Conclusions

Relative enthalpies for dissociative adsorption of Brønsted acids on basic metal oxides cannot be explained solely on the basis of gas-phase heterolytic bond dissociation energies. The phenomenological consequence is that in some cases aqueous dissociation constants correlate better with relative acidities in gas-solid surface reactions than do gas-phase acidities. The origin of this effect is a strong interaction between adsorbed conjugate base species and surface metal cations which results in some covalent bond formation, with concomitant reduction or delocalization of the negative charge on the conjugate base. The relative strengths of such surface-adsorbate interactions may be explained qualitatively

based upon the hard or soft acid-base characteristics of each, although a quantitative description is, to date, lacking.

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Registry No. ZnO, 1314-13-2; MgO, 1309-48-4; C₆H₅CCH, 536-74-3; CH₃OH, 67-56-1; C₂H₅OH, 64-17-5; CH₃SH, 74-93-1; C₆H₅OH, 108-95-2; HCN, 74-90-8; CH₃COOH, 64-19-7; C₆H₅SH, 108-98-5; HCOOH, 64-18-6; HCCH, 74-86-2.

Surface Photochemistry: On the Mechanism of the Semiconductor Photoinduced Valence Isomerization of Hexamethyl-Dewar Benzene to Hexamethylbenzene¹

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The CdS-, TiO₂-, and ZnO-photoinduced valence isomerization of hexamethyl-Dewar benzene to hexamethylbenzene has been investigated in methylene dichloride solution and found to be very efficient. The reaction appears to follow modified Langmuir-Hinshelwood and Eley-Rideal mechanisms. A surface cation radical chain mechanism is proposed since the reaction can be efficiently quenched by electron donors, and quantum yields greater than unity were obtained in TiO_2 and ZnO reactions. The quenching also followed modified Langmuir-Hinshelwood and Eley-Rideal pathways, in which the latter predominantly contributed to the overall quenching rates. CdS of different origins with different surface areas, purities, and structures were used, and the rates varied by a factor of 2.3. None of these functions appear to play a dominant role in the rate of reaction.

Introduction

The study of semiconductor-mediated photoassisted organic reaction is attracting increasing attention. Such reactions now include, aside from oxidation/reduction processes,² dimerization,^{3,4} cycloreversion,⁵⁻⁷ cis-trans isomerization⁸⁻¹³ and sigmatropic rearrangements.7 It has also been reported by Mukai7 and his collaborators that hexamethyl-Dewar benzene (HMDB) is isom-

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erized to hexamethylbenzene (HMB) over CdS, TiO₂, and ZnO in acetonitrile: A cation radical intermediate was proposed. We report here a more detailed study of this semiconductor-induced reaction in methylene dichloride, which reveals the occurrence of two mechanisms, both in the product formation and in the electron-transfer quenching of its formation.

The primary goals of this study are (a) to generalize a previously reported^{4,11} mechanistic model that provides a useful rationalization for the mechanism of semiconductor photoinduced reactions, and (b) to test for the occurrence of a chain reaction on a surface. The selection of valence isomerization of HMDB is based on two important facts: (a) HMDB absorbs in a relatively short wavelength region (<300 nm), and hence it is possible to test the model not only with CdS-photoinduced reaction^{4,11} but also with those of TiO_2 and ZnO; (b) the reaction is known, from previous work,¹⁴⁻¹⁷ to proceed very efficiently ($\phi \gg 1$) via a cation radical chain mechanism in homogeneous solution, and hence it is possible to test for the occurrence of a chain reaction on a surface.

Experimental Section

Methylene dichloride was of spectroscopic grade (Fisher) and was used without further purification. HMDB (Aldrich) was purified by passage rapidly through a very short column (4×0.5 cm) of dry silica gel (Merck, 230-400 mesh); pure HMDB

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^aSC, SC*, and SC(h⁺,e⁻) are the semiconductor in the ground state, the excited state (exciton), and after hole-electron separation, respectively. D and B (and their respective ions) are hexathethyl-Dewar benzene and hexamethylbenzene (and their ions). D_{ad} (Q_{ad}) and D_{sol} (Q_{sol}) are hexamethyl-Dewar benzene (the quencher) oh the surface and in solution.

(>99%) was obtained as revealed by GC and NMR analysis. All other substances were purified by distillation, sublimation, or recrystallization, as appropriate.

Unless otherwise stated CdS, (Strem, ultrapure, jurface area = 7 g/m^2 , lot no. 16693-S), TiO₂ (Fisher, lot no. 75250), and ZnO (Fisher, surface area 5 g/m^2 , lot no. 745055) were used throughout.

Typically, 0.05 M HMDB in methylene dichloride (6 mL) in the presence of CdS, TiO₂, or ZnO (50 mg) was irradiated, at $\lambda > 430$ nm (Corning filter 3-72) in the case of CMS and at λ > 360 nm (Corning filter 0-51) for TiO₂ and ZnO for 30 min, using a 150-W PRA xenon lamp. Prior to irradiation the mixture was sonicated for 5 min and was constantly stirred during the course of the irradiation. Compressed air was used as coolant and a water filter was used to remove IR radiation. The reaction vessel was open to the atmosphere via a reflux condensur. A known amount of *n*-dodecane, as calibrant, was added to the mixture before irradiation. After irradiation, the semiconductor was removed by filtration and the filtrate was analyzed with a Varian 3700 gas chromatograph equipped with a flame ionization detector, connected to a Hewlett-Packard 3390 A integrator. Analysis was performed on a 2 m \times 2 mm column packed with OV-101 (10%) on Chromosorb W(HP), 80-100 mesh. Unless otherwise stated, conversion for an arbitrary set of conditions was reproducible within $\leq \pm 5\%$ over the period required to complete a set of experiments. For quantum yield determinations a special aluminum block with a window $(1 \times 1.5 \text{ cm})$ was used to ensure that only the light from the lamp reached the reaction vessel. Potassium ferrioxalate (0.006 M) was used as actinometer. A Corning filter (CS7-60) was used which transmitted at 320-390 nm with a maximum at \sim 355 nm. Direct irradiation of HMDB (0.57 M) in methylene dichloride in this wavelength range produced no reaction. For the calculation of the quantum yield it was assumed that all radiation entering the reaction vessel was absorbed by the semiconductor; i.e., the scattered light was ignored

Results and Discussion

Irradiation of 0.05 M HMDB in methylene dichldride (6 mL) in the presence of CdS, TiO₂, or ZnO (50 mg) at & > 430 nm for CdS (band gap \sim 530 nm) and at $\lambda >$ 360 nm for TiO₂ and ZnO (band gaps \sim 400 nm) gave, readily, HMB. The reaction proceeded cleanly and rapidly: Appropriate control experiments confirmed that both light and semiconductor were required.

When a semiconductor particle absorbs light with an energy greater than the band gap the formation of an exciton results; charge separation may take place creating hole-electron pairs resulting in an injection of electrons into the conduction band and "holes" into the valence band.¹⁸ Donation of an electron from HMDB to the "hole", which is thermodynamically possible, (for

TABLE I: Quantum Yields of Valence Isomerization of HMDB to HMB Photomediated by CdS, TiO₂, and ZnO at Two Different **HMDB** Concentrations⁴

semiconductor	[HMDB], M	quantum yield (±10%)
CdS	0.13	0.29
	0.57	0.68
TiO ₂	0.13	0.84
-	0.57	1.23
ZnO	0.13	0.48
	0.57	1.23

^aHMDB solutions in methylene dichloride were irradiated for 30 min at 320-390 nm (Corning filter CS,7-60) in the presence of 50 mg of the semiconductor in air.

values of $E_{1/2}^{ox}$ and the valence bands; see "quenching studies" below) results in HMDB cation radical formation. In homogeneous solution the photosensitized valence isomerization of HMDB to HMB is known to proceed via such a cation radical,¹⁴⁻¹⁷ and, in fact, two cation radicals (HMDB⁺⁺ and HMB⁺⁺) are involved. The key step as shown below (S is the sensitizer) is the electron transfer from HMDB to HMB^{•+}: this permits the operation of a chain mechanism, as shown

HMDB
$$\xrightarrow{h\nu, S}$$
 HMDB^{•+} (+ S^{•−})
HMDB^{•+} → HMB^{•+}
HMB^{•+} + HMDB → HMDB^{•+} + HMB

This overall mechanism appears to be applicable to the semiconductor-mediated process, and our views, to be discussed below, are summarized in Scheme I. In particular, it should be noted that the reaction is proposed to occur both entirely on the surface of the semiconductor (Langmuir-Hinshelwood, LH, mechanism) and by collision of dissolved HMDB with surface-bound cation radical (Eley-Rideal, ER, mechanism).

Quantum Yield Determination. It has been reported that the rates of a variety of semiconductor-photoinduced reactions decrease nonlinearly with reduction in light intensity.^{4,9,19-26} This behavior has been explained on the basis that under very low light intensity the band bending in the space-charge layer of powdered semiconductor is enough to separate all the excitons into hole-electron pairs. However, with increasing light intensity the band bending tends to be decreased and a strong competition between electron-hole recombination in the bulk of the semiconductor and electron-hole separation may occur. Thus, at high light intensity it is expected that the electron-hole recombination process plays the crucial role and a minor portion of the exciton population has a chance to separate into electron-hole pairs. The quantum yields were, therefore, determined at relatively low light intensity (ca 25 mW/cm²):²⁵ a value of 1.2 (Table I) was obtained for ZnO and TiO₂ (0.57 M HMDB), which, depending, as it does, on electron-hole separation efficiency, implies that a chain process is involved. In this, an electron transfer occurs from HMDB, either adsorbed on the surface or diffusing to the surface, to the HMB cation radical on the surface.

Evans et al.¹⁴ have observed, in the photosensitized valence isomerization of HMDB with naphthalene, concentration-dependent quantum yields ranging up to ~ 80 . Peacock and

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Figure 1. Effect of HMDB concentration on rates of HMB formation (O) mediated by CdS. The solid curve was calculated from R = 0.541[D] + 0.506[D]/(1 + 13.83[D]). The overall rates are separated into LH (...) and ER (---) components. Each sample was irradiated at $\lambda > 430$ nm for 30 min.

Schuster,¹⁵ in an elegant recent study of the photosensitized valence isomerization of HMDB with a variety of sensitizers, have observed quantum yields of up to 213. The relatively low quantum yields for the semiconductor-photoinduced isomerization of HMDB, in comparison with homogeneous solution values, argue against the desorption of HMB cation radical into solution.

Kinetic Analysis. Although several studies have now been reported on semiconductor-photoinduced organic reactions in solution, in few cases has a model for the reaction been proposed. In an earlier study⁴ we have discussed our results concerning the CdS-mediated dimerization of *N*-vinylcarbazole (NVC) in terms of a combination of the LH model, in which the cation radical of NVC reacts with preadsorbed NVC, and the ER model, in which a neutral NVC molecule from solution collides with the NVC cation radical generated on the surface: a solution equivalent to the gas-phase Eley–Rideal process. A similar approach was successful in interpreting the quenching of this reaction⁴ and that of the cis–trans isomerization of some 4-substituted stilbenes.¹¹ We attempt to generalize its application here to include the CdS-, TiO₂-, and ZnO-mediated isomerization of HMDB.

The LH kinetic treatment is known to be a good model for the description of reactions taking place at the solid–gas interface.²⁷⁻²⁹ In order to extend this model to the solid–liquid interface, modification is necessary since the solvent occupies reactive sites.

The rate of reaction, R_{LH} , at the photosatationary state³⁰ will be given by equations of the following forms:

$$R_{\rm LH} = k_{\rm LH} \theta_{\rm D} = \frac{k_{\rm LH} K[{\rm D}]}{1 + K[{\rm D}] + K_{\rm s}[{\rm S}]} = \frac{k_{\rm LH} K'[{\rm D}]}{1 + K'[{\rm D}]} \quad (1)$$

where k_{LH} is the reaction rate constant, θ_D is the fraction of the surface covered by HMDB, K and [D] are the adsorption coefficient and the initial concentration of HMDB, K_s and [S] are the adsorption coefficient and the concentration of the solvent, and $K' = K/(1 + K_s[S])$. Since [S] \gg [D], however, $K_s[S]$ remains essentially constant at all HMDB concentrations used.

(30) The photostationary state concentration of HMB cation radical is

$$[SC^{*-}/B^{*+}] = \frac{k_2 k_4 I \theta_D}{k_7 (k_1 + k_2) (k_3 + k_4 \theta_D)}$$
(i)

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



Figure 2. Effect of HMDB concentration on rates of the HMB formation (O) mediated by TiO₂. The solid curve was calculated from R = 0.288[D] + 0.732[D]/(1 + 13.88[D]). The overall rates are separated into LH (...) and ER (---) components. Each sample was irradiated at $\lambda > 360$ nm for 30 min.



Figure 3. Effect of HMDB concentration on rates of the HMB formation (O) mediated by ZnO. The solid curve was calculated from R = 0.057[D] + 0.826[D]/(1 + 15.34[D]). The overall rates are separated in LH (···) and ER (---) components. Each sample was irradiated at $\lambda > 360$ nm for 30 min.

Equation 1 is a pseudo-first-order rate equation.

The ER kinetic treatment²⁹ would imply that reaction occurs between HMB cation radical and an HMDB molecule diffusing from the solution. The rate of reaction, R_{ER} , at the photostationary state³⁰ will be given by eq 2, which is a pseudo-first-order rate equation.

$$R_{\rm ER} = k_{\rm ER}[\rm D] \tag{2}$$

If both pathways are operating then the overall rate, R,³¹ should be given by eq 3.⁴

$$R = k_{\rm ER}[D] + \frac{k_{\rm LH}K'[D]}{1 + K'[D]}$$
(3)

Thus, in a plot of rate vs. concentration, as θ_D approaches a limiting value the overall increase in rate would be expected to approach linearity with further increase in HMDB concentration.

The effect of varying the concentration of HMDB (0.01–0.13 M) on the rates of isomerization over CdS, TiO₂, and ZnO (Figures 1–3) was investigated. In all three cases, at concentrations higher than ~ 0.06 M the overall rates of valence isomerization did, indeed, increase linearly with concentration. Similar observations have been reported in, for instance, the CdS-photoinduced dimerization of NVC in acetone⁴ and the gas-phase pho-

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Figure 4. Quenching of valence isomerization of HMDB to MHB: (0) 1,2,4,5-tetramethoxybenzene, the solid curve was calculated from ϕ^0/ϕ $= 1 + 1492.4[Q] + 716.7[Q]/(1 + 628.6[Q]); (\bullet) 1,2,4$ -trimethoxybenzene, the solid curve was calculated from $\phi^0/\phi = 1 + 685.9[Q] +$ $712.2[Q]/(1 + 777.4[Q]); (\Box) 1,4$ -dimethoxybenzene. CdS = 50 mg, HMDB = 0.05 M, 30-min irradiation.

tooxidation of carbon monoxide over TiO2³² and of propan-2-ol over ZnO.19

It was possible to fit³³ the data of rate vs. concentration for CdS-photoinduced valence isomerization of HMDB to a curve obtained by insertion of appropriate values for the constants in eq 3 (see the caption of Figure 1). Having these values, it became possible to separate the overall rates of isomerization into LH and ER components (Figure 1). Evidently, the ER pathway is the more important, and its importance increases as the HMDB concentration is increased. On the other hand, the fitting of the data in Figure 2 for TiO₂ reaction showed that the LH pathway is favored at low concentrations of HMDB but becomes comparable to the ER pathway at higher concentrations. The data for ZnO reaction (Figure 3) showed that, in contrast, the LH pathway was the more important contributor over a similar concentration range. These differences are not unexpected as the adsorption properties of HMDB on CdS, TiO₂, and ZnO surfaces are not expected to be the same.

A possible step, omitted from the scheme, is the desorption into solution of the long-lived HMB cation radical (solution lifetime ca. $4 \mu s$),¹⁵ after which reaction may proceed as in the sensitized reaction in homogeneous solution. This, from quantum yield measurements and from the fact that CdS-photoinduced isomerization of HMDB to HMB was considerably slower in more polar solvents such as methanol, acetone, and acetonitrile (in which the homogeneous sensitized reaction proceeds very well) appears unlikely. In addition, the semiconductor-mediated reaction requires the presence of oxygen.⁷ The function of the oxygen in this and other³⁻⁶ semiconductor-mediated reactions is to act as an electron trap, thus prolonging the lifetime of the "hole". The electron is trapped as surface-bound superoxide ion,³⁴ and the surface of the semiconductor is thus negatively charged and electrostatically opposes the desorption of positively charged species, especially in a solvent of medium dielectric constant.

Quenching Studies. The semiconductor-photoinduced valence isomerization of HMDB($E_{1/2}^{\text{ox}} = 1.58 \text{ V vs. SCE}$)¹⁴ to HMB ($E_{1/2}^{\text{ox}} = 1.62 \text{ V vs. SCE}$)¹⁴ may be quenched, in principle, by (a) donation of an electron by the quencher, Q, to the photogenerated "hole" competitively with the reactant, HMDB, and (b) interception of the cation radical of HMDB and/or the chain-carrying agent HMB cation radical by the quencher. 1,4-Dimethoxybenzene $(E_{1/2}^{\text{ox}} = 1.35 \text{ V vs. SCE})$,³⁵ 1,2,4-tri-methoxybenzene $(E_{1/2}^{\text{ox}} = 1.12 \text{ V vs. SCE})$,³⁵ 1,3,5-trimethoxy-benzene $(E_{1/2}^{\text{ox}} = 1.49 \text{ V vs. SCE})$,³⁵ and 1,2,4,5-tetramethoxy-



Figure 5. Quenching of valence isomerization of HMDB to HMB: (0) 1,2,4-trimethoxybenzene, the solid curve was calculated from $\phi^0/\phi = 1$ + 1101.3[Q] + 1207.9[Q]/(1 + 1183.9[Q]); (•) 1,3,5-trimethoxybenzene. $TiO_2 = 50$ mg, HMDB = 0.05 M, 30-min irradiation.



Figure 6. Quenching of valence isomerization of HMDB to HMB: (0) 1,2,4-trimethoxybenzene, the solid curve was calculated from $\phi^0/\phi = 1$ + $2044.8[Q] + 1285.5[Q]/(1 + 1178.8[Q]); (\bullet) 1,4-dimethoxybenzene.$ ZnO = 50 mg, HMDB = 0.05 M, 30-min irradiation.

benzene $(E_{1/2}^{\text{ox}} = 0.81 \text{ V vs. SCE})^{35}$ were tested as quenchers for CdS (valence band ~1.6 V vs. SCE), ³⁶ TiO₂ (valence band ~2.0 V vs. SCE),³⁷ and ZnO (valence band ~ 2.4 V vs. SCE)³⁶ photo induced reactions. Plots of ϕ^0/ϕ vs. [Q] are presented in Figures 4-6.

Figure 4 shows that, while 1,2,4-trimethoxybenzene and 1,2,4,5-tetramethoxybenzene quenched the CdS reaction efficiently, 1,4-dimethoxybenzene quenched the reaction only up to $\sim 17\%$ over a similar concentration range.

Figure 5 shows that 1,2,4-trimethoxybenzene quenched the TiO₂ reaction even more efficiently than that of the CdS reaction under similar conditions, but 1,3,5-trimethoxybenzene, however, did not. This was surprising since 1,3,5-trimethoxybenzene was expected to quench the "hole" very efficiently, though not the HMDB and HMB cation radicals.

1,2,4-Trimethoxybenzene quenched the ZnO reaction (Figure 6) not only more efficiently than that of the TiO_2 and CdS reactions but also more efficiently than the quenching of the CdS reaction by 1,2,4,5-tetramethoxybenzene. 1,4-Dimethoxybenzene, a poor electron donor toward both cation radicals but able, in principle, to quench the "hole" very efficiently, quenched the reaction up to 50% at the highest quencher concentration used: this is probably not to be attributed to "hole" quenching since this should be thermodynamically very efficient. It would thus seem that "hole" quenching is not importantly involved in the overall quenching process.

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Peacock and Schuster¹⁵ and Roth et al.¹⁶ have suggested that the lifetime of the HMDB cation radical in homogeneous solution is of the order of nanoseconds,^{15,16} while that of the HMB cation radical is of that of microseconds.¹⁵ On the assumption that surface does not drastically change the *difference* in the lifetimes of HMDB and HMB cation radicals it seems improbable that the HMDB cation radical be appreciably involved in the quenching of the CdS, TiO₂, and ZnO reactions. Accordingly, the quenching of the CdS-, TiO_2 -, and ZnO-mediated reactions with 1,2,4trimethoxybenzene and 1,2,4,5-tetramethoxybenzene involves essentially the cation radical of HMB.

Figures 4–6 show that at concentration higher than ~ 0.002 M of 1,2,4-trimethoxybenzene and 1,2,4,5-tetramethoxybenzene the rate of quenching of CdS, TiO₂, and ZnO reactions increases linearly with the quencher concentration.^{4,11} The data may be rationalized in terms of an LH mechanism, in which the cation radical of HMB is quenched by the preadsorbed quencher on the surface, together with an ER mechanism, in which the HMB cation radical is quenched by diffusion of the quencher from the solution and not the reverse.

Application of the steady-state hypothesis for the excited state and reactive intermediates leads to the quantum yield expression for the (chain pathway) product, in the absence of quencher

$$\phi^{0} = \frac{k_{2}}{k_{1} + k_{2}} \frac{k_{4}\theta_{D}^{0}}{k_{3} + k_{4}\theta_{D}^{0}} \frac{k_{6}}{k_{5} + k_{6}} \frac{k_{8}\theta_{D}^{0} + k_{9}[D]}{k_{7} + k_{8}\theta_{D}^{0} + k_{9}[D]}$$
(4)

where θ_D^0 is the fraction of the surface covered by the reactant, D, in the absence of the quencher. The formation of HMB via back electron transfer, by $k_7[SC^{\bullet-}/B^{\bullet+}]$, should depress the chain reaction.

The quantum yield expression, in the presence of the quencher is shown in eq 5.

$$\phi = \frac{k_2}{k_1 + k_2} \frac{k_4 \theta_D}{k_3 + k_4 \theta_D} \frac{k_6}{k_5 + k_6} \times \frac{k_8 \theta_D + k_9 [D]}{k_7 + k_8 \theta_D + k_9 [D] + k_{10} [Q] + k_{11} \theta_q}$$
(5)

The surface coverage, θ_D , in the presence of the quencher may be expressed in two extreme forms: either adsorption is sitecompetitive or it is not. When both the reactant, D, and the quencher, Q, are adsorbed on the surface without competing for the same sites but are competing independently with a constant concentration of the solvent, θ_D is considered to be constant (i.e., $\theta_D^0 = \theta_D$) and takes the form in eq 1 while θ_q takes the following forms:

$$\theta_{q} = \frac{K_{q}[Q]}{1 + K_{q}[Q] + K_{s}[S]} = \frac{K''[Q]}{1 + K''[Q]}$$
(6)

where K_q is the adsorption coefficient of the quencher and $K'' = k_q/(1 + K_s[S])$. Thus, eq 7 can be obtained when the quencher is adsorbed on the surface independently of the reactant,

$$\frac{\phi^0}{\phi} = 1 + A[Q] + \frac{B[Q]}{1 + C[Q]} \tag{7}$$

where $A = k_{10}/(k_7 + k_8\theta_D^0 + k_9[D]), B = k_{11}K''/(k_7 + k_8\theta_D^0 + k_9[D]), and C = K''.$

Equation 7 has the same general form of the equation derived previously.^{4,11}

The data of quenching of CdS, TiO₂, and ZnO reactions by 1,2,4-trimethoxybenzene fit³³ curves obtained with appropriate sets of constants in eq 7 as do the data of quenching of the CdS reaction by 1,2,4,5-tetramethoxybenzene (see captions to Figures 4–6). From the values of C and the ratios A/B, the quenching constants ratio k_{10}/k_{11} for CdS-, TiO₂-, and ZnO-mediated reactions, quenched by 1,2,4-trimethoxybenzene, are estimated to be ~750, ~1080, and 1870, respectively. Clearly, this shows that the ER pathway plays a crucial role in the quenching process.

Since the quenching constant k_{10} for the same quencher is expected to be the same for the CdS-, TiO₂-, and ZnO-mediated

TABLE II: Valence Isomerization of HMDB to HMB Initiated by CdS of Different Properties^a

		surf. area, ^b	cryst	
CdS supplier	purity, %	m²/g	struct ^b	yield, %
Strem (lot no. 16693-S)	≥99.99	7.1	$\alpha + \beta \; (\sim 1:1)$	90
Fisher (lot no. 792913)	99	12	β	73
Strem (lot no. NATL)	99.99	0.5	α	70
Aldrich (lot no. 053087)	98.8	7	β	68
Fluka (lot no. 249326-684)	99.999	1.4	α	64
Strem (lot no. NATL)	99	32.4	polytype	50
Aldrich (lot no. 1721PJ)	99.999	1.2	α	48
Strem (lot no. 16027-S ₁)	≥99.99	44	polytype	39

^a 0.062 M of HMDB in CH₂Cl₂ (5 mL) was irradiated in the presence of CdS (50 mg) at $\lambda > 430$ nm for 30 min with a 150-W xenon lamp. ^bSee ref 43.

reactions,³⁸ the lifetime of the HMB cation radical on the CdS, TiO₂, and ZnO surfaces should decrease in the following order: ZnO > TiO₂ > CdS, as indicated by the slopes of the linear section of the quenching plots (A values in eq 7; see captions to Figures 4–6). The fact that the lifetime of HMB cation radical on ZnO surface is then indicated to be longer than that on CdS provides one rationalization as to why 1,4-dimethoxybenzene quenched up to 50% of the ZnO reaction but only ~17% of the CdS reaction at a similar quencher concentration.

Since the quenching of the HMB cation radical should inhibit the chain but, nonetheless, gives the HMB produced from the HMDB cation radical, by $k_6[SC^{\bullet-}/D^{\bullet+}]$ and since up to ~96% of the reaction was quenchable, then extremely low concentrations of HMB cation radical should be produced by this route. This can be essentially rationalized in terms of the, generally accepted,^{4,9,19-26} view that only a small fraction of excitons generated have a chance to separate into hole-electron pairs at high light intensity (i.e., k_1 , in Scheme I, is greater than k_2). Thus, the fact that the reaction is extremely efficient (see Table I) supports the view that the reaction proceeds via a chain mechanism.

However, in contrast to the foregoing, when the reactant and quencher rate adsorbed competitively on the same sites together with the constant coverage of the solvent, the kinetic quenching treatment gives a power-series polynomial equation,⁴ which we were unable to fit to our data. Thus, the compatibility of the noncompetitive adsorption model with the isomerization quenching data suggests that the noncompetitive adsorption extreme ap-

$$k_{10} = \frac{2RT}{3000\eta} \left(\frac{r_{\rm c} + r_{\rm q}}{R_{\rm q}} + \frac{r_{\rm c} + r_{\rm q}}{R_{\rm s}} \right) \quad ({\rm M}^{-1} \; {\rm S}^{-1}) \tag{ii}$$

where T is the temperature, η is the solvent viscosity, r_c and r_q are the interaction radii of the HMB cation radical and the quencher, respectively, and R_q and R_s are the Stokes radii for the quencher and the semiconductor particle. If we assume, as in homogeneous solution, that $r_c = r_q = R_q = a$, since $R_s \gg a$, then eq ii takes the form

$$k_{10} = \frac{4RT}{3000\eta}$$
 (M⁻¹ S⁻¹) (iii)

in which k_{10} is equivalent to half the usual expression and independent of the exact size of the semiconductor particle. Accordingly, provided that the quenching efficiencies on contact be the same, the quenching constant, k_{10} , for the same quencher would be expected to be the same for CdS-, TiO₂-, and ZnO-mediated reactions.

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⁽³⁸⁾ According to the Einstien–Smoluchowski diffusion theory, and its approximation omitting the transfer component, and with the assumption of the applicability of Stokes law, the bimolecular quenching constant, k_{10} , of HMB cation radical adsorbed on the semiconductor by quenching by molecules discharged from solution is given approximately by³⁹

proximates the actual situation on the surface.

Effects of CdS Samples. CdS of hexagonal (α) and cubic (β) $(\sim 1:1)$ crystalline forms (Strem, ultrapure, lot no. 16693-S) was used in the above experiments. Mau et al.⁴⁰ have found that the crystal structure of the CdS particle influences the yield of hydrogen, with cubic β -CdS acting as a more active catalyst than hexagonal α -CdS. Conversely, Matsumura et al.⁴¹ have observed that CdS powder having a hexagonal crystal structure is much more efficient as a photocatalyst than that having a cubic one. Harvey et al.²⁰ have reported different rates and activation energies for the oxidation of liquid propan-2-ol on pure anatase, five doped rutile, and coated anatase and rutile pigments. Yanagida et al.42 have reported that ZnS with different surface areas, purities, particle sizes, and crystalline forms gave different quantum yields for hydrogen production in water/methanol systems. In a previous study,⁴ we have tested the dimerization of NVC on CdS from different sources with different structures, surface areas, and purities and have found that the rates varied by a factor of 4, with no direct relationship to either the surface areas or the purities of the samples. With the same CdS samples the reaction rates for valence isomerization are presented in Table II; they varied by a factor of only 2.3, again with no direct correlation with any of the physical properties.

Conclusions

The CdS-, TiO₂-, and ZnO-photomediated valence isomerization of hexamethyl-Dewar benzene to hexamethylbenzene has been investigated in methylene dichloride and found to be very efficient in all three cases. The effect of varying the concentration of HMDB on the rate of reaction at constant semiconductor mass showed mixed behavior. This behavior may be rationalized in terms of modified LH and ER pathways. A surface cation radical chain mechanism, as found in homogeneous systems, has been proposed as quantum yields greater than unity were obtained in the cases of TiO_2 and ZnO reactions, and the reaction can be quenched very efficiently by electron donors (methoxybenzenes). The quenching data has also been rationalized with LH and ER pathways; the latter contributed importantly to the overall quenching rates. CdS samples with different structures, surface areas, and purities were tested and found to affect the reaction rates by a factor of 2.3.

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Registry No. CdS, 1306-23-6; TiO₂, 13463-67-7; ZnO, 1314-13-2; hexamethyl-Dewar benzene, 7641-77-2; 1,2,4,5-tetramethoxybenzene, 2441-46-5; 1,2,4-trimethoxybenzene, 135-77-3; 1,4-dimethoxybenzene, 150-78-7; 1,3,5-trimethoxybenzene, 621-23-8.

Temperature-Programmed Desorption Study of H_2 - D_2 Exchange on Pt(111) and the **Role of Subsurface Sites**

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The adsorption of H_2 and D_2 has been studied on Pt(111) by temperature-programmed desorption. Exposures of at least 1000 Langmuir are required to saturate the surface. Below 120 K there is no exchange between $H_2(g)$ (or $D_2(g)$) and D(a)(or H(a)) on a fully saturated surface. Above 120 K, isotope exchange occurs readily with an activation energy of $1.1 \pm$ 0.1 kcal mol⁻¹. When the substrate is dosed at temperatures below 250 K the desorption of D_2 is complete at temperatures significantly below those for H₂ and HD irrespective of the order of adsorption. This isotope effect is attributed to the preferential accommodation of H into the near-surface region of Pt. There is no isotope effect in desorption after dosing above 250 K. This is interpreted in terms of surface-subsurface exchange (equilibration) during dosing. Within the framework of this model, the activation energy for recombination involving at least one subsurface H or D atom is 1.6 ± 0.1 kcal mol⁻¹.

Introduction

There is growing evidence for the formation of significant amounts of subsurface hydrogen during adsorption and desorption of H_2 on group VIII (groups 8-10)¹⁶ transition metals (other than Pd which is well-known to take up large quantities of hydrogen). Recently, Yates and co-workers¹ have reported the subsurface penetration of hydrogen isotopes into the (0001) surface of Ru. In temperature-programmed desorption (TPD) they observed that the high-temperature sides of the TPD curves for each of the hydrogen isotopes were clearly different. This difference was attributed to the preferential accommodation of H atoms into a subsurface site.

The adsorption of hydrogen in sites beneath the surface has also been suggested on Cu(100), Cu(111), polycrystalline Ni, Ni(111), and Pd(110) by Comsa and co-workers²⁻⁶ on the basis of the velocity distributions measured for desorbing H_2 and D_2 .

Comsa concluded that the "fast" velocity distribution measured was attributable to an elevated potential energy region that existed beneath the surface of the metal.

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