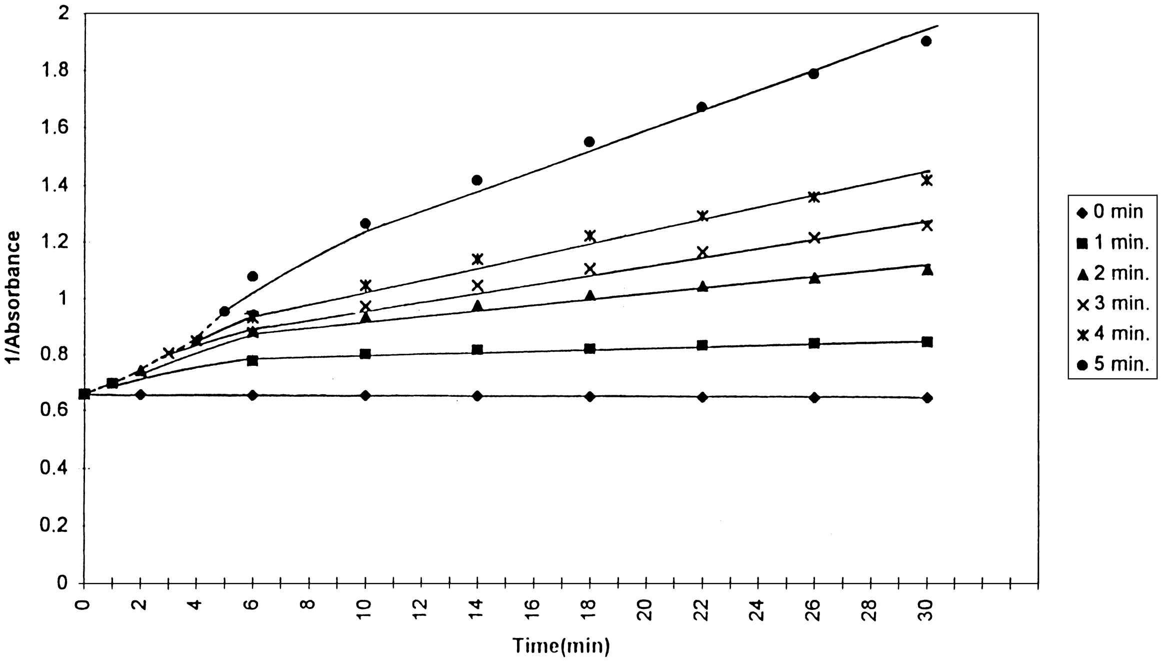


Fig. 3. Photolytic and photosensitised reactions of neutral red in cyclohexanone under aerobic conditions.

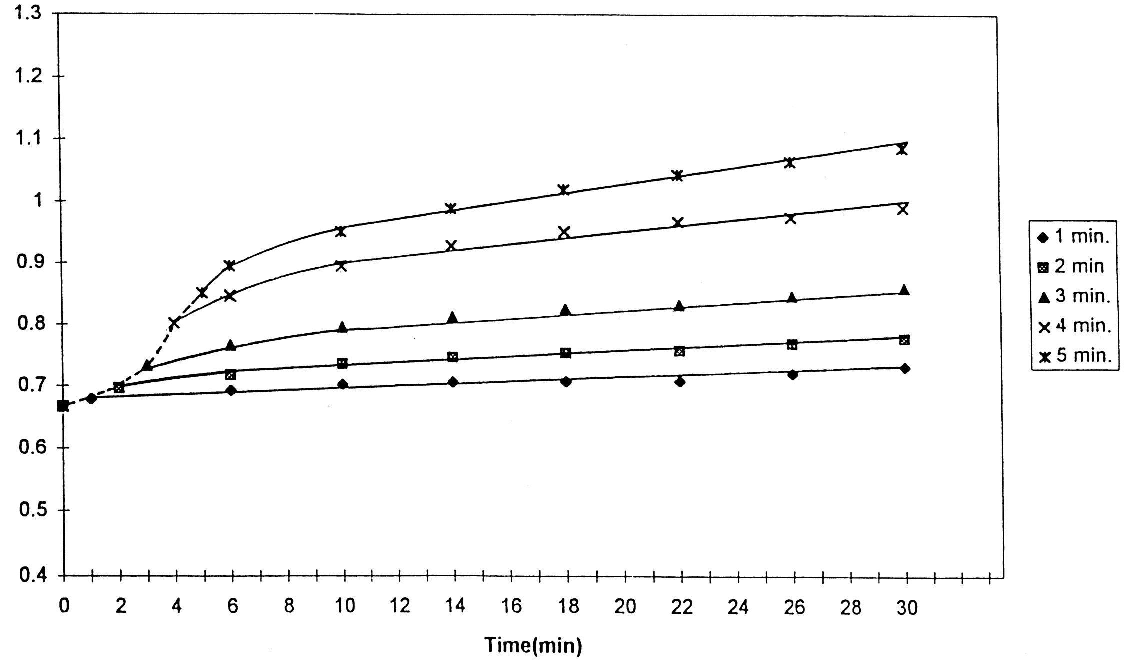


Fig. 4. Photolytic and photosensitised reactions of neutral red in cyclopentanone under aerobic conditions.

2. Photosensitised reactions followed second order kinetics in all cases (Figs. 3 and 4, in the cases of cyclohexanone and cyclopentanone, respectively under aerobic conditions, Figs. 5 and 6 under anaerobic conditions). The rates of these reactions after 4 min irradiation are recorded in Table 1. The rates were five times higher in the case of cyclohexanone than in the case of cyclopentanone under aerobic conditions and 7.77 times under anaerobic conditions.

A 1.5 ml dye–cyclopentanone solution of 2.33 absorbance was added to 1.5 ml of cyclopentanone preirradiated with

1. VIS radiation only
2. With mixed UV/VIS radiation

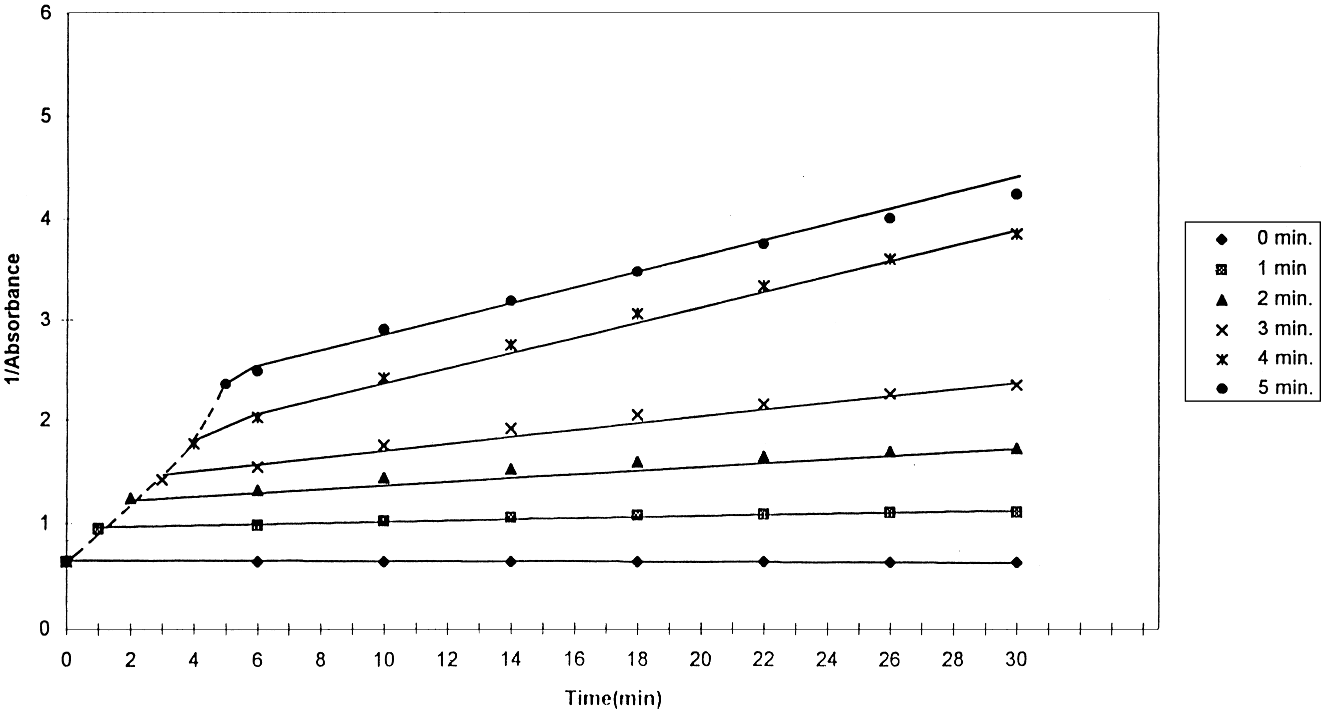


Fig. 5. Photolytic and photosensitised reactions of neutral red in cyclohexanone under anaerobic conditions.

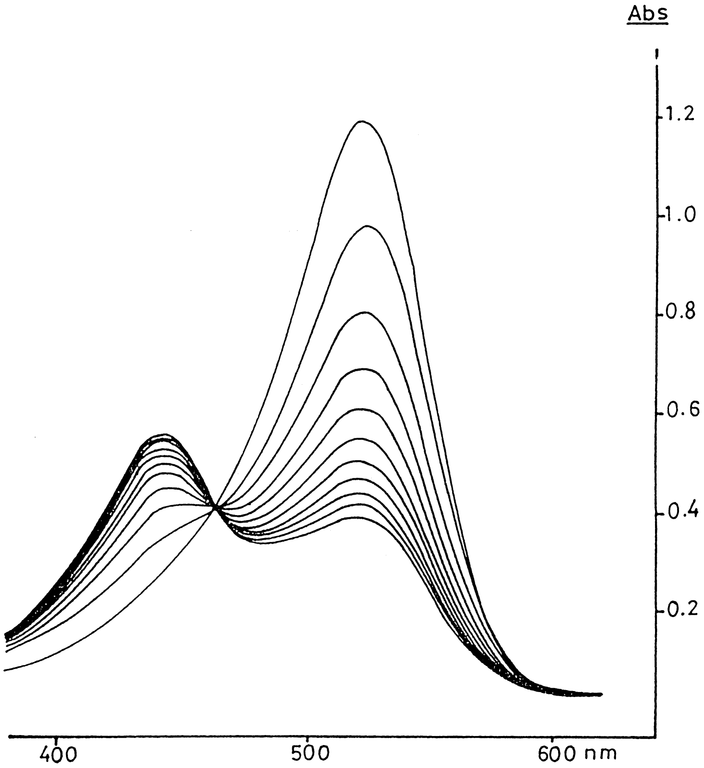


Fig. 6. Photolytic and photosensitised reactions of neutral red in cyclopentanone under anaerobic conditions.

No changes in the absorbance peak position were noticed and no other peaks appeared when visible radiation was used.

When mixed UV/VIS was used for preirradiation, the peak at 492 nm position did not appear but the peak at 444 position appeared and increased in height with time (Fig. 7).

The major part of the reaction followed second order kinetics (Fig. 8).

4. Discussion

It was observed that when neutral red was used as spectrometric probe of internal pH of thylakoid in photosynthetic reactions that the changes in the probe absorbance were consistent with acidification of the medium.

It was also observed at concentration above 1.85×10^{-4} M that there was a shift in the absorption towards shorter wave length from the original value. It was believed that the aggregation of neutral red occurs via hydrogen bonding [6].

In the present work the relation between absorbance and concentration obeyed Beer's law and no shift in λ_{max} of 527 or 522 nm was observed.

Spectral measurements for repetitive scans after the irradiation of the dye solution in cyclohexanone or cyclopentanone with UV/VIS radiation under aerobic condition showed a decrease in the absorbance at λ_{max} of 527 or 522 nm and the appearance of new peak of 444 nm position (Fig. 1(b) and (d)) and the color of the dye solution changed from red to yellow gradually during and after the irradiation.

When the photosensitised reaction was carried out under anaerobic conditions after irradiating the sample with UV and VIS radiation, another new peak appeared at λ_{max} 492 nm (Fig. 1(a) and (c)).

When the last reaction was repeated using VIS radiation only, the peak at 492 nm was more pronounced (Fig. 2(a) and (b)), but the peak at λ_{max} 492 nm, especially in the case of cyclohexanone (Fig. 2a and (b)).

The behavior when UV/VIS radiation was used suggests.

Table 1
Photolytic and photosensitised reactions by irradiating 1×10^{-5} M of dye solution under aerobic and anaerobic conditions for different time intervals with VIS radiation

Reactants	Rate of photolytic reaction (min^{-1})		Rate of photosensitised reaction ($\text{mol}^{-1}\ \text{min}^{-1}$)	
	Aerobic	Anaerobic	Aerobic	Anaerobic
Dye in cyclohexanone	0.070	0.253	0.020	0.070
Dye in cyclopentanone	0.043	0.092	0.004	0.009

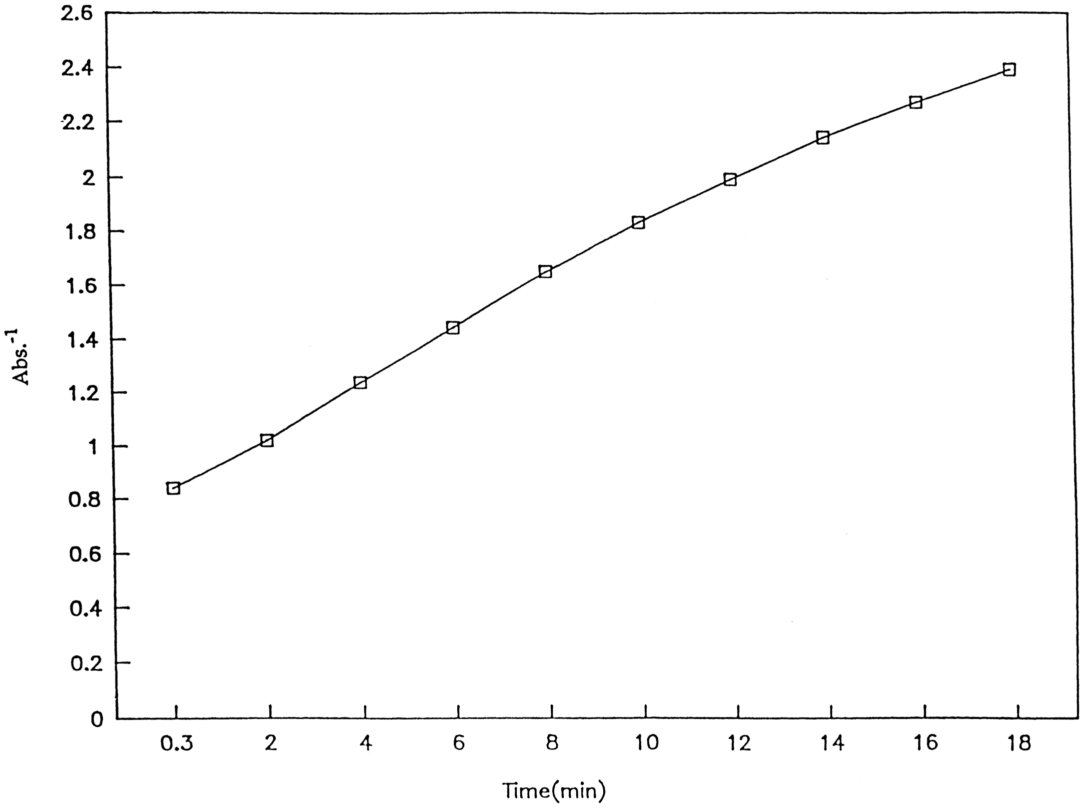


Fig. 7. Photosensitised reactions of neutral red with preirradiated cyclopentanone under anaerobic conditions.

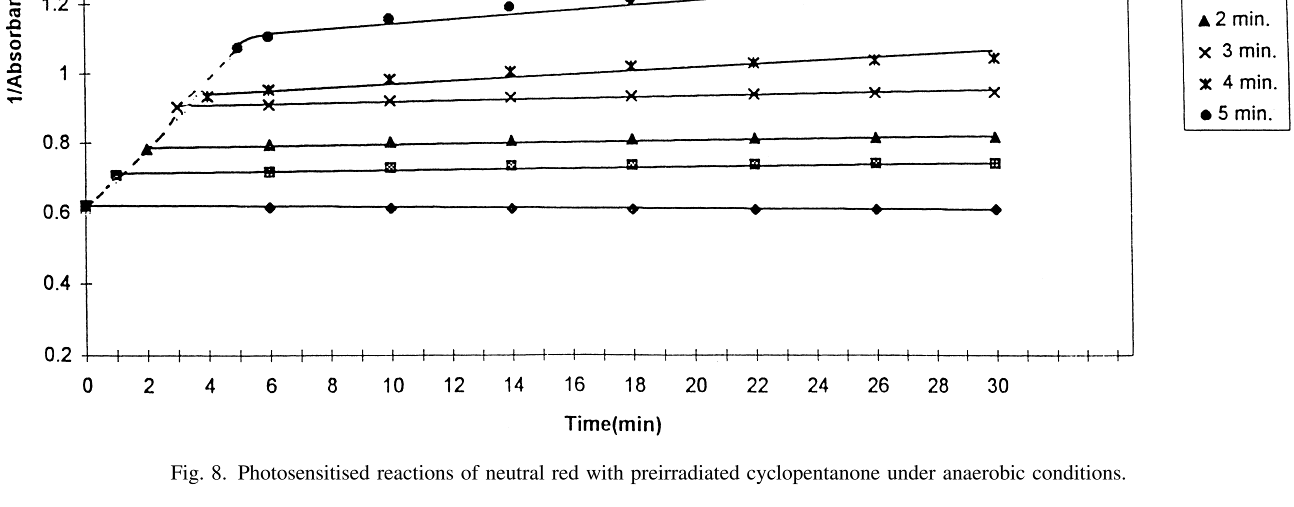
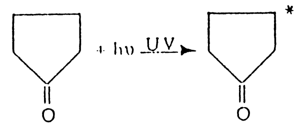


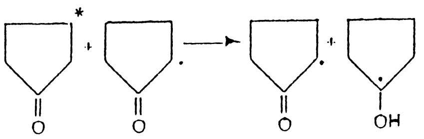
Fig. 8. Photosensitised reactions of neutral red with preirradiated cyclopentanone under anaerobic conditions.

Cyclopentanol or cyclohexanol is produced by the following reaction sequence [3,4]

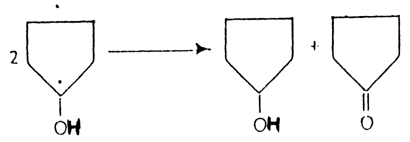


Cyclopentanone

(1)



(2)

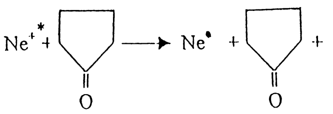


(3)

Cyclopentanol

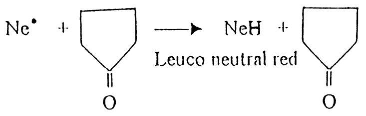
Dye radical is produced via the following routes [4]

$$Ne^{+} + h\upsilon \xrightarrow{VIS} Ne^{+*} \quad (4)$$



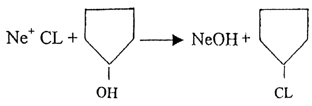
(5)

The dye radical $Ne^{\cdot}$ then reacts with cyclopentanone in the absence of oxygen as follows:



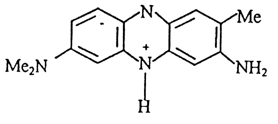
(6)

The peak at 492 nm was attributed to the formation of NeH. The peak of 444 nm was attributed to the formation of NeOH under the influence of UV photolysis as follows [5].

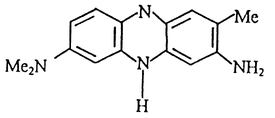


(7)

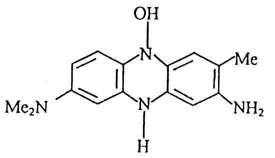
Here Ne^{+}, $Ne^{\cdot}$ and NeOH are the neutral red cation, the neutral red radical and neutral red leuco base respectively.



Ne+

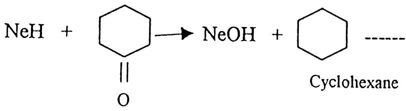


Ne



NeOH

Leuconeutral red NeH may react with cyclohexanone or cyclopentanone to produce the leucocarbinol neutral red NeOH as follows:



(8)

The small peak at 444 nm (Fig. 2(a) and (b)) may have appeared as a result of the last reaction (Eq. 8).

The photosensitised dark reaction of unirradiated dye solution with preirradiated cyclopentanone with UV radiation under anaerobic conditions followed second order kinetics for the major part of the reaction (Fig. 8). The peak at 492 nm position did not appear (Fig. 7). The appearance of the peak at 444 nm position is attributed to the reaction of the dye with cyclopentanol or cyclohexanol produced as a result of preirradiation of the solvent with UV radiation (Eqs. (2), (3) and (7)).

The slower rates of photolytic and photosensitised reactions under aerobic conditions (Figs. 3 and 4) compared with those under anaerobic conditions (Figs. 5 and 6 and Table 1) may be due to the reverse reactions as follows.

$$Ne^{\cdot} + O_2 \rightarrow Ne + O_2^{\cdot -}$$

This mechanism resembles the one suggested by P Resch et al. [7] for reoxidation of methylene blue radical.

The decay of the $Ne^{\cdot}$ radical was found by Marks et al. [8] to follow second order kinetics. In the present work the photosensitised dark reactions followed second order kinetics. This may indicate that the determining step in the present work is the decay of $Ne^{\cdot}$ radical (Figs. 4, 6 and 8).

The photolytic reactions followed first order kinetics in all cases. The rate determining step is not the decay of the dye radical as the dye with cyclopentanone or cyclohexanone under irradiation produces cyclopentanol or cyclohexanol Eqs. (1)–(3) in abundance. Thus the reaction is dependent on the dye concentration.

The peak at 492 nm position was more pronounced and distinct in the case of cyclohexanone and was attributed to the formation of NeH (Eq. 6). This indicates that cyclohexanone is more reactive than cyclopentanone [9], and this also explains the higher rates in all cases when cyclohexanone was used as solvent.

5. Conclusions

1. Using only VIS radiation for photolysis under anaerobic conditions produced a more pronounced peak at λ_{max} 492 nm which was attributed to the formation of leuconeutral red NeH validating the suggested mechanism [5] (Eqs. (4)–(6)).
2. The rate determining step in photosensitised reaction is the decay of the dye radical, while the rate determining factor in photolytic reactions is the dye cation concentration.

3. The photolytic reactions (under aerobic and anaerobic conditions) and phosensitised reactions in all cases are faster in cyclohexanone indicating the higher reactivity of cyclohexanone.

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