

Figure 5. Photosensitized debromination of *meso*-1,2-dibromostilbene (4) in a two-phase system.

the doubly reduced species C_8V is formed in the organic phase (Figure 2). This is a result of the induced disproportionation of C_8V^{2+} as described previously. Addition of 1,2-dibromostilbene to the ethyl acetate solution that contains the photoproduct C_8V yields *trans*-stilbene and the blue radical cation C_8V^{+} . All of these results demonstrate the photosynthetic formation of stilbene via oxidation of $(NH_4)_3EDTA$ by dibromostilbene in a cyclic process mediated by C_8V^{2+} (Figure 5). In this cycle, quenching of the excited $Ru(bpy)_3^{2+}$ by C_8V^{2+} ($k_q = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)²⁴ results in the photoproducts $Ru(bpy)_3^{3+}$ and C_8V^{+} . The oxidized photosensitizer $Ru(bpy)_3^{3+}$ oxidizes $(NH_4)_3EDTA$ and the sensitizer is recycled. The reduced photoproduct C_8V^{+} is extracted into the organic phase where it undergoes disproportionation to C_8V . The subsequent debromination of 1,2-dibromostilbene recycles the mediating electron acceptor C_8V^{2+} .

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Our previous discussion implies that such debromination processes should be unfavorable in a homogeneous solution that includes C_8V^{+} . This conclusion is based on the unfavored comproportionation of C_8V^{+} in a homogeneous phase ($K_d = 5 \times 10^{-8}$). Indeed illumination of an acetonitrile solution that includes $Ru(bpy)_3^{2+}$ as sensitizer, C_8V^{2+} as electron acceptor, triethanolamine as electron donor, and 1,2-dibromostilbene does not result in the formation of stilbene, despite the effective formation of C_8V^{+} . These results emphasize the importance of an organized two-phase media in driving a photosensitized single-electron-transfer product to a doubly reduced charge relay that is utilized in the chemical route.

Conclusions

We have demonstrated that a single-electron-transfer product can undergo an induced disproportionation process to the two-electron reduction product. The advantages of such transformation seem obvious: (i) The reduced form has a lower reduction potential than the one-electron reductant and can be utilized in versatile reduction processes. (ii) The comproportionation process establishes a charge relay of two reduction equivalents. Consequently, multielectron reduction reactions being mediated by such relays seem conceivable.

In nature multielectron-transfer processes are common, i.e., CO_2 or N_2 fixation, while the initial process are single-electron-transfer reactions. Since these reactions proceed in natural cellular media that include hydrophilic and hydrophobic microenvironments, similar mechanisms of induced disproportionation might lead to the multielectron charge relays.

Further developments of this system seem feasible. Introduction of coordination complexes into the organic phase might offer an active site that utilizes the multielectron relay in reduction processes. Also, design of amphiphilic dimeric electron acceptor can serve as four-electron charge delay relay via a similar disproportionation mechanism. These subjects are currently being examined in our laboratory.

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Surface Photochemistry: Semiconductor Photoinduced Dimerization of Phenyl Vinyl Ether¹

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Abstract: The dimerization of phenyl vinyl ether at an illuminated semiconductor surface has been demonstrated, and that reaction induced on ZnO was studied in detail. The involvement of surface-related processes has been shown to affect both the rate and stereochemistry of the system. Langmuir-Hinshelwood treatment has been found to be applicable for kinetic analysis. The effect of various quenchers has been described in terms of competitive adsorption with or without interference with electron-transfer processes on the surface. A reaction scheme involving the simultaneous formation of dimer both in the adsorbed state and in solution has been suggested, the former being the more important.

One of the most active areas of current photochemical research is the light-induced generation of fuels, and among these the use of semiconductors has been prominent. The use of semiconductors

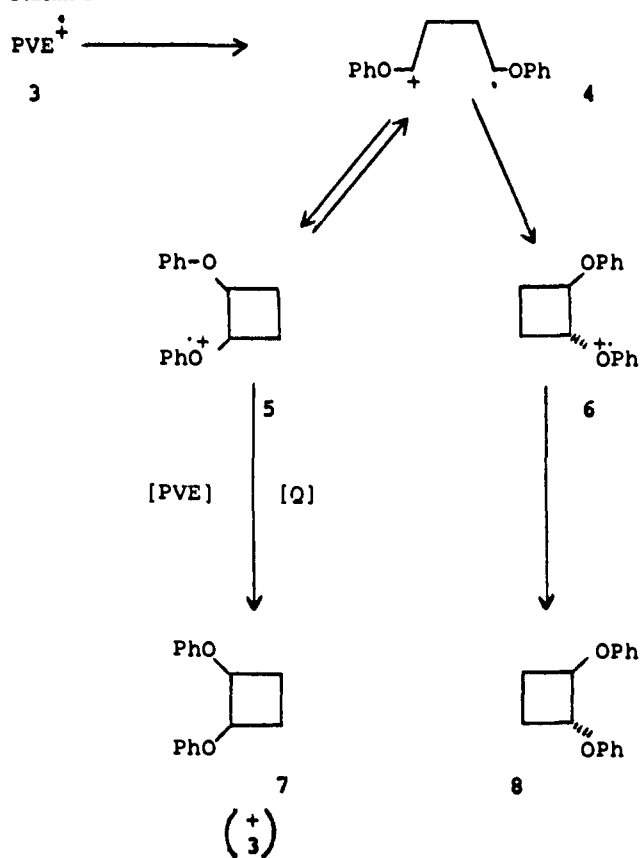
for other photochemical objectives has been far less and consists, essentially, of oxidative or reductive operations.³ Among the very few examples outside these main categories are the reports of the CdS powder photocatalyzed retrocycloaddition of **1** to give **2**,⁴

(1) Publication No. 327 from the Photochemistry Unit, University of Western Ontario.

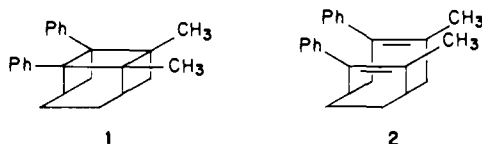
(2) On leave from the Indian Institute of Science, Bangalore.

(3) For an important and lucid review of semiconductors in organic photochemistry, see: Fox, M. A. *Acc. Chem. Res.* 1983, 16, 314.

Scheme I



the dissociation of dianthracene,⁵ and the [2 + 2] dimerization of phenyl vinyl ether (PVE).⁵ These reactions were suggested



to involve radical cations,⁶ and it is the purpose of the present report to describe our findings concerning the latter reaction in more detail: we believe these results have a more general implication for photoinduced organic reactions taking place at dispersed semiconductor interfaces.

Dimerization in homogeneous solution by electron-transfer sensitization has already been reported for PVE.^{13,17-22} For

Table I. Semiconductor Surface Areas

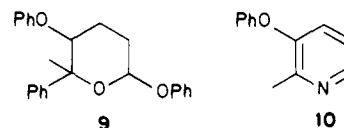
semiconductors	purity, %	area, m ² /g
ZnO (Fisher)	≥99	5
ZnO ^a (Aldrich)	99.9999	<0.5
TiO ₂ (Fluka, Anatase)	~99	5
TiO ₂ ^a (Aldrich, Anatase)	99.999	<0.5
TiO ₂ ^b (Degussa, P-25)	>99.5	48.9
CdS (Aldrich)	99.99	20
CdS (Aldrich)	99.999	1.2
Al ₂ O ₃ ^b (Degussa, C)	>99.6	93

^a Very small volume of nitrogen adsorbed renders value inaccurate. ^b Reference samples: areas determined by the manufacturer were 50 and 100 m²/g for TiO₂ and Al₂O₃, respectively.

comparison with our heterogeneous system, the most recent proposed view can be summarized as follows (Scheme I).

Electron transfer from PVE to the excited electron acceptor (e.g., 9,10-dicyanoanthracene) generates the PVE radical cation 3. This then adds to another PVE molecule to give the open dimer radical cation 4.²³ This may close to the cis (5) or trans (6) dimer radical cation. Quenching may be brought about by added quenchers, the acceptor radical anion, impurities in the system, or the neutral olefin. The latter step (5 → 7) constitutes a chain-propagation process. The product is a mixture of the cis (7) and trans (8) cyclobutanes. At concentrations of PVE >0.1 M the two isomers are produced in a ratio 7:8 of ~6:4.²²

Other, competitive, processes exist, such as the quenching of 3. The cation radical 4 has also been intercepted by added acetophenone to give 9 and by acetonitrile solvent to give 10 (plus phenol).¹⁸ Mixed adducts with ethyl vinyl ether²⁰ have been



reported when PVE was excited in the presence of that olefin but was not accompanied by the ethyl vinyl ether dimer. The absence of this substance was rationalized on the basis of the interception of 3 by the ethyl vinyl ether in competition with an efficient back electron transfer, leading to quenching of the ethyl vinyl ether radical cation.

It was found recently that the 8/7 ratio obtained was dependent on the PVE concentration, changing from the cis isomer being the major constituent to predominantly trans isomer below 0.03 M.²¹ An interpretation^{22,24} of this observation utilized the demonstrated^{18,22} isomerization of 7 to 8 by excited 9,10-dicyanoanthracene:PVE; 7 and 8 have similar oxidation potentials. The trans isomer was found to be stable under these conditions. At increased PVE concentrations more 5 is trapped (Scheme I) before reverting to 4. This varying product distribution with PVE concentration was used²² to determine the kinetics of the ring opening of 5 and that of the chain propagation step.

The following study shows that there are important differences between the homogeneous and heterogeneous systems although both involve electron transfer.

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 (5) Barber, R. A.; de Mayo, P.; Okada, K. *Chem. Commun.* **1982**, 1073.
 (6) The involvement of radical cation in cycloadditions, though not as well studied as that involving singlet or triplets, is nonetheless well established⁷⁻⁹ and includes the dimerization of some enamines,¹⁰ 1,1-diarylethylenes,¹¹ indenes,^{12,13} styrene,¹⁴ and phenylacetylenes.¹⁵ CIDNP has been of notable value in detecting the intervention of radical ions in pericyclic processes.¹⁶
 (7) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80 and references cited therein.
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 (20) Mizuno, K.; Ueda, H.; Otsuji, Y. *Chem. Lett.* **1981**, 1237.
 (21) Mizuno, K.; Kagano, H.; Kasuga, T.; Otsuji, Y. *Chem. Lett.* **1983**, 133.
 (22) Mattes, S. L.; Luss, H. R.; Farid, S. *J. Phys. Chem.* **1983**, *87*, 4779.
 (23) Whether the radical ion 4 be open chain or "long-bond" closed⁹ is not relevant to the present argument provided cis → trans isomerization be possible, even if slow.
 (24) A confusion in the literature with regard to stereochemical assignments has been resolved by X-ray analysis of the minor isomer.²² The C/T ratio earlier reported for CdS⁵ should be inverted.

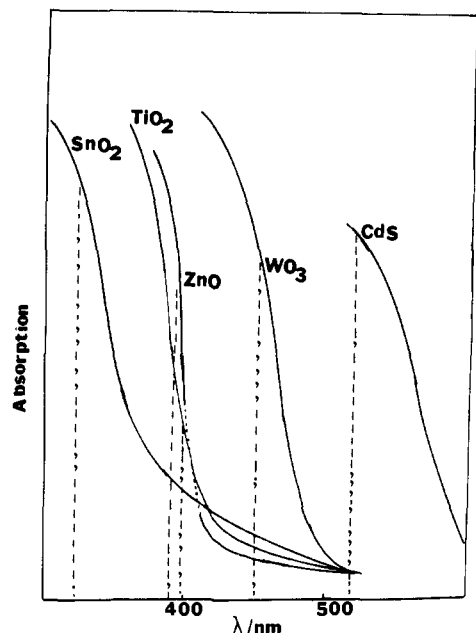


Figure 1. Photoacoustic spectra (solid lines) and reported band-gap energies (broken lines) of the powdered semiconductors.

Experimental Section

Materials. High-purity semiconductor powders (>99.99%) were Aldrich Gold Label. In addition, ZnO (>99%; Fisher) and TiO₂ (Anatase, ~99%; Fluka) were used.

Solvents used were all spectroscopic grade chemicals supplied by Fisher and were used without further purification. All other substances were supplied by Aldrich or Fisher and were purified by distillation, sublimation, or recrystallization. PVE was prepared by dehydrobromination of β -bromophenetole (Aldrich); β -bromophenetole (20 g), KOH (6 g), and water (10 mL) in dimethyl sulfoxide (200 mL) were maintained at 100 °C (stirring) for 5 h. After extensive dilution with water, the solution was extracted with ether. After the solution was washed and dried (MgSO₄), the ether was evaporated and the PVE was distilled under reduced pressure (bp 50 °C/14 mmHg). 1,2,4,5-Tetramethoxybenzene (TEMB) was prepared by the method of Benington et al.²⁵

Surface Area Determinations. These were made from BET plots obtained by N₂ adsorption from a N₂/He mixture at -195 °C. The amount of N₂ adsorbed was determined from the desorption peak by using a Perkin-Elmer Shell Model 212C sorptometer equipped with a thermal conductivity detector. The results are recorded in Table I.

Photoacoustic spectra were recorded by using an EDT Research Model OAS 400 spectrometer that use carbon black as reference. The powders (100–150 mg) were directly loaded into the sample cell (15 × 5 × 2 mm; aluminum). The spectra are recorded in Figure 1. The vertical broken lines indicate the wavelength corresponding to the band-gap energies.²⁶

Dimerization of Phenyl Vinyl Ether. All reactions were performed in a Pyrex tube using 5 mL of solvent, semiconductor (100 mg), and PVE (1.25 mmol). Prior to irradiation the mixture was sonicated for 15 min. Irradiation was carried out by using a 1-kW PRA Xenon lamp run at 880 W; the output was periodically checked with a Scientech 364 Power energy meter. Conversion relative to an arbitrary set of conditions was reproducible within $\pm 5\%$ over the period required to complete a set of experiments. During irradiations the mixture was constantly stirred. Compressed air was used as coolant, and a water filter removed IR radiation. Except for degassed samples the tubes 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 $< 2 \times 10^{-5}$ mmHg. After irradiation a known amount of calibrant (*n*-C₁₉H₄₀) was added to the mixture, which was then filtered. The filtrate was analyzed by using a Varian 3700 gas chromatograph, equipped with a flame ionization detector, which was connected to a Hewlett-Packard 3390 A integrator. Analyses were made on a 2 m × 2 mm column packed with Carbowax 20 M (5%) or OV-17 (3%) on Chromosorb W (Hp), 80–100 mesh. The peaks were identified by isolation by preparative chroma-

Table II. Solvent Effect on the Photocyclodimerization of Phenyl Vinyl Ether Initiated by Semiconductors at $\lambda > 340$ nm^{a,b}

	ZnO ^{c,d}	CdS ^{e,f}	TiO ₂ ^{g,h}	Ta ₂ O ₅ ^{e,f}	SnO ₂ ^{i,j}	Bi ₂ O ₃ ^{e,j}
dichloromethane	10	0.9	1.5	0.9	2.2	1.0
chloroform	4.8	0.03	0.2	0.05	1.5	0.45
carbon tetrachloride	3.6	0.6	0.4	ND ^k	2.0	1.15
acetonitrile	2.11	0.05	2.5	0.06	0.3	ND
acetone	2.01	ND	0.06	ND	ND	ND
benzene	ND	0.2	0.14	ND	ND	0.6
cyclohexane	ND					
<i>n</i> -hexane	ND					
tetrahydrofuran	ND					
dioxane	ND					
dimethyl sulfoxide	ND					
ethyl acetate	ND					
methanol	ND	ND	ND	ND	ND	ND

^a % yield of dimer under indicated conditions, PVE ~0.25 M, SC ~100 mg. ^b A T/C ratio of 0.49–0.56 was observed for all the semiconductors with no particular trend. ^c Fisher (>99%). ^d Irradiation time = 1.5 h. ^e Aldrich, Gold Label ($\geq 99.99\%$). ^f Irradiation time = 4 h. ^g Fluka, anatase (~99%). ^h Irradiation time = 3 h. ⁱ Aldrich (99.9%). ^j Irradiation time = 5 h. ^k ND = no dimer.

topography on silica gel followed by comparison of their ¹H NMR spectra with those reported earlier.^{17,20} Irradiation wavelengths were determined by using Corning glass filters 0–52 ($\lambda > 340$ nm), 0–51 ($\lambda > 360$ nm), and 3–72 ($\lambda > 430$ nm).

Formaldehyde Determination. The standard chromotropic acid method was used²⁷ for its determination when formed in the irradiation of MeOH over ZnO with and without PVE. Paraformaldehyde was used for preparation of the calibration curve, and measurements were made at 560, 570, and 580 nm.

Results and Discussion

The results of exploratory experiments with PVE photocyclodimerization with various semiconductors in different solvents are presented in Table II. Direct irradiation of PVE at $\lambda > 280$ nm did not result in dimer formation. The semiconductor suspensions were generally irradiated at $\lambda > 340$ nm. Under these conditions direct excitation of the semiconductors could be achieved, as can be seen from their photoacoustic spectra (Figure 1). Although the original semiconductor-induced dimerization was carried out with CdS, ZnO has now been found to be much more effective, followed, at some distance in efficiency, by TiO₂. In view of the similar absorption characteristics (Figure 1) and similar flat-band potentials²⁸ of TiO₂ and ZnO in acetonitrile, one might have expected more similar activity for both oxides in redox reactions, especially since the samples also had similar surface areas (Table I).

At the concentrations of PVE used, all effective semiconductors gave the same trans/cis (T/C) ratio, and this ratio was likewise independent of the solvent. However, although the T/C ratio was independent of the solvent, the rate of reaction was not, and of those tried (Table II) methylene dichloride was the most effective. No correlation could be found between dielectric constants or polarity (based on the E_T scale²⁹), but there was a general indication that the higher conversions were obtained with solvents of moderate polarity. Our interpretation is that the results were a consequence of surface phenomena. With high-polarity solvents there could be a successful competition for adsorption sites between the solvent and PVE. On the other hand the inability of the low-polarity solvents to displace active species or products from the surface could also result in low conversions. Specific surface interactions, including the quenching of intermediate cation radicals or more efficient donation of electrons to the semicon-

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Table III. Effect of Oxygen on the Photocyclodimerization of PVE^a Initiated by Semiconductors at $\lambda > 340$ nm

semiconductor	aerated sample			degassed sample		
	[PVE], M	dimer, %	T/C	[PVE], M	dimer, %	T/C
ZnO (Fisher)	0.18	20	0.53	0.22	0.25	0.39
TiO ₂ (Fluka)	0.21	1.6	0.52	0.22	0.15	0.39
CdS	0.20	0.9	0.50	0.22	0.01	0.26
Bi ₂ O ₃	0.24	0.4	0.54	0.16	0.06	0.27
Ta ₂ O ₅	0.29	0.9	0.49	0.23	0.01	
SnO ₂	0.2	2.4	0.56	0.23	0.07	

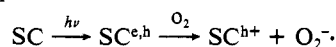
^aSolvent, CH₂Cl₂; irradiation time = 4 h.**Table IV.** Effect of Cutoff Wavelength on Dimerization

semiconductor	dimer, % ^a		
	$\lambda > 280$ nm	$\lambda > 340$ nm	$\lambda > 360$ nm
ZnO (Fisher)	31	21	12.5
TiO ₂ (Fluka)	2.8	1.6	0.5
SnO ₂	1.8	1.7	1.5
CdS	0.9	0.9	1.0
Bi ₂ O ₃		0.4	0.05

^aSolvent: CH₂Cl₂. Irradiation times: ZnO, 3 h; others, 4 h.

ductors than does PVE, are possible, as is the reaction of the solvent to give products which are inhibitors. For instance, the use of MeCN in the electron-transfer-sensitized reaction of PVE produces both phenol and a pyridine derivative.¹⁸ It has been shown elsewhere that both of these materials inhibit the photooxidation of isopropyl alcohol on ZnO.³⁰ Both photoassisted and thermally assisted reactions of methanol and acetone over ZnO and TiO₂ have been widely reported.³¹⁻³⁷

Table III records the differences in conversion under controlled conditions between aerated and degassed samples. As was noted earlier for CdS,⁵ in all cases the conversion is much higher for aerated systems. The simplest interpretation of this phenomenon is that the excited electron is trapped as superoxide ion, thus prolonging the life of the "hole" by delaying the collapse of the hole-electron pair:



It will also be noted that the stereochemical outcome from the cycloaddition in the degassed samples is different from that in the aerated specimens. The significance of this will be discussed in a later section.

Table IV indicates the relative extent of dimerization as a function of cutoff wavelength. The higher conversions obtained with $\lambda > 280$ nm are most probably to be attributed to the consequent increased intensity of the light. It is interesting to note that SnO₂ (band gap (3.8 eV) ~ 327 nm²⁶) is active at $\lambda > 340$ nm. The photoacoustic spectra of the semiconductors used (Figure 1) show absorption tails reaching to longer wavelengths than would be expected from the reported band-gap energies. Some conversion was detected from SnO₂ and TiO₂ even at $\lambda > 430$ nm.

It is usually considered that the presence of impurities in the lattice of the semiconductor affects the electron-hole population, which in turn affects the catalytic activity. Table V shows the comparison between high-purity ZnO and TiO₂ and their corresponding low-purity samples. However, it was also noted (Table I) that these samples differed considerably in surface area, that

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semiconductor	source	purity	dimer, %
ZnO	Fisher	≥ 99	11.1
ZnO	Fisher ^b	≥ 99	11.2
ZnO	Aldrich	99.9999	0.32
TiO ₂	Fluka	~ 99	1.1
TiO ₂	Aldrich	99.999	0.5

^aC_{PVE} ~ 0.25 M; semiconductor ~ 50 mg; irradiation time: ZnO, 1.5 h; TiO₂, 3 h. ^bZnO heated in vacuo, 300 °C/8 h.

of the pure samples being the lesser. Further, the absorption of the low-purity specimen in the photoacoustic spectra was about an apparent order of magnitude greater than for a similar layer of high-purity semiconductors.

The stability of the PVE dimers was tested by irradiation of a mixture (T/C = 0.59) in CH₂Cl₂ over a concentration range of 6×10^{-4} – 10^{-1} M in the presence of CdS and ZnO. No change in the total amount of dimers was observed after 12 h of irradiation. At the lower concentration ($< 10^{-3}$ M) some conversion of cis to trans was noted with an increase of T/C to 0.77. This parallels the observations made in homogeneous solution.²² At higher concentration (0.1 M), as previously reported,⁵ no change was observed. This suggested that the rate of conversion is slow and largely independent of the dimer concentration. As will be seen later this is consonant with the overall scheme to be proposed.

Kinetic Analysis

We have suggested above that surface-related processes were most probably playing an important role in PVE photocyclodimerization initiated by semiconductors. It is now necessary to examine whether (a) reaction is taking place in the adsorbed state, the products being desorbed into solution, (b) the surface merely provides an active species which, being desorbed into solution, therein reacts, or (c) surface reaction and solution-phase reaction occur simultaneously. Kinetic treatments have been used to discriminate among these possibilities. In the present instance we have subjected the ZnO catalyses process to detailed examination.

Of the many suggested kinetic equations for the description of catalytic systems, the best approximation are related to Langmuir-Hinshelwood treatments.³⁸⁻⁴⁰ These assume adsorption-desorption equilibria of the components of the reaction mixture on the catalyst surface. According to these treatments, a unimolecular surface reaction, where the reactant is significantly more strongly adsorbed than the product, will obey an equation of the form

$$r_0 = \frac{k_r K_1 c_1}{1 + K_1 c_1} \quad (1)$$

where r_0 is the rate of reaction, k_r is the reaction rate constant, and K_1 and c_1 are the adsorption constant and concentration of the reactant, respectively. Reorganization of (1) gives (2), which is more convenient.

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K_1} \frac{1}{c_1} \quad (2)$$

Similarly, a bimolecular surface reaction between two surface species (without significant mutual displacement) obeys eq 3

$$r_0 = \frac{k_r K_1 K_2 c_1 c_2}{(1 + K_1 c_1)(1 + K_2 c_2)} \quad (3)$$

which reduces to a form similar to that of eq 1 in instances where the concentration of one of these surface species remains constant.

In Figure 2 is illustrated the effect of PVE concentration on the rate⁴¹ of dimer formation, while the data are plotted according

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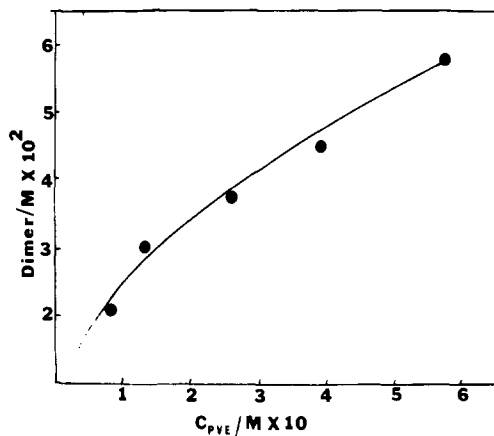


Figure 2. Effect of PVE concentration on the dimerization rate. For each experiment ZnO (90 mg) was used: irradiation time, 3 h; solvent, CH_2Cl_2 .

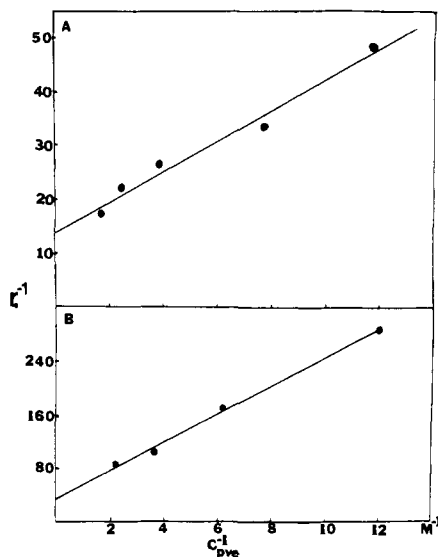


Figure 3. Application of Langmuir-Hinshelwood kinetic treatment (eq 2) to PVE photodimerization. (A) Data from Figure 2. (B) For each experiment ZnO (40 mg) was used: $\lambda > 360$ nm; irradiation time, 2 h ($r = 0.9986$).

to eq 2 in Figure 3A. Figure 3B represents a similar plot in an experiment wherein the conversion was maintained at $<5\%$ by the reduction of irradiation time and light flux. The straight line so obtained argues in favor of a surface reaction wherein the reactant is more strongly adsorbed than the product. Such plots are comprehensible in terms of a bimolecular photochemical reaction where the concentration of one species depends only on the light intensity, thus giving an apparent first-order dependence on PVE_{ad} at a photostationary state. (The concentration of this surface species will be low vis-à-vis that of PVE_{ad} and will not affect the concentration of the latter. This adequately rationalizes the fit of the data of Figure 3 to eq 2.) These experiments also indicate that saturation coverage of the semiconductor surface is not achieved at any concentration used (0.08–0.57 M). Owing to competition for adsorption sites between PVE and the solvent, eq 1 is more correctly shown to have the form in eq 4, where K_s is the adsorption constant and c_s is the concentration of the solvent.

$$r_0 = \frac{k_r K_1 c_1}{1 + K_1 c_1 + K_s c_s} \quad (4)$$

Since $c_s \gg c_1$, however, $K_s c_s$ remains essentially constant at all

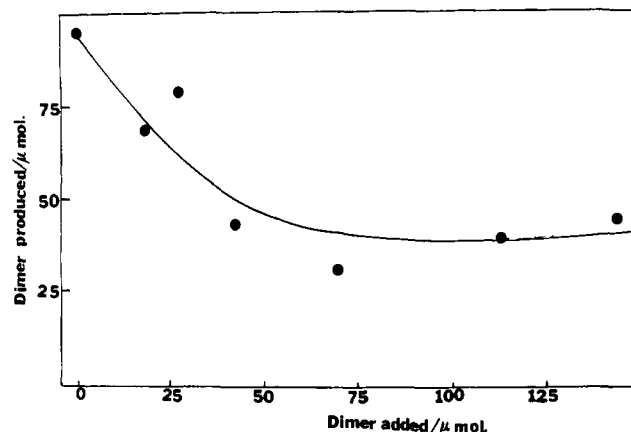


Figure 4. Effect of added PVE dimer to the reactant mixture on the rates of dimer formation: PVE, 0.25 M; ZnO, 100 mg, irradiation time, 3 h.

PVE concentrations used, and the data contained in Figure 3 are interpretable by eq 1. Other kinetic treatments based on a bimolecular surface reaction, where the two surface species compete with each other for surface sites, were not successful. Experiments were, therefore, performed to study the effect of added dimer on the reaction rate in the ZnO system. The results obtained (Figure 4) indicated an inverse relationship between the rate of dimer formation and the amount of dimer added, up to a limiting value: a result that suggests that probably more than one type of surface site is responsible for dimer formation. The impeding of the dimerization by the dimer itself is plausible in view of the similar oxidation potentials of the monomer and dimer¹⁸ and the observed slow conversion of cis dimer to trans. This effect was not noticed during the studies made on effect of PVE concentration (Figure 2) and in the subsequent kinetic analysis. The reason for this is our procedure wherein the total amount of PVE converted to dimer after 3 h of irradiation has been taken as proportional to the rate of reaction.⁴¹

Quenching Studies

Competitive adsorption is considered to be one of the most important phenomena for the inhibition of a surface reaction.

According to the Langmuir-Hinshelwood kinetic treatment the inhibition of a unimolecular surface reaction by competitive adsorption will obey an equation of the form shown in eq 5

$$r_\theta = \frac{k_r K_1 c_1}{1 + K_1 c_1 + K_\theta c_\theta} \quad (5)$$

where r_θ is the rate of reaction in the presence of the quencher and K_θ and c_θ are the adsorption constant and concentration of the quencher, respectively. Dividing eq 1 by eq 5 gives eq 6

$$\frac{r_0}{r_\theta} = 1 + \frac{K_\theta}{1 + K_1 c_1} c_\theta \quad (6)$$

which is similar in form to the Stern-Volmer equation. Hence, in the case of a photochemical reaction involving a surface, the observation of such a plot does not necessarily indicate the quenching of an excited state or the interception of a hole or an electron. Such is the case with isoprene.

Isoprene. This substance has a high-oxidation potential (1.84 V vs. Ag/Ag^+)⁴² as compared with PVE (1.25 V) and will not donate an electron to a semiconductor hole in competition with PVE. Furthermore, although its triplet energy is low the dimerization has been shown not to proceed via a triplet;¹⁷ singlet quenching would be endothermic. The plot according to eq 6 is linear (Figure 5), and extrapolation gives the expected intercept of unity.

However, in general terms, the rate constant in eq 5 is a pseudo-first-order function incorporating 3 in a photostationary

(41) The amount of PVE converted to dimer after irradiation for particular time periods (indicated in the captions to the plots) has been taken as proportional to the rate of formation of the dimer.

(42) Mann, G. K.; Barnes, K. K. "Electrochemical Reactions in Non-Aqueous Systems"; Marcel Dekker: New York, 1970.

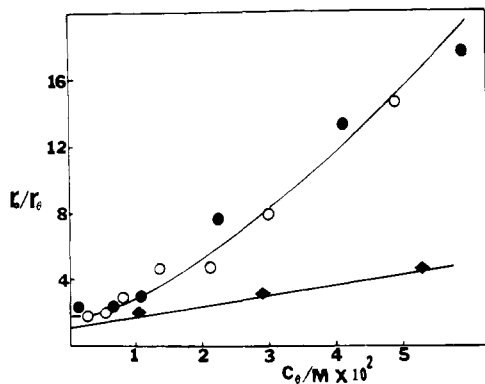


Figure 5. Plots of the data (eq 6) for the quenching effect of isoprene (\blacklozenge), TMB (O), and TEMB (\bullet); for each experiment ZnO, 100 mg; PVE, 0.25 M; irradiation time, 3 h.

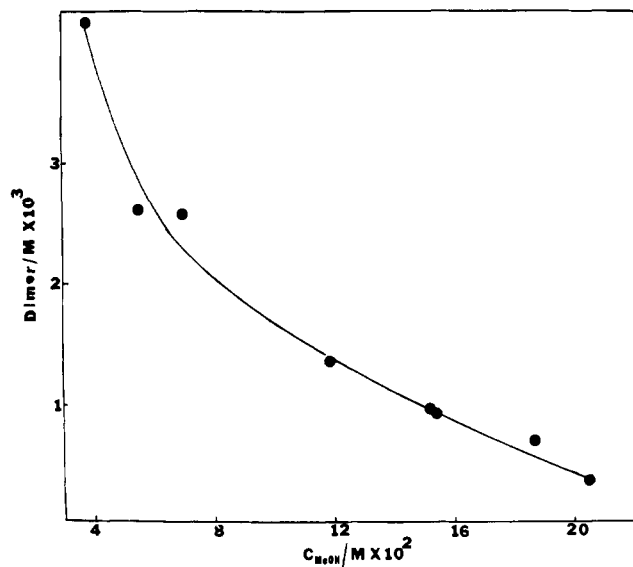


Figure 6. Effect of methyl alcohol on the rate of dimer formation: ZnO, 100 mg; PVE, 0.25 M, irradiation time, 3 h.

state. If the quencher is a species which can intercept a hole or 3, the value of the pseudo-first-order rate constant will be affected and eq 6 will not be applicable. In cases where the extent of trapping of the hole or radical cation is constant over a concentration region, a straight line could be obtained. Such a situation should only be obtained at relatively high concentrations of quencher.

Methoxybenzenes. 1,3,5-Trimethoxybenzene (TMB) and 1,2,4,5-tetramethoxybenzene (TEMB) were tested. Plots of the data (r_0/r_θ vs. c_θ) are presented in Figure 5. A good straight line is not obtained, indicating that, most probably, besides competitive adsorption, cationic interception is also occurring. In view of the oxidation potentials for TMB (1.49 vs. SCE)⁴³ and TEMB (0.81 vs. SCE)⁴³ this seems probable, but the similarity of the curves suggests that the competitive adsorption may be the dominant phenomenon.

Methyl Alcohol. In Table II it was noted that no dimer formation was observed when methanol was used as solvent. In view of the reported activity of metal oxides (including ZnO and TiO₂) in alcohol oxidation it seemed possible that the inhibition of dimerization could be attributable to competitive adsorption and/or surface interaction of the solvent. The effect of methanol on dimer formation was, therefore, studied, and conversion was plotted against methanol concentrations (Figure 6). A dependence was, indeed, found, and the data, plotted according to eq 5, are given in Figure 7. The scatter of the data ($r = 0.987$) argues that

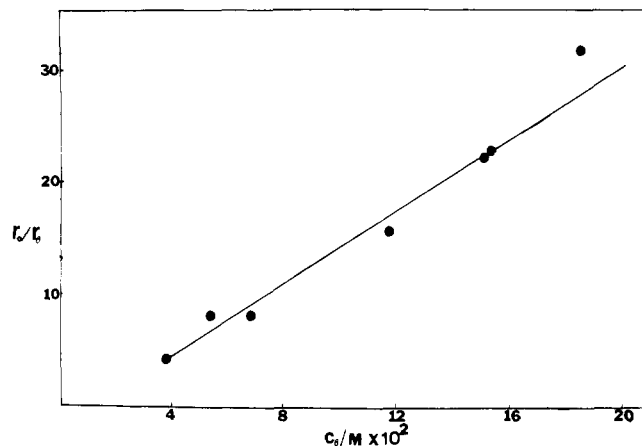


Figure 7. Plot of the data in Figure 6, according to eq 6 ($r = 0.987$).

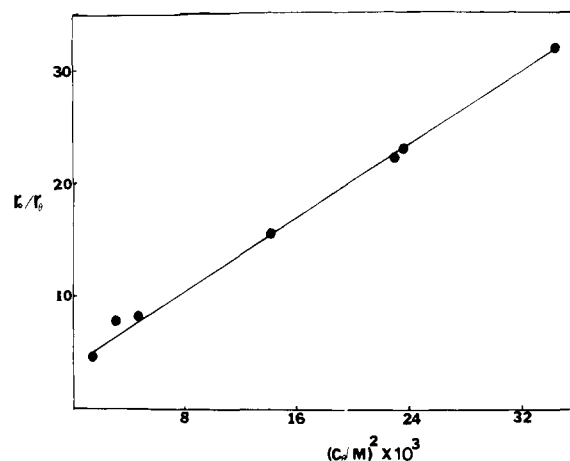


Figure 8. Plot of the data in Figure 6, according to eq 6 using the square root of c_{MeOH} ($r = 0.999$).

competitive adsorption is not the only process responsible for the observed retardation. Plotted (Figure 8) against c_θ^2 ($r = 0.999$) a better fit is obtained. This would be explicable if a situation could arise wherein reaction of the quencher at the surface generates products which compete with PVE for surface sites. In this case the extent of surface coverage by the product(s) would be proportional to the rate of the quencher reaction (r_p) at the surface (eq 7)

$$r_p = k_r' K_\theta^n c_\theta^n \quad (7)$$

where k_r' is the rate constant for the quencher reaction to give products and n is the order of the reaction. Complex reactions having fractional order dependency with respect to reactants are very common in heterogeneous catalysis,³⁸ and n may have any value greater than zero.

Introduction of this term into the Langmuir-Hinshelwood expression (eq 5) for inhibition of the photodimerization of PVE results in eq 8

$$r_\theta = \frac{k_r K_1 c_1}{1 + K_1 c_1 + K_p k_r' K_\theta^n c_\theta^n} \quad (8)$$

where K_p is the adsorption constant of the product. Taking $K_p k_r' K_\theta^n$ as equal to K_θ' gives eq 9

$$r_\theta = \frac{k_r K_1 c_1}{1 + K_1 c_1 + K_\theta' c_\theta^n} \quad (9)$$

A candidate for the oxidatively produced poison is the carboxylate ion, reported to be formed by primary (and secondary) alcohol oxidation on oxide surfaces^{35,36} and which is not easily desorbed. The formation, therefore, of formate ion from methanol would, therefore, not be unexpected. Analysis of the filtrate of

(43) Siegerman, H. In "Techniques of Chemistry"; Wienberg, N. L., Ed.; Wiley: New York, 1975; Vol. 5, Part 2, p 792.

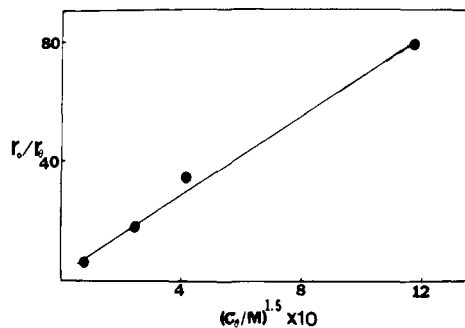


Figure 9. Quenching effect of EVE. Data plotted according to eq 6 using 1.5 power of c_{EVE} : ZnO, 100 mg; PVE, 0.25 M; irradiation time, 3 h.

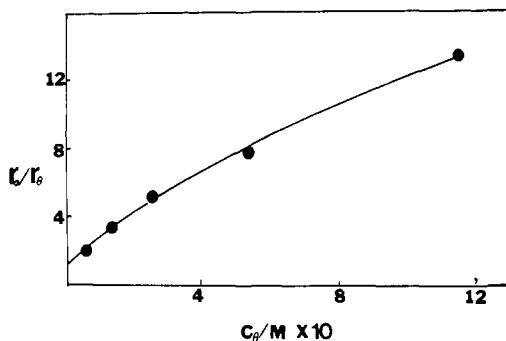


Figure 10. Quenching effect of furan (eq 6): ZnO, 100 mg; PVE, 0.25 M; irradiation time, 3 h.

a reaction mixture after 2 h of irradiation revealed the presence of formaldehyde, by the chromotropic acid test. Quantitative estimation showed that 1% of the methanol (33 mg, in CH_2Cl_2) was converted into formaldehyde. It was also observed that the presence of PVE (150 mg) in the reaction mixture did not affect the yield of formaldehyde and that some dimer formation still occurred. Similar experiments using various amounts of benzene and cyclohexane (<0.6 M) to quench the reaction on ZnO, TiO_2 , and CdS (in CH_2Cl_2 as solvent) did not lead to any significant decrease in dimer formation. In contrast, the addition of a small amount of methanol (~ 0.1 M) was sufficient to suppress completely the formation of PVE dimer on CdS and TiO_2 . These observations support the view, expressed above, that the solvent competes for adsorption sites at the surface.

Ethyl Vinyl Ether. Irradiation of an ethyl vinyl ether (EVE)-PVE mixture in the presence of ZnO in CH_2Cl_2 resulted in a rate of overall cycloaddition less than that of dimerization in the absence of the EVE. The formation of the PVE-EVE crossadduct was observed but not that of the EVE dimer. The ratio of the yield of crossadduct to that of PVE dimer increased with increasing EVE concentration, although the overall actual rate of formation of cycloadducts was decreased. Similar results have been reported for homogeneous solution by Mizuno et al.¹⁹ A plot of our data according to eq 6, using the 1.5 power of EVE concentration, is given in Figure 9: it is a straight-line plot over the range of concentration used. The decrease in the cycloaddition rate with increased EVE concentration suggests that interception of the photoinduced hole by EVE could be the dominant factor in this process, followed by the destruction of EVE^+ by back-electron transfer. The oxidation potential of EVE (1.26 V vs. Ag/Ag^+) is not appreciably different from that of PVE.

Furan and Methylfuran. Mizuno et al. have reported⁴⁴ the photoaddition of furan and methylfuran to various electron-rich aromatic olefins in the presence of electron-transfer sensitizers. However, comparison of the oxidation potentials of furan (1.46 V vs. Ag^+/Ag) and methylfuran (1.18 V vs. Ag^+/Ag) with that of PVE leads to the expectation that methylfuran should be effective in hole trapping in competition with PVE but not furan.

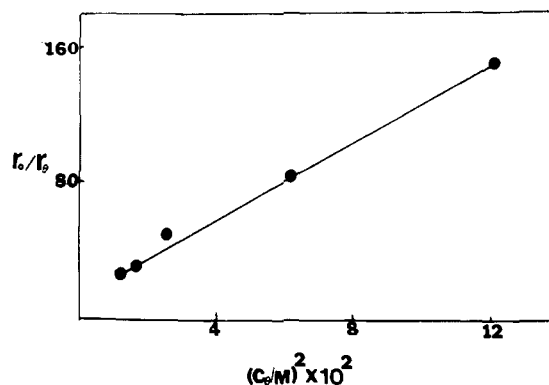


Figure 11. Quenching effect of methylfuran, (eq 6) using the square root of c_e . Conditions as in Figure 10 ($r = 0.993$).

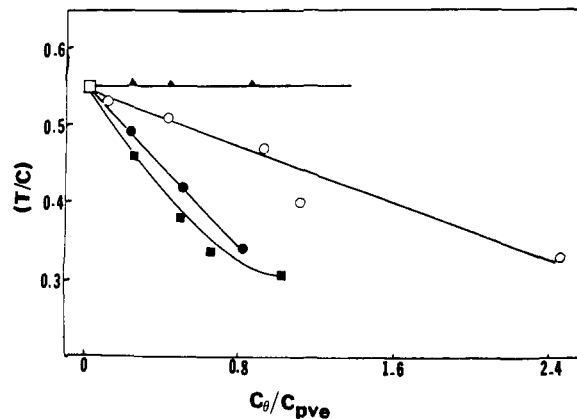


Figure 12. Effect of various quenchers on the T/C ratio in PVE photodimerization in the presence of furan (\blacktriangle); EVE (\circ), TMB (\bullet), and methylfuran (\blacklozenge) at constant PVE concentration (0.25 M).

The data for furan as quencher is plotted according to eq 6 in Figure 10. In the lower concentration range (<0.25 M) a straight line is obtained with an intercept of unity, suggesting that interception of the photoproducted hole and/or PVE^+ by furan is not very effective. The deviation in the high-concentration range (0.254–1.16 M) could be attributable to the saturation coverage of the surface by furan.

On the other hand, using methylfuran, an unidentified adduct was formed, and a plot of the data according to eq 6, using the square of the concentration, gave a straight line over the higher concentration region (<0.35 M) (Figure 11), suggesting a composite quenching function, including the formation of a semiconductor poison.

It is noteworthy that only those quenchers which can react under the prevalent conditions to generate products (e.g., methanol, EVE, and methylfuran) obey eq 9 with $n > 1$.

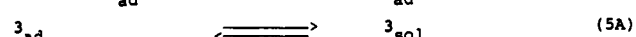
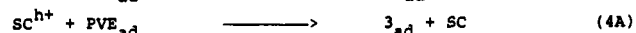
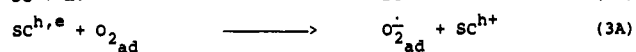
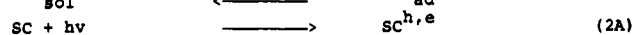
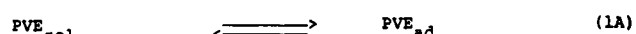
Stereochemistry. The following summarizes our present knowledge. A constant T/C ratio (~ 0.53) was observed for ZnO in CH_2Cl_2 . At low concentrations the slow conversion of the cis dimer to the trans dimer is observed both in solution and on ZnO. As would be expected, therefore, prolonged irradiation of PVE only shows a change in the T/C ratio when the initial concentration is low. Thus, a slight change in ratio (0.53–0.61) was observed when 0.025 M PVE was irradiated over ZnO (CH_2Cl_2) to 50% conversion. This is a reflection of the relative thermodynamic stability of the stereoisomer, as reported by Farid.²²

More surprising, various quenchers were found to affect the T/C ratio (Figure 12). First, furan, now believed to act by competitive adsorption and without electronic interference, does not quench dimer formation with a concomitant change of T/C ratio. On the other hand EVE, methylfuran, and TMB, now believed to quench by electron transfer, do change the ratio in the nonthermodynamic sense; i.e., T/C decreases. This can be interpreted on the basis of a lower concentration of 3_{ad} as discussed below.

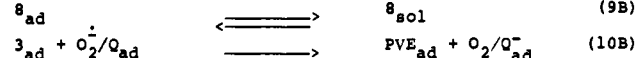
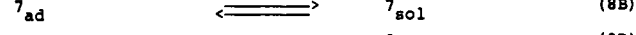
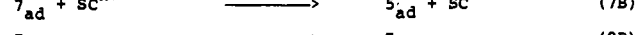
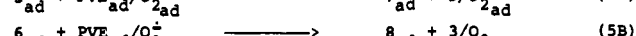
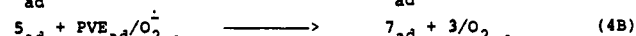
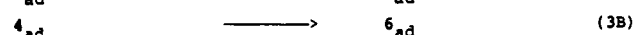
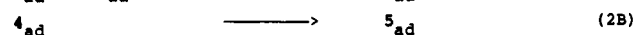
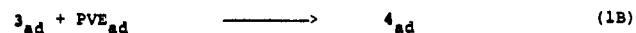
(44) Mizuno, K.; Kaji, R.; Okada, H.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* 1978, 594.

Scheme II

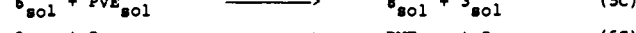
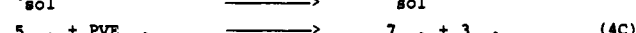
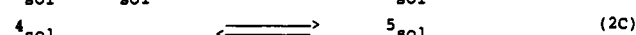
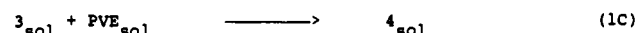
Elementary Processes



Surface reactions



Solution phase reactions



The T/C ratio was also affected by the concentration of the electron acceptor, oxygen (Table III), descending as low as 0.4 for ZnO and 0.26 for CdS. On the basis of the scheme following, the decrease in oxygen concentration results in the hole-electron collapse and a corresponding decrease in hole availability to oxidize adsorbed PVE. This drastically reduces the amount of adsorbed 3 and, consequently, even more the amount released into solution. Since the surface reaction is presumed to favor cis product (see below) the more reaction taking place in the adsorbed state, the smaller the T/C ratio of the product. It should be noted that the preference for adsorbed PVE to give cis product is general for all reactive semiconductors tested (Table III).

Minimal Scheme. From the foregoing results and observations it may be concluded that the dimerization of PVE occurs in the adsorbed state, with, however, some contribution from solution-phase reaction. The relative contribution of solution-phase reaction to the overall process of dimer formation determines the stereoselectivity of the system.

To accommodate these observations Scheme II is proposed as a *minimal* set of steps required, divided into three groups. The first group presents the steps required for the initiation of the reaction. The apparent applicability of the Langmuir-Hinshelwood kinetic treatment (Figure 3) would justify the reversible form of step 1A. The formation of the electron-hole pair (step 2A) on semiconductor powder surfaces under illumination with light of energy greater than the band gap is a widely reported and generally accepted phenomenon.⁴⁵ Similarly, the formation of $\text{O}_{2\cdot}$ by the trapping of a conduction-band electron by adsorbed

oxygen appears to be a general phenomenon.⁴⁶ Attempts to demonstrate that superoxide existed in solution during the semiconductor-induced oxidation of alkenes were unsuccessful,⁴⁷ and it was suggested that superoxide ion is restricted to the surface: The same may be true in the present instance. Lattice oxygen is evidently not essential since the reaction can be induced by CdS.

The formation of the radical cation of PVE in the adsorbed state (step 4A) finds analogy in the work of Grätzel⁴⁸ and Fox⁴⁹ in flash photolytic studies of colloidal semiconductors. The former observed a Langmuir adsorption isotherm-type behavior for hole scavenging by halide ion, SCN^- , and SH^- in colloidal TiO_2 and CdS. It was also observed⁴⁸ that the rate of electron transfer in colloidal TiO_2 from the interior of the semiconductor particle to the interface was faster than the rate of recombination, resulting in a very efficient electron transfer to solution. A large driving force was required for the transfer of a hole from the interior of the semiconductor to the interfaces. However, because of the presence of surface hydroxyl and surface defects the hole was efficiently scavenged before reaching the interface. This suggests that for formation of 3 PVE has to compete with other hole scavengers and that efficient competition is only possible if PVE is also adsorbed on the surface.

Section B comprises surface processes, and section C comprises those in solution. The latter follows that of Farid,²² as represented in Scheme I.

After the formation of 3 in the adsorbed state, there is competition between reaction with another adsorbed PVE molecule (step 1B) and desorption into solution (step 5A). The extent of the competition will depend upon the relative concentration of 3_{ad} and PVE_{ad} . To account for our stereochemical observations we presume that the conversion of 4 to 5 (step 2B) is preferred to a greater degree over (3B), on the surface, than is (2C) over (3C) in solution. The observed conversion of cis dimer to trans dimer appears to justify the inclusion of steps 7b and 8b.

The T/C ratio (~ 0.53) is lower than the value observed (~ 0.65)²² in homogeneous systems, but the difference is not dramatic. We assume a contribution for a solution-phase reaction (desorption of 3 (step 5A) and subsequent reaction as in section C) as well as possible desorption of 5 (step 6B) and reversal to 4,²³ leading to both isomers.

Thus, any process which decreases the rate of desorption to solution of 3_{ad} or 5_{ad} (step 5A and 6B) should lead to a lowering of the T/C ratio. This could be achieved by decreasing the hole availability (step 4A) which decreases 3_{ad} or by efficient interception of 3_{ad} and 5_{ad} by PVE_{ad} (steps 1B and 4B) in comparison with steps 5A and 6B. The decrease in T/C ratio in deoxygenated samples or in the presence of quencher may be attributed to this phenomenon. In contrast the higher T/C ratio observed at lower (0.025 M) PVE concentration could be attributable to the reverse: i.e., the less efficient interception of 3_{ad} (step 1B) as compared to desorption (step 5A). If the concentration of 3_{ad} produced is, as appears to be the case, zero order with respect to PVE_{ad} , no decrease in the concentration of 3_{ad} is to be expected, and thus less efficient interception by PVE_{ad} (step 1B), because of its lower concentration, will occur.

The observed difference in the activity of ZnO and TiO_2 may be related to the differences in the nature and reactivity of the adsorbed O_2 species. Irradiation of PVE in the presence of high-surface-area TiO_2 (Degussa) resulted in complete destruction of PVE and a yellow coloration of TiO_2 .

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Conclusions

We believe the foregoing shows that surface-related processes play an important role in controlling the rate of reaction and stereochemical behavior of the semiconductor photoinduced dimerization of PVE. Simple kinetic analysis based upon Langmuir-Hinshelwood treatment has been successfully applied. This procedure can rationalize the different effects of various quenchers on the reaction, and the overall pathway emerges as a complex sequence of steps involving both surface reaction and reaction in solution.

Acknowledgment. We thank Professor J. S. Sheasby, Material Engineering, UWO, for providing facilities for surface area

measurement, Professor J. Cunningham, University College, Cork, Ireland, for providing reference samples (TiO₂, Al₂O₃, Degussa) for surface area measurements, and Dr. N. S. McIntyre and D. Johnston, "Surface Science", UWO, for their help in the photoacoustic studies of the semiconductors. We thank the Natural Science and Engineering Research Council of Canada for financial support.

Registry No. 7, 35370-71-9; 8, 35370-70-8; PVE, 766-94-9; TMB, 621-23-8; TEMB, 2441-46-5; EVE, 109-92-2; ZnO, 1314-13-2; TiO₂, 13463-67-7; CdS, 1306-23-6; Al₂O₃, 1344-28-1; Ta₂O₅, 1314-61-0; SnO₂, 18282-10-5; Bi₂O₃, 1304-76-3; WO₃, 1314-35-8; isoprene, 78-79-5; furan, 110-00-9; 2-methylfuran, 534-22-5; β -bromophenetole, 589-10-6.

Structure, Conformation, and Ligand Binding in Fe(CO)₄(C₂H₄) and Some Derivatives. A Theoretical Study

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Abstract: Iron-olefin complexes of the general formula Fe(CO)₄(C₂X₄), where X = H, F, Cl, and CN, were studied by molecular orbital methods. Calculated ΔE 's for the reactions Fe(CO)₄(C₂H₄) + C₂X₄ → Fe(CO)₄(C₂X₄) + C₂H₄ are found to vary in the order F >> CN > Cl and are consistent with available experimental data on related systems. The conformational preferences of these complexes have also been investigated. All derivatives studied here were found to prefer a trigonal-bipyramidal structure with the ethylene occupying a position in the equatorial plane. The nature of the metal-olefin bond is discussed and illustrated with electron density difference contour maps and localized molecular orbitals (LMO's) in the metal-olefin region. The relative binding energies of cis and trans 1,2-disubstituted olefins were also calculated and are discussed.

The chemistry of olefins in transition-metal complexes has been a topic of discussion for some time. As a result, numerous theoretical studies of metal-olefin complexes have appeared in the literature.¹⁻¹³ These studies have employed a large variety of quantum chemical methods ranging from empirical and semi-empirical schemes such as extended Hückel, CNDO, INDO, and HFS(X- α) to all electron ab initio calculations. While approximate methods provide a means of systematically studying real olefin complexes, they are often insufficient for the prediction of molecular properties, particularly the total energy. First-principle calculations on real transition-metal-olefin systems are difficult, however, because the formidable size of such computations places them out of reach of most quantum chemists. Recently, the PRDDO approximations¹⁴ have been extended through the first

transition series.¹⁵ Although PRDDO is an approximate method, it closely reproduces ab initio minimum basis set calculations with only a fraction of the computational effort. This allows a systematic study of real olefin complexes without sacrificing the quantitative accuracy of the ab initio approach. In this paper, we present the first PRDDO calculations on metal-olefin systems.

The most widely accepted scheme of metal-olefin bonding comes from Dewar¹⁶ and Chatt and Duncanson.¹⁷ They proposed that the bonding consists of a two-way donor-acceptor mechanism: σ donation of the π -bonding electrons of the olefin to vacant orbitals on the metal, and π back donation of metal d electrons to the π^* orbital of the olefin. Their picture has served as the starting point for rationalizing olefin site preference, rotational barriers, and substituent effects observed in a wide range of metal-olefin systems. Many of these arguments were pioneered by Hoffmann et al.^{1,2}

Limited to the first transition series, some of the most interesting olefin complexes to study are iron-olefin complexes of the general formula Fe(CO)₄(C₂X₄), where X = H, F, Cl, or CN. Experimentally, all are known to exist;¹⁸⁻²² however, they are thermally

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