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SURFACE PHOTOCHEMISTRY

THE CdS PHOTOINDUCED DIMERIZATION OF N-VINYLCARBAZOLE†

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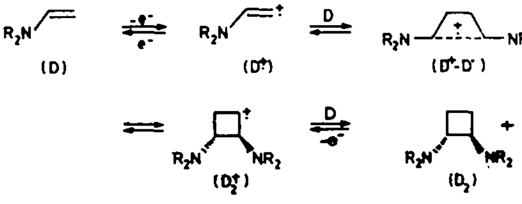
Abstract—The CdS dispersion mediated photoinduced dimerization of N-vinylcarbazole (NVC) has been investigated and found to be efficient. The rate of reaction is not affected over quite a wide range of CdS masses at constant NVC concentration in solution. The reaction requires the presence of oxygen. At low light intensities the rate is linearly related thereto. A cation radical mechanism is proposed since the reaction can be efficiently quenched by electron donors. The dimerization appears to follow the Langmuir–Hinshelwood and modified Eley–Rideal mechanisms, as does the quenching. CdS of different origins with different surface areas, purities and structures were used and the rates varied by a factor of four. None of these functions appears to play a dominant role in the rate of dimerization. The variation in rates and in activation energies suggested the importance of traps located close to the conduction band.

INTRODUCTION

While photosensitized electron transfer organic reactions have received considerable attention,[1] comparatively little is known about semiconductor photoinduced electron transfer processes. Although, CdS has attracted much attention, the major part of this work has been directed to the development of solar cells[2] and much less to the use of CdS to induce organic reactions. Amongst the few examples, excluding oxidation/reduction processes,[3] are instances of the CdS photocatalysed dimerization of phenyl vinyl ether,[5] reterocycloaddition,[4a,5,6] *cis-trans* isomerization of some styrene derivatives,[7] valence isomerization[5] and a [1,3]-sigmatropic rearrangement reaction.[5] We wish to report here, in some detail, the CdS photoinduced cyclodimerization of N-vinylcarbazole (NVC).

The cyclodimerization of NVC to *trans*-1,2-dicarbazylcyclobutane in solution occurs via a cation radical chain mechanism (Scheme 1), as was established by Ledwith and co-workers.[8] It occurs readily via many types of oxidative routes including thermal (metal catalysis[9]), electrochemical (anodic[10]), photochemical (sensitization[11]), and by pulse radiolysis.[12] Other examples of cation radical cyclodimerization have also been reported.[13]

Bauld *et al.*[14] have pointed out that these reactions involve a [2+1]cycloaddition. Although the [2+1] process remains symmetry forbidden, more detailed calculations by Bauld *et al.*[14] have shown that, with respect to the thermal [2+2]cycloaddition, the process is enormously favoured whether the addition be synchronous or not. The "cyclobutane cation radical" exists preferentially in an unsymmetric structure (Scheme 1; $D^+—D^·$), which has one long, one-electron carbon–carbon σ bond. The reversibility ($D^+—D^· \rightleftharpoons D_2^{+·}$) in Scheme 1 has been recognized by Ledwith and co-workers.[15] Similarly, *cis*-1,2-diphenoxycyclobutane has been reported to isomerize to the *trans*-isomer via its cation radical.[16]



Scheme 1.

EXPERIMENTAL

Acetone used was of spectroscopic grade (Baker, New Jersey) and was used without further purification. Methyl ethyl ketone (Fisher, New Jersey certified) was used after distillation. All other substances were purified by distillation, sublimation or recrystallization, as appropriate.

CdS of different sources, surface areas, crystalline structures, and purities were used throughout this work (for detailed CdS specification see Table 1).

Typically, 0.22 M NVC in acetone (6 ml) in the presence of CdS (42 mg) was irradiated at $\lambda > 430$ nm (Corning Filter 3-72) for 30 min, using a 150 W PRA xenon lamp run at 140 W; the output of the lamp was periodically checked with a Scientech 364 power energy meter. Prior to irradiation the mixture was sonicated for 10 min. The mixture was constantly stirred during the course of irradiation. Compressed air was used as coolant and a water filter was used to remove IR radiation. Except for undegassed samples the reaction vessels were open to the atmosphere via a reflux condenser. For degassed samples three freeze–thaw cycles were used before sealing to a residual pressure of less than 2×10^{-5} mm Hg. A known amount of n-hexadecane as calibrant, was added to the mixture before irradiation. After irradiation, the CdS was removed by filtration. The filtrate was analysed using a Varian 3700 gas chromatograph equipped with a flame ionization detector, which was connected to a Hewlett–Packard 3390 A integrator. Analysis was performed on a 2 m/2 mm column packed with OV-101 (3%) on Chromosorb W(HP) 80–100 mesh. For quantum yield determinations a special block was used to ensure that only the light from the lamp reached the reaction vessel. Potassium ferrioxalate (0.15 M) was used as actinometer. In calculating the quantum yield it was assumed that all radi-

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Table 1. Dimerization of N-vinylcarbazole initiated by CdS of different properties[a]

CdS-supplier	Purity (%)	Surface area ($m^2\ g^{-1}$)[b]	Crystalline structure[b]	Relative yield[c]	Activation energy ($kJ\ mol^{-1}$)
Strem (lot No. = NATL)	99	32.4	polytype	1.00	
Strem (ultrapure) (lot No. = 16027-S1)	⩾99.99	44	polytype	0.80	7.1
Strem (luminescent) (lot No. = NATL)	99.99	0.5	α	0.74	
Aldrich (gold label) (lot No. = 1721PJ)	99.999	1.2	α	0.65	
Fluka (puriss) (lot No. = 249326-684)	99.999	1.4	α	0.59	
Aldrich (gold label) (lot No. = 0897)	99.99+	20	polytype	0.59	
Fisher (lot No. = 792913)	99	12	β	0.32	
Strem (ultrapure) (lot No. = 16693-S)	⩾99.99	7.1	$\alpha+\beta$ (~1:1)	0.31	
Aldrich (lot No. = 053087)	98.8	7	β	0.24	17.6

[a] 0.22 M of NVC in acetone (6 ml) was irradiated in the presence of CdS (42 mg) at $\lambda > 430$ nm for 30 min with a 150 W xenon lamp.

[b] See Ref. 34.

[c] The highest dimer yield (0.05 M) was obtained with Strem (99%).

ation entering the reaction vessel was absorbed by the CdS, i.e. the scattered light was ignored. A Corning filter (CS 5-58) was used which transmitted at 360–470 nm with a maximum at ~405 nm. Direct irradiation of NVC (0.33 M) in acetone at these wavelengths did not induce any dimerization. For light intensity dependent experiments, calibrated metal gauze filters were used. The effective transmission of these filters was measured by means of a power energy meter (Scientech 364). For activation energy determinations, 0.33 M of NVC in methyl ethyl ketone (7 ml) was irradiated under the usual conditions using a thermomix-1420 (B. Braun Melsugen AG) to control the temp (±0.1°).

RESULTS AND DISCUSSION

Irradiation of NVC 0.22 M in acetone in the presence of CdS at $\lambda > 430$ nm (CdS band gap, 2.4 eV, ~530 nm) gave, readily, *trans*-1,2-dicarbazylcyclobutane,† white needles, m.p. 195–196°.[17] The reaction can be made almost quantitative, if irradiation is prolonged. Appropriate control experiments indicated that both light and CdS were required.

CdS photoinduced reactions are based on the formation of electron–hole pairs upon absorption of light; these can react, in principle, following migration of the "holes" to the surface, with species in solution or adsorbed on the surface, to produce oxidized forms. Thus, donation of an electron from NVC to the "hole" results in a cation radical intermediate which may react in the sequence shown in Scheme 1.

In agreement with Ledwith and co-workers[15] an essential feature of this mechanism (Scheme 1) is the interconvertibility of the cation radicals D^+—$D^{\cdot}$ and $D_2^{\dot{+}}$. Thus, when the dimer was irradiated in the presence of CdS under the same conditions used to induce the dimerization of NVC, about 2.5% of the dimer was converted to NVC; indicating the reversibility of the reaction. The inefficient cleavage of the dimer suggests that the rate of electron transfer to $D_2^{\dot{+}}$ is much faster than the rate of conversion of $D_2^{\dot{+}}$ to D^+—$D^{\cdot}$.[18]

Effect of oxygen

In CdS photocatalysed processes (retrocycloaddition,[4a,5,6] valence isomerization,[5] [1,3]-sigmatropic rearrangement[5] and dimerization[4]) previously examined it was generally found that oxygen enhanced the rate of reaction. Similar behaviour was observed in the CdS photoinduced dimerization of NVC. When NVC was irradiated in the presence of CdS for 1.5 h, the yields of the dimer for aerated vs degassed samples decreased from 62 to 1.5%. In contrast to the NVC dimerization in homogeneous solution systems in which the relative yields of the dimer and polymer of NVC depend, respectively, on the presence or absence of oxygen,[8] the dramatic decrease in the dimer yield in the absence of oxygen in our system is not accompanied by polymer formation. The simplest interpretation of this phenomenon is that the excited electron is trapped as surface-bound superoxide ion,[19] thus prolonging the life of the "hole" by delaying the collapse of the electron–hole pair[4b,5]

$$SC \xrightarrow{h\nu} SC(h^+,e^-) \xrightarrow{O_2} SC(h^+) + O_2^{\dot{-}}.$$

This is compatible with the suggested role of oxygen in electron-transfer dimerization of NVC in homogeneous solution. Here, it has been found that catalytic amounts of molecular oxygen enhance the quantum yield of the reaction[8b,11a] and it has been proposed that superoxide ion, formed through secondary electron transfer from the sensitizer anion radical to oxygen, is a "more stable" counterion for the cation radical chain reaction.[8b]

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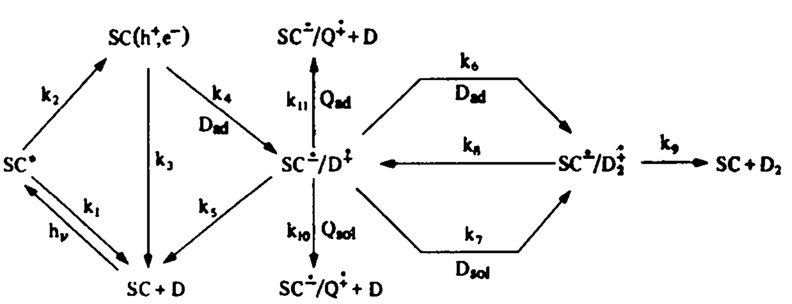
† ^{1}H-NMR ($CDCl_3$): showed aromatic protons centred at $\delta = 8.42$ (4H) and 7.38 (12H), methine protons centred at $\delta = 6.30$ (2H) and methylene protons centred at $\delta = 3.10$ (2H) and 2.72 (2H); MS, *m/e* 386 (M^+). These spectral data were in excellent agreement with the literature.[17]



Scheme 2. SC, SC* and SC (h^+, e^-) are the semiconductor in the ground state, excited state (exciton) and after electron–hole separation, respectively. D and D_2 (and their respective ions) are NVC and its dimer, while D_{ad} and D_{sol} are the NVC on the surface and in solution.

Kinetic analysis

It was desired to ascertain whether the dimerization of NVC takes place totally from species in the adsorbed state, or whether neutral NVC from the solution collides with the NVC cation radical generated on the surface: a solution equivalent to the gas phase Eley–Rideal process. We have attempted to discriminate between these possibilities.

In a previous study[7b] we have found that the Langmuir–Hinshelwood kinetic treatment for reaction in the adsorbed state was compatible with the isomerization data for *cis*-stilbene, and have suggested that the surface of CdS (Aldrich, gold label, lot No. = 0897) used approaches homogeneity. On the other hand, the somewhat greater compatibility of the Freundlich kinetic treatment *vis-à-vis* the Langmuir–Hinshelwood treatment with the isomerization data of *cis*-stilbene when CdS (Fisher, lot No. = 792913) was used has suggested that this surface is more heterogeneous though a detailed model was lacking. The dimerization of NVC, being a bimolecular reaction, opens up a variety of possibilities for reaction pathways. For example, while the *cis*-stilbene cation radical needs only isomerization to form the product cation radical, the NVC cation radical reacts on the surface either with an NVC molecule preadsorbed on the surface or with one which diffuses from the solution to the surface. In both cases the NVC cation radical has to encounter a neutral NVC molecule to form the dimer cation radical; a process which seems to be a rate-determining step. For this reason, and for its compatibility with other observations to be detailed below, a combination of the Langmuir–Hinshelwood, and the Eley–Rideal pathways, rather than a single pathway, was considered. It is important to note that, owing to the electrostatic interaction on the surface, desorption of NVC radical cation into solution appears improbable.

The Langmuir–Hinshelwood (LH) kinetic treatment is known to be a good model for the description of solid–gas reactions;[20] it also seems to be a good approximation for the description of a solid–liquid system.[20,21] This treatment assumes that a reaction surface be homogeneous, that adsorption forces be independent of surface coverage, and that the rate of reaction be proportional to the surface coverage (θ_D). If these conditions hold, then the rate of reaction, at the photostationary state concentration of the NVC cation radical, where the reactant is significantly more strongly adsorbed than the product, will be given by

$$R_{LH} = k_{LH}\theta_D = \frac{k_{LH}K[D]}{1+K_s[S]+K[D]} \tag{1}$$

or

$$R_{LH} = \frac{k_{LH}K[D]}{a+K[D]} = \frac{k_{LH}K'[D]}{1+K'[D]} \tag{2}$$

where R_{LH} is the rate of reaction, k_{LH} the reaction rate constant, K the adsorption coefficient of the reactant, θ_D the fraction of the surface covered by the reactant, [D] the initial concentration of the reactant, K_s the adsorption coefficient of the solvent, S and $a = 1+K_s[S]$. Since the concentration of the solvent is much higher than that of NVC and remains essentially constant, the part of the CdS surface covered by the solvent is approximately unchanged at all NVC concentrations used and its presence is included in "a".[22b] From Scheme 2, the concentration of the NVC cation radical at the photostationary state is

$$[SC^{-}/D^{+}] = \frac{k_2k_4I\theta_D}{k_5(k_1+k_2)(k_3+k_4\theta_D)} \tag{3}$$

where I is the flux, constant during the experiment. When the rate of electron transfer from NVC to the "hole" $k_4\theta_D[SC(h^+, e^-)]$ is much greater than electron–hole recombination, $k_3[SC(h^+, e^-)]$, k_3 can be neglected *vis-à-vis* $k_4\theta_D$, then $[SC^-/D^+] \approx$ constant.

The model of the Eley–Rideal (ER) kinetic treatment assumes that a reaction occurs between the NVC cation radical on the surface and a neutral NVC molecule from the fluid;[22] the rate of reaction, at the photostationary state concentration of the NVC cation radical on the surface, will obey

$$R_{ER} = k_{ER}[D] \tag{4}$$

where k_{ER} is the reaction rate constant. Equation (4) is a pseudo-first-order rate equation. The term $[SC^-/D^+]$ is already included in k_{LH} and K_{ER} in Eqs (2) and (4).

If both Eqs (2) and (4) are operative, then mixed behaviour for the reaction rate vs concentration of NVC is to be expected. The overall rate of dimerization of NVC, R,† may then be described as

$$R = k_{ER}[D] + \frac{k_{LH}K'[D]}{1+K'[D]}. \tag{5}$$

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†The rates, R, were taken throughout this study, as the amount of product produced after irradiation for particular time periods (indicated in the caption to the plots) with constant light flux. The part of the surface covered by oxygen is unchanged as the reaction vessels were open to the atmosphere via a reflux condenser.

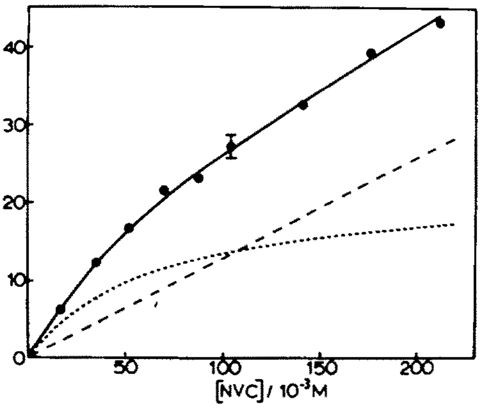

Fig. 1. Effect of NVC concentration on the rates of dimer formation (●). The curve is calculated from $R = 0.129[D] + 0.349[D]/(1 + 15.6[D])$. The overall rates are separated into LH (----) and ER (——) components. Each sample was irradiated at $\lambda > 430$ nm for 30 min with a 150 W xenon lamp. These irradiation conditions were used throughout this work.

Thus, in a plot of rate vs concentration when θ_D almost attains a limiting value, thereafter the overall rate of dimerization is expected to increase linearly with further increase in NVC concentration.

The effect of varying the concentrations of NVC (0.022–0.22 M) on the rate of dimerization at constant CdS mass (42 mg) was investigated and is shown in Fig. 1. At concentrations higher than 0.1 M, the overall rates of dimerization increase linearly with the concentration. Similar observations have been reported as, for instance, in the gas-phase photo-oxidation of carbon monoxide on TiO_2[23] and of propan-2-ol on ZnO.[24] This behaviour has, in fact, been interpreted on the basis that the experimentally observed data arose from separate contributions by two photoassisted mechanisms to the overall rate of photo-oxidation.[23,24] The data may be explained in terms of both the LH and ER pathways.

The data in Fig. 1 fit† nicely a curve obtained by insertion of the values of the constants in Eq. (5)

$$R = 0.129[D] + 0.349[D]/1 + 15.6[D].$$

Having these values, k_{ER}/k_{LH} is estimated to be 6, which clearly indicates that the ER pathway is favoured. Similarly, using these values, it became possible to separate the overall rates of dimerization into LH and ER components (Fig. 1).

On the basis of the above discussion, coupled with quenching data and quantum yield determination (to be discussed below), the overall mechanism is outlined in Scheme 2. The effect of oxygen, considered to be constant, is omitted.

CdS *mass effect*

The rate of dimer formation as a function of the amount of CdS at constant NVC concentration (0.22 M) was found to be constant over the range 10–75 mg of CdS (Fig. 2). However, when 5 mg of CdS were used, the rate was halved. Similar observations have been previously reported, for instance, in the CdS photoinduced isomerization of *cis*-stilbene,[7b] in the selective photocatalytic oxidation of alkanes on TiO_2[25] (where the catalyst was spread out in the reactor as a thin homogeneous layer) and in the oxidation of propan-2-ol either in the liquid phase with suspended TiO_2[26] or in the vapour phase over a thin uniform film of TiO_2.[24] This behaviour was attributed to the complete absorption of radiation near the surface of the semiconductor. In all the above-mentioned systems a plateau was observed at a semiconductor mass of greater than 100 mg;[24–26] in the CdS photoinduced dimerization of NVC it has been found that 10 mg of CdS was enough to achieve maximum activity. The unchanged rates of dimerization of NVC over the range of 10–75 mg of CdS may be explained in terms of either or both of the following factors: (a) light entering the reaction vessel is completely absorbed by CdS (i.e. little scattered light) and (b) the major part of the reaction follows the ER pathways where the concentration of NVC in solution is almost constant. That the rate of reaction decreased to half when 5 mg of CdS were used then implies incomplete absorption of the light by the CdS.

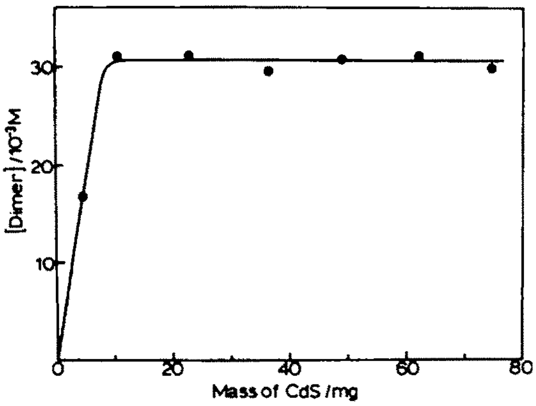

Fig. 2. Influence of the mass of CdS on the rate of dimer formation.

Quenching studies

One mode of demonstrating the involvement of the cation radical in a reaction scheme is the observation of its quenching by an electron donor. 1,3,5-Trimethoxybenzene ($E^{ox}_{1/2} = 1.49$ V vs SCE),[27] 1,2,4-trimethoxybenzene ($E^{ox}_{1/2} = 1.12$ V vs SCE)[27] and 1,2,4,5-tetramethoxybenzene ($E^{ox}_{1/2} = 0.81$ V vs SCE)[28] were tested as quenchers. Plots of $(\phi^{\circ}/\phi - 1)$ vs [Q] for 1,3,5- and 1,2,4-trimethoxybenzenes are shown in Fig. 3. While 1,2,4-trimethoxybenzene quenched the reaction efficiently, the 1,3,5-isomer did not exhibit any quenching ability over a similar concentration range. 1,2,4,5-Tetramethoxybenzene, on the other hand, quenched the reaction dramatically (Fig. 4) at a lower concentration range. Thus, for the same concentration (~0.006 M), 1,2,4,5-tetramethoxybenzene was found to quench the reaction about ten times more efficiently than 1,2,4-trimethoxybenzene. The inability of 1,3,5-trimethoxybenzene to quench the "hole" (valence band 1.6 V vs SCE[29])—quenching of the $(NVC^{\dot{+}})$ is thermodynamically very slow—may be understood in terms of the low concentration of the quencher, the

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† A nonlinear least square method program was used to fit the data.

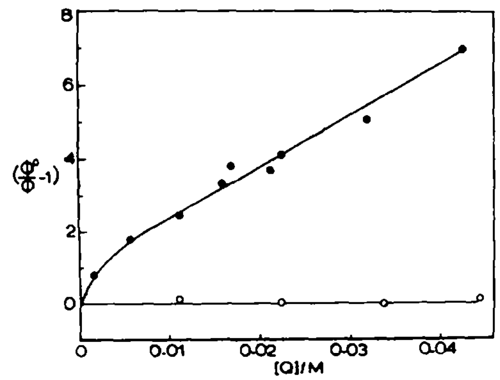

Fig. 3. Effect of 1,2,4-trimethoxybenzene (●) and 1,3,5-trimethoxybenzene (○), as quenchers, on the rate of dimerization of NVC. The curve is calculated from $\phi^\circ/\phi = 1+127[Q]+3096[Q]/(1+1314[Q])$.

high concentration of NVC ($E^{ox}_{1/2} = 1.12$ V vs SCE), and the short life-time of the "hole". Accordingly, the quenching with 1,2,4-trimethoxybenzene and 1,2,4,5,-tetramethoxybenzene involves essentially the cation radical of NVC.

Figure 4 shows that at concentrations higher than 0.001 M of 1,2,4,5-tetramethoxybenzene the rate of quenching increases linearly with the quencher concentration. Similar behaviour was observed with 1,2,4-trimethoxybenzene. This behaviour is similar to that discussed above for the relationship of dimerization rates to concentration of NVC (Fig. 1). The data seem to arise from separate contributions from two quenching mechanisms to the overall quenching process. Again, the data may be explained in terms of an LH mechanism in which the cation radical of NVC should be quenched by the preadsorbed quencher on the surface together with an ER mechanism in which the NVC cation radical is quenched by diffusion of the quencher from the solution.

To rationalize these data kinetically the following treatment is proposed. On the assumption that under our conditions only cation radical (NVC^{+}) quenching is important, and that the quenching involves surface (LH) and solution (ER) pathways, we arrive at Scheme 2 as a minimal representation of the processes.

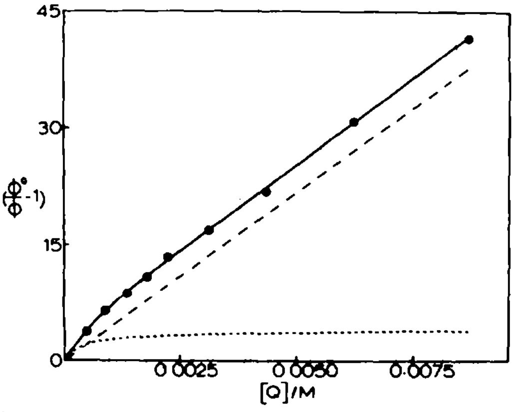

Fig. 4. Quenching of the dimerization of NVC by 1,2,4,5-tetramethoxybenzene (●). The curve is calculated from $\phi^\circ/\phi = 1+4353[Q]+8484[Q]/(1+2046[Q])$. The overall quenching rates are separated into LH (----) and ER (---) quenching components.

Application of the steady-state hypothesis leads to the quantum yield expression, in the absence of quencher

$$\phi^\circ = \frac{k_2}{k_1+k_2}\cdot\frac{k_4\theta_D^\circ}{k_3+k_4\theta_D^\circ}\cdot\frac{k_6\theta_D^\circ+k_7[D]}{k_5+k_6\theta_D^\circ+k_7[D]}\cdot\frac{k_9}{k_8+k_9} \quad (6)$$

where θ_D° is the fraction of the surface covered by the reactant, NVC, [D] the initial concentration of the reactant, and the rate constants are as indicated in the scheme. The quantum yield for the conversion of the final cation radical, $D_2^{\dot{+}}$, to product is assumed to be not more than unity, i.e. that no chain reaction is involved.

The quantum yield expression, in the presence of the quencher, is

$$\phi = \frac{k_2}{k_1+k_2}\cdot\frac{k_4\theta_D}{k_3+k_4\theta_D} \times \frac{k_6\theta_D+k_7[D]}{k_5+k_6\theta_D+k_7[D]+k_{10}[Q]+k_{11}\theta_q}\cdot\frac{k_9}{k_8+k_9}. \quad (7)$$

When both the reactant, D, and the quencher, Q, adsorb on the surface without significant competition for the same sites, then θ_D is considered to be constant (i.e. $\theta_D^\circ = \theta_D$) and θ_q takes the following forms

$$\theta_q = \frac{K_q[Q]}{1+K_s[S]+K_q[Q]} = \frac{K_q[Q]}{a+K_Q[Q]} = \frac{K''[Q]}{1+K''[Q]} \quad (8)$$

where $K'' = K_q/a$. Dividing Eq. (6) by Eq. (7) gives

$$\frac{\phi^\circ}{\phi} = 1 + \frac{k_{10}[Q]}{k_5+k_6\theta_D+k_7[D]} + \frac{K_{11}\theta_q}{k_5+k_6\theta_D+k_7[D]}. \quad (9)$$

Substitution of Eq. (8) in Eq. (9) gives

$$\frac{\phi^\circ}{\phi} = 1+A[Q]+\frac{B[Q]}{1+C[Q]} \quad (10)$$

where

$$A = \frac{k_{10}}{k_5+k_6\theta_D+k_7[D]},$$

$$B = \frac{k_{11}K''}{k_5+k_6\theta_D+k_7[D]}$$

and

$$C = K''.$$

The quenching data in Fig. 4 fit a curve obtained by use of the following set of constants in Eq. (10): $A = 4353$, $B = 8484$, $C = 2046$.† From the value of K'' and the ratio A/B, which is shown to be 0.513, k_{10}/k_{11} is estimated to be 1049. Similarly, the ratio k_{10}/k_{11}, in the case of 1,2,4-trimethoxybenzene, is estimated to be 54 (for A, B and C values, see caption of Fig. 3). Actually, the ratios k_{10}/k_{11} for both quenchers strongly argue in favour of the ER quenching pathway. Having A, B and C it is possible to assign the LH and ER components to the overall quenching rate (Fig. 4).

However, when both the reactant, D, and the quencher, Q, are considered to compete for the same

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†A nonlinear least square method program was used to fit the data.

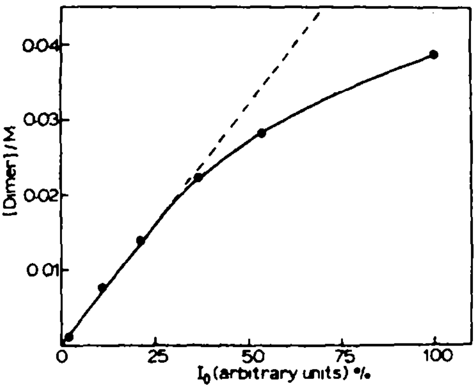

Fig. 5. Effect of variation of light intensity upon rates of dimerization of NVC.

sites, then θ_D and θ_q take the following forms

$$\theta_D = \frac{K[D]}{1+K_s[S]+K[D]+K_q[Q]} \tag{11}$$

$$\theta_q = \frac{K_q[Q]}{1+K_s[S]+K_q[Q]+K[D]}. \tag{12}$$

Substitution of Eqs (11) and (12) in Eq. (7) and then dividing Eq. (6) by Eq. (7) gave a power series polynomial equation which we were unable to fit to our data. Thus, the compatibility of the non-competitive adsorption model with the quenching data suggests that the non-competitive adsorption extreme approximates the actual situation on the surface.

Light intensity effect and quantum yield

The rate of dimer formation was studied as a function of light intensity (Fig. 5). Reduced intensities are expressed as percentages of that of the full arc ($\lambda > 430$ nm). It was found that the reaction rate decreased nonlinearly with reduction in light intensity down to about 35% of full intensity. However, with further reduction in intensity, down to 2% of full light intensity the reaction then decreased linearly. Similar observations have been reported for, at least, the following photocatalytic processes: (a) the *cis–trans* isomerization of *cis*-stilbene on CdS,[7b] (b) the oxidation of propan-2-ol in the vapour phase over a thin uniform of TiO_2,[24] (c) the oxidation of liquid propan-2-on suspended TiO_2,[26] (d) the gas-phase photo-Kolbe reaction of acetic acid over Pt/TiO_2[30] and (e) a photoelectrochemical cell system when a Pt electrode coated with TiO_2 powder was used as a photoanode.[31] The rates in most of these reactions, were linearly dependent on the square root of light intensity. No satisfactory linear relationship can be obtained for the rate vs $\sqrt{I}$ in CdS photoinduced dimerization of NVC; this is most probably to be attributed to the negligible occurrence of electron–hole recombination up to ~35% of full light intensity. By analogy,[24,26,30,31] this behaviour may be explained on the basis that under weak illumination the band bending in the space charge layer of powdered CdS is enough to separate all hole–electron pairs. However, with increasing light intensity a strong competition between processes involving hole–electron recombination and those involving participation of photogenerated "holes" in surface photo-oxidation may occur, the band bending tending to be decreased. The linear behaviour suggests that the electron–hole recombination process is negligible in this range (2–35% of full light intensity). Accordingly, the quantum efficiency for the CdS (h^+, e^-) formation by the excited CdS may be considered to be unity in this range. Extrapolation of the linear segment (Fig. 5) to 100% light intensity and dividing the observed rate at this light intensity by the extrapolated value allows an estimation of ~0.6 for the quantum efficiency for the CdS (h^+, e^-) formation at this light intensity. Thus, to eliminate the electron–hole recombination process, extremely low light intensities compatible with the obtention of meaningful measurements were used in the quantum yield determination: the value for CdS photoinduced dimerization of NVC (0.33 M) was found to be 0.33 ± 0.03.

Ledwith and co-workers[8a] have measured the quantum yield for the photosensitized dimerization of NVC for chloranil and fluorenone. They reported[8a] quantum yields of 8.5 and 3.6 for aerated acetone solutions of NVC (0.1 M), and have suggested that the reaction proceeds via the chain mechanism shown in Scheme 1. The relatively low quantum yield for the CdS photoinduced dimerization of NVC, in comparison with that in homogeneous solution, suggests that such a chain mechanism does not seem to be important in CdS photoinduced dimerization of NVC.

CdS *samples and the temperature effect*

The experiments described were performed on CdS of polycrystalline form (Strem, ultrapure, lot No. = 4840). Bard and co-workers[2a] have found recently that the crystal structure of the CdS particle influences the yield of hydrogen, with cubic β-CdS acting as a more active catalyst than hexagonal α-CdS. Rudham and co-workers[26] have reported different rates and activation energies for the oxidation of liquid propan-2-ol on pure anatase, five doped rutiles and coated anatase and rutile pigments. Under these conditions, they have obtained an activation energy which ranged from 31 to 91 kJ mol^{-1} and have attributed these results to the presence of traps with different depths below the conduction band. Yanagida *et al.*[32] have reported that ZnS with different physical properties such as purity, particle size, surface area and crystalline form gave different quantum yields for hydrogen production in water/methanol systems. We have, therefore, studied the cyclodimerization of NVC on CdS from different sources with different structures, surface areas and purities. The surface area, purities, crystalline structures of different CdS samples together with the relative reaction rates are presented in Table 1. The data shows that the rates vary by a factor of four with no direct relationship to either the surface areas or the purities of the samples. This is not surprising since different surface states (vacancies, lattice defects, impurities) localized between the top of the valence band and the bottom of the conduction band, acting as donor or acceptor centres may well be present. The generation of these states depends on the method of preparation of the CdS sample, the impurity levels and the photochemical effects. In analogy with Rudham and co-workers'[26] observations, one possible explanation for this variation in reaction rates is

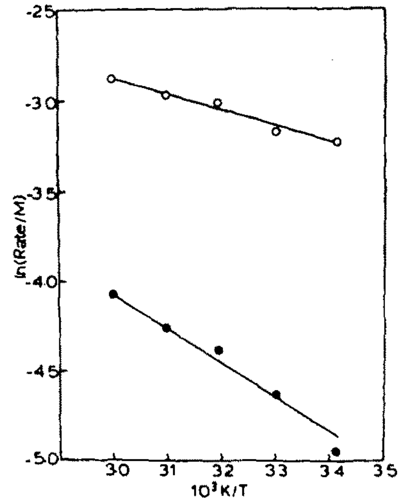

Fig. 6. Arrhenius plots of ln (rate) against $1/T$ for the dimerization of NVC using two different CdS samples: Strem, ○; Aldrich, ●.

the different trapping efficiencies of the photoelectron by traps at different depths below the conduction band of CdS. Supporting evidence for this conclusion may be found in the activation energies data. Thus, the effect of temperature (293–333 K) on the rate of dimerization was studied with two selected samples of CdS. The Arrhenius plots are represented in Fig. 6 and the corresponding activation energies included in Table 1. The different activation energies suggest that these energies are associated with processes within the semiconductor rather than with the photocatalysed dimerization of NVC. The low activation energies suggest the presence of traps of different depths below the conduction band; the location of these traps should be very close to the conduction band of CdS. Traps at different depths (0.05, 0.14, 0.25, 0.41, 0.63 and 0.83 eV) have been reported in CdS single crystal investigations.[33] The low activation energies seem to be required to promote a photoelectron from these traps into the conduction band and hence increase the efficiency of superoxide ion formation; a process which has shown to be very important for CdS photoinduced dimerization of NVC.

CONCLUSIONS

The CdS powder photomediated dimerization of NVC has been investigated. The reaction rates are unchanged over the range 10–75 mg of CdS at constant NVC concentration but is very much affected by oxygen. The effect of varying the concentration of NVC on the rate of dimerization at constant CdS mass showed a complex behaviour. The data may be rationalized in terms of Langmuir–Hinshelwood and modified Eley–Rideal mechanisms. A cation radical process has been proposed as the reaction can be quenched very efficiently by electron donors (methoxybenzenes). The quenching data have also been rationalized with the Langmuir–Hinshelwood and the Eley–Rideal quenching pathways. The rates of reaction were linearly dependent on the light intensity up to 35% of full illumination indicating that the hole–electron recombination process is negligible at this range of light intensity. The quantum yield was found to be 0.33 ± 0.03. CdS samples with different structures, surface areas and purities were tested and found to affect the reaction rates by a factor of four.

Different activation energies were obtained using different CdS samples which suggests that these are associated with processes within the catalyst rather than the photocatalytic dimerization of NVC.

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