

Reduction of Dyes by Photogenerated Ketyl Radicals

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Various dyes such as methylene blue (MB), rhodamine-B, rose bengal and 1,10-phenanthroline have been used in photoelectrochemical (PEC) cells in order to test their efficiency as mediators in PEC cells. MB is found to be the most efficient of all the mediators tried. A two-compartment PEC cell, in which the photoanode compartment is filled with a solution of alcohol, benzophenone and dye and the dark cathode with $1 \text{ mol dm}^{-3} \text{ HClO}_4$ has been used. Both medium pressure mercury vapour lamp and sunlight have been used as light sources for the photoreaction. The reduction of the dye is reversible in the dark and the time taken to attain the original state is quite long with a conversion efficiency of 11.6%. The current produced depends on [dye] and [sensitizer]. Possible mechanisms are discussed.

The use of photoelectrochemical (PEC) cells in the conversion of light energy into electrical energy and involving many endothermic processes, has attracted attention in recent years. Among these processes water splitting reaction¹⁻⁵, metal ion redox reactions^{6,7} and organic redox reactions⁸⁻¹¹ have been extensively studied in solution phase systems with dyes or other mediators as electron carriers. It is now well known that triplet benzophenone abstracts H-atom from alcohols to produce highly unstable ketyl radicals¹²⁻¹⁴ which have reducing properties¹⁵⁻¹⁷. Anodic oxidation of these reducing substrates generates photocurrent when connected to a suitable cathode. Some progress has been made in this direction using viologens as mediators^{16,17}. To increase the efficiency of this type of PEC cells, we have presently tried methylene blue (MB), rhodamine-B (Rh-B), 1,10-phenanthroline (PA) and rose bengal (RB) along with benzoyl viologen (BV) for comparison as mediators and found MB to be the most efficient of all.

Materials and Methods

All the chemicals used were of extra pure quality and wherever necessary, these were purified by standard methods¹⁹ just before use. 4,4'-Dibenzoyl viologen was prepared according to the procedure cited elsewhere²⁰.

UVS-500 medium pressure mercury vapour lamp (HANOVIA) was employed as the standard light source. Intensity measurements were carried out by ferrioxalate actinometry²¹. The cell was exposed at various distances from the light sources to vary the intensity. All the experiments were repeated in sunlight.

The photoelectrochemical cell consisted of two identical parts, each being a cylindrical tube with B₁₄

sockets and a side arm. Platinum electrodes were fused to the B₁₄ cones with mercury contact. The side tube was used for inserting the salt bridge. The cathode half-cell was filled with 1.0 mol dm^{-3} perchloric acid and the anode with solutions of various concentrations of benzophenone and the dye in 1:1 2-propanol-water mixture. Potassium chloride (0.2 mol dm^{-3}) was used as a supporting electrolyte. Filter paper dipped in saturated KCl was used as salt bridge. Photocurrents and photopotentials were measured with PI.DG 100 multimeter. The load resistance was $10^3 \text{ K}\Omega$ and the internal resistance of the cell was negligible ($< 10^{-6} \text{ K}\Omega$). The maximum photopotential obtained was stable as long as the cell was exposed to light. The stability of the cell was calculated from the time taken by the cell to attain the original (initial) current and voltage values after switching off the light.

Power conversion efficiency was calculated by Eq. (1), dividing power output by power input in watts.

$$\text{Conversion efficiency (\%)} = \frac{\text{Power output}}{\text{Power input}} \times 100$$

$$\text{Power input} = \frac{\text{Einsteins}}{8.37 \times 366 \times 10^{-9}} \text{ W}$$

where 366×10^{-9} is the wavelength of light absorbed by the system and

$$\text{Power output} = (I_{\text{max}} \times V_{\text{max}}) \times 2 \text{ W}$$

The output was multiplied by 2 since each photon caused the transfer of two electrons.

Results and Discussion

To improve the photovoltage and efficiency of the PEC cell, various mediators were tried. Reduction of methylene blue (MB) by photogenerated ketyl radicals

is discussed first and later compared with other mediators. After the dark currents have been stabilized (≈ 15 min), the anode half-cell was exposed to the light and increase in the photocurrent and photopotential noted at regular intervals. At peak photocurrent and photopotential, the reactions at the photoanode are assumed to have attained a stationary state. The photocurrent (I_{max}) of the cell was calculated by subtracting the dark current (I_{dark}) from the observed maximum current (I_{obs}). Similarly the photopotential was obtained as the difference between V_{obs} and V_{dark} .

In the absence of MB very small photocurrents developed and the addition of MB enhanced both I_{max} and V_{max} (Fig. 1). When the cell was brought back into dark it took 30 min to attain the original I_{dark} and V_{dark} values in the absence of MB and 4 to 5 hr in the presence of MB. After 15 min of irradiation, MB got reduced to leucomethylene blue (LMB) as indicated by the complete bleaching of the solution and the solution remained colourless as long as the cell was exposed to light. As soon as the light was switched off, LMB was oxidized back to the blue MB and the current and potential dropped slowly.

Under identical conditions irradiation of the anode compartment by the light of wavelength >400 nm (tungsten lamp) did not result in the development of photocurrent. Also the dye was not reduced and the blue colour of the solution persisted. In the absence of benzophenone, even if the cell was exposed to medium pressure Hg vapour lamp no photocurrent could be detected.

When the surface area of the Pt electrode was increased from 0.01 cm^2 to 5.00 cm^2 the I_{max} and V_{max} values increased from 1.00 μA to 65.0 μA and 5.00 mV to 195 mV respectively. Similarly increase in surface

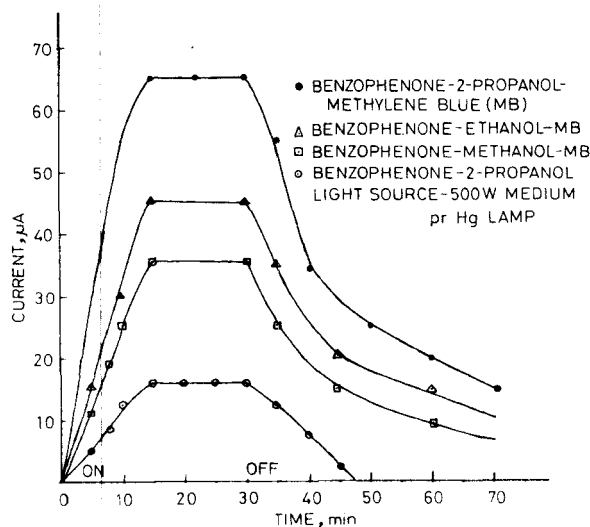


Fig. 1—Variation of photocurrent with time of illumination in presence and absence of mediators ($[B]=0.1$ $mol\ dm^{-3}$; $[MB]=4.5 \times 10^{-4}$ $mol\ dm^{-3}$)

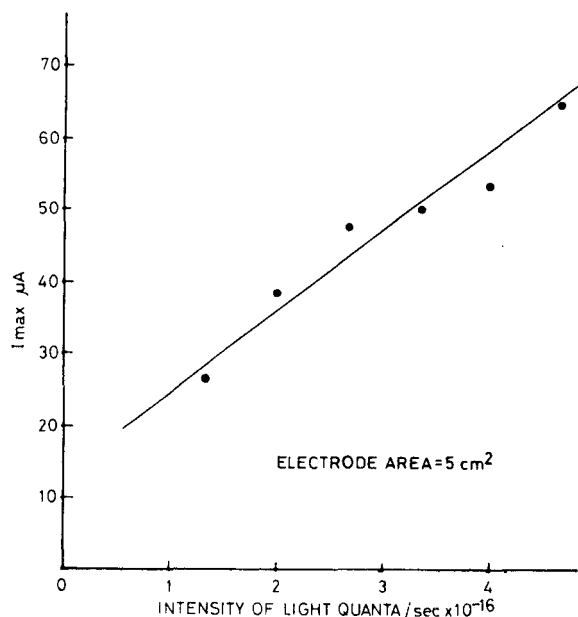


Fig. 2—Variation of photocurrent with intensity of light ($[B]=0.1$ $mol\ dm^{-3}$; $[MB]=4.5 \times 10^{-4}$ $mol\ dm^{-3}$)

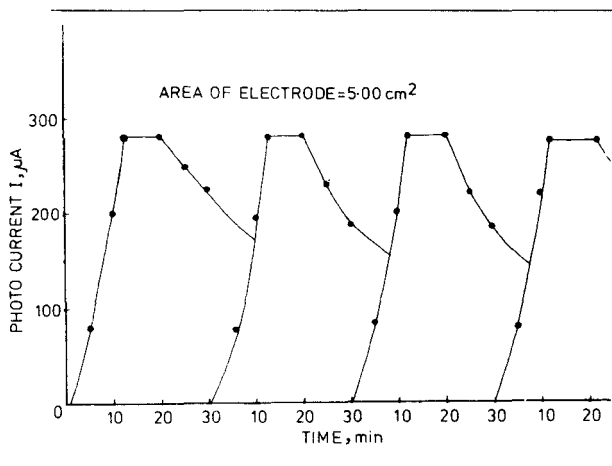


Fig. 3—On-off cycles of benzophenone-2-propanol-MB system solar cell ($[benzophenone]=0.1$ $mol\ dm^{-3}$; $[KCl]=0.2$ $mol\ dm^{-3}$, $[MB]=4.5 \times 10^{-4}$ $mol\ dm^{-3}$)

area of salt bridge from 48.0 cm^2 to 225 cm^2 increased I_{max} and V_{max} values from 38.0 μA to 68.0 μA and 115 mV to 195 mV respectively. In all other experiments the surface areas of electrode and salt bridge were kept at the optimum level such that maximum current and voltage were obtained. Under the conditions $[MB]=4.5 \times 10^{-4}$ $mol\ dm^{-3}$, $[KCl]=0.2$ $mol\ dm^{-3}$, (Intensity $=6.1 \times 10^{15}$ q/s) in 1:1 2-propanol-water mixture, an increase in [benzophenone] (from 0.30 to 0.14 $mol\ dm^{-3}$) brought about increase in both I_{max} and V_{max} upto a certain level ($I_{max}=255$ μA and $V_{max}=430$ mV at benzophenone conc. 0.1 $mol\ dm^{-3}$) and thereafter both I_{max} and V_{max} showed a decreasing trend. At higher [benzophenone]

formation of benzpinacol was observed (the white precipitate formed was identified as benzpinacol). With increase in [MB] both I_{max} and V_{max} also increased upto a saturation point, i.e. at [MB] = 45.0×10^{-5} mol dm⁻³. Beyond this concentration there was no perceptible variation in both I_{max} and V_{max} at content [B] (0.1 mol dm⁻³). This observation indicates that MB is the electroactive species.

The current produced in the PEC cells with benzophenone-2-propanol-MB showed strong dependence on light intensity at 366 nm. At higher wavelength (>400 nm) photocurrents were not obtained. The photocurrents were directly proportional to intensity and a linear plot was obtained (Fig. 2).

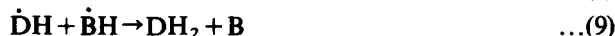
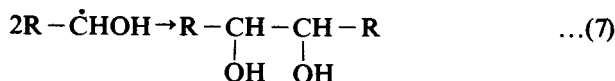
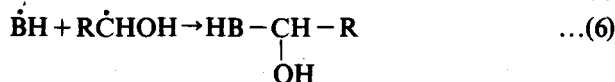
Similar results were obtained with sunlight as the light source and Rh-B, PA, RB and BV as mediators (Table 1). Except RB all other dyes, viz. MB, Rh-B, PA, and BV were reduced by the ketyl radicals (as indicated by bleaching of the dye colour) and generated photocurrent. Methylene blue was the most effective of all dyes with maximum efficiency. The gas evolved at cathode was identified as hydrogen. The cell could be recycled several times (Fig. 3).

The above results show that benzophenone is the photon receptor and the excited dye cannot directly abstract hydrogen atom from alcohol, since at higher wavelengths where benzophenone does not absorb there is no reaction. Small amounts of photocurrents observed in the absence of the dye could be due to the oxidation of ketyl radicals at the Pt electrode^{16,17}. The formation of ketyl radicals in such a system has been proved earlier²¹ using quenchers. The total reactions in the two compartments of PEC cell may be divided into three parts and written as in Scheme 1.

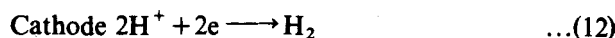
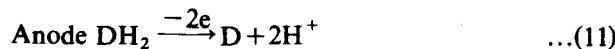
(i) Photochemical reactions



(ii) Solution phase reactions



(iii) Electrode reactions



where B stands for benzophenone and D for dye in general.

Scheme 1

In Scheme 1, the reactions (1 to 7) are all well established^{12,13,26} and the reactions (8-10) appear to be mainly responsible for the increase in photocurrent in the presence of dye. The oxidation of alcohol can be taken as the ultimate step in the solution phase reaction which is known¹⁷ to be endothermic to the extent of 90.3 kJ mol⁻¹. Either DH or DH₂ is the

Table 1— I_{max} and V_{max} Values Obtained in Presence of Various Mediators in Sunlight

[B] = 0.1 mol dm⁻³; [KCl] = 0.2 mol dm⁻³
 [MB] = 4.50×10^{-4} mol dm⁻³
 [BV] = 3.0×10^{-3} mol dm⁻³
 [Rh-B] = 1.50×10^{-3} mol dm⁻³
 [RB] = 1.01×10^{-3} mol dm⁻³
 Area of electrodes = 5 cm²

Mediator	Power input (W × 10 ⁻³)	I_{max} (μA)	V_{max} (mV)	Stability (hr)	% conversion efficiency
1 MB-2-propanol	2.2	265	480	5	11.6
MB-ethanol	2.2	190	325	4	5.6
MB-methanol	2.2	160	315	4	4.5
2 PA-2-propanol	2.2	110	340	4	3.4
3 Rh-B-2-propanol	2.2	200	420	5	7.6
4 BV-2-propanol	2.0	135	375	0.5	5.1
5 RB-2-propanol	2.0	50.00	110	0.5	0.5
6 2-propanol	2.0	50.00	110	0.5	0.5

electroactive species and responsible for the enhancement of I_{\max} and V_{\max} . Increase in [B] increases I_{\max} since triplet benzophenone is the initiator (step-4)^{12,13}. Quenching of excited benzophenone (step-3) and the ketyl radicals (steps 5 and 6) appears to be responsible for the decrease in I_{\max} after saturation. Since alcohol has been taken in excess, reaction(7) has no significance in the present study. Reactions (11 and 12), the two electrode processes, account for the increase in I_{\max} and V_{\max} with increase in [MB].

Among the different substituted viologens studied it has been reported that BV gives maximum conversion efficiency¹⁶. However, under the present conditions BV gave only 135 μA whereas MB and Rh-B gave 265 μA and 200 μA respectively (Table I). The photovoltages were also higher with MB (480 mV) and Rh-B (420 mV) as compared to that (375 mV) with BV.

Though such cells using photoredox systems do give encouraging results, they cannot be used for the conversion of solar energy commercially, since only very small part of the solar spectrum (2.7% of total irradiation since only light of wavelength 366 nm is absorbed by the system^{2,3}) is involved.

Acknowledgement

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