Photobleaching in Methylene Blue Sensitization
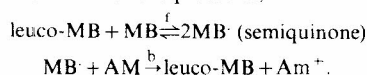
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Methylene Blue (MB) is reduced to leuco-MB by methanol (k_{ol}) and amines (k_{Am}) with $k_{ol} \simeq k_{Am}/10$. The bleaching in methanol does not go to completion and the cessation is attributed to the deactivation of ^{3}MB by leuco-MB through an electron transfer process. The final e.m.f. (platinum electrode versus SCE) reached is independent of [Am] and the effect of varying [MB] and light intensity is in accordance with the processes;

$$\text{leuco-MB} + \text{MB} \overset{f}{\rightleftharpoons} 2\text{MB}^{\cdot} \text{ (semiquinone)}$$

$$\text{MB}^{\cdot} + \text{AM} \overset{b}{\rightarrow} \text{leuco-MB} + \text{Am}^{+}.$$

The temperature effect indicates a somewhat higher E_a for path-b as compared to path-f. The results on the effect of change of dielectric constant of the medium suggest some ineffective deactivation of ^{3}MB competing with the net initial electron transfer reaction;

$$^3\text{MB} + \text{Am} \rightarrow \text{MB}^{\cdot} + \text{Am}^{+}.$$
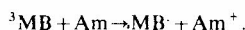
The difference between the maximum e.m.f. (0.282 to 0.302 V) and the rate of approach to this limiting condition in the case of the five amines, viz. *o*-toluidine, N-ethylaniline, diphenylamine, N-methyldiphenylamine, N,N-dimethylaniline have been rationalised through (a) triplet exciplexation; (b) availability of hydrogen on nitrogen because of a possible initial hydrogen atom transfer to the dye; and (c) stability of the aminium radical cation because of a back reaction.

Dye sensitization has an important role in many photooxidations[1] and in the techniques being developed for the utilisation of solar energy[2]. In most of these systems dyes undergo reversible redox reactions. Methylene blue [(MB, phenothiazin-5-ium-3, 7-bis(dimethylamino chloride)] is reported to be a good electron acceptor[3]. The molecular orbital calculations on MB, taking the participation of d orbitals of sulphur into account, predict leuco methylene blue (leuco-MB) to be excellent electron donor[4].

Japanese workers have observed in alkaline solutions containing amines, phenazine and thiazine dyes, concomitant oxidation of amines and the photoreduction of the dyes[5]. In a study of the photobleaching of MB with primary, secondary and tertiary ethylamines it has been postulated that protonated dye after photooxidation gives an intermediate with the amines which decomposes to leuco-MB and amine oxide[6]. Steiner *et al.*[7] and Kayser and Young[8] have been able to identify the intermediates and have measured some of the rate constants, employing flash photolysis technique. However, the steady illuminations need not follow the same course of the reaction because of the large density of intermediates in the flash experiments.

In view of the significance of the dye sensitization and many unknown features of these reactions, the present investigation was undertaken.
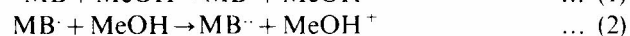
Materials and Methods

Oxygen was vigorously excluded in all the systems and photobleaching was monitored through both spectrophotometric and redox potential measurements. Merck reagent grade MB was used as such. The other reagents were of high purity and were crystallised or fractionally distilled before use. White light made parallel with convex lenses system was used for illumination. The reaction cell consisted of a square tube (ACE Glass Inc., USA); 20 mm^2 × 80 mm and fitted with a side tube. The solutions were flushed with purified nitrogen before illumination. Saturated calomel electrode was used as a reference electrode. Dynamaster recorder (Elliott; 1PH570-51, London) was employed for recording the potential-time curves. Chemical actinometer, dimethylfuran, was used for light intensity measurements.

Results and Discussion

The redox potential at the platinum electrode in MB sensitized photooxidation of amines in deaerated solutions in methanol gives a measure of the extent of photoreduction of the dye[9]. In the absence of amine the solvent methanol also reduces the dye and in both the cases, i.e. in the presence and absence of amines the photoproduct is leuco-MB as evidenced by repeated complete recovery of the dye on oxygenation of the photolysed solution. That the final e.m.f. reached corresponds to complete bleaching of the dye in the presence of amine and only partial bleaching in the

neat solvent is shown by the plots in Fig. 1. The intensity of light absorbed changes with the irradiation time and this factor when taken into account shows that saturation actually takes place after a much longer period. In view of the low singlet and triplet levels of the dye[10], $\varnothing_{isc} = 0.52$ (ref. 11) and even amines not quenching the excited singlet dye[12], it can be surmised that it is the triplet state which is reduced in the present experiments. In the absence of any substrate, the bleaching can be explained by the sequence of reactions (1-3)

$$^3MB + MeOH \rightarrow MB^- + MeOH^+ \qquad ... (1)$$
$$MB^- + MeOH \rightarrow MB^{--} + MeOH^+ \qquad ... (2)$$
$$MB^- + MB^- \rightarrow MB + MB^{--} \qquad ... (3)$$

(MB is a univalent cation, MB· is neutral semiquinone radical, MB·· is univalent leuco dye anion).

Semiquinone radicals have been directly observed in flash photolysis of MB and a rapid dismutation rate has been reported for their disappearance[13]. MeOH⁺ is expected to give alkyl hydroxy radicals in analogy with radioloysis systems where this species is certainly produced[14]. However, hydroxyl radicals are not produced here since in their presence dye is expected to be consumed which is not true. Methanol bleaches the excited dye in the beginning of photolysis but this process does not go to completion. The cessation of bleaching appears to be due to the quenching of the reaction by a product. Quenching by any of the oxidation products of methanol at the concentrations involved is ruled out. Leuco dye is a good electron donor and a reasonable net quenching process appears to be:

$$^3MB + MB^{--} \rightarrow MB^- + MB^- \rightarrow MB + MB^{--} \qquad ... (4)$$
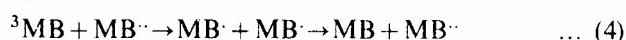
The deactivation here is suggested to involve an electron transfer chemical reaction since (i) electronic energy dissipation is less likely because of low [MB⁻] and (ii) the rate can not be considered higher than the diffusion-controlled rate.

In the presence of amines, photobleaching is 10 times faster (cf. Fig. 1) and any reaction with the solvent can be neglected. The effect of varying concentration of the amine has been examined and the results are graphically shown in Fig. 2. The curves have similar shape and the final e.m.f. reached is the same. However, the time required to reach the maximum e.m.f. increases with decrease in [Am].

The effect of varying [dye] is shown in Fig. 3. An increase in [dye] increases the time to reach the final equilibrium. This is an unexpected observation. A comparison of curves III and IV shows that whereas in curve III a steady slow reaction (which is absent in curve I) precedes the final flattening; in curve IV the initial slow reaction is further slowed down and equilibrium is not reached upto the observed extent of
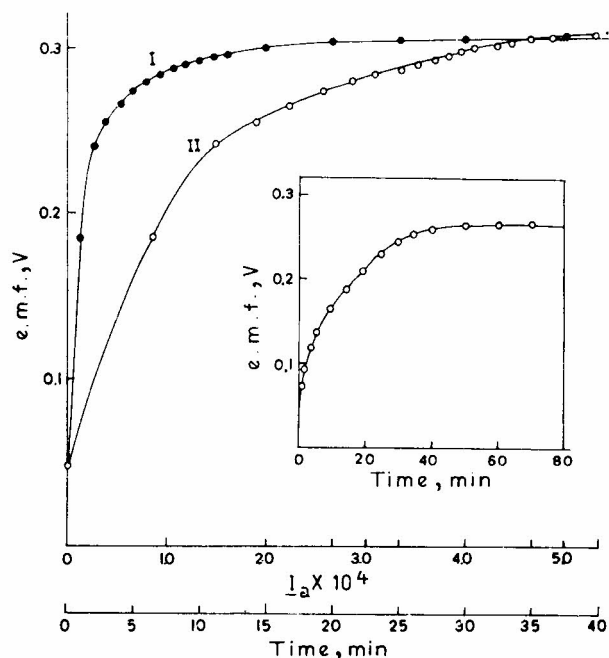

Fig. 1—Effect of change in absorbed light intensity during photolysis of MB in the presence of diphenylamine (Curve I, e.m.f. versus time and curve II, e.m.f. versus absorbed light intensity. [MB] $=0.8 \times 10^{-5}$ M, [DPA] $= 1.0 \times 10^{-2}$ M; solvent = CH₃OH-H₂O (2:1); temp = 31 C; and $I_0 = 1.76 \times 10^{-4}$ Einstein litre⁻¹ min⁻¹. Inset curve; [DPA] = 0; [MB] = 0.8 × 10⁻⁵ M; solvent = CH₃OH; temp = 29 C; and $I_0 = 1.76 \times 10^{-4}$ Einstein litre⁻¹ min⁻¹)
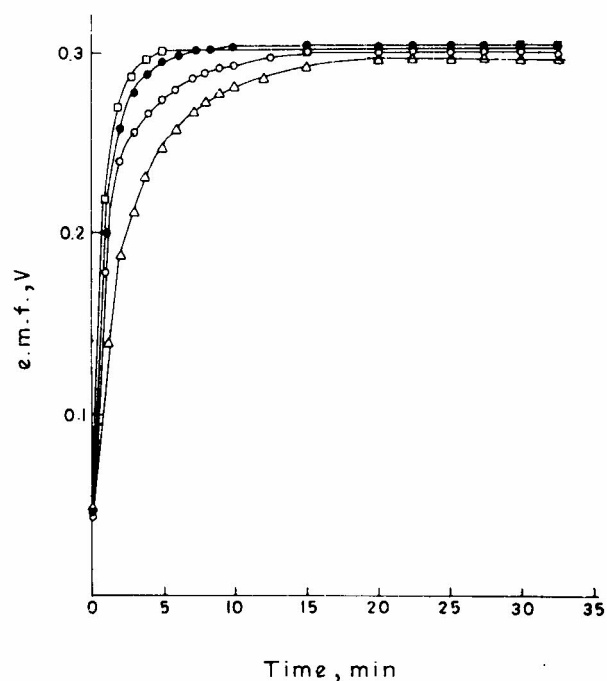
Fig. 2 —Effect of varying [diphenylamine] on the photolysis of MB [Curves □ ··□, ●··●, ○ ─○, △ ─△, are for [DPA] = 5.0 × 10⁻², 1.0 × 10⁻², 0.5 × 10⁻² and 0.05 × 10⁻² M respectively. [MB] = 0.8 × 10⁻⁵ M; solvent = CH₃OH-H₂O (2:1); temp = 32.5 C; and I_0 = 1.76 × 10⁻⁴ Einstein litre⁻¹ min⁻¹)
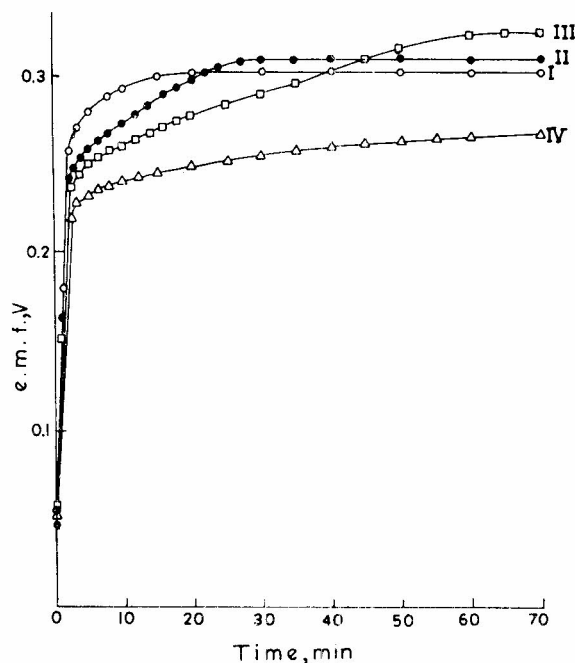
Fig. 3 —Effect of varying [dye] on its photolysis in the presence of diphenylamine (Curve I, II, III, IV are for [MB] = 0.8×10^{-5}, 4.0 $\times 10^{-5}$, 8.0×10^{-5} and 40.0×10^{-5} M respectively. [DPA] = 1.0 $\times 10^{-2}$ M; solvent = CH$_3$OH-H$_2$O (2 : 1); temp = 33 C and I_0 = 1.76 $\times 10^{-4}$ Einstein litre^{-1} min^{-1})
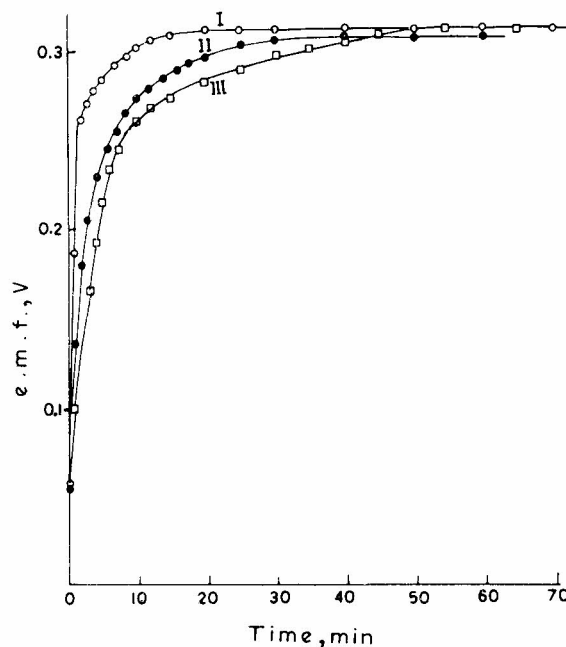
Fig. 4—Effect of light intensity on the photolysis of MB in the presence of diphenylamine (I_0 = 1.76 × 10^{-4} (I), I_0 = 0.65 × 10^{-4} (II) and 0.47 × 10^{-4} (III) Einstein litre^{-1} min^{-1}. [MB] = 0.8 × 10^{-5} M; [DPA] = 1.0 × 10^{-2} M; temp = 34°C; and solvent = CH$_3$OH-H$_2$O (2 : 1))

the reaction. It is apparent that the approach to final equilibrium is slowed by the dye. With increase in [dye] the concentration of the primary short-lived intermediates is expected to be high — a result also expected from increased incident intensity. The effect of change in incident intensity is given in Fig. 4 and an opposite effect is observed. Curve III at low light intensity resembles the high [dye] experiment. It is thus apparent that the observed effect is not due to a localised high concentration of excited dye molecules, radicals or ions. At high [MB] and low absorbed intensities (I_a) a new region of reaction before the flat maximum appears. At lower I_a, [³MB] is small and it suggests a similar result at high [MB] implying deactivation to occur by the reaction (5)

$$^3MB + MB \rightarrow 2MB \qquad \ldots (5)$$

This type of deactivation is well known in other sensitized systems. However, it has been observed in the photooxidation of amines that when [Am] ≫ [O₂] the initial interaction is between ³MB and amine and an increase in [dye] does not lead to deactivation and furthermore the oxidation is independent of the intensity absorbed[15]. It thus appears that the deactivation of the excited dye is not the cause of the observed effect.

In view of these observations, one needs to consider the reactions (6) and (7)

$$MB^{..} + MB \rightleftharpoons MB^. + MB^. \qquad \ldots (6)$$

$$MB^. + Am \rightarrow MB^{..} + Am^+ \qquad \ldots (7)$$
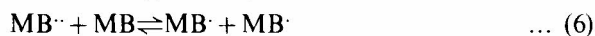
The equilibrium is in favour of semiquinone in the presence of large excess of the dye and of necessity the reaction between MB and amine is a slow one. A higher equilibrium concentration of the semiquinone is expected in curve IV (Fig. 3) and this is in accordance with the observation of Michaelis et al.[16] that in partly reduced solution of MB in dilute acid a little percentage of the total dye can be present as semiquinone[16]. At lower light intensities the relative concentration of MB before the final equilibrium is expected to be higher and this is as observed.

The dielectric of the medium plays an important role in the reactions where the amines are involved or where the transition state has some charge separation[17], and the effect of this parameter was examined by varying the proportion of water in methanol. Figure 5 shows that the bleaching rate increases with an increase in the dielectric constant of the medium. Viscosity of the medium can also influence the reaction but addition of water to methanol does not change it. This suggests that some ineffective deactivation of ³MB competes with the electron transfer reaction (8)

$$^3MB + Am \rightarrow MB^. + Am^+ \qquad \ldots (8)$$
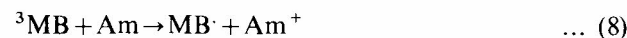
which is likely to be the rate-determining process.

Temperature effect studies are mechanistically very revealing in appropriate reactions. In the present system the absorption process is not affected by
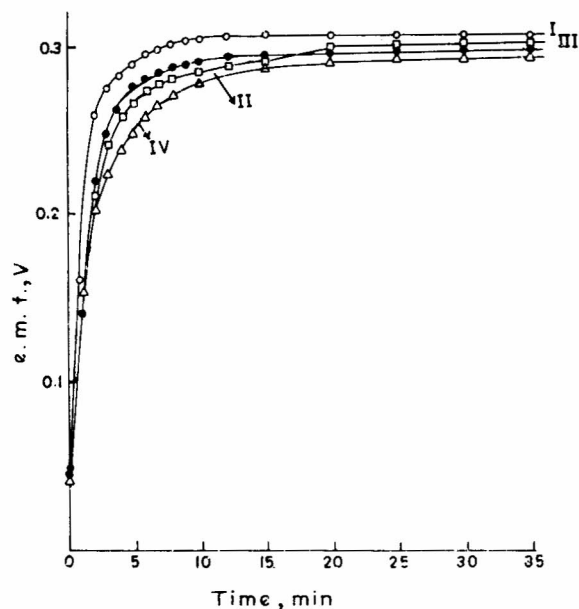
Fig. 5—Effect of dielectric constant of the medium on the photolysis of MB in the presence of diphenylamine ([MB] = 0.8×10^{-5} M; [DPA] = 1.0×10^{-2} M; temp = $34°C$; and $I_0 = 1.76 \times 10^{-4}$ Einstein litre^{-1} min^{-1}. Curve I, CH$_3$OH/H$_2$O = 2 (by volume), $\varepsilon = 51.10$; curve II, CH$_3$OH/H$_2$O = 3, $\varepsilon = 46.76$; curve III, CH$_3$OH/H$_2$O = 4,ε = 44.09; and curve IV, CH$_3$OH, $\varepsilon = 32.70$. Dielectric constant values (ε) were calculated from the equation

$$\varepsilon_0 = \varepsilon_{01} + W(H_2O - \varepsilon_{01})$$

where ε_{01} and ε_{H_2O} are the dielectric constants of methanol and water respectively and W is the weight of water added per g of the total solvent)

temperature and it is felt that in the event of particularly any of the secondary processes having some activation energy the temperature effect may reveal the nature of the transition state of that process. Figure 6 shows that a change in temperature by $26.5°C$ does not alter the reaction to any appreciable extent. The final e.m.f. and the net rate of approach to equilibrium register only slight increase at higher temperature. This can be taken to suggest a somewhat higher activation energy for the backward reaction in Eq. 6 as compared to that for the forward reaction.

The effect of changing the substrate amine was next examined. The results are given in Fig. 7. For the five amines examined the maximum e.m.f. varies from 0.282 to 0.302 V. The rate of bleaching is observed to be slowest in N,N-dimethylaniline and the e.m.f. versus absorbed intensity curve clearly shows a central linear portion which needs to be compared with the [dye] effect (cf. Fig. 3). ^{3}MB is a reductant and can give exciplexes with amines. Exciplexes have been reported with triplet benzophenone and anilines[18]. Electron transfer has also been postulated through triplet excimers in the thionine and electron donor substrate system[7]. It, thus, appears reasonable to postulate the formation of a charge transfer complex between ^{3}MB and Am.
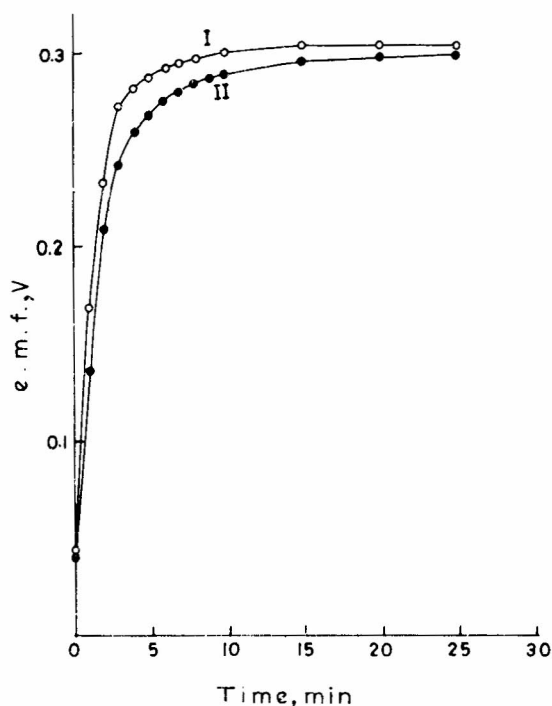

Fig. 6— Effect of varying temperature on the photolysis of MB in the presence of diphenylamine (Temp = 35.5 (I) and 9.0°C (II). [MB] = 0.8×10^{-5} M; [DPA] = 1.0×10^{-2} M; solvent = CH$_3$OH-H$_2$O (2:1); and $I_0 = 1.76 \times 10^{-4}$ Einstein litre^{-1} min^{-1})
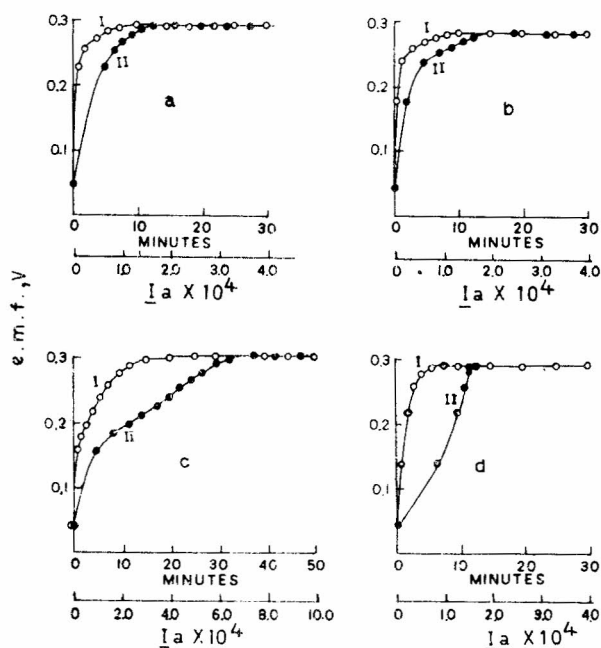

Fig. 7 – Change of e.m.f. during photooxidation of amines, viz. o-toluidine (a), N-ethylaniline (b), N-methyldiphenylamine (c), and N,N-dimethylaniline (d) in the presence of MB (Curve I, e.m.f. versus time; and II, e.m.f. versus absorbed light intensity. [MB] = 0.8 $\times 10^{-5}$ M; [Am] = 1.0×10^{-2} M; solvent = CH$_3$OH-H$_2$O (2:1), temp = 34.5°C (for a), 35 (for b), 33 (for c), and 34 (for d); $I_0 = 1.76 \times 10^{-4}$ Einstein litre^{-1} min^{-1})

$$^3MB + Am \rightarrow {}^3(MB...Am) \qquad ... (9)$$

A study of the substituent effect on the interaction of triplet dye with amines supports the formation of a charge transfer intermediate[19]. Such processes are expected to depend upon the ionization potential of the substrate. The reported data on ionization potentials of the amines[20], however, do not reveal any simple relationship with the ionization potential and rate of the redox reaction. However, an electron abstraction followed by proton transfer with or without the participation of the exciplex is equivalent to hydrogen atom transfer and it remains to be established what actually happens[21]. It is likely that hydrogen atom is first transferred to the interacting dye and the semiquinone results later through the loss of a proton. In such a situation availability of hydrogen on the nitrogen of the amine can play an important role and this appears to be true from the present results. Another important factor particularly with respect to the back electron transfer reaction is the stability of the aminium radical cation. A markedly faster rate with N-methyldiphenylamine as compared to that with the N,N-dimethylaniline can be attributed to considerably large stability (in terms of resonance structures) of the cation arising from the former amine.

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