Micellar effects on dye sensitized photooxidation of phenothiazine

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Methylene blue sensitized photooxidation of phenothiazine (PTH) in sodium dodecylsulphate, cetyl trimethylammonium bromide and brij-35 in methanol-water, ethanol-water and acetonitrile-water gives phenothiazine-3-one (PTN) and phenothiazine sulphone as the products at low conversion. A small shift in the \( \lambda_{\text{max}} \) indicates the formation of an additional product, which is destroyed during the separation. An inverse relationship between \( \log \Phi \) (\( \Phi \) quantum yield of PTN formation) and \( 1/C \_0 \) (\( C \_0 \) = dielectric constant of the medium) supports the participation of singlet oxygen \( \left( O\_2 \right) \) at low [PTH]. A mechanism consistent with the results showing the participation of \( O\_2 \) at low [PTH] and electron transfer-exciplex formation at high [PTH] is postulated. The formation of phenothiazine sulphone has been suggested to be through the phenothiazinyl radical.

The presence of surfactants in the photochemical system influences the reactions by means of possible change in the mechanism\(^{1,2}\) and/or product distribution and increase in the solubility of singlet oxygen \( \left( O\_2 \right) \) and substrate\(^{3-5}\). The photooxidation is reported to proceed both by singlet oxygen\(^{6-10}\) and electron transfer mechanisms in micellar\(^{11-15}\) as well as non-micellar media\(^{16,17}\) where both substrates and solvent play an important role in sorting out the applicability of the two mechanisms\(^{18}\). The photoysis of phenothiazine (PTH) in sodium dodecylsulphate (SDS) micellar solution has been found to result in the photoionization and PTH triplet formation\(^{19}\). The lifetimes of both PTH\(^{+}\) and PTH triplet are much more in micellar solution as compared to methanolic solution possibly because of their slow exit from micellar interior. The participation of \( O\_2 \) has been reported in the photooxidation study of tetramethylene-10-methyl phenothiazine system in micellar medium\(^{20}\). The mechanism of photooxidation of PTH in liquid and frozen (77 K) aqueous micellar solutions of SDS has been studied by ESR and the reaction involves the reduction of molecular oxygen dissolved in the aqueous bulk phase\(^{21}\). The phenothiazine derivative promotes micellar photooxidation of sulfides to sulfoxides\(^{22}\). A majority of reports available on photooxidation in micellar media involve \( O\_2 \) as a reactive intermediate although a few papers\(^{23,24}\) are available describing both \( O\_2 \) and electron transfer mechanisms. The present studies aim at laying down the mechanistic details of methylene blue sensitized photooxidation of PTH in SDS, cetyl trimethylammonium bromide (CTAB) and brij-35 (BJ-35) micellar solutions.

Experimental

PTH was crystallized from benzene-petroleum ether to give a sharp m. pt. (180°C). The surfactants (SDS, CTAB and BJ-35) and methylene blue (MB) (Sigma Aldrich) were of guaranteed reagent grade. Other solvents were of high purity grade and were distilled before use.

A rectangular pyrex glass cell (1×4 cm\(^3\)) was used for carrying out the photolysis. A high pressure mercury lamp (250 watt, Philips) with a stabilized power supply was used as light source. A 510 nm optically flat glass cut off filter was placed in between the collimator and the photolysis cell.

The extent of reaction was monitored spectrophotometrically on Shimadzu (UV-1700) spectrophotometer. For kinetic runs, the photolysis cell was directly placed in the spectrophotometer housing at known times and absorbance measured at 500 nm (\( \lambda_{\text{max}} \) of the coloured product). The cell was again placed in front of the light source after absorbance measurements. Light intensity was measured with the help of 2,5-dimethylfuran actinometer\(^{25}\).

Results and discussion

Solutions containing PTH (I) (8.0×10\(^{-4}\) mol dm\(^{-3}\)), MB (12.5×10\(^{-5}\) mol dm\(^{-3}\)) and SDS (8.0×10\(^{-3}\) mol dm\(^{-3}\)) in aqueous organic solvents (three solvent systems: methanol-water, ethanol-water and acetonitrile-water containing 20% water) upon photolysis gave the product mixture. The product mixture when separated on TLC plates gave two bands, which were characterized as phenothiazine-3-one (PTN) (II) and phenothiazine sulphoxide (III) by the method reported elsewhere\(^{26}\). A comparison of visible spectra of photolysed solutions and authentic sample of PTN (Fig. 1) shows that the curves differ in
the absorption maximum indicating the formation of another product absorbing in the visible region which is destroyed in the process of separation since no other coloured product could be detected when the reaction mixture was irradiated up to 20 min.

The formation of phenothiazine nitroxide has been reported in an ESR study of photooxidation of PTH\(^7\) where phenothiazinyl (IV) and phenothiazine nitroxide (V) radicals show the combined absorption. Not only that the nitroxides are observed with PTH, but photooxidation of diphenylamine has been shown to give diphenyl nitroxide\(^26\)\(^30\). This can, therefore, be considered only an indication of the formation of phenothiazine nitroxide but not conclusive evidence because we were not able to detect this on TLC. On prolonged photolysis, however, a minor violet coloured product was detected on TLC, which can be the result of secondary reactions. This was avoided by carrying out the reaction up to low conversions. A similar study with CTAB and BJ-35 as surfactant micelles gave the same products in all the three solvent systems showing that the nature of the product is independent of the nature of surfactant. The linear increase in the absorbance with irradiation time shows the concomitant formation of the products and under the given set of conditions the combined absorbance has been taken for the kinetic study. The product III, being colourless, does not give any absorbance in the visible region.

Methylene blue is the light absorbing species and its concentration is expected to strongly influence the reaction. There is an initial increase in the quantum yield with an increase in [MB] which becomes practically constant beyond \(10^{-5}\) mol dm\(^{-3}\). Thus, a concentration of \(12.5\times10^{-5}\) mol dm\(^{-3}\) MB which corresponds to the complete absorption region was used for the kinetic runs. The dielectric constant of the medium has been shown to strongly influence the sensitized photooxidations\(^31\). Table 1 exhibits an increase in the quantum yield of the product formation (\(\Phi\)) with the increase in the dielectric constant (\(\varepsilon_0\)) of the medium.

The effect has been studied by varying the proportion of water in organic solvents. The quantum yield increases with the increase in the dielectric constant \(\varepsilon_0\) of the medium and the linear plots are obtained between \(\log \Phi\) and \(1/\varepsilon_0\) for three systems separately with negative slopes. The different slopes in three solvent systems point to some other effect as well in addition to the dielectric effect of the medium because if dielectric would have been the only factor responsible for higher quantum yield at high dielectric constant then the combined plot of \(\log \Phi\) versus \(1/\varepsilon_0\) for the three systems should have given a straight line which was not observed. The other possible parameters, which can influence the quantum yield, are the viscosity, nature of the surfactant and the dye-solvent interaction. Thus, the detailed

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### Table 1 — Effect of dielectric constant of the medium ([PTH] = 8.0\(\times\)10\(^{-4}\) mol dm\(^{-3}\), [MB] = 12.5\(\times\)10\(^{-5}\) mol dm\(^{-3}\), [SDS] = 8.0\(\times\)10\(^{-4}\) mol dm\(^{-3}\), [CTAB] = 8.0\(\times\)10\(^{-4}\) mol dm\(^{-3}\), [BJ-35] = 0.4% (v/v), \(\varepsilon_0\) = Dielectric constant of the medium calculated from \(\varepsilon\) of the medium)

<table>
<thead>
<tr>
<th>Solvent % (v/v)</th>
<th>Dielectric constant (\varepsilon_0)</th>
<th>SDS</th>
<th>CTAB</th>
<th>BJ-35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water in methanol</td>
<td>08</td>
<td>36.73</td>
<td>2.20</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>41.32</td>
<td>3.19</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>45.45</td>
<td>4.02</td>
<td>3.47</td>
</tr>
<tr>
<td>Water in ethanol</td>
<td>08</td>
<td>29.65</td>
<td>0.61</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>34.78</td>
<td>1.11</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>39.72</td>
<td>1.16</td>
<td>1.40</td>
</tr>
<tr>
<td>Water in acetonitrile</td>
<td>08</td>
<td>42.73</td>
<td>0.36</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>46.50</td>
<td>0.70</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>50.13</td>
<td>0.80</td>
<td>1.30</td>
</tr>
</tbody>
</table>

\(\varepsilon_0 = \text{Dielectric constant of the medium calculated from the relationship } \varepsilon_0 = \varepsilon_{\text{organic solvent}} + W(\varepsilon_{\text{water}} - \varepsilon_{\text{organic solvent}})\)

\(W = \text{Weight of water added per gram of the total solvent.}\)
A tentative mechanism is as given in the Scheme 1.

\[\begin{align*}
 Mb & \xrightarrow{hv} k_1 Mb \\
 Mb & \xrightarrow{k_2} Mb + \Phi \\
 Mb & \xrightarrow{k_3} Mb + [O_2] \\
 Mb & \xrightarrow{k_{PTH}} Mb + [PTH] \\
 \end{align*}\]

**Scheme 1**

Since various pathways are affected by the presence of surfactants, the effect of varying surfactant concentration was studied. The results showed an initial decrease in the quantum yield, which increased further after reaching a minimum value with the increase in surfactant concentration with all the three surfactants. The surfactants decrease the concentration of excited singlet MB when added in small amounts resulting in decrease in triplet MB concentration, which is produced through intersystem crossing process of singlet MB. Since triplet MB is a reactive intermediate for the product formation, its concentration plays an important role while measuring the quantum yield of the product. The singlet lifetime decreases with the increase in the surfactant concentration and aggregation may account for such a decrease. Hydrophobic ion pairs formed in the pre-micellar region are surrounded by the hydrocarbon chains of the surfactants when concentration is increased further.

The proximity of the dye molecules in the aggregates results in the rapid deactivation of excited states resulting in the shortening of triplet lifetime of MB. The increase in the quantum yield beyond minima could be attributed to the protection of excited state of MB encapsulated in micelles from bimolecular deactivation. Although the decay rate \(k_3\) of triplet MB decreases in micellar solution, the initial decrease in the quantum yield could be solely attributed to the decrease in singlet lifetime of MB in the pre-micellar region. The decreased decay rate of triplet MB increases the quantum yield of the product formation through steps \(k_4\) followed by \(k_5\) where the surfactant concentration is high. The reaction is also expected to be enhanced if it goes through step \(k_7\).

The fractions of the reaction going through the competitive reactions (steps \(k_4\) and \(k_7\)) are dependent upon the relative concentrations of \(O_2\) and [PTH] in the complete absorption region. The effect of varying [PTH] was, therefore, examined and the results are given in Figs 2 to 4 where quantum yield has been plotted against [PTH]. Inverse plots (Φ\(^{-1}\) versus [PTH]\(^{\beta}\)) have also been included in the figures as insets. The results show an initial increase in the quantum yield which decreases after reaching a maximum value with increase in [PTH] at constant [MB], [O\(_2\)], and [surfactant] in all the three solvent systems. The initial increase in the quantum yield is in accordance with Eq. (1) (derived on the basis of steady stated treatment of Scheme 1 when steps \(k_7\) and \(k_8\) have not been included), which predicts a flattening (not observed) at high [PTH] when \(\beta \ll [PTH]\).

\[
\Phi = \Phi'(O_2) \alpha [PTH]/([PTH] + \beta) \quad \cdots (1)
\]

where \(\beta = k_3/k_6\), \(\alpha\) is the fraction of reaction giving products via \(k_4\), and

\[
\Phi'(O_3) = k_2 k_3 [O_2] / (k_1 + k_2) (k_3 + k_4 [O_2])
\]

In the complete absorption region, Eq. (2) gives the quantum yield of product formation:

\[
\Phi = \{k_2 [PTH]/(k_1 + k_2)\} \{k_7 + k_4 [O_2] / (k_3 + k_6 [PTH])\} \\
\{1 / (k_1 + k_4 [O_2] + k_7 [PTH])\} \quad \cdots (2)
\]

Fig. 2 — Plots of Φ versus [PTH]. Curves I to III are for SDS, CTAB and BJ-35, respectively. Inset represents Φ\(^{-1}\) versus [PTH]\(^{\beta}\) plots ((O) SDS, (●) CTAB and (●) BJ-35. SDS = 8.0 × 10\(^{-4}\) mol dm\(^{-3}\), CTAB = 8.0 × 10\(^{-4}\) mol dm\(^{-3}\), BJ-35 = 0.4% (v/v), MB = 12.5 × 10\(^{-3}\) mol dm\(^{-3}\), Solvent methanol : water, 4 : 1).
where $k_8$ has not been included in view of it being probable only at very high [PTH].

Equation (2) does not give a simple relationship between $\Phi$ and [PTH]. At low [PTH], process ($k_4$) is more favorable and Eq. (2) in the inverted form (Eq. 3) predicts a linear relationship between $\Phi^{-1}$ and [PTH]^{-1} when $k_7$ becomes insignificant.

$$\Phi^{-1} = \frac{(k_1+k_2) (k_3+k_4 [O_2])/k_2 k_4 [O_2])}{(1+k_5 [PTH]/k_6)} ... (3)$$

The steady state treatment of Scheme 1 taken all steps together gives:

$$\Phi^{-1} = \frac{(k_1+k_2) k_7+ (k_3+k_4 [O_2])/k_8 (k_5+k_6 [O_2])}{k_2 (k_7+k_8 [O_2])} ... (4)$$

Equation (4) includes certain assumptions at high [PTH] in micellar media where processes ($k_3$) and ($k_1$) are less favorable.

The [PTH] effect can be explained with the help of Eqs (3) and (4). The two parts of inverse plots can be explained by the two equations. The first part is in accordance with Eq. (4) which predicts an inverse relation between $\Phi$ and [PTH] whereas the second part obeys Eq. (3). At intermediate [PTH], however, neither of the two equations is valid and the reaction may be going through both the mechanisms ($^1O_2$ and electron transfer). The results, therefore, show that the MB sensitized photooxidation of PTH undergoes through $^1O_2$ participation at low [PTH] and electron transfer-excioplex formation at high [PTH].

Phenothiazine sulfoxide cannot be formed through an energy transfer from triplet MB to PTH since the process would be endothermic by 88.2 kJ$^{34,35}$. The direct photolysis of PTH has been shown to give phenothiazine sulfoxide through phenothiazinyl radical$^{36}$ which can be possible in our system as well by an attack of $^1O_2$ on the radical. The low quantum yield and monitoring difficulty did not allow the kinetic analysis of this product.

References