

## On the Mechanism of the Cadmium Sulphide Sensitized Photoreduction of Heptylviologen in Nonaqueous Solution

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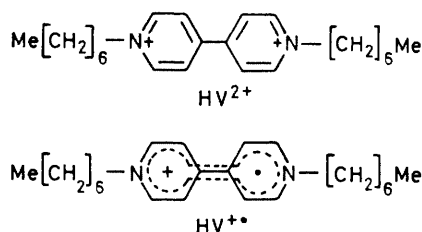
*Summary* The heterogeneous cadmium sulphide (CdS) sensitized photoreduction of heptylviologen ( $HV^{2+}$ ) in deoxygenated non-aqueous solution, which occurs by an electron-transfer process whereby the photo-excited electron in the conduction band of CdS is transferred to adsorbed  $HV^{2+}$ , is greatly enhanced ( $> 10^2$ ) by the addition of triethanolamine.

THERE is considerable interest in the application of semiconductor photo-electrodes for converting solar energy into chemical fuels and/or electricity.<sup>1,2</sup> Pigment dispersions

can also be employed for solar energy utilization and this has recently been reviewed by Bard.<sup>3</sup> In order to explore the full potential of this area of research an understanding of the reversible and irreversible interfacial redox processes, *i.e.*, photo-injection of holes (oxidation) and electrons (reduction), as well as the effect of additives on these processes is essential. This mechanistic information will be important for the design of novel semiconductors and charge transport molecules as well as exploring novel photosynthetic applications. Bard,<sup>4</sup> for example, has recently demonstrated that amino acids can be produced

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by irradiating platinumized titanium dioxide powder in the presence of ammonia and methane



We describe here the results of a mechanistic study of the heterogeneous cadmium sulphide photoreduction of heptylvologen ( $\text{HV}^{2+}$ ) tetrafluoroborate to its paramagnetic highly coloured cation radical ( $\text{HV}^{+\bullet}$ ) in nonaqueous media (see Figure)

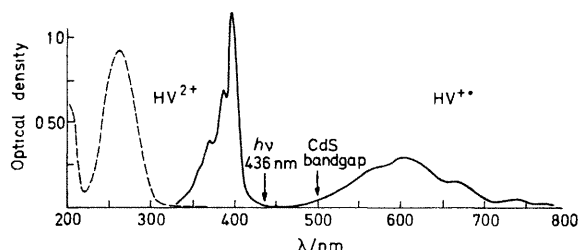


FIGURE Absorption spectra of  $\text{HV}^{2+}$  and  $\text{HV}^{+\bullet}$  in MeCN

Irradiation of a semiconductor with  $h\nu >$  band gap creates a hole in the valence band as a result of the excitation of an electron to the conduction band. The valence band 'hole' is an oxidizing species while at the same time the electron in the conduction band is a potential reducing agent prior to electron-hole recombination within the semiconductor.

Harbour and Hair<sup>5</sup> have reported the use of 5,5-dimethyl-1-pyrroline 1-oxide (DMPO) as a spin trap for superoxide anion  $\text{O}_2^{\cdot-}$  produced by irradiating aqueous dispersions of CdS in the presence of molecular oxygen. Enhancement of  $\text{O}_2^{\cdot-}$  production was observed upon the addition of amines such as ethylenediaminetetra-acetic acid.

As an extension of those investigations the cadmium sulphide sensitized photo-oxidation of an aryl amine (leuco-Crystal Violet) in non-aqueous media using both e s r and spectrophotometric techniques was studied.<sup>6</sup> We have now investigated the effect of additives, especially surfactants and supersensitizers, on the steady state rate of CdS sensitized photoreduction of heptylvologen. The reduced viologens are of interest since they are known to reduce water to molecular hydrogen in the presence of a Pt catalyst.<sup>7</sup>

The concentration of the reduced heptylvologen ( $\text{HV}^{+\bullet}$ ) was monitored spectrophotometrically after irradiating CdS dispersions at 436 nm in MeCN,  $\text{CH}_2\text{Cl}_2$ , or in mixtures of the two solvents with and without additives. The wavelength of irradiation lies outside the region of absorption of  $\text{HV}^{2+}$  and is of greater energy than the band gap of CdS (see Figure). The ratio of CdS powder, with an average particle size of ca  $1 \mu\text{m}$ , to solution was kept constant at  $1.0 \text{ mg cm}^{-3}$  throughout this study. The precise quantum yield for  $\text{HV}^{+\bullet}$  was not recorded owing to the difficulty in correcting for light scattering by the CdS particles. The initial rates of

photoreduction of  $\text{HV}^{2+}$  were measured for  $< 1\%$  conversion of  $\text{HV}^{2+}$  in any kinetic run. When a large concentration of  $\text{HV}^{+\bullet}$  is produced side reactions occur e.g., disproportionation which make the analysis of the kinetics difficult. The possible retention of photoactivity by the CdS particles has not been investigated yet.

A plot of the half wave reduction potential ( $E_{1/2}^{\text{red}}$ ) for  $\text{HV}^{2+}$  as a function of solvent dielectric constant in MeCN ( $\epsilon$  ca 38)– $\text{CH}_2\text{Cl}_2$  ( $\epsilon$  ca 9) is linear. As the solvent dielectric constant increases, the reduction potential becomes more cathodic. The less polar solvent appears to stabilize the monocation,  $\text{HV}^{+\bullet}$ , relative to the dication  $\text{HV}^{2+}$ .

The electrochemical results indicate that the lowest unoccupied molecular orbital (LUMO) of  $\text{HV}^{2+}$  lies at lower energy in  $\text{CH}_2\text{Cl}_2$  than in MeCN. It would be expected that the rate of  $\text{HV}^{+\bullet}$  production would be faster in  $\text{CH}_2\text{Cl}_2$  than in MeCN based on a purely thermodynamic argument. This assumes that the conduction band (CB) and valence band (VB) levels of the CdS are solvent independent.

Experimentally the rate of photoreduction of  $\text{HV}^{2+}$  was found to be ca 10 times faster in MeCN than in  $\text{CH}_2\text{Cl}_2$ . A plot of the log of the rate  $\{\log(d[\text{HV}^{+\bullet}]/dt)\}$  as a function of solvent dielectric constant indicates that the rate of photo-production of  $\text{HV}^{+\bullet}$  increases as the solvent dielectric constant increases. This is the reverse of that expected based on the thermodynamic reduction potential for  $\text{HV}^{2+}$  in the solvents employed. The photoredox reaction appears then to be kinetically rather than thermodynamically controlled.

Electrophoretic measurements (using a Rank Bros 'Model II' instrument with the flat cell configuration) indicate that the CdS particles possess a *negative* surface charge in MeCN and a *positive* surface charge in  $\text{CH}_2\text{Cl}_2$ . Upon the addition of  $\text{HV}^{2+}$  to the dispersion of CdS particles in MeCN the CdS particle surface charge changes from negative to positive. This indicates that  $\text{HV}^{2+}$  is adsorbed on the CdS. However, no change in surface charge was observed when  $\text{HV}^{2+}$  was added to the dispersion in  $\text{CH}_2\text{Cl}_2$ . It appears that the rate enhancement in MeCN over  $\text{CH}_2\text{Cl}_2$  is due primarily to the surface adsorption of  $\text{HV}^{2+}$  on the CdS particles.

Obviously something must be oxidized in the additive-free system to prevent the buildup of holes. Independent studies<sup>8</sup> have shown that the photolysis of aqueous CdS dispersions leads to the dissolution of CdS through the oxidation of  $\text{S}^{2-}$ . This is consistent with the oxidation potential of CdS<sup>9</sup> ( $E^\circ = 0.1 \text{ V}$ ) which lies far above the level of the hole. Hence, the reductant in this system is probably the CdS itself.

It was found also that the addition of the surfactant hexadecyltrimethylammonium chloride (ca  $1.0 \times 10^{-4} \text{ M}$ ) to the suspension of CdS particles in  $\text{CH}_2\text{Cl}_2$  changes the surface charge from positive to negative. The addition of  $\text{HV}^{2+}$  caused the charge to become less negative, indicating surface adsorption of  $\text{HV}^{2+}$ . The rate of photoreduction of  $\text{HV}^{2+}$  is enhanced by the addition of this surfactant, further indicating the importance of surface adsorption of the electroactive species, i.e.,  $\text{HV}^{2+}$ .

E s r experiments were also carried out on these systems by monitoring the formation of the  $\text{HV}^{+\bullet}$  species. This radical gives a characteristic e s r spectrum abundant in hyperfine splittings. Qualitative agreement with the optical results was obtained as expected.

The rates of photoreduction of  $HV^{2+}$  were found to be enhanced by the addition of certain amines as in the photoreduction of molecular oxygen. The addition of an electron donor such as triethanolamine (TEA), for example, has a profound effect on the rate of photoreduction of  $HV^{2+}$ . The addition of  $10^{-2}$  M TEA to the dispersion in MeCN increases the rate of photoreduction by a factor of *ca.* 250 while the addition of  $10^{-4}$  M TEA increases the rate by a factor of *ca.* 50. Control experiments without CdS did not yield  $HV^+$ . TEA's effect on the rate presumably arises from electron donation to the valence band hole prior or subsequent to electron injection, thus regenerating the neutral particle.

The results of this study using the acceptor  $HV^{2+}$  are in agreement with the previous investigations by Harbour

and Hair employing molecular oxygen as an electron acceptor. The concepts found in this study therefore may be generally applied. Also, the photoreduced viologen can be employed to produce molecular hydrogen in the presence of water and a platinum catalyst, if desired, at the expense of the consumption of TEA. In addition these results show that non-aqueous solvents may be successfully employed to carry out useful heterogeneous photochemistry.

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