Methylene blue sensitized oxidation of 2-imidazolidinethione in microheterogeneous medium

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The methylene blue (MB) sensitized photooxidation of 2-imidazolidinethione (IT) in sodium dodecylsulphate (SDS) aqueous micellar solution gives 2-imidazolidine-2-yl-sulphinic acid as the primary product. Higher quantum yields of product formation at high [SDS] are due to the increased efficiency of energy transfer/electron transfer processes in MB-\( \text{O}_2 \)/MB-IT pairs respectively. The effect of various kinetic parameters establishes the reaction to proceed through the participation of singlet oxygen. The ionic mechanism is suggested at higher IT concentration. Salt effect supports the stabilization of polar transition state/formation of dye rich micellar aggregates.

A large amount of work has been done on the photooxidation of various substrates using different dyes as sensitizers both in homogeneous and heterogeneous media\(^{1-9}\). The photooxidation is reported to involve singlet oxygen (\( \text{O}_2 \)) as a reactive intermediate in addition to the electron transfer-exciplex formation and the efficiency of the two processes depends upon the concentration of the substrate\(^2,4-6\). The kinetic investigation of sulphide oxidation has been reported to proceed via nucleophilic attack on \( \text{O}_2 \) in homogeneous medium\(^7\). Dye sensitized oxidation of thiourea and diphenylthiourea\(^8,9\) proceeds via \( \text{O}_2 \) mechanism. The presence of surfactants in a photochemical system can be taken to influence the reaction by means of possible change in mechanism and/or product distribution and increase in the solubility of \( \text{O}_2 \) and substrates\(^1,11,12\). The lowering of threshold energy for electron transfer and reduction in the geminate pair reverse reaction by the surfactant has also been reported in micellar systems\(^1\).

The available reports show that a little amount of work has been done on the photooxidation of sulphides and thioureas especially in heterogeneous medium. The present investigation has been carried out in order to look into the mechanistic aspects of methylene blue (MB) sensitized oxidation of 2-imidazolidinethione (IT) in sodium dodecylsulphate (SDS) aqueous micellar solutions.

Materials and Methods

2-Imidazolidinethione was prepared by the method reported elsewhere\(^14\) and SDS (Glaxo, GR) was crystallized from absolute ethanol. Other reagents were of high purity grade and were crystallized/distilled before use. The photolysis were carried out in a flat bottom pyrex cell (5 cm dia and 10 cm length) with a high pressure mercury lamp (250 W, Philips) and halogen lamp (1000 W, Philips) with a stabilized power supply. The incident light was filtered through an optically flat glass filter with cut off at 470 nm. The products were monitored conductometrically with a precalibrated digital conductometer (Toshniwal) by inserting the conductivity cell directly into the reaction mixture. The irradiations were stopped with the help of a wooden shutter during measurements. The conductivity cell was taken out of the photolysis cell during irradiations. Pressurized oxygen gas was passed through the solution at suitable flow rate. The light intensity was changed by inserting a wire gauge in between the light source and photolysis cell.

Results and Discussion

The lone product formed in the reaction mixture, containing 7.5 x 10\(^{-4}\) mol dm\(^{-3}\) IT, 6.0 x 10\(^{-5}\) mol dm\(^{-3}\) MB and 4.0 x 10\(^{-2}\) mol dm\(^{-3}\) SDS in water which was photolysed for 90 minutes, was identified as 2-imidazolidine-2-yl-sulphinic acid (ISH) by the methods reported elsewhere\(^15\). For kinetic runs the products were monitored conductometrically since IT and ISH are colourless and optical density cannot be used. The added ionic substances, whose concentration does not change with time, will contribute to the
The observed value of conductance which has been cancelled by subtracting the conductance of unirradiated solution from that of irradiated solution at different times.

The incident light is essentially absorbed by MB because IT is transparent in the visible region (irradiations were made at wavelengths greater than 470 nm). The effect of varying MB concentrations shows that the quantum yield of product formation first increases and then becomes practically constant with the increase in [MB] which seems reasonable because at lower [MB] the absorption of incident radiation is incomplete. All the incident light is absorbed by MB when its concentration reaches $5.0 \times 10^{-5}$ mol dm$^{-3}$ and further increase in MB ceases to affect the quantum yield and hence flattening is observed. The lower quantum yields at [MB] higher than flattened region could be due to the deactivation of triplet dye by dimeric MB species$^{15}$.

The reaction kinetics in heterogeneous system appears to be somewhat similar to that in homogeneous system because same product is formed in both the cases. Various steps leading to the product formation are, however, expected to be influenced by the presence of SDS because the surfactants are reported to have an increasing effect on energy transfer rate and decreasing effect on the decay rate of the sensitizer$^{11}$ in the micellar region. The quenching of the excited states by oxygen is also favourable in the presence of surfactants$^{17}$.

The fluorescence intensity of dyes has been reported to be decreased by the surfactants in premicellar region$^{16,20}$ and dye rich premicellar aggregates are responsible for the effect on absorption characteristics of the dyes$^{11}$. The effect of varying SDS concentration (Fig. 1) shows that the quantum yield decreases continuously during the progress of the reaction which finally reaches zero value. The decrease in the quantum yield is not due to any depletion in [IT] because the IT concentration used here is such that beyond this the quantum yield does not increase (cf. IT concentration effect). The quantum yield of product formation as evidenced by the overall reaction extent first decreases and then increases with increase in [SDS]. The surfactants decrease the concentration of excited singlet MB when added in small amounts$^{20}$ resulting in decrease in triplet [MB] which is a reactive intermediate for product formation. The singlet lifetime decreases with increase in surfactant concentration in the premicellar region and aggregation may account for the same$^{21}$ and thus the initial decrease in quantum yield could be solely attributed to the decrease in the singlet lifetime of MB in premicellar region. The absorption characteristics of MB may not significantly affect the quantum yield as the [MB] used here is such that it essentially absorbs all the incident radiations. Higher quantum yields at high [SDS] are due to the increased efficiency of energy transfer/electron transfer processes in MB-$O_2^{-}/$MB-IT pairs respectively which are responsible for the product formation and the decreasing effect on the deactivation rate of triplet MB$^{16}$. The slowing down of the reaction during its course may be attributed to some quenching effect. As the reaction proceeds acid is formed whose concentration builds up with time. When the reaction extent is more the reaction is slowed down at lower irradiation times as compared to that in lower reaction extents. The effect shows that the product may be acting as a quenching species whose minimum concentration required for quenching builds up at relatively lower irradiation times when the reaction extent is higher. In the absence of SDS the slowing down effect is at higher irradiation times because the reaction rate is lower in the initial stages. The overall lower conversion at low [SDS] as compared to the system where SDS is not present shows that SDS not only enhances the reaction in the initial stages but...
it also helps in quenching by the product in the final stages.

The concentration of IT is expected to strongly influence the reaction as it can compete with $O_2$ in the energy transfer process of triplet MB. The results of varying concentration of IT are given in Fig. 2. The reaction extent first increases and then decreases after reaching a maximum value with the increase in [IT] both in the premicellar (1 mM SDS) and postmicellar (10 mM SDS) regions. A similar effect was observed in homogeneous medium with the difference that the change in the conductivity versus irradiation time plots are observed to be S-shaped showing a slow and steady reaction initially which rapidly accelerates after certain time and then stops. Two pathways leading to the products may be represented as shown in Scheme 1.

The relative efficiency of steps $k_1$ and $k_2$ determines the overall reaction extent. As the concentration of IT increases more and more reaction goes through process $k_3$ whose efficiency is several times lower than that of process $k_1$ (ref. 22). The initial increase in the rate with increase in IT concentration is in accordance with the fact that rate is proportional to the [substrate] if the reaction goes through step $k_1$ alone as has been reported in other systems$^{2,25}$. A similar study in SDS free system shows that process $k_3$ starts operating at relatively lower [IT] in the presence of SDS than in its absence showing that the electron transfer-exciplex formation mechanism is more facilitated by SDS possibly through the stabilization of ionic intermediates.

Light intensity in all the experiments was kept constant as the reaction extent was found to be dependent on the intensity of light. The reaction decreases with the decrease in light intensity. The decreased light intensity not only results in the overall lesser reaction extent but also shifts the flattening to longer irradiation times showing the quenching effect due to the product itself. It requires a relatively lesser time to reach the minimum concentration of the product at higher light intensity as compared to a system irradiated with low light intensity.

The flattening is neither due to depletion in IT...
concentration nor in oxygen concentration as the reaction extent practically remains the same when the oxygen concentration was increased from $2.28 \times 10^{-4}$ mol dm$^{-3}$ to $1.14 \times 10^{-3}$ mol dm$^{-3}$ (Fig. 3). The reaction extent when the gas is continuously bubbled through the solution (Fig. 3, curve II) as compared to the case when the solution was flushed with O$_2$ for 15 minutes before photolysis (Fig. 3, curve I) can be attributed to (a) stirring of the reaction mixture, (b) accumulation of impurities present in oxygen and (c) part of the reaction occurring at the interface of the oxygen bubble. The stirring has no effect because the mechanical stirring of the reaction mixture does not alter the reaction extent. The oxygen gas was of 99.9% purity and the level of impurities could be of the order of $10^{-6}$ mol dm$^{-3}$ which can influence the reaction because of quenching of excited states by impurities with diffusion controlled rate$^{24,25}$. In the event of such quenching the reaction extent should have been lower instead of higher when oxygen gas is bubbled through the solution. It appears, therefore, that a part of the reaction occurs at the interface of the oxygen bubble where the deactivation by the solvent is minimized.

In order to establish the ionic mechanism, the effect of added salts (NaCl, KCl and KNO$_3$) was examined. The higher reaction extent in the presence of the salts can be attributed to (a) stabilization of polar transition state/ionic intermediates and (b) lowering in critical micelle concentration$^{26}$ resulting in the formation of dye rich micellar aggregates and electron transfer is facilitated$^{27}$. The electron transfer efficiency has been shown to be enhanced even in the premicellar region$^{28,29}$ and the effect could be due to the formation of dye rich induced micelle. Such an effect is expected to be more in the presence of dye rich micellar aggregates as compared to the dye rich induced micelles.

The results presented above, in addition to the observed decrease in pH of the reaction mixture with irradiation time, confirm the formation of sulphinic acid (ISH) the dissociation of which leads to an increase in [H$^+$] which is responsible for lowering of pH.

The observed results establish that MB sensitized photoxidation of IT in SDS micellar solutions proceeds through the involvement of O$_2$ and ionic intermediates and the kinetic features show the similarity in heterogeneous and homogeneous systems. However, SDS influences the energy transfer/electron transfer processes in addition to the formation of dye rich micellar aggregates in the presence of added salts.

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**References**