

intermediates may be able to achieve cyclic forms conducive to δ - and ϵ -H shifts. Future studies of the chemistry of transition metal ions with larger, labeled alkanes should provide further insights into this area.

Summary

The purpose of the present study was to examine the effect of the chain length in the reaction pathways of Co^+ with some monofunctional organic molecules and to suggest an ordering for preferred site of attack of skeletal bonds. In the study of a series of straight-chain alkyl chlorides and alcohols, increases in the chain length lead to a rich chemistry in both cases.

Metal ions such as Co^+ react with longer chain *n*-alkyl chlorides and normal alcohols by mechanisms similar to alkanes, i.e., by inserting into the skeletal C-C bonds. This leads to the formation of metal-olefin complexes in the case of *n*-alkyl chlorides and metal ion-small alcohols complexes in the case of alcohols. This is consistent with the proton affinity rule⁹ for competitive ligand loss.

Metal insertion into the polar bonds of C-OH and C-Cl in larger alcohols and alkyl chlorides is not a major pathway, as it is for the small alkyl chlorides and alcohols ($n < 4$).

Long-chain alkyl chlorides exhibit some similarities with alkanes concerning the ordering (pattern) for preferred site of insertion by Co^+ . For alcohols, the increase in the chain length has a more "dramatic" effect on the reaction products. Since $\text{PA}(\text{alcohols}) > \text{PA}(\text{alkyl chlorides})$, there is a relatively strong initial cobalt ion-alcohol interaction on complexation. A mechanistic sequence consisting of a metal-carbon atom interaction via the formation of cyclic five- or six-membered ring intermediates and a further insertion into the skeletal C-C bonds which come into close proximity with the metal accounts for most of the products observed.

Since the initial interaction between Co^+ and alkyl chlorides is less than that with alcohols, we do not see the complexa-

tion/five-or-six-membered ring intermediate process playing as important a role for the chloroalkanes. The effect due to the presence of the chlorine is less dominant than that of the OH group. Also, when complexation of Co^+ to the chlorine atom of an alkyl chloride occurs, metal insertion into the C-Cl bond occurs, favored by the strong Co^+-Cl bond. Since the Co^+-OH bond^{2d} is weaker than the Co^+-Cl bond,²⁴ and C-OH bonds are stronger than C-Cl bonds,¹⁴ attack at the functional group is less important on complexation for the alcohols.

Concerning the mechanistic step of the β -H shift following metal insertion into a C-C bond and the formation of an intermediate containing two alkyl groups bound to the metal center, the alkyl group carrying no functional group usually provides the H that shifts onto the metal center, with the exception of the $-(\text{CH}_2)_4\text{OH}$ group.

Further studies of Co^+ with bifunctional organic molecules (halo alcohols and dihaloalkanes) containing two or more carbon chains are now under way, in order to better understand how the chain length affects the reactivity and the preferred site of attack.

Registry No. $\text{C}_3\text{H}_7\text{Cl}$, 540-54-5; $\text{C}_3\text{H}_7\text{OH}$, 71-23-8; $\text{C}_4\text{H}_9\text{Cl}$, 109-69-3; $\text{C}_4\text{H}_9\text{OH}$, 71-36-3; $\text{C}_5\text{H}_{11}\text{Cl}$, 543-59-9; $\text{C}_5\text{H}_{11}\text{OH}$, 71-41-0; $\text{C}_6\text{H}_{13}\text{Cl}$, 544-10-5; $\text{C}_6\text{H}_{13}\text{OH}$, 111-27-3; $\text{C}_7\text{H}_{15}\text{Cl}$, 629-06-1; $\text{C}_7\text{H}_{15}\text{OH}$, 111-70-6; $\text{C}_8\text{H}_{17}\text{Cl}$, 111-85-3; $\text{C}_8\text{H}_{17}\text{OH}$, 111-87-5; CO^+ , 16610-75-6.

(24) From the appearance potential of CoCl^+ ion obtained from the mass spectral studies of $\text{Cl}_3\text{SiCo}(\text{CO})_3\text{PF}_3$ and $\text{Cl}_3\text{SiCo}(\text{CO})_2(\text{PF}_3)_2$ (18.7 ± 0.4 and 18.9 ± 0.5 eV, respectively)²⁵ and using the values of $\Delta H_f(\text{CO}) = -26.4$ kcal/mol,²¹ $\Delta H_f(\text{PF}_3) = -219.6$ kcal/mol,²¹ $\Delta H_f(\text{SiCl}_2) = -37.66$ kcal/mol,²⁶ $\Delta H_f(\text{Cl}_3\text{SiCo}(\text{CO})_3\text{PF}_3) = -548 \pm 10$ kcal/mol²⁵ and $\Delta H_f(\text{Cl}_3\text{SiCo}(\text{CO})_2(\text{PF}_3)_2) = -748 \pm 10$ kcal/mol,²⁵ we can estimate the bond strength between Co^+ and Cl, $D(\text{Co}^+-\text{Cl}) = 91.4 \pm 19.2$ kcal/mol.

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Surface Photochemistry: CdS-Mediated Dimerization of Phenyl Vinyl Ether. The Dark Reaction¹

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Abstract: The dimerization of phenyl vinyl ether can be induced by light in the presence of CdS. We report here that certain samples of CdS induce the same cycloaddition in the dark, the reaction being attributed to the presence in the CdS of acceptor-type surface states. These surface states could also be produced by treatment of an inactive CdS specimen with sulfuric acid or by the coadsorption of the electron acceptors maleic anhydride and tetrachlorophthalic anhydride. Neither CdS particle size, surface area, nor crystal structure (cubic, hexagonal, or polytype) appeared to be significant factors in the dimerization.

Photochemical reactions involving electron transfer at semiconductor surfaces have been for the last few decades, and continue to be, an area of intensive research. Much of this work has been motivated by the desire to achieve the light-induced generation of fuel (e.g., the photolysis of water). Cadmium sulfide, having a small band gap and good spectral response in the visible region, has been an important focus of attention. However, more attention has been paid to the development of solar cells (the photoproduction of hydrogen) and much less to the development of the use of CdS for other organic electron-transfer reactions. Among the few photoreactions using CdS dispersions reported, other than

oxidation/reduction,² are the dimerization of phenyl vinyl ether³ (PVE) and the cis-trans isomerization⁴ of styrene derivatives. It was in connection with the former that a slow, but significant, dark reaction occurred which could be used as a probe of the physical condition of the CdS dispersion utilized. The present contribution reports how modification of the surface or the purity

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Table I. Details of CdS Samples Used

sample no.	supplier	grade	lot. no.	purity	surface area, ^a m ² g ⁻¹	structure
1	Aldrich	Gold Label	1721 PJ	99.999	1.2	α
2	Strem	Luminescent	NATL	99.99	0.6	α
3	Fisher		792913	~99	12.0	β
4	Aldrich		JC053087	98.8	7.0	β
5	Aldrich	Gold Label	0897	99.99	20.0	polytype ^b
6	Strem	Ultrapure	16027-S1	≥99.99	44.0	polytype ^b
7	c			>99.99		β

^aSurface area determined as described in ref 3a. ^bSamples 5 and 6 are both polytypes but are different from each other. Sample 6 has the lesser stacking disorder and is nearer to a cubic structure. ^cPrepared in the laboratory (see text).

of the CdS and its structure can affect the reactivity of the semiconductor. This is, to our knowledge, the first observation of an electron-transfer reaction involving cation radicals in the dark at room temperature induced by CdS.⁵

Interfacial electron-transfer studies have been performed using CdS as a colloid,⁶ as a dispersed powder,⁷ or as a single-crystal electrode.⁸ As is the case with other heterogeneous catalysts, characterization of the CdS surface in its working state is not clearly established yet; analogy has to be made with studies reported on single crystals or polycrystalline powders.

One profitable route to characterizing the CdS in its various forms is the study of its luminescent⁹ and conductive properties.¹⁰ It has been surmised that there are several energy levels¹¹ in the forbidden zone attributable to surface states (vacancies, lattice imperfections, impurities) acting as donor or acceptor centers.^{10,11} The CdS spectral response, including the infrared region,¹² has been attributed to transitions between these energy levels,^{9,13} including the valence and conduction bands. Adsorbed electron-acceptor molecules also modify the CdS properties in that they reduce the dark conductivity.¹⁴

The generation of these surface states has been shown to depend on the mode of the preparation of the CdS,¹⁵ subsequent heat treatment,¹⁵ purity levels,¹⁵ and the nature of any molecules adsorbed on the surface.^{14a,16} The method of preparation of the

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(16) Among the most important applications of adsorbed molecules in the modification of the CdS surface is the recent use of RuO₂ or Pt (or both)¹⁷ as dopants which facilitate hole or electron transfer to adsorbed species.

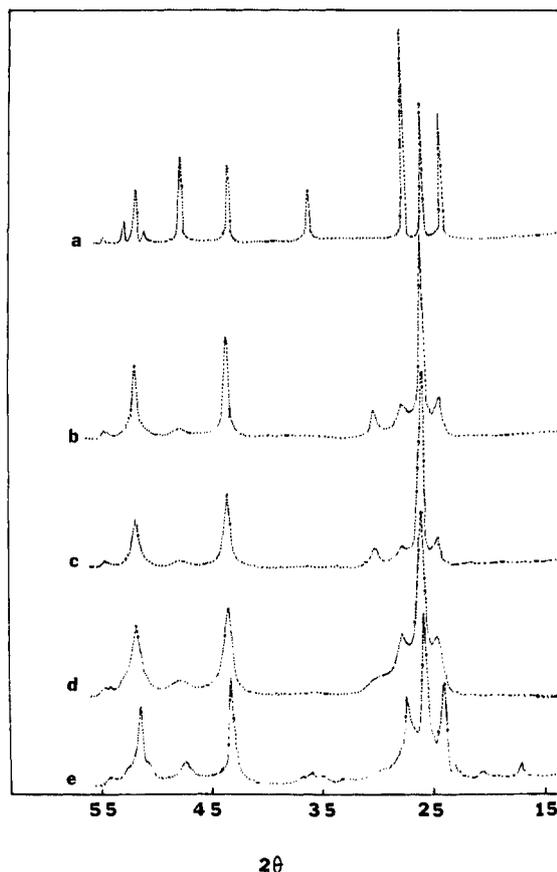


Figure 1. X-ray diffractograms of various CdS samples: (a) samples 1 and 2 (α), (b) samples 3 and 4 (β), (c) sample 7 (β), (d) sample 6 (polytype), and (e) sample 5 (polytype).

CdS determines whether the product will be α -CdS (hexagonal), β -CdS (cubic),¹⁸ or polytype. The hexagonal and cubic forms are reported to have a small (~ 0.2 eV) difference in band gap,¹⁹ but this is not considered likely to have a profound effect on the electron-transfer properties. Changes in conductivity under pressure with a simultaneous transformation from hexagonal to cubic form are attributed to changes in the defect levels and not to changes in the band gap.^{10c} However, reports that CdS (as does ZnS) exhibits polytypism²⁰ and that the electronic band type of the polytype crystals varies with polytype periodicity are relevant to the present discussion.²¹ Thomas and co-workers²² have re-

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ported that colloidal CdS was more efficient than a polycrystalline powder dispersion for electron transfer. This has been attributed to the modification in crystal structure in colloidal CdS; the X-ray diffractogram of the colloidal CdS, having a broad band, resembles that of a polytype. Very recently Bard and his co-workers²³ have suggested, for CdS immobilized in a polymer (Nafion) matrix, that the β form is more active than the α form, when platinized, for the photoproduction of hydrogen.

Experimental Section

Materials. Most of the CdS samples were commercial products and are listed in Table I. Samples were also prepared as described below. TiO₂ was Fluka (>99%, ~5 m² g⁻¹). Dichloromethane (Baker, spectral grade) was used as received. All other substances were purified by distillation, sublimation, or recrystallization, as appropriate. PVE was prepared as described elsewhere.^{3a}

CdS Preparation.¹⁸ Hydrogen sulfide (Canadian Liquid Air, C.P. Grade) was passed through a solution of CdSO₄ (Aldrich, 99.999%, 200 mL, 0.2 M) for 10 min. For the preparation of cubic (β) CdS a boiling solution acidified with H₂SO₄ (pH ~2.5)²³ was used. The precipitate was filtered and washed several times with conductivity water, after which it was dried at 100 °C at 2×10^{-5} torr for 3–4 h.

Loading of Iron and Other Substances on CdS. (a) A known amount of FeCl₃(aq) (0.5–3% with respect to CdS) was mixed with CdS (sample 1, Table I) and the mixture sonicated until a thick paste was obtained. This was dried at 100, 150, and 200 °C. Similarly, CdO (99.9999%) or CdSO₄ (99.999%, Aldrich), to the amount of 1.0% CdS, was sonicated in methylene chloride with CdS to dryness.

(b) A known amount of FeSO₄ was added to aqueous CdSO₄ and H₂S passed, the sulfide being washed and dried, all as before.

Methods. Reaction of PVE. PVE (150 mg) in CH₂Cl₂ (total 5 mL, ~0.25 M) was mixed with 100 mg of CdS in a Pyrex tube. The mixture was sonicated for 10 min, after which it was either irradiated or kept in the dark. Details of the irradiation procedure have been described elsewhere.^{3a} For the dark reaction the tubes were wrapped in black tape and stirred constantly. After the desired period had elapsed, the calibrating compound was added (C₁₆H₃₄); then the reaction mixture was filtered (CH₂Cl₂ wash) and analyzed by GLC.^{3a} The peaks were identified by MS and ¹H NMR spectra after separation by preparative TLC.

X-ray Diffraction (XRD) Analysis. The analysis was performed on a Rigaku diffractometer using Cu K α radiation. The diffractograms were compared with those reported²⁴ for standard CdS samples. Diffractograms having broad and diffuse peaks and having some extra, or missing some standard peaks were identified as polytypes by comparison with those reported for CdS and ZnS.²⁰ However, no detailed characterization of the polytype crystals was performed. Figure 1 presents diffractograms of some of the cadmium sulfide samples. From the XRD line width the average crystal size of these samples was estimated to be of the order of 80 Å for sample 6, and ~400 Å for sample 1. The particle size was roughly related to the surface area: the higher the surface area, the smaller the size.

ESR Studies. The ESR measurements were performed on a Varian E-12 EPR spectrometer equipped with a Varian E-257 temperature controller and interfaced with a Nicolet 2090-III transient recorder and a Nicolet 1180 computer system for the acquisition of spectra. The powdered samples were transferred to 4.0-mm o.d. quartz tubes, which were then introduced into the insert Dewar of the temperature controller in the EPR cavity. All the spectra were recorded at 90 K with modulation amplitude of 1 mT; microwave power 10 mW at 9.04 GHz. Sample 2 had only one ESR signal at $g = 1.8$, sample 2A (see Table II) had ESR signals at $g = 1.8, 2.003$, and 2.169, while sample 3 had ESR signals at $g = 1.778, 1.931, 1.98, 2.003, 2.033, 2.157, 2.55$, and 4.283.

Results

The activities of the CdS from various sources and treatments for the dimerization of PVE both in the dark and with illumination are listed in Table II. Of the untreated specimens only samples 3 and 4 were effective in the dark, giving both the dimer 1,1-diphenoxycyclobutane (DCB) and 1,1-diphenoxyethane (DPE). Traces of phenol were also detected. The formation of the later suggested that the DPE was formed by addition of phenol to PVE,

Table II. Catalytic Activity of Various CdS Samples for PVE. Conversions to DCB and DPE

sample no.	dark reaction ^a			illuminated reaction ^a		
	time (h)	DCB (%)	DPE (%)	time (h)	DCB (%)	DPE (%)
1	40	0	0	4	1.92	0.07
	138	0.4	0.06			
2	45	0	0	4	3.1	0.06
2A ^b	18	9.9	8.2			
3	4	1.8	12.4	4	3.3	17
	18	12.1	23.9			
3A ^c	22	14.3	16.4			
3B ^d	19	0.8	10.8			
4	20	8.6	12.7	2	1.1	0.33
				4	2.8	5.6
5	45	0	0	4	2.8	2.2
	138	0.8	3.8			
6	20	0.02	0.04	2.5	0.05	0
	45	0.05	0.05	4	0.4	0.15
7 ^e	18	0	0			
7A ^f	16	3.95	13.4			

^aPVE ~0.25 M (CH₂Cl₂, 5 mL), CdS ~100 mg, room temperature, $\lambda > 430$ nm for illuminated reactions; conversion expressed as % PVE converted to a particular product. ^bSample 2 was washed with acidified 200 mL (pH ~2.5) water and dried in air at 100 °C. ^cSample 3 was wetted with water and dried in air at 100 °C overnight. ^dSample 3 was washed thoroughly with water and dried in air at 100 °C overnight. ^eAll CdS (β) samples prepared in the lab were inactive including that (i) dried in air at room temperature, (ii) dried at 100 °C in air, (iii) dried in vacuo at 50 °C, and (iv) dried in vacuo at 100 °C. ^fPrepared in the same way as sample 7, but the precipitate was not washed.

a known process.²⁵ The generation of DCB cannot, however, be easily rationalized via a simple cationic mechanism, and the intermediacy of a cation radical^{3a,28} appeared probable.

Sample 7 had a cubic structure as did samples 3 and 4, but was inactive in the dark. This indicated that the crystal form was not the determining factor with regard to activity in the dark. Drying the washed precipitate of sample 7 at 50 °C overnight in vacuo, at 100 °C in air or at 160 °C in vacuo did not induce any dark activity. Similarly, the fact that samples 1–4 and 7 had particle sizes in the same range (~300–400 Å) precluded this factor, also as being responsible for activity.

In view of the high impurity levels in samples 3 and 4 the possibility of a dopant cannot be ignored. However, it should be noted that *under illumination* samples 1–5 have comparable activities with regard to dimerization. The analysis provided by the supplier of sample 3 indicated the presence of 0.4% SO₄²⁻ and 0.007% iron. However, doping samples 1 and 2 with CdSO₄, Fe³⁺ (as FeCl₃), Fe²⁺ (as FeS), or CdO did not result in any dark activity.

The trans to cis ratio (T/C) in the dimers of PVE obtained from samples 3 and 4 were similar and were ~0.1, both in the dark and under illumination. Samples 1, 2, and 5, on the other hand, gave a T/C value of ~0.52 as was previously reported for a group of semiconductors.^{3a} DPE was only observed using samples 3 and 4 whether with or without light. Sample 6, which had the highest surface area (~44 m² g⁻¹), was inactive in PVE conversion both in the dark and with illumination. It was, however, active in olefin isomerization.²⁶

The formation of cation radicals by adsorption of polycyclic aromatic hydrocarbons onto alumina, silica, and silica-alumina has been widely reported²⁷ and has been attributed to the participation of both Lewis and Brønsted acid sites on the adsorbent surface;^{27a,c} a role for oxygen as an electron acceptor or as a charge-transfer agent has also been suggested.²⁷ Since β -CdS is

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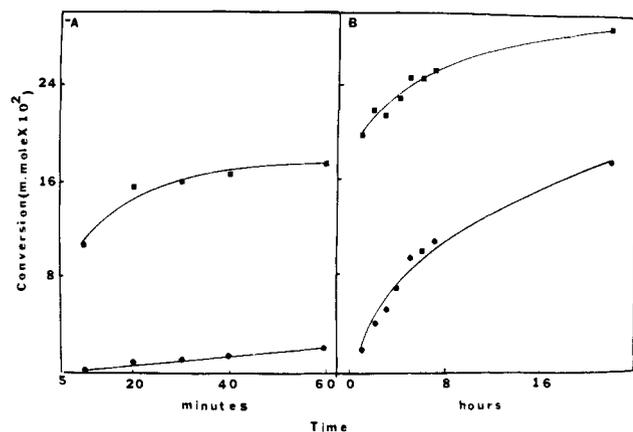


Figure 2. Time-dependent studies of PVE conversion to DCB (●) and DPE (■) induced by CdS (sample 3) in the dark; for both A and B, CdS ~ 100 mg, PVE ~ 0.25 M (solvent CH_2Cl_2 , volume of solution 5 mL). A and B are two separate experiments. The value of DPE after 60 min in case A is not the same as in B. Error in determination is $\pm 8\%$.

usually prepared from an acidified cadmium salt solution, it seemed possible that the dark activity of samples 3 and 4 might be attributable to residual acid following inadequate washing of the precipitate during the CdS preparation. That such was, indeed, the case was rendered more probable by the observation that washing sample 2 (sample 2A) with a dilute acid solution (200 mL of water at pH 2.5, H_2SO_4), or not washing the β -CdS precipitate gave material (sample 7A) which was active in the dark. In addition, while wetting of sample 3 followed by drying (sample 3A) had no significant effect on the activity, the source material washed with water and dried (sample 3B) was rendered largely inactive with respect to dimerization though DPE formation was unaffected.

Drying samples at above 100°C affects the dark reactivity. Some reduction was observed (for both DCB and DPE formation) when samples were dried at 160°C ($< 2 \times 10^{-5}$ torr); while drying at temperature $> 200^\circ$ (vac) considerable loss of activity resulted, possibly because of annealing.

For the further results here reported, CdS as in sample 3 was used.

Reaction Course with Respect to Time. In Figure 2 is shown the amount of PVE converted to DCB and DPE with time. The initial rate of DPE formation is very fast; $> 50\%$ of the total DPE produced was formed in the first 20 min as against only 4% of the total DCB. In the latter part of the reaction the rates are comparable.

It was also observed that the dimer formed initially (conversion 0.11%, 10 min) was almost 100% trans isomer. However, the T/C ratio decreased to 0.21 after 20 min, arriving ultimately at a constant value of ~ 0.1 after 4 h. Phenol, presumed formed during the reaction to rationalize DPE formation, was present to the extent of only 1.2% of the original PVE concentration after 10 min and was reduced to 0.15% at the end of the reaction.

Effect of Concentration. The amount of PVE converted in the dark to product over a fixed time (18 h) varies with PVE concentration (Figure 3). For DCB formation the increase is roughly linear above 0.1 M. On the other hand, the DPE reaches a limiting value at ~ 0.1 M after which there may be a slight decrease; the experimental error renders this point uncertain. Again, at a low concentration of PVE (~ 0.06 M) the T/C ratio of the DCB (0.66) was similar to that observed for DCB formation from PVE using organic electron-transfer sensitizer.²⁸ The amount of dimer ($\sim 0.5\%$) produced was very small. However, the T/C ratio reached 0.1 at higher concentration of PVE. This decrease in the T/C ratio is in sharp contrast to the homogeneous system²⁸ where an increase in the T/C ratio had been observed with increase in PVE concentration. It has also been observed previously^{3a} that DCB was stable under our reaction conditions, in the presence

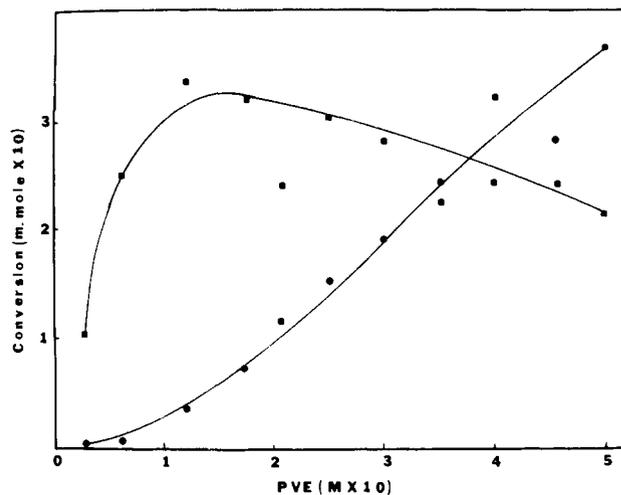


Figure 3. Effect of PVE concentration on PVE conversion to DCB (●) and DPE (■) induced by CdS (sample 3) in the dark. For each experiment: CdS ~ 100 mg, time 18 h, solvent CH_2Cl_2 , total solution 5 mL.

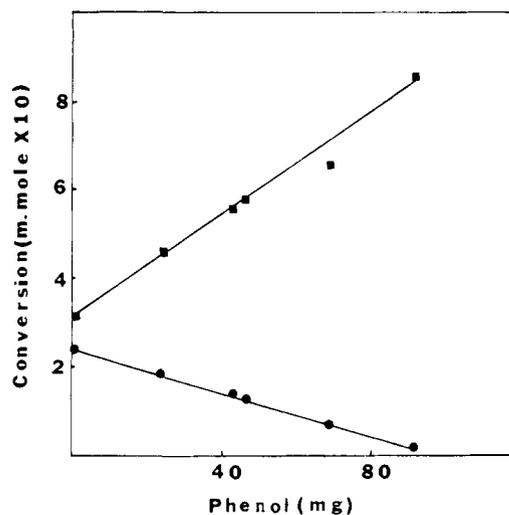


Figure 4. Effect of phenol on PVE conversion to DCB (●) and DPE (■) induced by CdS (sample 3). For each experiment: CdS ~ 100 mg, PVE ~ 2.25 M (in CH_2Cl_2), total solution 5 mL, time 18 h.

of UV illumination, and similar results were obtained for the dark reaction in the present case. This change in the T/C ratio may indicate the existence of two kinds of sites for dimer formation on the CdS surface. If such be the case, the trans sites must be fast, limited in number, and rapidly poisoned; in contrast, the cis sites should be present in large number, but be slow in reaction at first (an induction period).

The behavior of the DPE curve could likewise be attributed to a limited number of active sites which also become rapidly poisoned; thus the amount of DPE produced reaches a limiting value and does not increase at higher PVC concentration.

Effect of Phenol and Pyridine. Addition of phenol to PVE/CdS in the dark and reaction for 18 h (Figure 4) results in an increase in DPE formation and a corresponding decrease in DCB formation. In these experiments the consumption of the phenol was near 100%; the amount of unreacted phenol was $< 1\%$. This supports our earlier contention that the addition of phenol to PVE is a very fast reaction. The appropriate control experiments established that CdS (sample 3) was necessary for this reaction, and that high-purity CdS (sample 1 or 2) was ineffective.

A small amount of pyridine (0.036 vs. 0.25 M PVE in CH_2Cl_2) was sufficient to inhibit completely both DPE and DCB formation; the PVE was recovered quantitatively. However, 64% of the pyridine was not recovered; no products could be detected on GLC. It is presumed that the pyridine was irreversibly adsorbed on the surface and that CH_2Cl_2 was not sufficiently active to induce

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Table III. Oxidation Potentials of Various Quenchers and Their Quenching Effect on PVE Conversion to DCB Induced by CdS in the Dark

quencher	oxidation potential, ^a V	R_0/R_θ ^b
1,2-DMB ^c	1.45	2
1,3-DMB	1.38	1.5
1,4-DMB	1.34	1.4
1,3,5-TMB ^d	1.49	7.25
1,2,3-TMB	1.42	2.4
1,2,4-TMB	1.12	2.9

^aOxidation potential vs. SCE (ref 29). ^b R_0/R_θ is the ratio of dimerization in the absence of any quencher (R_0) to that in the presence of quencher (R_θ) at $C_\theta = 2 \times 10^{-3}$ M. ^cDMB = dimethoxybenzene. ^dTMB = trimethoxybenzene.

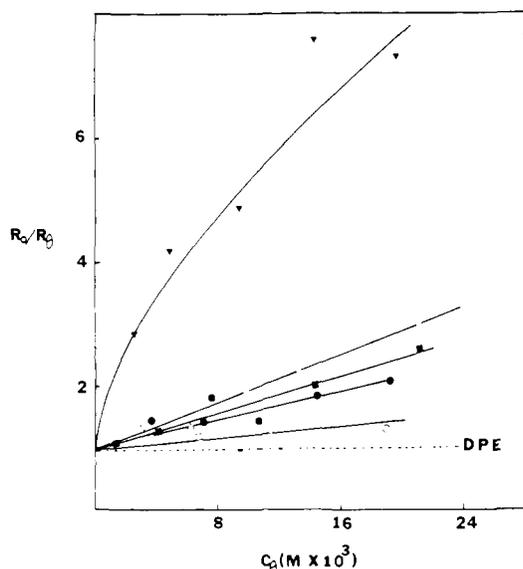


Figure 5. Effect of various quenchers on the dimerization of PVE induced by CdS (sample 3) in the dark (solid lines): \blacktriangledown , 1,3,5-TMF; \square , 1,2,4-TMB; \blacksquare , 1,2,3-TMB; \bullet , 1,2-DMB; \triangle , 1,3-DMB; \circ , 1,4-DMB. DPE (broken lines) was unaffected by all these quenchers. R_0 is the rate in the absence of any quencher; R_θ , rate in the presence of quencher. For each experiment: CdS \sim 100 mg, PVE \sim 0.25 M (in CH_2Cl_2), time 18 h.

desorption. While not being able to compete ($E_{1/2}^{\text{ox}} = 1.82$ V vs. Ag/Ag^+)²⁹ with PVE ($E_{1/2}^{\text{ox}} = 1.28$ V vs. Ag/Ag^+ ,^{30a} 1.75 V vs. SCE^{30b}) in ability to quench a hole or PVE^+ , pyridine is basic and may cover the active sites of the CdS, thus inhibiting PVE adsorption. The acid sites used for DPE formation would also be neutralized.

Quenching Experiments. If DCB, in the dark reaction, was formed via a cation radical, quenching by electron donors should be possible. The methoxybenzenes (Table III) are suitable substances, being more efficient donors than PVE; their effect is shown in Figure 5. The quenching effects, while not large, roughly follow, with the exception of 1,3,5-trimethoxybenzene, the order of the oxidation potentials, slight variations being attributable to different adsorptivities. The nonquenching of DPE formation confirms its genesis by an independent route.

Furthermore, no change in the T/C ratio (\sim 0.1) was observed in the dark reaction. A decrease in the T/C ratio of DCB in the presence of electronic quenchers had been observed before during the photoinduced dimerization of PVE both in homogeneous²⁸ and heterogeneous^{3a} systems; the extent of the decrease in the T/C ratio was greater in the heterogeneous system.

The behavior of 1,3,5-trimethoxybenzene is at present difficult to explain. Some special interaction of the three components may

Table IV. Effect of MA or TCPA on PVE Conversion Induced by CdS^a

anhydride	conditions	time (h)	DCB ^b (%)	DPE (%)
MA	dark	17	22	20
	$h\nu$	4	22	20
TCPA	dark	20	39	35
	$h\nu$	4	39	35

^aCdS (sample 2) \sim 100 mg, MA \sim 70 mg, TCPA \sim 50 mg, $\lambda >$ 430 nm (for light-induced reactions). ^bT/C of DCB = \sim 0.1.

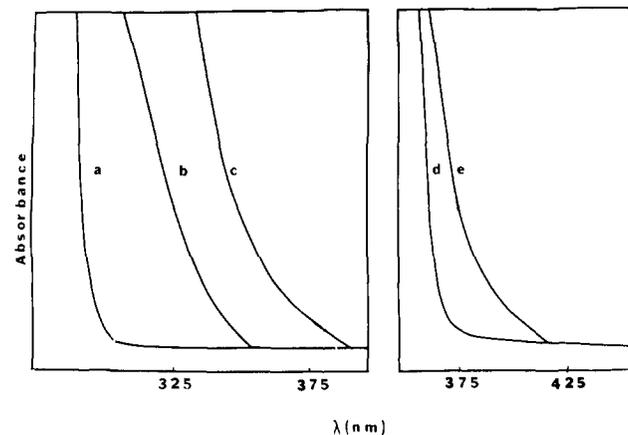


Figure 6. UV spectra of (a) PVE, (b) MA (0.14 M), (c) mixture of PVE (0.28 M) + MA (0.14 M), (d) TCPA (0.05 M), and (e) mixture of PVE (0.25 M) + TCPA (0.035 M). Solvent CH_2Cl_2 .

be involved because the nature of the dispersion in the product had changed, and the mixture had to be filtered with an ultrafine sintered glass filter in this case only. Furthermore, the change in the CdS dispersion required the presence of PVE. The nature of this interesting phenomenon was not investigated further.

Addition of Electron Acceptors. From previous work it has been suggested that oxygen acts as an electron acceptor in the light-induced CdS-catalyzed dimerization of PVE.³ It, therefore, seemed possible that replacement of oxygen by a more efficient electron acceptor might enhance the rate of dimerization. Maleic anhydride (MA; $E_{1/2}^{\text{red}} = -0.84$ V vs. SCE²⁹) and tetrachlorophthalic anhydride (TCPA; $E_{1/2}^{\text{red}} = -0.86$ V vs. SCE²⁹) appeared to be suitable candidates. Indeed, inactive sample 1 or 2, in the presence of MA, gave both DPE and DCB together with a trace of phenol (Table IV). The T/C ratio observed was \sim 0.1. No conversion was observed in the absence of CdS. Furthermore, reaction could not be attributed to the formation of free acids from the anhydrides by the action of adsorbed water since substitution of maleic acid for the anhydride did not lead to reaction.

In Table IV is recorded the effect of MA and TCPA on the reactions of PVE in the dark and under illumination catalyzed by sample 2 CdS. Comparison of these results with those in Table II (for instance, samples 3 and 4) reveal that the anhydrides are very effective, and that the increased reaction rate does not change the T/C ratio. A time-dependent study of the MA-PVE-CdS (sample 2) dark reaction gave similar plots for DCB and DPE formation as observed previously with sample 3 without the addition of MA (Figure 2). Degassing of the MA-PVE-CdS mixture did not affect the rate of reaction both in the dark and under illumination.

It had been reported³¹ that both dimethylmaleic anhydride and TCPA form charge-transfer complexes with PVE. This has been confirmed for MA also (see Figure 6). Furthermore, irradiation of the complex leads to dimer formation. We have found that irradiation of a degassed sample of PVE with MA or TCPA at $\lambda >$ 430 nm, the cutoff used for CdS illumination, did not result in any reaction, confirming the part played by CdS in our irradiations. On the other hand, irradiation of similar mixtures with light of $\lambda >$ 340 nm resulted in the formation of DCB only, with

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(30) (a) Mizuno, K.; Ueda, H.; Otsuji, Y. *Chem. Lett.* **1981**, 1237. (b) Evan, T. R.; Wake, R. W.; Jaenicke, O. In "The Exciplex"; Gordon, M.; Ware, W. R., Eds.; Academic Press: New York, 1975; p 345.

(31) Farid, S.; Hartman, S. E.; Evans, T. R. In ref 30b, p 327.

Table V. Reported g Values for Various Paramagnetic Species/Centers on CdS

paramagnetic species/centers	ESR signals	ref
donor center	$g = 1.79$ ($g_{\parallel} = 1.8, g_{\perp} = 1.79$)	33
(formed by a sulfur vacancy)	$g = 1.77$	34
F ⁺ center	$g_{\parallel} = 2.00, g_{\perp} = 1.98$	33
(defect-consisting of a sulfur vacancy acting as electron acceptor)	$g = 2.027$	35
	$g = 2.003$	36, 37
acceptor state	$g_{\parallel} = 2.12/2.08$	33
(attributed to clusters of cadmium vacancies, 0.7 eV above valence band)	$g_{\perp} = 2.10/2.07$	
hole trapped on a sulfur vacancy adjacent to a cadmium vacancy	$g_{\parallel} = 2.0018, g_{\perp} = 2.0592$	34
O ₂ ⁻	$g_{\parallel} = 2.442, g_{\perp} = 1.949$	37
O ⁻	$g_{\parallel} = 1.972, g_{\perp} = 2.309$	37
O ₂ ⁺	$g_x = 1.986, g_y = 2.002,$ $g_z = 2.002$ $g_{av} = 2.006$	37

a T/C ratio of ~ 0.67 . This phenomenon was of importance with regard to other semiconductors. Thus irradiation of PVE/TiO₂ at $\lambda > 384$ nm, in the presence of MA, where the CT complex absorbs a negligible amount of light (Figure 6) resulted in no dimer formation. Under the same conditions, but using TCPA, the complex of which absorbs up to $\lambda \sim 410$ nm (Figure 6), about 20% DCB was obtained (T/C ~ 0.67). Irradiation of the degassed mixture with omission of the TiO₂ resulted in about 4% DCB (T/C ~ 0.67). It seems probable, therefore, that in the former case the adsorbed complex is being excited. Conversely, because of the above observations and, because the same T/C ratio, ~ 0.5 , was observed in the photodimerization induced by TiO₂ and CdS (sample 1) in the absence of anhydrides, it could be reasonably concluded that the dark reaction of PVE with CdS in the presence of MA or TCPA did not arise from the CT complex of PVE with MA or TCPA.

Various other electron acceptors were also studied; however, for various reasons³² they were not suitable.

ESR Studies. The g values of the various peaks observed were listed earlier (see Experimental Section). Listed in Table V are the g values reported in the literature for various paramagnetic centers on CdS. The high-purity material (samples 2, 2A) is not as complex as the less pure (sample 3). Sample 2 has only one sharp peak with $g = 1.8$. A similar peak has been observed by Brailsford et al.³³ for CdS and was assigned by them to an electron donor center derived from a sulfur vacancy. The CdS treated with H₂SO₄ (sample 2A) has two additional peaks, one very broad ($g = 2.003$), the other small but sharp ($g = 2.167$). A peak at $g = 2.003$ has been detected by many workers^{33,35-37} and has been assigned to an F⁺ center formed from a sulfur vacancy with a trapped electron. Interaction of the F⁺ center with adsorbed oxygen on CdS has been shown³⁶ to be responsible for the

(32) These reasons can be summarized as follows: (a) absorption of light of higher wavelength by the electron acceptors, e.g., *p*-benzoquinone, fluorenone, benzil, naphthoquinone; (b) formation of a colored CT complex between PVE and the electron acceptors, e.g., TCNE; (c) chemical reactivity of the electron acceptors, e.g., TCNE; (d) chemical reactivity of the electron acceptors, resulting in adduct formation with PVE, e.g., fumaronitrile; (e) the very low or negligible solubility of the electron acceptors in CH₂Cl₂, e.g., phthalic anhydride. Other solvents were not considered suitable.^{3a}

(33) Brailsford, J. R.; Wood, J. J. *Phys. C* **1968**, *1*(2), 1213.

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(37) (a) Sootha, G. D.; Padam, G. K.; Gupta, S. K. *Phys. Status Solidi A* **1979**, *52*, K125. (b) *Ibid.* **1980**, *58*, 615. (c) *Ibid.* **1980**, *60*, 599. (d) Padam, G. K.; Singh, B.; Gupta, S. K.; Sootha, G. D. *Ibid.* **1982**, *71*, K37. (e) *Ibid.* **1982**, *71*, K169.

Table VI. Possible Paramagnetic Species/Center on Various CdS Samples^a

species/center	sample 2	sample 2A	sample 3
electron-donor center	+	+	+
F ⁺ /O ₂ ⁺	-	+	+
electron-acceptor centers	-	?	?
O ₂ ⁻	-	-	?
O ⁻	-	?	?
Fe ³⁺	-	-	+

^a + = present, - = absent.

broadness of this peak. The peak at $g = 2.169$ could not be assigned (vide infra). The peak at $g = 1.8$ in sample 3 is similar to that exhibited by the pure samples and is similarly assigned. The peak at $g = 2.003$ is comparatively sharp and has two small satellites at $g = 1.98$ and $g = 2.033$. A similar ensemble of peaks ($g_x = 1.986, g_y = 2.002, g_z = 2.022$) with $g_{av} = 2.006$ has been assigned to an O₂⁺ species,³⁷ which is thus a possible candidate.

The signal at $g = 4.283$ can be assigned to Fe³⁺ impurity,³⁸ the supplier's analysis indicating the presence of 0.007% iron. A very broad signal (width ~ 40 mT) was also observed in sample 3. Owing to drifting in the base line at lower field, the center of this line could only be roughly estimated to be at $g = 2.55$. Superoxide ion, O₂⁻ has been reported to have $g_{\parallel} = 2.442$ and $g_{\perp} = 1.949$ on CdS³⁷ (2.487 and 1.928, respectively, on (cubic) CdO).^{37d} In view of the fact that the CdS used in earlier studies was hexagonal and that sample 3 is cubic (Table I), the possibility that signals with $g \approx 2.55$ and $g = 1.931$ are attributable to O₂⁻ cannot be excluded. In the same way the signal in sample 2A (hexagonal) at $g = 2.169$ and in sample 3 (cubic) at $g = 2.157$ may have the same origin, differing only in environment. The firm assignment of these signals (at $g = 2.169$ and $g = 2.157$) is difficult from the available literature reports. However, Gupta et al.^{37d} have reported the presence of O⁻ on CdO with $g_{\parallel} = 2.003$ and $g_{\perp} = 2.141$. It is possible that such species (both samples 2A and 3 also have signals at $g = 2.003$) are responsible for these signals and that, owing to its similar structure, the signal from β -CdS (sample 3) is nearer to that of CdO. Another signal source could be the presence of acceptor-type surface states derived from cadmium vacancies. Brailsford et al.³³ have observed a broad (~ 13 mT) signal varying in g value with specimens of CdS ($g_{\parallel} = 2.08, 2.12; g_{\perp} = 2.07, 2.10$). The variation in shape and g value were attributed to different concentrations of various possible clusters of vacancies contributing to the signal. For this reason we are inclined to exclude the possibility that acceptor levels consisting of clusters of Cd vacancies could be responsible for our observed signals. Table VI contains the list of various species detected or expected on a CdS surface from the ESR studies.

These observations suggest that sample 2 has no chemisorbed oxygen on the surface while both samples 3 and 2A have. Since only samples 3 and 2A are active in electron transfer in the dark, then F⁺/O₂⁺ center, O⁻, or acceptor levels are likely candidates for reaction initiators.

Discussion

The results presented may be summarized as follows.

(a) High-purity CdS (samples 1 and 2) did not show any activity in the dark in the conversion of PVE to DCB or DPE, in contrast to (b) lower purity CdS (samples 3 and 4) which were so active. (c) High-purity samples, when treated with dilute sulfuric acid (pH ~ 2.5) or when in the presence of MA or TCPA become active. (d) ESR spectroscopy (Table VI) showed the presence, in all the CdS samples studied, of sulfur vacancies acting as electron donors. The modified high-purity CdS (sample 2A) shows the presence of F⁺/O₂⁺ centers, together with another signal which could not be uniquely assigned. (e) The less pure CdS (sample 3), in addition to the above species, shows the presence of other paramagnetic centers, one of which was attributed to Fe³⁺; the presence of superoxide was also a possibility. (f) The T/C

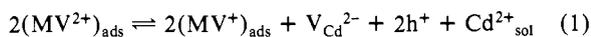
(38) Pimenov, Yu. D.; Kholmogorov, V. E. *Kinet. Catal. (Engl. Transl.)* **1969**, *10*, 135.

ratio of the dimers changes during the course of the reaction and is different from that obtained under the influence of light, with high-purity CdS.

The presence of various energy levels in the forbidden zone of CdS acting as donor or acceptor centers have been widely reported.¹¹ These levels have been associated with lattice defects, e.g., cadmium vacancies (V_{Cd}),^{9-15,33} sulfur vacancies (V_S),^{9-15,33,34} impurity ions,⁹⁻¹⁵ or adsorbed molecules.¹⁴

The formation of acceptor-type surface states attributable to surface-adsorbed oxygen has been frequently reported,^{14a,b} and, even at low temperatures, oxygen has been described as decreasing the dark conductivity of CdS. This decrease has been attributed^{14a} to the transfer of conduction band electrons from the CdS to the adsorbed oxygen, thus decreasing the number of majority charge carrier. A similar decrease in the dark conductivity was a consequence of *p*-benzoquinone adsorption.^{14c} Early ESR studies of the adsorption of *p*-benzoquinone, tetracyanoethylene, and chloranil on CdS at room temperature³⁸ revealed that electron transfer, with formation of the anion radical, had occurred. The efficiency of the transfer was related to the electron affinity of the acceptor; trinitrobenzene, a comparatively weak acceptor, did not induce any ESR signal.

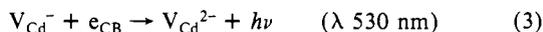
Recently Grätzel and co-workers³⁹ have observed the appearance of a green luminescence ($\lambda_{max} \sim 530$ nm) when methyl viologen (MV^{2+}) was used for the quenching of photoluminescence in studies with colloidal CdS. This luminescence appeared when higher concentrations ($>10^{-5}$ M) of MV^{2+} were used and was preceded by an induction period which was MV^{2+} concentration dependent. A mechanism was proposed for the generation of this emission where adsorbed MV^{2+} interacted with CdS, according to eq 1 to produce cadmium vacancies (V_{Cd}^{2-}).



It was suggested that these vacancies were in equilibrium with holes (h^+) with the generation of V_{Cd}^- :



The Fermi level associated with V_{Cd}^- was considered to be near the valence band, and the emission was associated with interaction with conduction band electrons:



A subsequent trapping of a hole by V_{Cd}^{2-} regenerated the (V_{Cd}^-) center. The presence of (V_{Cd}^-), acting as an electron acceptor, had been reported earlier, and had been assigned an energy level 0.7 eV above the valence band.³³

We suggest a similar route for the formation of DCB in the dark. Following the generation of V_{Cd}^{2-} by the interaction of MA, TCPA, or H_2SO_4 with CdS, which then leads to the formation of V_{Cd}^- , electron transfer from PVE could produce the required cation radical. Alternatively, since it has been shown that electron acceptors (e.g., *p*-benzoquinone) form donor-acceptor-type complexes with CdS³⁸ (observed in their UV spectra) and since it has also been reported^{12d} that donor-acceptor pairs on Cu-doped CdS crystals can be dissociated with IR illumination in the temperature range -123 to $+77$ °C, then it is possible that electron transition from the valence band to V_{Cd}^- or the donor-acceptor complex may occur, again leading to the PVE radical cation through the transfer of the resulting free hole, in the valence band, to PVE. Further reaction with another PVE molecule gives the dimer radical cation, the quenching of which, by V_{Cd} or any other donor, produces DCB and restores the original state.

The suggestion that a Brønsted acid site can act, as do quinones and tetracyanoethylene, as electron acceptors is not new. It has been proposed that such a site, on the surface of alumina or silica-alumina, can accept electrons from, for instance, perylene.²⁷ The extent of cation-radical formation was influenced by the acid strength of the solid. We propose that such acid sites are also responsible for DPE formation via a normal cation mechanism

involving the addition of phenol to PVE.

We have no direct evidence for the formation of PVE cation radical on the CdS surface. Harbour et al.,⁴⁰ using CdS from the same source as our sample 3, have suggested that in ambient light the preparation of Cd phthalocyanine on CdS (CdPc), a photon with $E > E_b$, will create hole/electron pairs, the electrons of which can reduce a surface CdPc and the hole of which can oxidize a spatially separated CdPc surface molecule. No change in radical concentration, as indicated by the ESR signal, was observed on illumination. There appears, to the best of our knowledge, to be no other report of the "dark" generation of cation radicals on CdS.

Our ESR studies suggest the presence of paramagnetic centers on CdS attributable to oxygen species. However, the dark activity of CdS (samples 3 and 4 or samples 1 and 2 in the presence of MA or TCPA), as well as the T/C ratio (~ 0.1), was unaffected by the presence or absence of oxygen. This is in sharp contrast to our previous studies³ where irradiation of the degassed samples of PVE (in the presence of high-purity CdS, ZnO and TiO_2) resulted both in the decrease of the T/C ratio (from 0.52 to 0.26 for CdS) and in the rate of the dimer formation in comparison to the aerated samples. It might be presumed that oxygen did not play a major role in the dimerization of PV owing to the presence of other electron-acceptor centers/species on CdS in the present system. However, our degassing procedure^{3a} was probably insufficient to remove chemisorbed oxygen from the surface and this view must be tentative.

The stereochemistry of the reaction merits some comment. The T/C ratio (0.1) for DCB formed in the dark on the CdS surface is quite different from that observed previously (T/C ~ 0.5) for the photodimerization of PVE by various semiconductors,^{3a} including high-purity CdS. Reduction in the T/C ratio was observed only for degassed samples of CdS, TiO_2 , and ZnO, or in the presence of electronic quenchers on the ZnO surface. It was proposed previously^{3a} that the formation of cis dimer was preferred over trans dimer, both in the adsorbed state and in the solution phase. However, the conversion of PVE to cis dimer was preferred to a greater degree on the surface than in solution. The decrease in the T/C ratio of the DCB in the absence of oxygen or in the presence of quencher was attributed to the decrease in contribution of solution-phase reaction. In the present case, owing to the presence of various defect centers in low-purity CdS (samples 3 and 4) as well as in the modified CdS (sample 2A), most probably the radical cation (or dimer radical cation) is quenched before it can escape into solution. More reaction, proportionately, therefore, takes place on the surface with a consequent lower value of T/C. We are presently unable to rationalize the preference for the trans isomer exhibited in the early reaction stages.

Conclusions

We have shown that the dimerization of PVE can be achieved by CdS in the dark as well as by the previously known photo-reaction. The efficiency of various forms of the semiconductor has been examined and the rate of the reaction found to be dependent on defects. Such defects can be induced in pure, ineffective CdS by treatment with H_2SO_4 . The coadsorption of electron acceptors (maleic anhydride, tetrachlorophthalic anhydride) is also effective. The particular crystal form, cubic or hexagonal, used appears irrelevant. The reaction is rationalized, tentatively, on the basis of the generation of cadmium vacancies.

Acknowledgment. We thank Professor H. de Lasa (Chemical Engineering, U.W.O.) for providing facilities for surface area measurements, Professor M. E. Fleet and Ms. C.-C. Cheng (Geology, U.W.O.) for X-ray diffraction analyses, and Professor V. Ramamurthy (Bangalore) for the initial PVE-maleic anhydride- TiO_2 ($\lambda > 340$ nm) experiment. Special thanks are due to Dr. A. R. McIntosh for his help in the ESR Studies. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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