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# Photoinduced reactions of neutral red with cyclohexanone

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**Abstract**

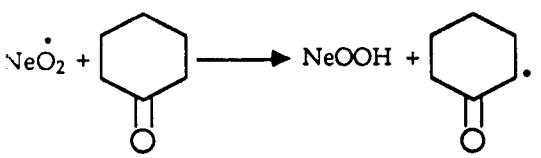
Photoinduced reactions of neutral red with cyclohexanone were studied at 23 °C under anaerobic conditions. A new peak appeared at wavelength 492 nm. The initial relative rate of photoinduced reaction under anaerobic conditions was 2.1 times faster than that under aerobic conditions. Leucocarbinol neutral red was produced as a result of the formation of cyclohexanol.

*Keywords:* Photoinduced reactions; Neutral red; Cyclohexanone

## 1. Introduction

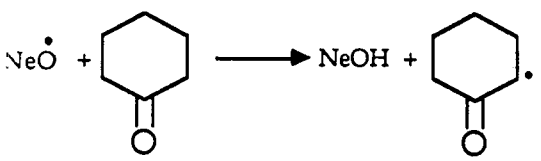
It was found in previous work [1–3] that electron transfer takes place from cyclohexanone to neutral red dye through photochemical formation of species that have an appreciable lifetime. The studies were carried out under aerobic conditions. The results suggested that oxygen was involved in the following steps [3]:

$$Ne^{\cdot} + O_2 \longrightarrow NeO_2^{\cdot} \quad (1)$$




(2)


(3)




(4)

The aim of the present work is to further investigate the role of oxygen in the mechanism by studying the reactions under anaerobic conditions.

## 2. Experimental details

Neutral red (CI 50040) and cyclohexanone were BDH grade. Cyclohexanone was 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 the required initial absorbance in the region 300–700 nm using a Perkin–Elmer 559 UV–visible spectrophotometer. The reaction kinetics were studied by measuring the changes in absorbance with time directly after the termination of irradiation.

Irradiation of samples was carried out using an Osram ME/D box-type, 250 W, medium pressure mercury lamp fitted with a quartz window. The quartz cell carriage was mounted on an optical bench 7.5 cm from the light source.

The dark reaction of the dye with pre-irradiated cyclohexanone was carried out by adding 1.5 $cm^3$ of irradiated cyclohexanone to 1.5 $cm^3$ of unirradiated dye–cyclohexanone solution; 20 s after mixing, the absorbance changes were monitored.

Air evacuation from the samples was carried out using a rotary pump. A liquid nitrogen trap was used to trap any grease or mercury vapour traces in the vacuum line. The air pressure was measured using a Pirani 11 gauge.

## 3. Results

(1) The photoinduced dark reaction following 4 min irradiation of dye–cyclohexanone solution of initial absorbance 1.46 under aerobic and anaerobic conditions was studied. It was found that:

(a) in both cases the reaction followed neither first- nor second-order kinetics;

(b) the initial relative rate of reaction under anaerobic conditions (0.12 $min^{-1}$) was 2.1 times faster than

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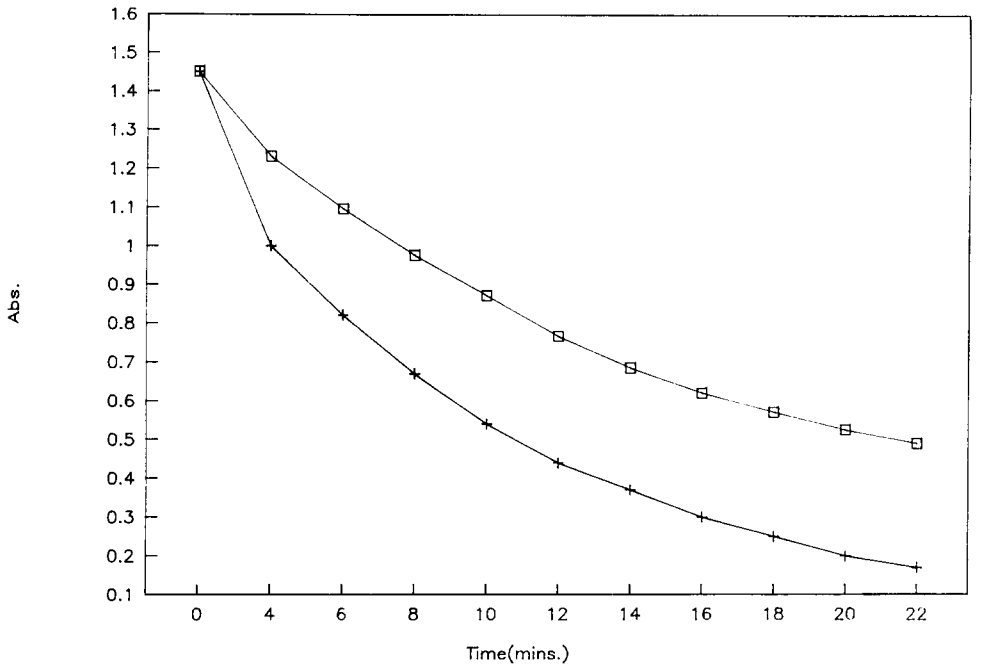



Fig. 1. Photoinduced reactions of neutral red: □, aerobic conditions; +, anaerobic conditions.

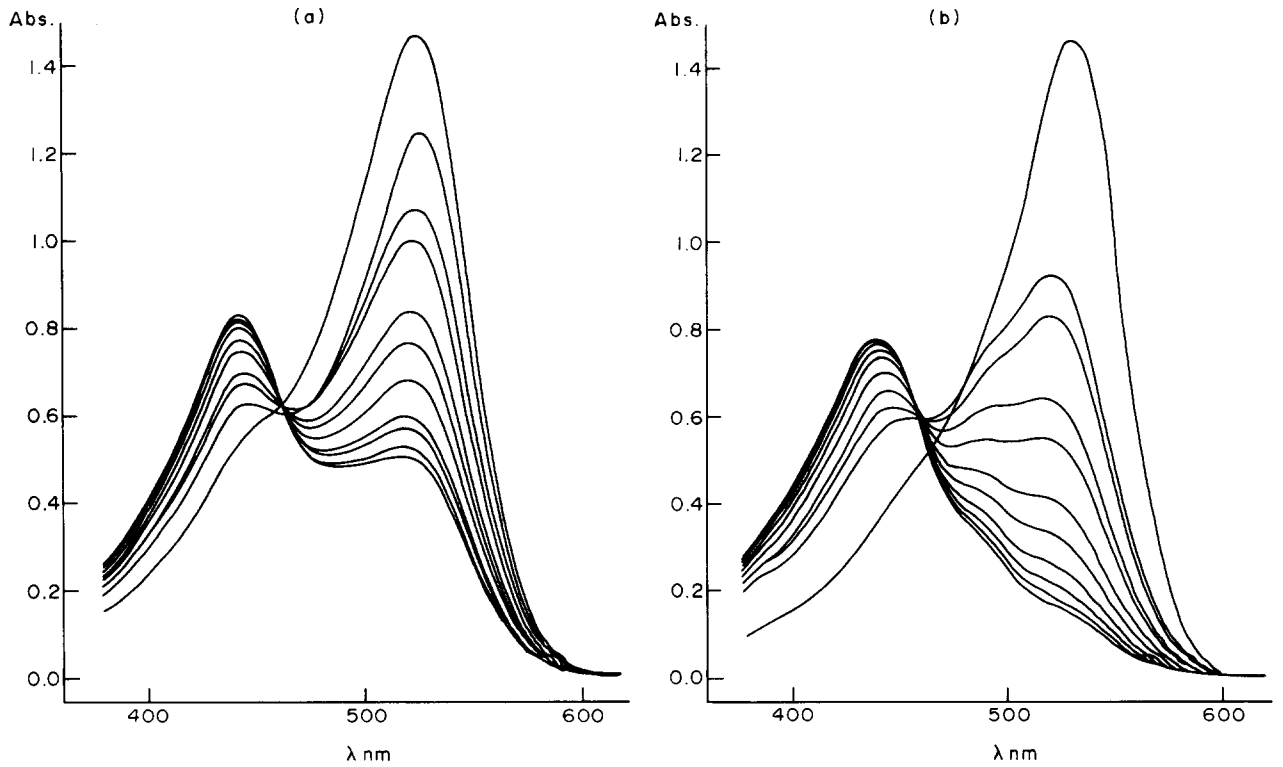



Fig. 2. Photoinduced reactions of neutral red with cyclohexanone: (a) aerobic conditions; (b) anaerobic conditions.

that under aerobic conditions (0.057 $min^{-1}$) (Fig. 1);

(c) a new peak at wavelength 492 nm appeared in the case of reaction under anaerobic conditions (Fig. 2(b)).

(2) The photoinduced dark reaction of dye solution (of absorbance 2.33) with cyclohexanone pre-irradiated for 10 min was studied under anaerobic conditions. It was found that:

(a) the peak at 492 nm did not appear (Fig. 3(a));

(b) the major part of the reaction followed second-order kinetics (Fig. 3(b)).

(3) 0.5 $cm^3$ of cyclohexanol was added to 2.5 $cm^3$ of $10^{-5}$ M dye–cyclohexanone solution. The changes in absorbance

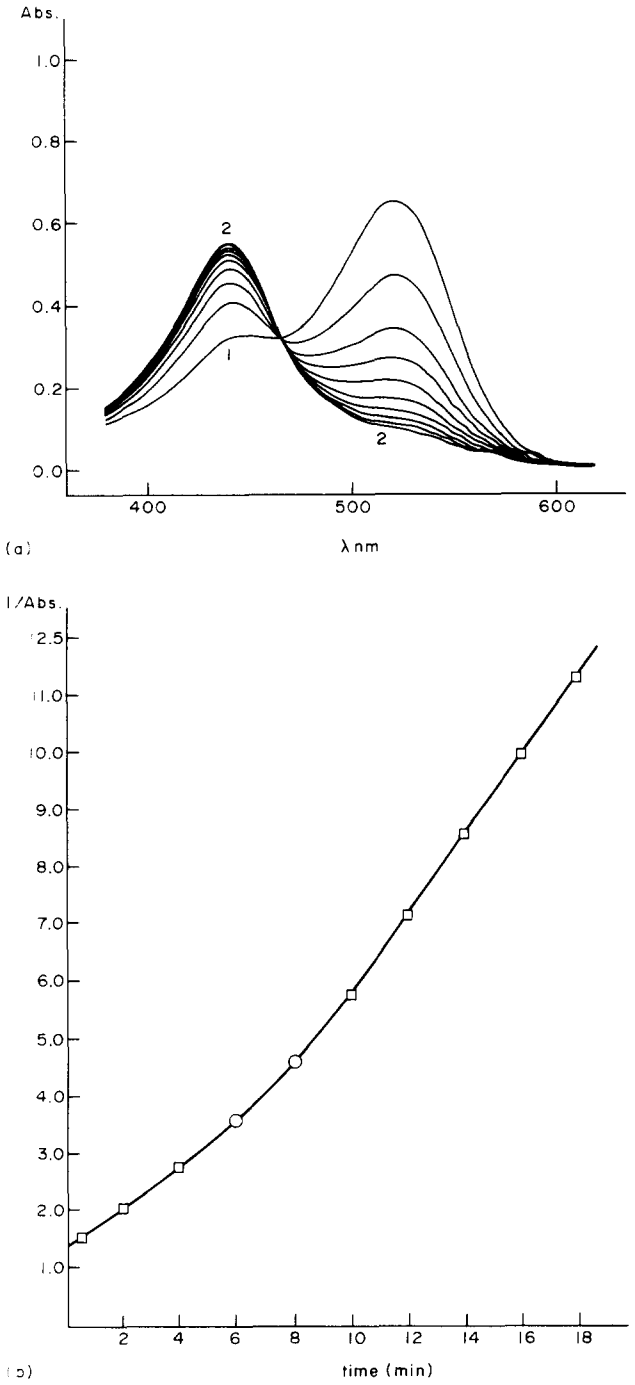



Fig. 3. (a) Photoinduced dark reaction of neutral red with pre-irradiated cyclohexanone under anaerobic conditions. (b) Photoinduced reaction of neutral red with pre-irradiated cyclohexanone under anaerobic conditions.

were followed 20 s after mixing. It was found that the peak height at wavelength 527 nm decreased (from 1.38 to 0.53), a new peak appeared at 444 nm (Fig. 4) and the colour of the dye solution changed from red to yellow.

## 4. Discussion

Neutral red is a dye with the azine structure which has been used as an acid–base indicator [4]:

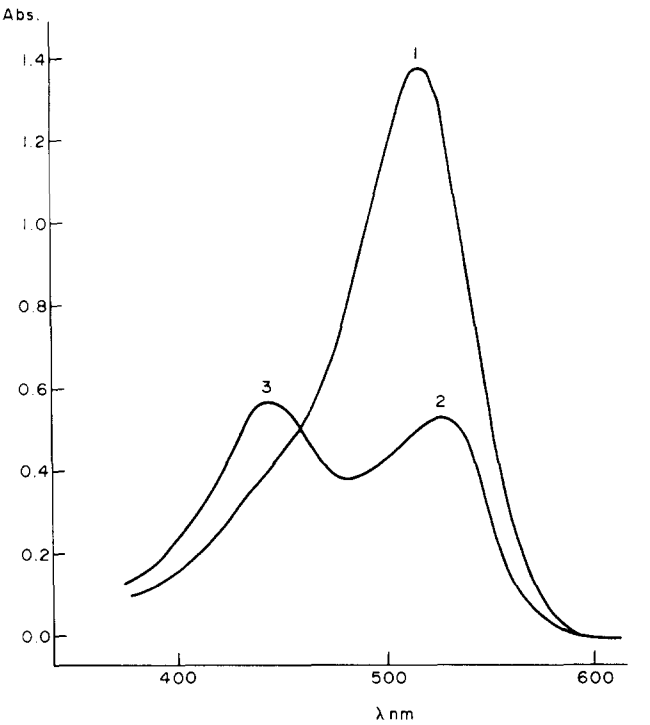
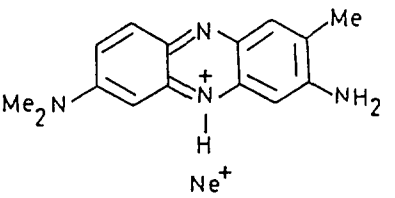



Fig. 4. Spectra of neutral red in cyclohexanone: 1, before addition of cyclohexanol; 2, 3, after addition of cyclohexanol.

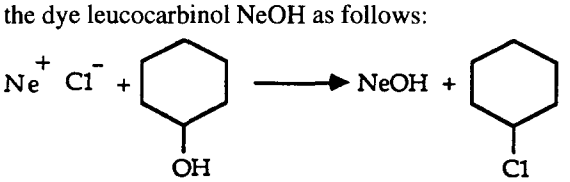



Neutral red cation

Spectral measurements by repetitive scans after irradiation of the dye in cyclohexanone under aerobic conditions showed a decrease in absorbance at $\lambda_{max} = 527$ nm and the appearance of a new peak at 444 nm [3]. Production of the leucobase of the dye was indicated by the increase in absorbance at wavelength 444 nm after addition of 0.1 N NaOH to the irradiated dye solution and also by the change in colour of the dye solution from red to yellow during and after irradiation [3].

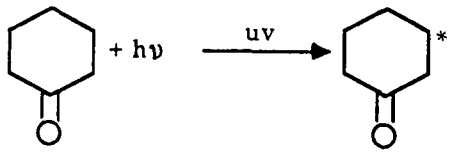
In the present work the spectral measurements were carried out under anaerobic conditions. It was found that a new peak at wavelength 492 nm appeared after irradiating the dye–cyclohexanone solution, which decreased gradually in height during the course of the reaction (Fig. 2(b)).

Addition of cyclohexanol to dye–cyclohexanone solution caused a decrease in peak height at 527 nm and the appearance of a peak at 444 nm (Fig. 4). A change in colour of the dye solution from red to yellow was also observed. This indicates that cyclohexanol reacted with the dye cation $Ne^+$ to form the dye leucocarbinol NeOH as follows:

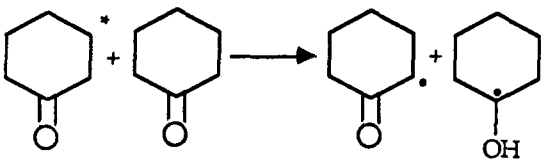



(5)

The occurrence of dark reaction following the addition of pre-irradiated cyclohexanone to dye–cyclohexanone solution under anaerobic conditions 35 min after the end of irradiation indicates that long-lived stable species were formed through a photochemical process. These species appeared to be cyclohexanol formed [3] as follows:




(6)

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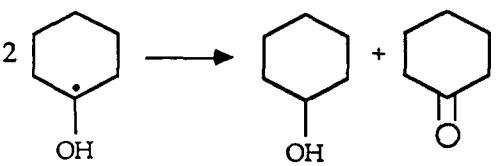
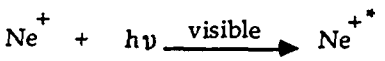



Cyclohexanol

(8)

Cyclohexanol then reacts with the dye cation as in Eq. (5).

Since oxygen is absent in the case of photoinduced reaction under anaerobic conditions, the peak at 492 nm may be attributed to leuco neutral red NeH [5,6] as follows:

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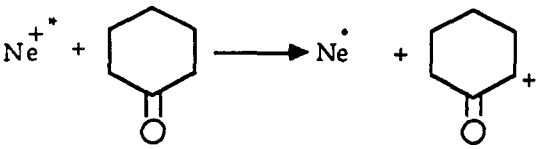


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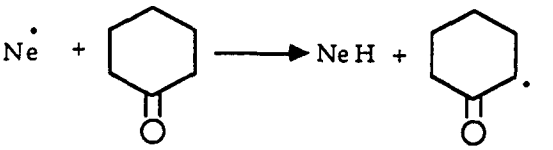


(11)

Eqs. (9)–(11) may explain the formation of leuco neutral red NeH and the appearance of the new peak at 492 nm. They may also explain the absence of this peak when only cyclohexanone was pre-irradiated (Fig. 3(a)), since the appearance of this peak requires the production of neutral red radical through irradiation as in Eqs. (9)–(11).

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