

Photoredox reactions of methylene blue on zinc oxide

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Photoreduction of methylene blue (MB^+) at 366 nm (3.4 eV) in a heterogeneous medium containing ZnO (band separation = 3.2 eV) has been carried out. In oxygen-free media the product has been found to be leuco-MB which is fully converted into MB^+ on air oxidation. An analysis of the results shows that ZnO is the absorber and negligible light absorbed by MB^+ cannot explain the observed conversions. Concentration of ZnO in the medium plays a more important role at higher concentrations of MB^+ . Also reaction extent decreases with increase in dye concentration but at low concentrations it is proportional to dye concentration. A unique feature of the reaction is that it is quenched by the product. Photoreduction is more efficient in solvents of high dielectric and in solvents with easily available hydrogens. Different samples of ZnO prepared from different salts behave differently in this photoreduction due to different reflectance and absorbance characteristics of these samples. A mechanism explaining the observed data and consistent with the known features of such systems have been proposed.

Although the interest in solar energy utilisation via conversion of photons into chemical potential at the semi-conductor-electrolyte interface has waned, the mechanistic studies of photocatalytic and photosensitized processes in such heterogeneous media continue to attract attention (i) for many fundamental questions remain unanswered and (ii) the commercial viability of synthetic potential is yet to be fully exploited. Aqueous or aerosol suspensions of most semiconductor materials have been found to photocatalyse the reaction for this type of energy conversion. Zinc oxide redox system has been studied by many workers because of its high photoactivity and extensive background information is available on its photocatalytic, photoluminescent and photoconductive behaviour¹⁻⁵. An important characteristic of ZnO is that it does not undergo photoreduction like many other metal oxides⁶.

In most of the homogeneous photoreactions, quantum efficiencies are far below unity and the wastage is usually attributed to either the degradation of electronically excited species or a reversible fast electron transfer process^{7,8}. In select systems, however, one of the processes predominates. It is important to distinguish between the two processes and one of the methods is to employ a system where only electron transfer is possible. In the present study, the interface of ZnO, a n-type semiconductor, which allows electron transfer, has been exploited.

Materials and Methods

Zinc oxide (BDH, LR) was washed with distilled

water and dried in an oven. Samples of ZnO prepared by ignition of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and zinc carbonate were also employed after washing and drying. Methylene blue (Sigma Chemicals, USA, extra pure) was purified by repeated crystallisation from ethanol. Purified nitrogen⁹ was used for deoxygenation of solutions.

The light source was a medium pressure mercury lamp (125 watt, Philips) with an integrated filter having maximum emission at 366 nm. The photolysis cell was made of a clean pyrex glass tube fitted with a threaded leak proof cork. The light beam falling on the cell was rendered parallel using a blackened glass tube. The contents of the photolysis cell were continuously stirred to keep the ZnO particles suspended during photolysis. The progress of the reaction was monitored by directly transferring the cell to the cell housing of the spectrophotometer (Erma model LS-7, Japan) after the settling down of ZnO particles by centrifugation. Spectrophotometric and thin layer chromatographic techniques were used for the identification of the products.

Results and Discussion

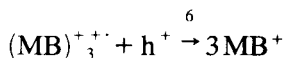
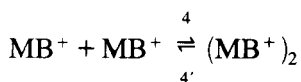
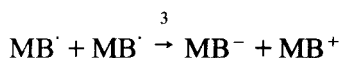
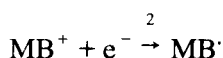
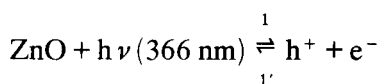
In deoxygenated aqueous solutions, methylene blue (MB^+) does not undergo any reaction when irradiated with 366 nm light in the absence of ZnO. However in the presence of ZnO, MB^+ is quantitatively reduced to leuco-MB and on aeration of the photolysed mixture, MB^+ is completely recovered.

Absorption of 3.4 eV (366 nm) photons by ZnO raises electrons to conduction band from the valence band (band separation = 3.2 eV). MB^+ has a

poor absorption in this region of spectrum ($OD_{366\text{ nm}} = 0.018$ at the maximum concentration employed) and approximate calculations show that it absorbs less than 4% of incident radiation. In view of the leuco-dye being the only product and apparent high quantum yields as noted in Table 1, it is obvious that in the present system no reaction takes place through excited MB^+ .

It has been observed that at lower MB^+ concentrations, the reaction extent per unit time is proportional to the MB^+ concentration as shown in Figs 1 and 2. But at higher MB^+ concentrations, the dye quenches the reaction as is clear from the data in Table 2.

These observations and the known features of such systems are suggestive of a mechanistic pathway shown in Scheme 1.



(MB^{\cdot} = Semiquinone radical; MB^- = Leuco-MB).

Scheme 1

Table 1—Initial apparent quantum yields of MB^+ disappearance in different solvents*

$[MB^+] = 1.07 \times 10^{-5} \text{ mol dm}^{-3}$; $[ZnO] = 2 \text{ g dm}^{-3}$;
 $I_0 = 5.87 \times 10^{-10} \text{ E s}^{-1}$

Sl. No.	Solvent	$a\phi_{0(-MB^+)}$
1	Ethylene glycol	0.00
2	Ethylene glycol + 10% isopropanol	0.04
3	Acetonitrile	0.07
4	Water	0.09
5	Methanol	0.12
6	Isopropanol	0.14

*6% (v/v) water has been added to increase the solubility of the dye.

The potential barrier at the surface of the semiconductor repels electron while holes are attracted to the surface by surface potential¹⁰. It has been observed that MB^+ is a good electron acceptor¹¹. Step-2 in Scheme 1 is in agreement with the observed extent of reaction being proportional to MB^+ concentration in a given set (Fig. 1). Resonance stabilized semiquinone radicals have been directly observed and are known to disproportionate at a diffusion-controlled rate¹². The effect of ZnO concentration in the suspension supports step-3 of Scheme 1. Whereas no effect is observed at low

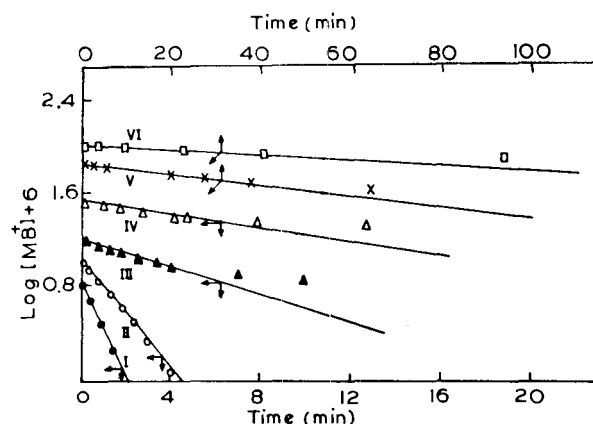


Fig. 1—Plots of $\log [MB^+]$ versus photolysis time at different MB^+ concentrations ($I_0 = 1.28 \times 10^{-9} \text{ E s}^{-1}$; solvent = water; $[ZnO] = 2 \text{ g dm}^{-3}$; concentration of MB^+ : I, 0.071×10^{-4} ; II, 0.107×10^{-4} ; III, 0.178×10^{-4} ; IV, 0.355×10^{-4} ; V, 0.710×10^{-4} and VI, $0.890 \times 10^{-4} \text{ mol dm}^{-3}$)

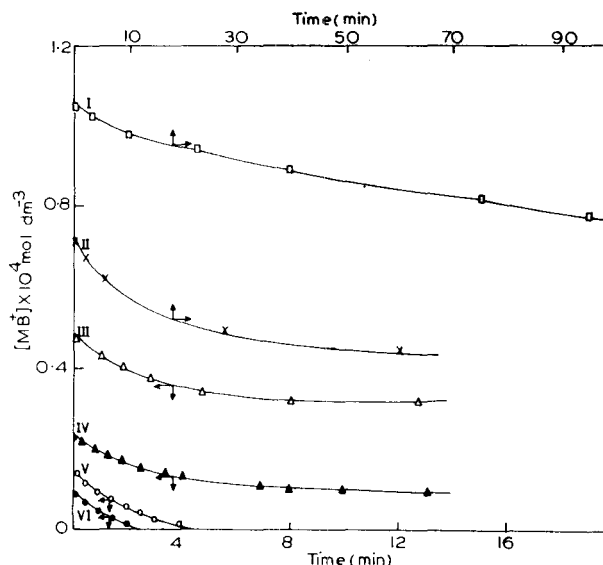


Fig. 2—Rate of disappearance of MB^+ with time ($I_0 = 1.28 \times 10^{-9} \text{ E s}^{-1}$; solvent = water; $[ZnO] = 2 \text{ g dm}^{-3}$; concentration of MB^+ : I, 0.890×10^{-4} ; II, 0.710×10^{-4} ; III, 0.355×10^{-4} ; IV, 0.178×10^{-4} ; V, 0.107×10^{-4} and VI, $0.071 \times 10^{-4} \text{ mol dm}^{-3}$)

Table 2—Apparent* quantum yields of MB^+ disappearance at zero times for different initial substrate concentrations in water

$I_0 = 1.30 \times 10^{-9} \text{ E s}^{-1}$; $[\text{ZnO}] = 2 \text{ g dm}^{-3}$

Sl. No.	$[\text{MB}^+] \times 10^4$ mol dm^{-3}	$a\phi_0 \times 10$
1	0.071	0.70
2	0.107	0.94
3	0.178	0.80
4	0.355	0.51
5	0.710	0.30
6	0.890	0.20

*Apparent because the yields are in terms of incident intensity.

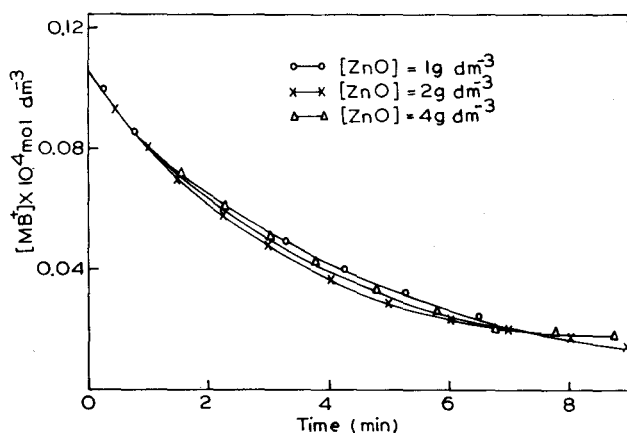


Fig. 3—Photoreduction of MB^+ at different suspended concentrations of zinc oxide (solvent = water; $[\text{MB}^+] = 1.07 \times 10^{-5} \text{ mol dm}^{-3}$; $I_0 = 5.87 \times 10^{-10} \text{ E s}^{-1}$)

MB^+ concentration (Fig. 3), the quantum efficiency increases with increase in ZnO concentration at higher MB^+ concentration as shown in Fig. 4. Under these conditions, step-5 of Scheme 1 involving dimers is in competition with step-3 and higher light absorption density favours radical-radical reaction. It has been observed that apparent quantum yields at zero time ($a\phi_0$) decrease with increase in dye concentration (see Table 2). Association of the dye is necessary to explain this. The aggregation can occur at the surface or in the bulk. A study of visible spectrum at different MB^+ concentrations has revealed that significant dimerisation occurs in water solutions even at 10^{-5} M concentration¹³. On the other hand, addition of more ZnO to dye solution has no effect on its absorbance (cf Fig. 4). For step-4 and step-4', k has been estimated¹⁴ as 4×10^3 at 30°C . This gives the fraction of monomer dye which exists as dimer equal to 0.05, 0.07, 0.11, 0.18, 0.27 and 0.29 for zero time concentrations, respectively of the dye noted in Fig. 2. Thus it is apparent that the light wastage is enhanced by the associated species present in the bulk.

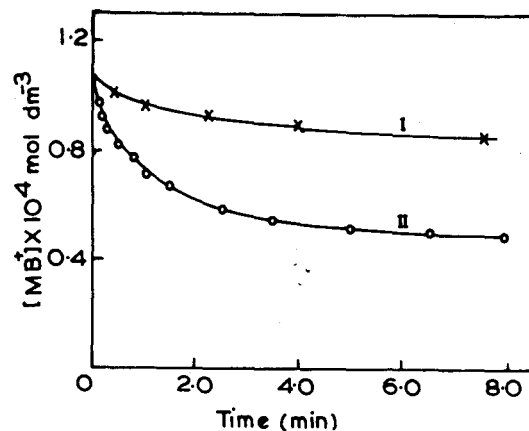


Fig. 4—Plots of $[\text{MB}^+]$ versus time of photolysis at different zinc oxide concentrations (solvent = water; $[\text{MB}^+] = 1.07 \times 10^{-4} \text{ mol dm}^{-3}$; $I_0 = 1.28 \times 10^{-9} \text{ E s}^{-1}$; ZnO conc.: I and II, 2 and 4 g dm^{-3} respectively)

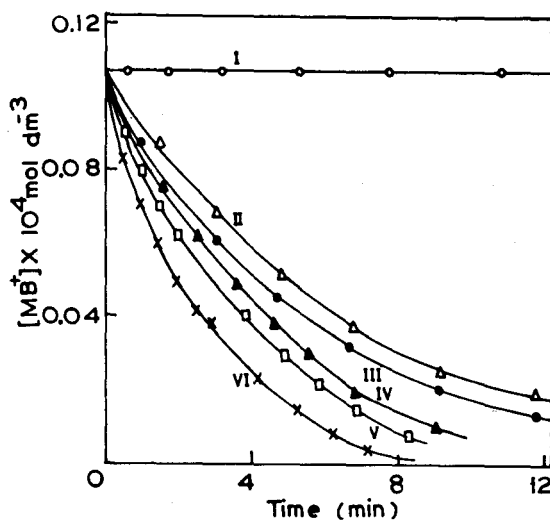


Fig. 5—Plots of $[\text{MB}^+]$ versus time of photolysis in different solvents ($I_0 = 5.87 \times 10^{-10} \text{ E s}^{-1}$; $[\text{MB}^+] = 1.07 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{ZnO}] = 2 \text{ g dm}^{-3}$; solvent: I, ethylene glycol containing 6% water; II, ethylene glycol containing 6% water and 10% isopropanol; III, acetonitrile containing 6% water; IV, water; V, methanol containing 6% water and VI, isopropanol containing 6% water)

A very important feature of the reaction is that at higher concentrations of dye, it stops much before completion as shown in Fig. 2, which evidences quenching by the product. Leuco- MB is an excellent electron donor¹¹ and an electron transfer to the surface competes with an electron transfer from the surface. It has been shown, particularly in n-type semiconductors, that charge transfer to a redox couple can compete with semiconductor decomposition even though thermodynamics predicts that electron transfer across the interface between full and empty states has a low probability¹⁵. Zinc oxide does photo-oxidise as well and oxidation of isopropanol and thiocyanine dyes has been report-

ed^{16,17}. In the absence of dimers, the competition is in favour of electron transfer from the surface.

Figure 5 shows that the reaction ceases in ethylene glycol medium [$k_{\text{diff}}(\text{glycol})/k_{\text{diff}}(\text{water}) = 26$] because it limits the diffusion-controlled step. It has been observed that semiquinone disproportionation increases with solvent polarity¹⁸. It is, however, difficult to correlate the observed changes in reaction efficiency in different solvents with their basic properties. It appears that the solvents have a specific effect on charge transfer processes in this system.

Zinc oxide prepared from various salts by heating at 700°C for different periods of time showed different efficiencies. The variation in efficiency is very large as is clear from Fig. 6. The wide variation can be attributed to the fact that the activity of ZnO (n-type semiconductor) is due to non-stoichiometry and different samples can have different amounts of zinc¹⁹. Variation in activity could also be due to var-

iation in surface area, particle size and the presence of various decomposition products^{20,21}.

Acknowledgement

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References

- 1 Kodama S, Yabuta M Anpa & Kobukawa Y, *Bull chem Soc Japan*, 58 (1985) 2307.
- 2 Steinbach F, *Z physik Chem (Neue folge)*, 61 (1968) 235.
- 3 Weiher R L & Tait C W, *Phys Rev*, 185 (1969) 1114.
- 4 Nink R Z, *Naturforsch*, 24 (1969) 1339.
- 5 Nobbs J Mck, *J phys Chem (solids)*, 29 (1968) 439 and references cited therein.
- 6 Domeneck J & Prieto A, *Electrochem Acta*, 31 (1986) 1317.
- 7 Kuzmin M G & Soboleva I V, *Prog Reaction Kinetics*, 14 (1986) 157.
- 8 Kavarnos G J & Turro N J, *Chem Rev*, 81 (1986) 401.
- 9 Gegion D, Huber J R & Weiss K, *J Am chem Soc*, 92 (1970) 5058.
- 10 Morrison S R, *Surface Sci*, 15 (1969) 363.
- 11 Pullman B & Pullman A, *Biochem Biophys Acta*, 35 (1959) 535.
- 12 Bartholomew R F & Davidson R S, *J chem Soc, C*, (1971) 2342.
- 13 Michaelis L & Granick S, *J Am chem Soc*, 67 (1945) 1212.
- 14 Sandro L Fornili, Giuseppe Sgroi & Vincenzo Izzo, *J chem Soc Faraday Trans I*, 79 (1983) 1085.
- 15 Memming R, *J electrochem Soc*, 125 (1978) 117.
- 16 Kavassails C & Spittler M T, *J phys Chem*, 87 (1983) 3166.
- 17 Thampi K R, Reddy T V, Ramakrishnan V & Kuriacose J C, *Electrochem Acta*, 28 (1983) 1869.
- 18 Bryce D Smith (Senior Reporter), *Photochemistry Vol. 7* (The Chemical Soc, London), 1976, pp 567.
- 19 Cartmell E, *Principles of crystal chemistry*, (Royal Institute of Chemistry, London), 1971, pp 66.
- 20 Sugunadevi B, Ramakrishnan V & Kuriacose J C, *Indian J Chem*, 19A (1980) 402.
- 21 Kalyanasundram K, *Energy resources through photochemistry and catalysis*, edited by M Gratzel (Academic Press, New York) 1983, pp 217-260.

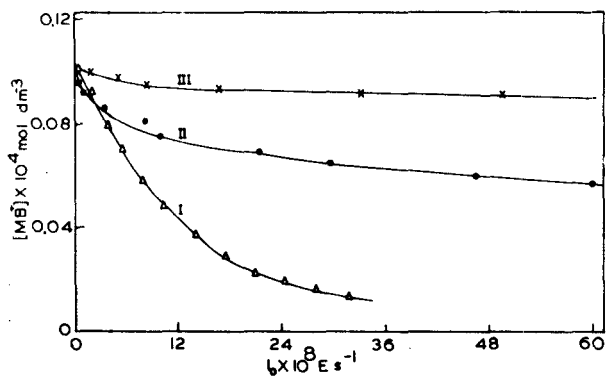


Fig. 6—Plots of $[\text{MB}^+]$ versus I_0 for different samples of zinc oxide (solvent = water; $[\text{MB}^+] = 1.07 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{ZnO}] = 2 \text{ g dm}^{-3}$; I, commercial sample of ZnO; II and III, ZnO prepared in the laboratory using zinc carbonate and zinc nitrate respectively)