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Mechanism of the Cadmium Sulphide Sensitized Photo-oxidation of Leuco Crystal Violet in Nonaqueous Solution

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Summary The cadmium sulphide sensitized photo-oxidation of Leuco Crystal Violet in oxygenated MeCN occurs initially by an electron transfer mechanism until superoxide anion concentration increases sufficiently to compete by a hydrogen atom abstraction process.

THE use of semiconductor photoelectrodes has recently been receiving increased attention as a means of converting solar energy into chemical fuels and/or electricity.[1,2] Further advances in semiconductor photoelectrochemistry will require detailed knowledge of interfacial oxidation and reduction processes as well as the effect of secondary components such as oxygen. This mechanistic information may in turn lead to more general applications of semiconductors in synthesis and in the decomposition of pollutants as has been proposed by Bard for aqueous systems.[3,4]

We describe here the results of a mechanistic study of the heterogeneous cadmium sulphide photo-oxidation of Leuco Crystal Violet (L-CV) to Crystal Violet (CV) in acetonitrile solution.

$(p\text{-}Me_2NC_6H_4)_3CH$	$(p\text{-}Me_2NC_6H_4)_3C^+$
L-CV	CV
ϵ (MeCN; 303 nm) 7700	ϵ (586 nm) 104,000

Irradiation of a semiconductor with radiation 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[5] have recently reported the use of 5,5-dimethyl-Δ^1-pyrroline 1-oxide (DMPO) as a spin trap for superoxide anion $O_2^{\cdot-}$) produced by irradiating aqueous dispersions of CdS in the presence of molecular oxygen. Enhancement of $O_2^{\cdot-}$ production was observed upon the addition of amines such as ethylenediaminetetra-acetic acid.

As an extension of these investigations the rate of L-CV to CV oxidation was investigated under a variety of experimental conditions with the objective of obtaining more detailed information concerning the photoredox behaviour of semiconductors. CV concentration was monitored spectrophotometrically after irradiating CdS dispersions at 436 nm in a stirred MeCN solution of L-CV within an optical cell and centrifuging of the pigment. The wavelength of irradiation is outside the region of absorption of L-CV and is of greater energy than the band gap of CdS.

The initial rate of oxidation of L-CV in air-saturated MeCN using 1·0 mg CdS cm^{-3} of $1{\cdot}0 \times 10^{-4}$M L-CV in MeCN was $1{\cdot}6 \times 10^{-8}$ mol l^{-1} s^{-1}. Oxidation to CV was not observed in unirradiated samples containing CdS during the timescale of the experiment. Also, irradiating the L-CV solutions, without CdS, as a control for our light filtering system yielded a rate *ca.* 10^3 slower than in the presence of CdS. Degassing the solvent produced a decrease in rate of greater than a factor of 10 while saturating the solvent with oxygen increased the rate of oxidation by a factor of *ca.* 20 over the degassed reaction, indicating the importance of molecular oxygen to the oxidation process. Replacement of the hydrogen on the α-carbon of L-CV with deuterium results in a primary deuterium isotope effect, k_H/k_D, of 4·2, indicating that hydrogen is lost in a rate-determining step. The addition of 10 vol. % of H_2O to the dry acetonitrile slows the rate of oxidation by a factor of *ca.* 5. When D_2O is employed in place of H_2O a further decrease in rate of *ca.* 2 is observed. The decrease in rate due to the addition of protic solvents to the MeCN is consistent with the equilibrium nature of the deprotonation of the $L\text{-}CV^+$ and reprotonation of the L-CV radical as previously proposed.[6]

Spin trapping experiments with DMPO in MeCN show that the concentration of $O_2^{-\cdot}$ increases upon addition of low concentrations ($<10^{-2}$M) of L-CV, and decreases upon the addition of higher concentrations ($>10^{-2}$M) of L-CV. From the spin trapping and kinetic experiments we conclude there are two oxidation mechanisms simultaneously leading to CV. The initial rate of appearance of CV is attributed primarily to the one-electron oxidation of L-CV by the photogenerated hole in the CdS valence band when the concentration of $O_2^{-\cdot}$ is low, based upon the spin trapping results and magnitude of the primary deuterium isotope effect.[6] It appears that oxygen acts as a trap for the conduction band electron thus allowing the CdS to regenerate its original state and therefore functioning as a photocatalyst. As the concentration of $O_2^{-\cdot}$ increases hydrogen atom abstraction then can compete[7] with the cation radical mechanism as demonstrated by $O_2^{-\cdot}$ quenching when the L-CV concentration is $>10^{-2}$M. Both mechanisms produce the L-CV radical which may form CV by transferring an electron to molecular oxygen producing more $O_2^{-\cdot}$ or to the photogenerated hole in CdS. The fact that H_2O does not completely quench the oxidation process is evidence that superoxide is not the predominant oxidizing species since $O_2^{-\cdot}$ is known to react vigorously with water undergoing disproportionation to molecular oxygen and peroxide.[8] Hydrogen peroxide has been found not to be an active oxidant under our reaction conditions.

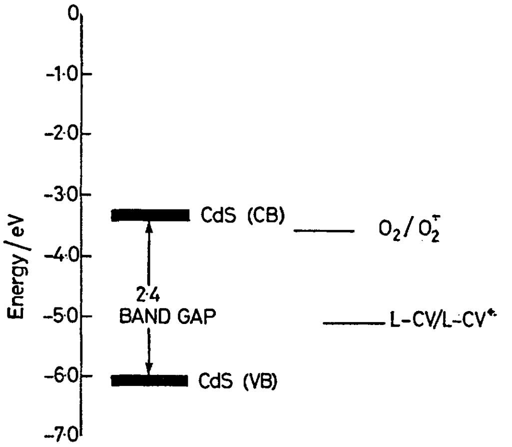

FIGURE. Absolute positions of valence (VB) and conduction band (CB) levels of CdS along with redox levels of O_2 and L-CV.

The absolute positions of the valence (VB) and conduction bands (CB) of CdS[9] relative to the redox levels of $O_2/O_2^{-\cdot}$,[10] and the redox levels of $L\text{-}CV/L\text{-}CV^{+\cdot}$[6] are in the Figure, and are consistent with the electron transfer oxidation mechanism represented by the reactions in the Scheme. Electron transfer from L-CV to the hole in the CdS valence band is thermodynamically favoured by *ca.* 20 kcal/mol while electron transfer from the conduction band to molecular oxygen in MeCN solvent is thermodynamically favourable by *ca.* 0·7 kcal/mol. Electron transfer from L-CV radical to oxygen is also thermodynamically feasible.[6] The involvement of singlet oxygen in the oxidation process was eliminated by the absence of significant quenching by 1,4-diazabicyclo[2.2.2]octane.

$$\begin{aligned}
&CdS + h\nu \longrightarrow CdS^*\\
&CdS^* \longrightarrow CdS\\
&CdS^* + L\text{-}CV \longrightarrow CdS^- + L\text{-}CV^{+\cdot}\\
&L\text{-}CV^{+\cdot} \xrightarrow{\text{slow}} L\text{-}CV\cdot + H^+\\
&L\text{-}CV\cdot + A \longrightarrow CV + A^-\\
&CdS^- + A \longrightarrow CdS + A^-\\
&O_2^{-\cdot} + L\text{-}CV \longrightarrow HO^-_2 + L\text{-}CV\cdot\\
&CdS^* + A \longrightarrow CdS^+ + A^-\\
&CdS^+ + L\text{-}CV \longrightarrow CdS + L\text{-}CV\cdot
\end{aligned}$$

SCHEME. $A = O_2$, hole in valence bond.

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