PHOTOSENSITIZED OXIDATION OF 2-IMIDAZOLIDINETHIONE

VEENA RANI, NATHU RAM DAHMIWAL and K. S. SIDHU
Department of Chemistry, Punjabi University, Patiala 147002 (India)
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Summary

The methylene-blue-sensitized photo-oxidation of 2-imidazolidinethione (IT) in water gives 2-imidazolin-2-yl-sulphinate as the primary and only product. The quantum yield ϕ of photo-oxidation increases and then decreases to a zero value during the course of the reaction. The dye undergoes photobleaching in the absence of oxygen. A mechanism involving interaction of the triplet dye with $O_2(^3\Sigma_g^-)$ and/or IT and leading to products through the participation of $IT^{+\cdot}$ and $O_2^{-\cdot}$ is suggested. The effect of singlet oxygen quenchers is discussed.

1. Introduction

It is widely accepted that dyes are convenient sensitizers in photosensitized oxidation reactions [1 - 4]. Dyes have also been used for the *in situ* formation of singlet $O_2(^1\Delta_g)$ [5 - 7]. In the absence of singlet oxygen the process involves initial electron transfer from the substrate to the triplet dye followed by proton transfer from the radical ion.

The oxidation of thioureas has been of considerable interest because of their industrial applications and the mechanism of total oxidation has been reported in many publications [8]. Oxidation of 2-imidazolidinethione (IT) with sodium hypochlorite in acidic or neutral medium leads to ethylene urea, 1-(2′-imidazoline-2′-yl)-2-imidazolidinethione and ethylenediamine [9]. However, in acetonitrile, bis(2-imidazolin-2-yl) disulphide has also been detected [10]. In acetone with riboflavin as sensitizer, the intermediacy of singlet oxygen has been suggested [11]. Furthermore, allyl thiourea has been used as a singlet oxygen trap in many studies [12]. From the available reports on thioureas and the corresponding results on the photosensitized oxidation of amines it appears that the mechanistic features of the photo-oxidation of thioureas have not been studied in detail particularly at low conversions (at higher conversions secondary reactions mask the all important mechanistic features of the initial reactions) and therefore an investigation of the methylene-blue(MB)-sensitized oxidation of IT was proposed. We report here the results of this investigation.

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2. Experimental details

Conductivity water and freshly distilled BDH (India) AnalaR grade solvents were used. IT was prepared by adding ethylenediamine (15 g) dropwise with vigorous shaking to carbon disulphide (25 g) [13]. The mixture was refluxed for 30 min and cooled. After pouring off the excess CS_2, the residual mass was dissolved in 50 ml of warm distilled water. Hydrochloric acid (4 - 5 ml) was added and again refluxed at 100 °C for 1 h. IT separated out on cooling and was recrystallized twice from alcohol. Further purification was carried out by column chromatography on silica gel using ethanol as eluent. The eluted fraction was recrystallized to a sharp melting point of 197 °C. The other reagents were recrystallized to sharp melting points.

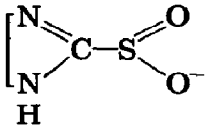
The photolysis assembly consisted of a halogen lamp (Philips, India; 1000 W), a 470 nm cut-off filter, a quartz cell with two optically flat windows and with circulating cold water as a heat sink and a photolysis cell made of a Pyrex tube (30 mm in diameter and 200 mm in length) which was flattened at the bottom and was fitted with a narrow capillary along the walls through which gases could be passed. The cell was placed in a water thermostat (30 ± 0.2 °C). Presaturated gases were passed through the solution at suitable flow rates. To change the light intensity, wire gauze was inserted in between the heat sink and the lamp.

The reaction mixture containing 5.0×10^{-4} M IT and 1.5×10^{-4} M MB in water was photolysed in the presence of oxygen at constant temperature for 2 h. After distilling off the excess solvent under reduced pressure, the concentrate was separated on a thin layer chromatography (TLC) plate. The products were analysed by means of TLC and UV spectroscopy.

The products were monitored conductimetrically using a precalibrated Toshniwal (India) conductimeter. The pH changes were recorded on a pH meter by directly inserting the glass electrode into the reaction cell. The irradiation was stopped during measurements.

3. Results and discussion

The reaction mixture when separated on a TLC plate (silica gel G; methanol:acetic acid, 9:1) showed the presence of only one product. A comparison of the R_f value ($R_f = 0.25$) and the UV spectrum with the reported data indicated that the product was 2-imidazolin-2-yl-sulphinate I [10]:



I

It may be noted that thioureas have been observed to give sulphinic acids in eosin- or protoporphyrin-sensitized auto-oxidation [14].

The unirradiated solution contains essentially the phenothiazine-5-ium-3,7-bisdimethylamine ion, the chloride ion and the ions resulting from the dissociation of water. On irradiation the product formation is expected to increase the conductivity particularly as a result of the formation of H_3O^+ (*cf.* the ionic mobilities [15]) and to decrease the pH without affecting the concentration of the ionic species initially present. Plots of the change $\Delta\lambda$ in conductivity *versus* the time of irradiation are S shaped (Fig. 1). It appears that there is a slow and steady reaction initially which rapidly accelerates after a certain time and then stops. In view of the formation of only one product all the operating reaction paths yield the same sulphinic acid.

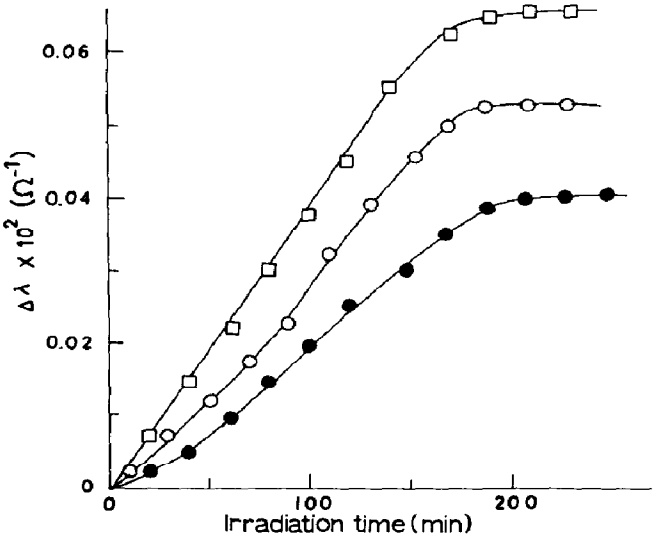


Fig. 1. Effect of the IT concentration ([MB] = 1.7×10^{-4} M): ●, 0.71×10^{-2} M; ○, 2.84×10^{-2} M; □, 11.36×10^{-2} M.

The flattening of the curve at first sight may appear to be due to the complete consumption of the substrate since the light absorbed did not change with time as shown by the constant absorbance around 652 nm and oxygen was bubbled continuously through the solution. Figure 1 shows the effect of the concentration of IT. At the highest concentration (11.36×10^{-2} M) of IT used the first part of the S-shaped curve disappears. The flattening, however, appears at the same value of the total light absorbed. A comparison of the three curves shows that the flattening is at higher conversions in concentrated solutions and that this is not because of any significant depletion in IT.

The effect of varying the light intensity I_a was examined next and the results are given in Fig. 2. With decreases in the light intensity the flattening occurs at a net lower extent of reaction and the point of inflection shifts to longer irradiation times. This suggests that the quenching is caused by a product of the reaction and that the concentration of the species to be

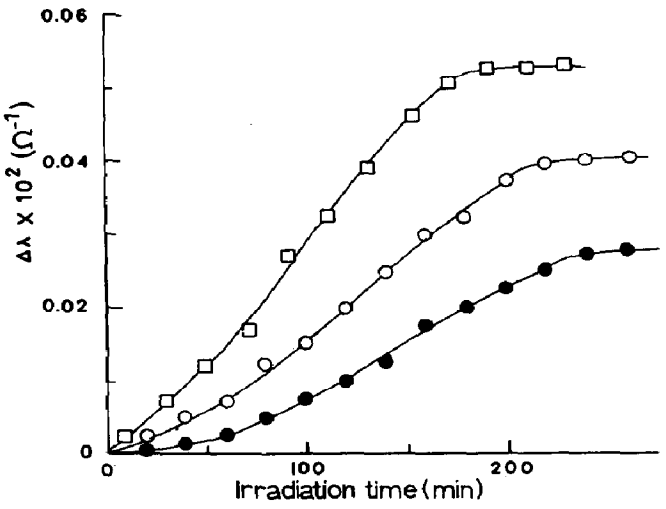


Fig. 2. Effect of the absorbed light intensity ([MB] = 1.7×10^{-4} M; [IT] = 2.84×10^{-2} M): I_a (●) < I_a (○) < I_a (□).

quenched is proportional to the absorbed light intensity and the substrate concentration.

The absorption spectra of MB in the visible region in the presence of various amounts of IT show that there is no possibility of any complexation between IT and ground state MB. MB has a quantum yield ϕ_{ISC} of intersystem crossing of 0.5 from its excited singlet state [16] and although some quenching of the excited singlet dye has been reported at high amine concentrations [17] it is the triplet state of the dye which is more important here because the concentrations of IT used are low. Amines quench triplet dyes at a rate competitive with energy transfer to $O_2(^3\Sigma_g^-)$ and the relative importance of the two reactions depends on [amine]/$[O_2(^3\Sigma_g^-)]$ [6, 17 - 19]. Sulphides and disulphides, like amines, have been shown to be attacked by electrophilic singlet oxygen, leading to partial or complete charge transfer intermediates [20 - 24]. In the MB-sensitized photo-oxidation of di-*n*-butyl sulphide in ethanol, both processes are equally important [25]. It is thus possible that the triplet dye (which is electrophilic like singlet oxygen) may interact at the nitrogen or sulphur atom of IT. This interaction was examined in both water and methanol. A solution of 8.4×10^{-6} M MB and 3.4×10^{-4} M IT in water and another of 1.05×10^{-5} M MB and 4.25×10^{-4} M IT in methanol were degassed through freeze–thaw cycles and sealed. On photolysis, bleaching was observed in both cases as shown in Figs. 3 and 4. However, a shift in the absorption maximum in methanol represents some chemical reaction other than pure bleaching of the dye. On exposure to air the dye was restored in water solution with the near disappearance of the shoulder at 600 nm which corresponds to the dimeric dye species [26]. However, it was restored with a shift in the maximum in methanol solution. The observations suggest that the leuco dye may not be the bleached species because it is known to oxidize to the dye itself [27]. The following processes

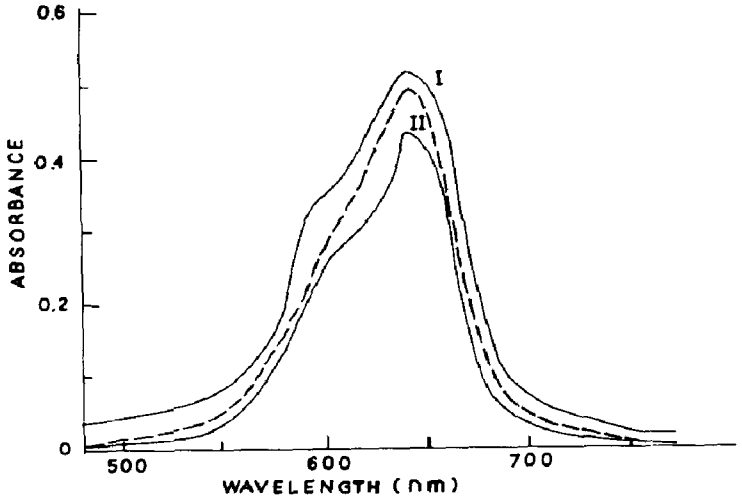


Fig. 3. Absorption spectra of oxygen-free and air-exposed reaction mixtures in water ([MB] = 8.4×10^{-6} M; [IT] = 3.4×10^{-4} M): curve I, unphotolysed; curve II, photolysed for 75 min; – – –, photolysed for 75 min and then exposed to air.

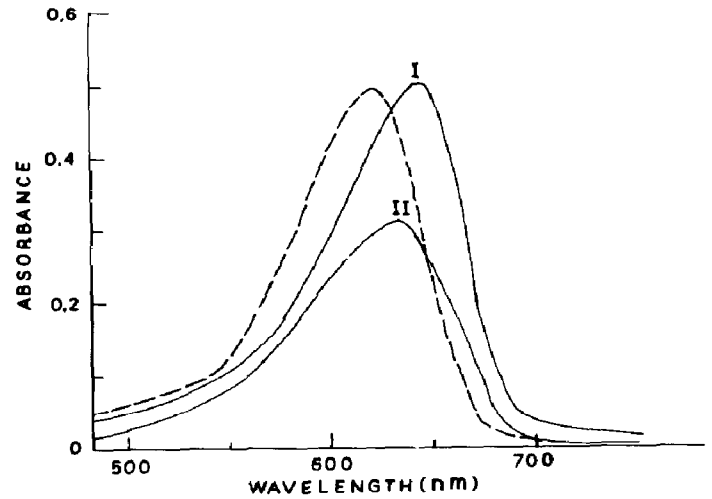


Fig. 4. Absorption spectra of oxygen-free and air-exposed reaction mixtures in methanol ([MB] = 1.05×10^{-5} M; [IT] = 4.25×10^{-4} M): curve I, unphotolysed; curve II, photolysed for 80 min; – – –, photolysed for 80 min and then exposed to air.

need consideration in the absence of oxygen (there may be some charge separation in the triplet complex):

$$^3D + IT \longrightarrow {}^3(D^{\cdot}\cdot\cdot IT) \quad (1)$$

$$^3(D^{\cdot}\cdot\cdot IT) \longrightarrow DH^{\cdot} + IT^{\cdot} \quad (2)$$

$$DH^{\cdot} + DH^{\cdot} \longrightarrow D + DH_2 \quad (3)$$

$$DH^{\cdot} + IT \longrightarrow DH^{-} + IT^{+} \quad (4)$$

$$DH^{\cdot} + IT^{+} \longrightarrow DH_2 + IT^{\cdot} \quad (5)$$

$$IT^{+} + H_2O \longrightarrow IT^{\cdot} + H_3O^{+} \quad (6)$$

$$^3(D^{\cdot\cdot\cdot}IT) \longrightarrow D + IT \text{ or some unstable product} \quad (7)$$

There is enough evidence for processes such as (1) [28]. There is no spin restriction on process (2). Process (3) has been put forth by Hatchard and Parker [29] for the oxidation of Fe^{2+} with triplet MB in flash photolysis, but because the absorbed light intensity is of the order of 10^{-4} einsteins $cell^{-1}$ min^{-1} in the present experiments, this process need not be important. Phenothiazine is known to undergo very slow oxidation in the dark. $DH^{\cdot}$ is a substituted phenothiazine in which the *para* positions with respect to the nitrogen of the ring are blocked and it certainly cannot undergo fast auto-oxidation at room temperature. Thus $DH^{\cdot}$ is unlikely to be formed because of the fast recovery of the bleached dye on exposure to air. In the absence of step (3), step (4) followed by step (5) can produce a leuco dye. Step (6) is energetically feasible because of the availability of bonding and resonance energies of $IT^{\cdot}$, and step (7) explains the observed change in the absorption spectra of the oxidized bleached dye.

In the presence of oxygen the triplet dye can transfer energy to oxygen in competition with its interaction with IT, resulting in the formation of singlet oxygen:

$$^3D + O_2(^3\Sigma_g^-) \longrightarrow D + O_2(^1\Delta_g) \quad (8)$$

Process (8) is expected to be more important at higher oxygen concentrations. The effect of varying the oxygen concentration was studied and the results are given in Fig. 5. The rate is higher at higher oxygen concentrations. The rate cannot increase indefinitely because of the processes [30 - 33]

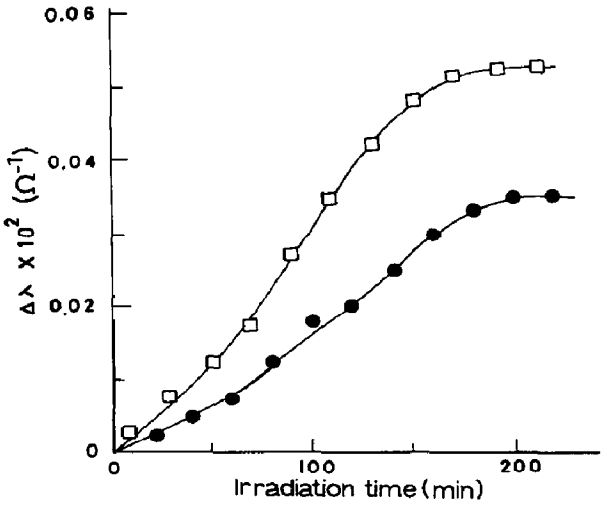


Fig. 5. Effect of the oxygen concentration ([MB] = 1.7×10^{-4} M; [IT] = 2.84×10^{-2} M): ●, [O_2] = 2.28×10^{-4} M; □, [O_2] = 11.41×10^{-4} M).

$$O_2(^1\Delta_g) + O_2(^3\Sigma_g^-) \longrightarrow 2O_2(^3\Sigma_g^-) \quad (9)$$

$$O_2(^1\Delta_g) + {}^3D \longrightarrow O_2(^3\Sigma_g^-) + D \quad (10)$$

To examine the role of singlet oxygen further the effect of adding well-known singlet oxygen quenchers [34, 35] (β-carotene and 1,4-diazabicyclo-[2.2.2]octane (DABCO)) was studied at both high and low oxygen concentrations. The results are given in Figs. 6 and 7. β-Carotene quenches via an energy transfer mechanism at a diffusion-controlled rate [36, 37], whereas DABCO quenches singlet oxygen by a charge transfer mechanism [38, 39] with a rate constant of the order of 10^7 M^{-1} s^{-1} [38 - 41]. The ratio k_q(β-carotene)/k_q(DABCO) = δ of the quenching rate constant for β-carotene to that for DABCO should be of the order of 10^3 in terms of the diffusion-controlled quenching by β-carotene and the charge transfer quenching by DABCO. This value is much higher than the corresponding value determined from the results of Fig. 6 which gives δ = 19. The observed δ is low possibly because of a larger value of k_q(DABCO) which necessitates the quenching of a species other than singlet oxygen:

$$^3(D\cdots IT) + DABCO \longrightarrow (D\cdots IT\cdots DABCO) \downarrow D + IT + DABCO \quad (11)$$

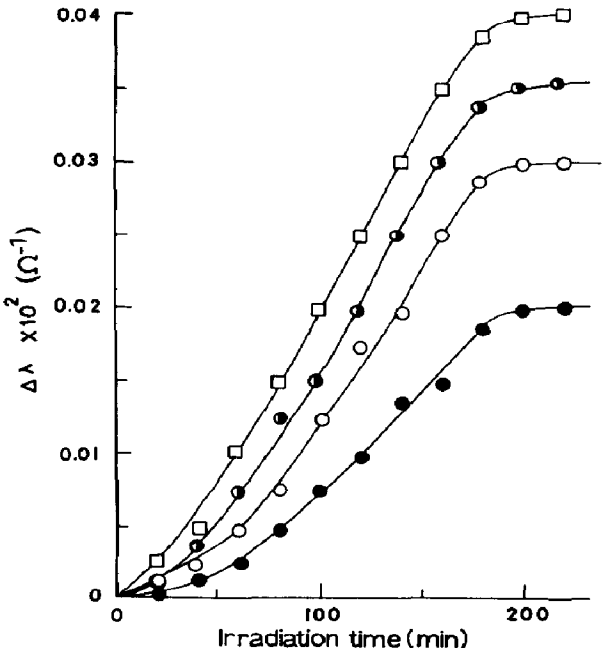
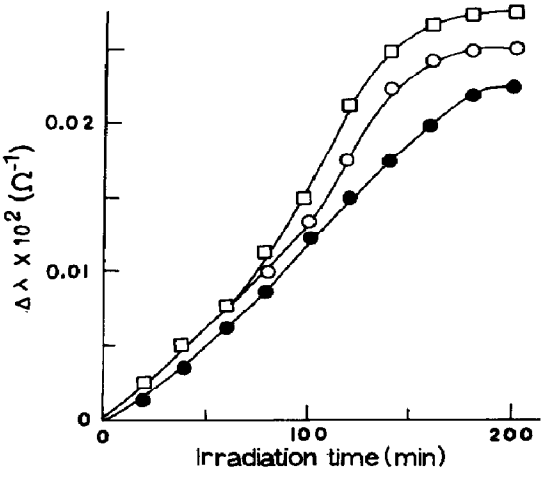


Fig. 6. Effect of singlet oxygen quenchers ([MB] = 1.7 x 10^{-4} M; [IT] = 7.0 x 10^{-3} M; [O_2] = 11.41 x 10^{-4} M): □, no quencher; ●, 1.26 x 10^{-2} M DABCO; ○, 1.31 x 10^{-3} M β-carotene; ●, 2.62 x 10^{-3} M β-carotene.



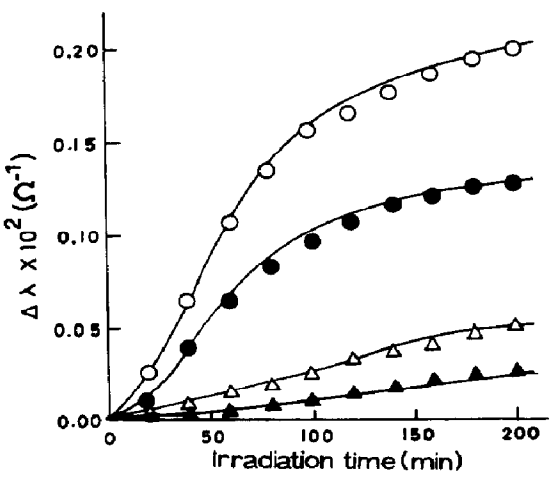


Fig. 7. Effect of singlet oxygen quenchers ([MB] = 1.7×10^{-4} M; [IT] = 7.0×10^{-3} M; [O_2] = 2.28×10^{-4} M): □, no quencher; ○, 1.26×10^{-2} M DABCO; ●, 2.6×10^{-3} M β-carotene.

Fig. 8. Effect of D_2O ([IT] = 1.4×10^{-2} M; [MB] = 1.7×10^{-4} M): ○, ▲, D_2O; ●, △, H_2O; ○, ●, oxygen gas bubbled continuously through the solutions.

The results at lower oxygen concentrations give $\delta = 10$ (Fig. 7) which is in agreement with step (11) since a lower singlet oxygen concentration is expected here. At these quencher concentrations the triplet dye can also be quenched. However, the results (Fig. 8) of the effect of D_2O clearly show the participation of singlet oxygen in the system particularly at higher oxygen concentrations. At lower oxygen concentrations the lower rate in D_2O is apparently due to a specific primary isotope effect.

The change in pH during photolysis in the presence of singlet oxygen quenchers was examined at both high and low oxygen concentrations and the results are given in Figs. 9 and 10. The pH of the reaction mixture initially decreases and then becomes constant. Plots of Δ(pH) *versus* time of irradiation resemble the corresponding conductivity curve but the flattening here occurs at lower irradiation times. The δ values obtained from the results of Figs. 9 and 10 compare favourably with the values obtained from the conductivity data and this supports the participation of singlet oxygen. A mechanism consistent with the results is as follows:

$$^1D_0 + h\nu \longrightarrow {}^1D_1 \qquad (12)$$

$$^1D_1 \longrightarrow {}^1D_0 \qquad (13)$$

$$^1D_1 \longrightarrow {}^3D_1 \qquad (14)$$

$$^3D_1 \longrightarrow {}^1D_0 \qquad (15)$$

$$^3D_1 + {}^3O_2 \longrightarrow {}^1D_0 + O_2(^1\Delta_g) \qquad (16)$$

$$^3D_1 + IT \longrightarrow {}^3(D\cdots IT) \qquad (1)$$

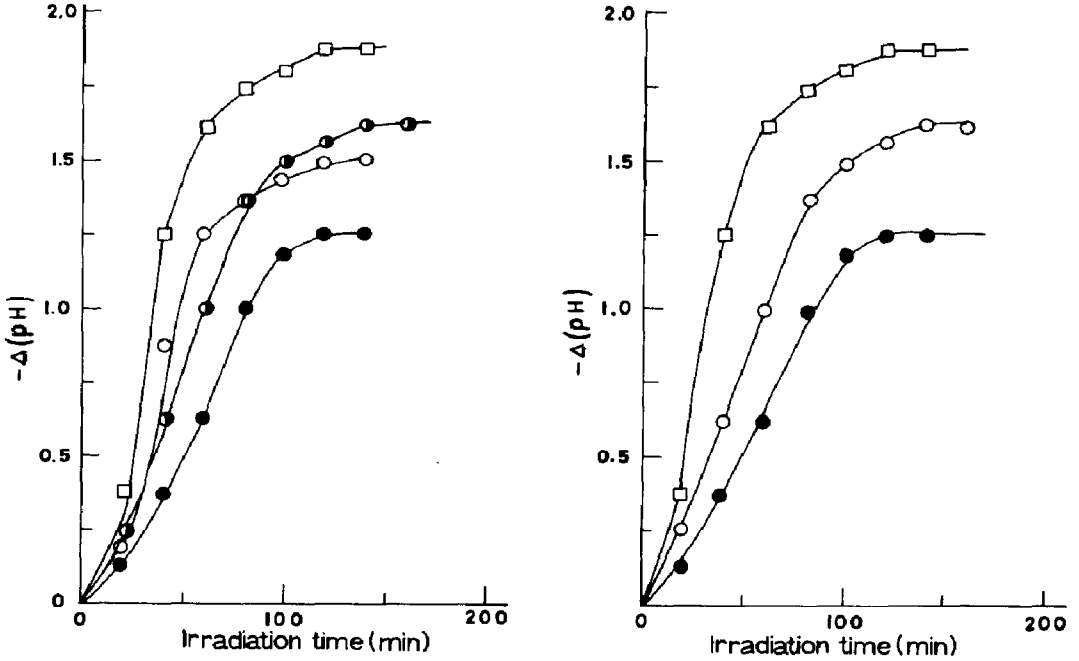


Fig. 9. Effect of singlet oxygen quenchers ([MB] = 1.7×10^{-4} M; [IT] = 7.0×10^{-3} M; [O_2] = 11.41×10^{-4} M): □, no quencher; ◑, 1.26×10^{-2} M DABCO; ○, 1.31×10^{-3} M β-carotene; ●, 2.62×10^{-3} M β-carotene.

Fig. 10. Effect of singlet oxygen quenchers ([MB] = 1.7×10^{-4} M; [IT] = 7.0×10^{-3} M; [O_2] = 2.28×10^{-4} M): □, no quencher; ○, 1.2×10^{-2} M DABCO; ●, 2.62×10^{-3} M β-carotene.

$$^3(D\cdots IT) \longrightarrow D^{\cdot-} + IT^{\cdot+} \quad (17)$$

$$D^{\cdot-} + IT^{\cdot+} \longrightarrow D\dot{H} + IT^{\cdot} \quad (18)$$

$$D^{\cdot-} + {}^3O_2 \longrightarrow D + O_2^{\cdot-} \quad (19)$$

$$IT + {}^1O_2 \longrightarrow {}^1(IT\cdots O_2)$$

$$^3(IT\cdots O_2) \rightleftharpoons IT^{\cdot+} + O_2^{\cdot-} \quad (20)$$

$$\longrightarrow IT + O_2$$

$$O_2^{\cdot-} + IT^{\cdot+} \longrightarrow IT^{\cdot} + HO_2^{\cdot} \quad (21)$$

$$IT^{\cdot} + HO_2^{\cdot} \longrightarrow \text{product (PH)} \quad (22)$$

$$PH \rightleftharpoons P^- + H^+ \quad (23)$$

$$O_2^{\cdot-} + H^+ \longrightarrow HO_2^{\cdot} \quad (24)$$

In view of the lower range of concentration of IT used (from 7.4×10^{-4} to 11.36×10^{-2} M) any interaction of the singlet dye with IT is unlikely.

Reaction (16) is expected to be diffusion controlled because it involves exothermic energy transfer. The present results also require step (1) and, at comparable concentrations of oxygen and IT, $k_1 \approx k_{16}$. The exciplex may dissociate to give semiquinone dye (step (17)) which has been observed in MB sensitization of amines [1]. The semiquinone gives a semileuco dye (step (18)) within or outside the solvent cage. The enhancement in the reaction rate after a certain time as a result of the formation of a product requires steps (19) and/or (20) because $H\dot{O}_2$ has been shown to be the reactive oxidizing species in the photolysis of H_2O_2 in the presence of ascorbic acid [42] and the observed increase in the reaction rate during photolysis is through reaction (24). In the initial stages step (22) following from step (21) explains the product formation. Step (23) gives the excess H^+ required to explain the enhancement in the reaction rate. Step (20) includes a back electron transfer process in which light is wasted; this step is most probable especially within the solvent cage if this process proceeds through a charge transfer complex in which the singlet and triplet levels are expected to be very close (*cf.* DABCO quenching [34]). Steps (19) - (21) are further supported by the sensitized oxidation of 9,10-dicyanoanthracene [43] carried out in acetonitrile–water (4:1) as solvent where the products and the basic features are the same.

The complete cessation of the reaction is certainly caused by a product of the reaction. The quenched species can be either ^3D or $^3(D\cdots IT)$ since sulphinic acid is the only observed product. Although the effect of the IT concentration can be explained through the quenching of both ^3D and $^3(D\cdots IT)$ the effect of the oxygen concentration suggests competitive quenching of ^3D only. The quenching of the triplet dye was investigated further by adding diphenylamine to the system because diphenylamine is known to give the oxidation product *N*-phenyl-*p*-benzoquinoneimine through both the singlet oxygen mechanism and the electron transfer mechanism originating from ^3D [44]. The formation of *N*-phenyl-*p*-benzoquinoneimine stops after 220 min. This shows that the prequenching time is longer in this case compared with that for the results shown in Fig. 1, on account of the fact that some ^3D reacts with diphenylamine, resulting in a lower rate of quencher product formation and thus supporting ^3D as a species that can be quenched.

In the presence of singlet oxygen quenchers the rate of product formation is suppressed and the flattening should be expected at longer irradiation times, which is not observed. It appears that reaction with singlet oxygen is very fast but the percentage of ^3D quenched by $O_2(^3\Sigma_g^-)$ is very small.

The pH plots flatten at lower irradiation times because the steady state concentration of H^+ is reached before the limiting concentration of the quencher as explained through steps (23) and (24).

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