J. Am. Chem. Soc. 1983, 105, 27-31

Electrochemical Investigation of the Energetics of Particulate Titanium Dioxide Photocatalysts. The Methyl Viologen–Acetate System

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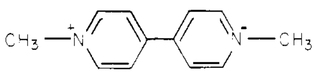
Received June 14, 1982

Abstract: Addition of methyl viologen (MV^{2+}) enhances the anodic currents observed for TiO_2 suspensions under illumination by trapping of photogenerated electrons with formation of $MV^{+}\cdot$. The magnitude of the photocurrent depends upon the relative location of the semiconductor Fermi level and E_{redox} of the $MV^{2+}/MV^{+}\cdot$ couple. The location of the Fermi level in the anatase powders was estimated as -0.05 V vs. NHE (pH 0) based on the observed variation of photocurrent with pH. The shift in the quasi-Fermi level with light intensity is also discussed.

Introduction

Particulate suspensions and colloidal dispersions of TiO_2 and other semiconductors have been shown to be photocatalysts for a number of reactions.[1-6] These include the photodecomposition of acetic acid, hydrocarbons, and numerous other reactions. Recent reports have described the splitting of water (to H_2 and O_2) on suitably prepared TiO_2 colloids.[7] Most studies involving these materials have been concerned with product formation or rate of removal of substrate under irradiation rather than investigations of the energetics, kinetics, and mechanisms of the processes at the semiconductor surface.

Recent papers from this laboratory have described an electrochemical method of probing the behavior of these particles by collection of photogenerated charge (either on the particles or in products formed in solution) on an inert collector electrode immersed in the irradiated suspension.[8-10] These studies have supported the model in which the semiconductor particles are analogous to single crystal semiconductor electrodes. That is, upon illumination, electron–hole (e^-h^+) pairs are formed at the surface of the particle. Indeed, electrochemical experiments have shown that electrons accumulated on the surface can be collected at an inert electrode to produce current. Unfortunately, the physical nature of the particles prevents investigation of the doping levels and flat band potentials, e.g., by the conductance or impedance measurements (Mott Schottky plots) which have been useful for single crystal semiconductor electrodes.[11] Recently, we reported that conduction band electrons on TiO_2 particles could be trapped by electron acceptors (Fe^{3+}, Cu^{2+}), decreasing the extent of e^-h^+ recombination.[10] This latter process is significant in particles of these dimensions, as a space charge layer of dimensions sufficient to separate the e^-h^+ pair is absent. We have now utilized this phenomenon to explore the energetics of semiconductor particles which govern their fundamental behavior. Specifically, we describe herein the use of methyl viologen dication (MV^{2+}) as an electron trapping agent and discuss the effect of light intensity and pH on the Fermi level energy for TiO_2 particle suspensions.



MV^{2+}

Experimental Section

Reagent grade TiO_2 (Matheson, Coleman and Bell, MCB) was used in all experiments. The powder was confirmed to be in the anatase form by X-ray diffraction with a grain diameter of 0.2 μm by scanning electron microscopy (SEM). The suspensions were prepared by addition of 0.25 g of TiO_2 powder to 100 mL of triply distilled H_2O containing 0.1 M KNO_3 (Mallinkrodt) and 1.0 M sodium acetate (Baker). Vigorous stirring of this mixture resulted in a finely divided TiO_2 suspension. SEM of the dried TiO_2 powder after suspension showed the same grain size as the original material. All suspensions were degassed for at least 2 h with prepurified nitrogen prior to photochemical experiments. In the experiment with rutile particles, the rutile structure was obtained by heating the anatase particles in air. The particles which were partially converted to rutile (3–5% conversion) were heated at 800 °C for 16 h. The particles which were completely converted were heated at 1100 °C for 24 h. Structures were determined by X-ray powder diffraction analysis.

Experiments were performed in a 200-mL Pyrex H-cell, equipped with a flat optical window sufficiently large to allow illumination of the entire width of the cell. The collector electrode used was a platinum flag (20 × 20 × 0.25 mm). The counterelectrode was a large platinum flag placed in a compartment separated from the slurry compartment by a fine porosity glass frit. A saturated calomel electrode (SCE) was used as a reference electrode; all redox potential values are reported vs. the SCE. A Corning Model 12 pH meter was used to monitor the pH of the suspension; the pH electrodes were immersed in the suspension through ports in the side of the photocell. The pH of the photocell was adjusted by addition of small amounts of either 1.0 M HNO_3 or 1.0 M NaOH after the current from the previous measurement decayed to zero. As the amounts added between measurements were generally small (<0.1 mL), only a short degassing was necessary after addition. Methyl viologen (Sigma Chemical Co.) was added to the photocell directly before the experiment.

Photocurrents and cyclic voltammograms were recorded with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR Model 175 Universal programmer, and a Houston Instruments Model 2000 X–Y recorder. The illumination source was a 3.0-kW Xe arc lamp (Christie Corp., Los Angeles, CAc, Model VF30KK) operated at 1.6 kW. Light intensity was adjusted with neutral density filters (Muffaletto Optical Co.). A 10-cm water bath was placed between the

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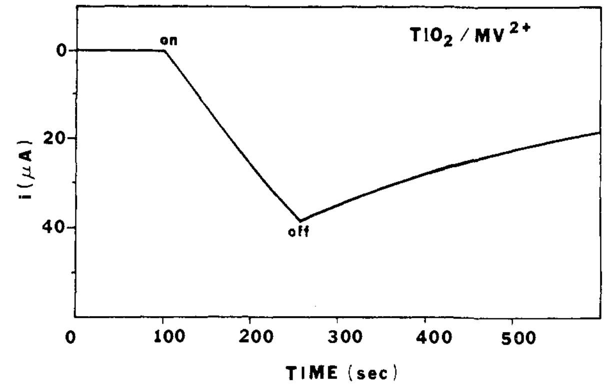


Figure 1. Photocurrent vs. time for stirred TiO_2 suspension photocell containing MV^{2+}. Cell conditions: TiO_2 powder (250 mg); H_2O (100 mL); [NaOAc] = 1.0 M; [KNO_3] = 0.1 M; [MV^{2+}] = 1 mM. Platinum collector electrode at –0.20 V vs. SCE, N_2 purged. Time: 0 to 100 s, preirradiation light level; 100 s, light on; 250 s, light off.

lamp and the cell in all experiments. The part of the total energy output absorbed by the TiO_2 slurry in a Pyrex cell (300–405 cm) was determined by integration of the Xe lamp spectrum and corrected for illumination area. The photon flux thus determined was 6.6×10^{18} photons s^{-1}.

Results

Effects of Methyl Viologen on Photocurrent. As reported previously, when a stirred TiO_2 suspension ($\simeq$2.5 mg/mL) in acetate medium (1.0 M NaOAc, pH $\simeq$8) containing a platinum collector electrode (4 cm^2, held at –0.2 V vs. SCE) was illuminated ($h\nu > Eg \simeq$ 3.2 eV), a small photocurrent was observed.[8,9] This current grew for a short period of time, achieving a maximum of 4 μA in ~1 min. The magnitude of the current was independent of the position and orientation of the collector electrode and decreased to essentially zero if the stirring was stopped. These observations illustrate that the measured current originates from charges on the bulk suspension, *not* from light impinging on the collector electrode itself. The anodic photocurrent results from the production of electron–hole (e^-h^+) pairs followed by depletion of holes by reaction with acetate and collection of electrons at the electrode.[8,9] The current is limited by the accumulation of electrons on the particles which increases the rate of e^-h^+ recombination.

The additon of a substance to the solution that is capable of reacting with the photogenerated electrons to form a reduced product oxidizable at the electrode can significantly increase the photocurrent.[11] Thus the addition of small amounts (~1.0 mM) of methyl viologen dication (MV^{2+}) to stirred TiO_2 suspensions resulted in a large enhancement of the anodic photocurrent (i) produced by these cells, when the collector electrode was held at –0.2 V (Figure 1). Under illumination ($h\nu > Eg$, $\simeq$390 nm) a steadily increasing current was observed, concomitant with the appearance of the blue methyl viologen radical cation ($MV^{+}\cdot$). When the light was removed, the anodic current persisted and decayed slowly to zero as $MV^{+}\cdot$ was oxidized at the electrode. During this decay, the blue color of $MV^{+}\cdot$ diminished; at zero current only colorless MV^{2+} was apparent. Therefore, this behavior is similar to that previously reported for TiO_2 suspensions containing Fe^{3+} and Cu^{2+} ions.[10] Both the rate of photocurrent increase ($\Delta i/\Delta t$) and its decay in the dark were proportional to MV^{2+} concentration. Accurate determination of the $\Delta i/\Delta t$ (initial slope, i.e., linear region for times up to 100 s after onset of irradiation) dependence on [MV^{2+}] at low concentrations (0.01–0.1 mM) was difficult because of the decomposition of small amounts of MV^{2+} under the experimental conditions. However, $\Delta i/\Delta t$ reached a maximum at [MV^{2+}] > 0.5 mM, similar to the behavior observed for TiO_2 suspensions containing Fe^{3+} ion.

The results obtained were independent of the position of the collector electrode within the cell. Moreover, when the stirring was stopped, the observed current immediately returned to zero. These observations indicate that the enhanced photocurrent arises from *bulk* effects, not from light impinging on the collector electrode. Because these suspensions were rather opaque and light did not appear to penetrate very deeply into the cell, TiO_2 particles were probably illuminated only when they passed close to the illuminated cell window.

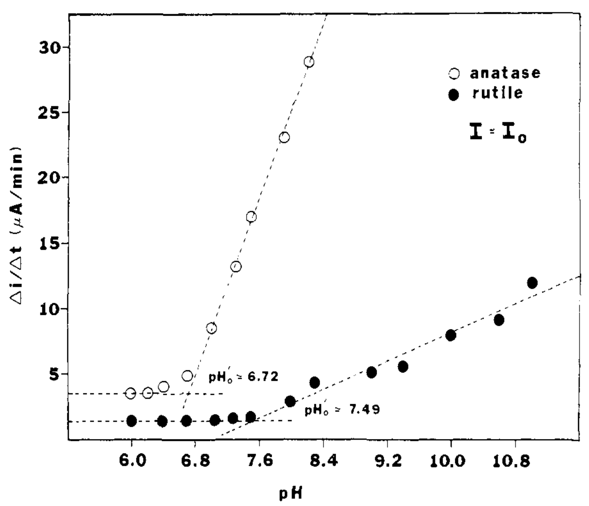


Figure 2. Dependence of rate of the change of photocurrent with time ($\Delta i/\Delta t$) on pH for stirred TiO_2 suspension photocell. Cell conditions: TiO_2 powder (250 mg); H_2O (100 mL); [NaOAc] = 1.0 M; [KNO_3] = 0.1 M; [MV^{2+}] = 1 mM. Platinum collector electrode at –0.20 V vs. SCE, N_2 purged; rutile powder 3–5% converted.

Introduction of air into the suspension resulted in an immediate decay of the observed anodic current, concomitant with the loss of the blue color of $MV^{+}\cdot$. This observation is in accord with the thermodynamically favorable O_2 reduction by $MV^{+}\cdot$. Therefore, N_2 was bubbled through the suspensions during the experiments to exlude air from the photocells.

Effect of pH on Photocurrent. The ability of MV^{2+} to react with photogenerated electrons depends upon the reduction potential of these electrons, which is a function of the location of the Fermi level, E_F, at the surface of the particles. For oxide semiconductors, E_F depends upon the pH of the contacting solution. Indeed, the rate of photocurrent increase during illumination, $\Delta i/\Delta t$, was found to depend on the pH of the TiO_2 suspension containing MV^{2+}. As the pH of the suspension was increased by incremental addition of 1.0 M NaOH solution, $\Delta i/\Delta t$ increased significantly and eventually reached a plateau at very high pH values (pH >13). Most experiments to illustrate pH dependence were performed over a more narrow pH range so that introduction of O_2 (during pH adjustment by addition of acid or base) could be minimized; this resulted in better and more reproducible results. Typical data from one such experiment are depicted in Figure 2. Note that the region in which pH has the greatest effect on $\Delta i/\Delta t$ is fairly linear; generally correlation coefficients of 0.985 or greater were obtained for all such plots (vide infra). The observed photocurrent decreased monotonically with decreasing pH until a baseline current was achieved. This baseline current was identical with that observed for TiO_2 alone; i.e., at or below this pH, termed pH_0, no MV^{2+} reduction occurs. While the precise determination of this point was difficult because the data show some curvature in the region close to the baseline, extrapolation of the linear region of this curve to the baseline current could be performed with a precision of ±0.05 pH unit. This procedure yields a value of pH_0 = 6.72. Similar experiments were also performed with rutile powder. As has often been observed for TiO_2 photocatalysts, the rate of reaction was slower than for anatase. Specifically, a pH_0 value of 7.49 was obtained for the powder which had been partially converted to rutile (3–5%), along with diminished baseline currents. Powder which had been completely converted to rutile yielded no photoreduction of MV^{2+} and negligible baseline photocurrents at any pH.

Light Intensity Effects. The light intensity of the 1600-W Xe lamp was varied by placing neutral density filters between the cell (containing TiO_2 and 1 mM MV^{2+}) and the lamp. Light intensity had a significant effect on the observed photocurrent;

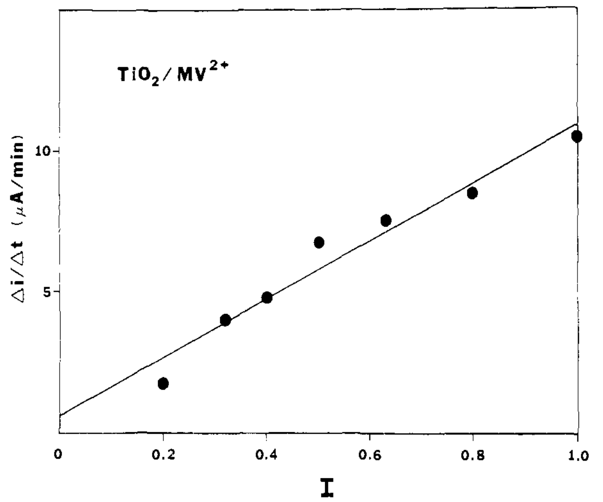


Figure 3. Dependence of rate of the change of photocurrent with time ($\Delta i/\Delta t$) on normalized intensity for stirred TiO_2 (anatase) suspension photocells containing MV^{2+}. Cell conditions: TiO_2 powder (250 mg); H_2O (100 mL); [NaOAc] = 1.0 M; [KNO_3] = 0.1 M; [MV^{2+}] = 1 mM. Platinum collector electrode at −0.20 V vs. SCE, N_2 purged.

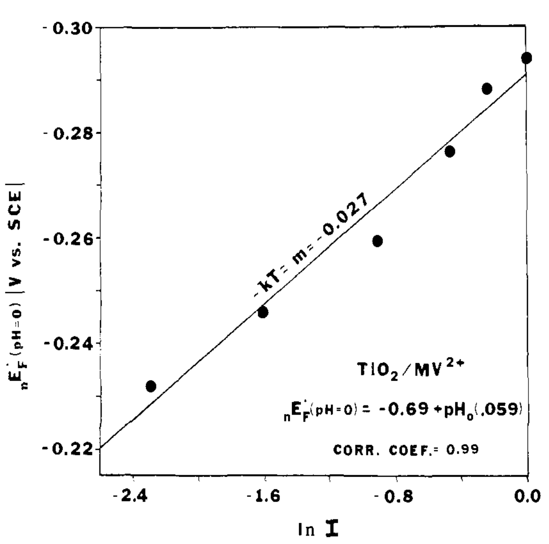


Figure 4. Variation in $_nE^*_F$ (pH 0) with ln (normalized intensity) for stirred TiO_2 suspension photocells containing MV^{2+}. Cell conditions: TiO_2 (anatase) powder (250 mg); H_2O (100 mL); [NaOAc] = 1.0 M; [KNO_3] = 0.1 M; [MV^{2+}] = 1 mM. Platinum collector electrode at −0.20 V vs. SCE, N_2 purged.

a plot of $\Delta i/\Delta t$ vs. normalized intensity (I) was fairly linear (Figure 3). Light intensity also had an effect on the pH dependence of the photocurrent for these suspensions. In addition to the expected smaller photocurrents for diminished intensities, extrapolation of the linear portion of $\Delta i/\Delta t$ vs. pH curves to the baseline current for various light intensities gave different pH_0' values, with pH_0' shifting to more positive values with decreasing light intensities. When values of pH_0' thus determined were plotted vs. ln I, a straight line with a slope of −27 mV was obtained (Figure 4).

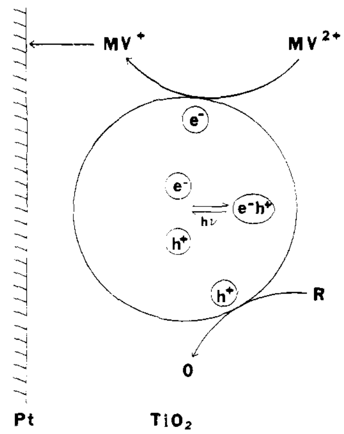
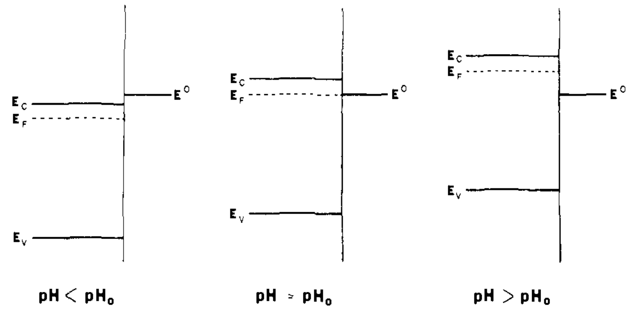


Figure 5. Schematic representation of the particle and collector electrode reactions occurring in TiO_2 suspension photocells: R = acetate, O = CH_4, CH_2H_2, CO_2.

Scheme I

$TiO_2 + h\nu \rightarrow TiO_2(e^-h^+)$	
$TiO_2(e^-h^+) + HOAc \rightarrow TiO_2(e^-) + CO_2 + CH_4$	(hole reaction)
$TiO_2(e^-h^+) \rightarrow TiO_2$	(recombination)
$TiO_2(e^-) + MV^{2+} \rightarrow TiO_2 + MV^{+\cdot}$	(electron trapping)
$MV^{+\cdot} \rightarrow MV^{2+} + e^-$	(at collector electrode)

Scheme II



Discussion

Semiconductor particles such as TiO_2 behave as short-circuited photoelectrochemical cells, where both cathodic and anodic reactions occur on the same particle. In these experiments, anodic photocurrent from illuminated TiO_2 suspensions arises from transfer of photogenerated electrons on the particle to the collector electrode or from oxidation of photoreduced species at the collector electrode. The anodic currents that result from electrons trapped on the particle (e.g., as Ti^{3+} center)[12] are rather small, probably because the accumulation of electronic charge on the particle increases the rate of e^-h^+ recombination. The role of MV^{2+}, similar to that described for Fe^{3+} and Cu^{2+} in our previous report, is the removal of electrons from e^-h^+ recombination sites with the production of an oxidizable species, $MV^{+\cdot}$. This reduction occurs if the condition exists that the potential of the photogenerated electrons in TiO_2 is negative of the redox potential of the $MV^{2+}/MV^{+\cdot}$ couple (−0.69 V vs. SCE). The reduced form, $MV^{+\cdot}$, is then oxidized at the collector electrode, which is held at a potential positive of the redox potential of the couple (Figure 5). The process can be represented by Scheme I.

The role of acetate ion is rapid removal of photogenerated holes in an irreversible fashion.[13,14] The presence of acetate essentially precludes oxidation of H_2O,[15] thus preventing formation of O_2 which would be deleterious to $MV^{+\cdot}$ generation. The presence of a reactive hole scavenger also prevents "short circuiting" of the particle by MV^{2+} (i.e., by the reaction $MV^{+\cdot} + h^+ \rightarrow MV^{2+}$), thus allowing the observation of a *net* photocurrent.

pH Effects. Since the redox potential of the $MV^{2+}/MV^{+\cdot}$ couple is pH independent, the observation of a pH effect on the photocurrent produced by these cells must be related to changes within or on the surface of the TiO_2. The most likely source of this effect is shifting of the Fermi level energy, E_F, with pH. For TiO_2 the position of the Fermi level, as determined by the flat

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band potential, V_{fb}, shifts with pH because the adsorption of excess H^+ or OH^- produces a potential drop across the Helmholtz layer.[16-18] This shift, given by

$$\Delta V_{fb} = -0.059 \text{ pH} \qquad (1)$$

$$E_F = E_F \text{ (pH 0)} - 0.059 \text{ pH (at 25 °C)} \qquad (2)$$

results in the electron having a greater reducing power (i.e., a more negative electrode potential) as the pH increases. Since the redox potential for the $MV^{2+}/MV^{+\cdot}$ couple equivalent to an energy level, E_{redox}, is independent of pH, E_F will shift with respect to E_{redox} with changes in solution pH, as shown in Scheme II. As a first approximation, when E_F is below E_{redox}, reduction of MV^{2+} by photogenerated electrons does not occur. As E_F increases in energy above E_{redox} (i.e., as V_{fb} becomes more negative with respect to the standard potential of the redox couple), the driving force or overpotential for the reduction increases. According to usual electrochemical and heterogeneous electron transfer concepts,[19-21] this increases the rate of the reaction. The results of the variation on reduction rate (represented by the slope $\Delta i/\Delta t$) with pH generally agree with this model. The pH value of the extrapolated increase of $\Delta i/\Delta t$ with pH to the background level yields the pH value where $E_F = E_{redox}$, pH_0 (Figure 2). Thus from eq 2, and taking E_{redox} to be the standard potential of the $MV^{2+/+\cdot}$ couple (−0.69 V vs. SCE), we obtain

$$E_F \text{ (pH 0)} = -0.69 + 0.059 \text{ pH}_0 \qquad (3)$$

From the pH_0 value of 6.72 at maximum lamp intensity, we obtain a value of E_F (pH 0) equivalent to a potential of −0.29 V vs. SCE (or −0.05 V vs. NHE).

Gratzel and co-workers[22] have recently described an analogous method involving the spectroscopic determination of the $MV^{2+}/MV^{+\cdot}$ ratio at colloidal TiO_2 and estimated an electron energy at −0.38 V vs. SCE. The difference between these values might be attributed to differences in light intensity used as discussed below, to differences in the nature of the material, or to the slightly different method of estimating E_{redox}.

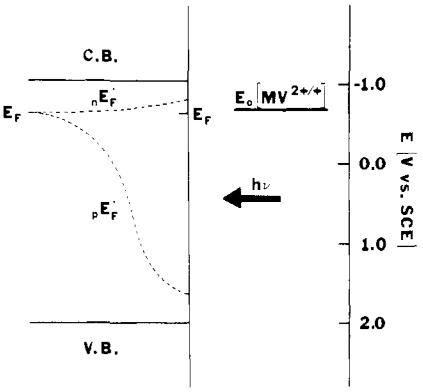
The pH_0 value for partially converted (3–5%) rutile powder, 7.49, corresponds to −0.25 V vs. SCE (−0.01 V vs. NHE). This positive shift is consistent with the smaller bandgap of rutile present in the partially converted powder. The fact that 100% rutile powder yields no photoreduction of MV^{2+} is consistent with previous results from this laboratory which indicated that rutile was 100-fold less efficient in the photo-Kolbe oxidation of acetate than anatase.

Intensity Effects. The observation of a linear dependence of $\Delta i/\Delta t$ on light intensity suggests that (e^-h^+) recombination is not significant under these conditions. Derivations from linearity at higher intensities are generally thought to arise from significant (e^-h^+) recombination.[23,24] In the case presented here, a linear relationship is not surprising as $\Delta i/\Delta t$ is measured near the beginning of illumination, where a large excess of MV^{2+} is present and little buildup of electrons or holes in the semiconductor has occurred. Under these conditions, the first term in the expression

$$\text{rate of electron transfer to } MV^{2+} = k[e^-][MV^{2+}] - k_r[e^-][h^+] \qquad (4)$$

dominates. The linear dependence arises since the formation of $[e^-]$ is directly proportional to light intensity.

Scheme III



The energy of the photogenerated electrons is represented by the Fermi level energy, E_F, associated with n-TiO_2. The Fermi level is fixed at equilibrium in the dark with respect to the conduction band edge, E_C; the difference $E_F - E_C$ is determined by the doping density of the n-TiO_2. However, under illumination of the semiconductor suface, the energy of the electron is represented by the quasi-Fermi level (see Scheme III).[24,25] The energy of this level, represented by $_nE^*_F$ depends on the density of carriers initially present, n_0, and the excess carriers generated by the light, Δn^*, as shown in eq 5. For moderately doped n-type semiconductors, $n_0 \gg p_0$, and illumination usually results in relatively small differences between $_nE^*_F$ and E_F. However, for TiO_2 powder, which is not reduced or purposely doped, n_0 is small and probably dominated by impurities in the material. The magnitude of Δn^* depends upon the light intensity (I), recombination rate, and the rate of electron transfer to a solution species. The increase of Δn^* with intensity results in a shift of $_nE^*_F$ to higher values (corresponding to more negative potentials) as the light intensity reaching the semiconductor surface increases. If one assumes that Δn^* is proportional to light intensity and $(\Delta n^*/n_0) \gg 1$, then

$$_nE^*_F = E_F + kT \ln [1 + (\Delta n^*/n_0)] \qquad (5)$$

$$_nE^*_F = \text{constant} + kT \ln (I) \qquad (6)$$

A plot of $_nE^*_F$ (represented as potential) vs. ln (I) should have a slope equal to $-kT$ (at 25 °C, 0.0257 V). This shift of the Fermi level, made manifest in the different pH_0' values found for different light intensities, is shown in Figure 4 and is in agreement with the above prediction. Conceptually different pH_0' values arise because the Fermi level must be raised (i.e., the pH increased) at lower intensities for MV^{2+} reduction to occur. Alternatively, at higher light intensities the electron concentration at the semiconductor surface increases, so that the potential for reduction becomes more negative. Electrophoretic measurements[26] performed on TiO_2 suggested that the electronic buildup of charge on the TiO_2 particles under illumination from the same light source as was employed in the present studies was 1.5 μC cm^{-2} when no electron scavenger was present in solution. This corresponds to approximately 10^{19} electrons cm^{-2}. Since the doping level of the powder is probably $<10^{15}$ cm^{-2}, the condition $\Delta n^*/n_0 \gg 1$ appears reasonable. The concentration of electrons would be lower in the presence of a reducible species such as MV^{2+}. However, the observation of a linear relationship between ln (I) and $_nE^*_F$ with a slope of $-kT$ suggests that light intensity does indeed dominate in determining $\Delta n^*/n_0$. More importantly, these results suggest that light intensity must also be considered in determination of energy levels of particulate semiconductors, particularly materials with low doping levels.

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Conclusions

We have demonstrated that markedly enhanced photocurrents can be obtained from illuminated TiO_2 suspensions when methyl viologen dication is present in the suspension. The observation of this behavior is consistent with electron trapping by MV^{2+}, thus preventing deleterious (e^-h^+) recombination. This behavior has led to insight into the energetics of TiO_2 particles in that shifting of Fermi level with pH can be observed, and the location of the Fermi and quasi-Fermi levels can be estimated. Methyl viologen is useful in these studies as it is soluble over a wide range of pH values, unlike previously reported electron trapping agents Fe^{3+} and Cu^{2+} which form insoluble compounds in basic solutions. These measurements emphasize the utility of electrochemical techniques in characterizing heterogeneous photocatalysts. In agreement with the photochemical results of Gratzel et al.,[22] photogenerated electrons in anatase preparations are sufficiently negative to cause proton reduction.

Acknowledgment. The support of this research by the Robert A. Welch Foundation and the National Science Foundation (CHE 8000682) is gratefully acknowledged.

Registry No. TiO_2, 13463-67-7; NaOAc, 127-09-3; MV^{2+}, 4685-14-7.

Theoretical Models for Solvation and Catalysis in Carbonyl Addition

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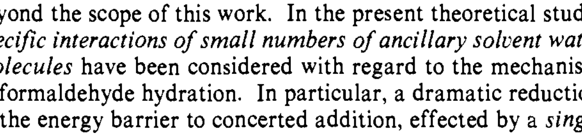
Abstract: Alternative modes of catalysis of formaldehyde hydration by a single ancillary water molecule are investigated by ab initio calculations at the STO-3G level. A cyclic transition state ($FW2^*$) involving formaldehyde with two molecules of water is characterized and is only 0.8 kcal mol^{-1} higher in energy than the isolated reactants. The results indicate that gas-phase formaldehyde hydration probably proceeds via $FW2^*$ in a concerted mechanism with a Gibbs free energy of activation of 27 kcal mol^{-1}. Addition of a water dimer to formaldehyde via $FW2^*$ is predicted to occur in water with a Gibbs free energy of activation of 16 kcal mol^{-1}, in agreement with experiment. Empirical extrapolation to the liquid phase of entropies of activation calculated for reaction of one or two waters in the gas phase suggests that a mechanism involving three water molecules would be consistent with experiments for dioxan solution. Specific solvation by four water molecules is predicted to stablize the zwitterionic adduct $H_2O^+CH_2O^-$ (an unbound state in the gas phase) by 111 kcal mol^{-1} relative to $H_2O^+CH_2O^-$ and $4H_2O$ or by 37 kcal mol^{-1} relative to $(H_2O)_3$ and $CH_2O{\cdot}2H_2O$. Thus a stepwise mechanism for formaldehyde hydration also may be feasible, although the energy barrier to formation of a solvated zwitterionic intermediate has not yet been calculated.

Nucleophilic addition of water to formaldehyde may be envisaged as occurring either by stepwise or concerted mechanisms to yield methanediol. If the processes (see Scheme I) of heavy-atom reorganization (HAR), i.e., C—O σ-bond making and C=O π-bond breaking, are accomplished in an initial step followed by the necessary proton transfer (PT) in a second step, then a zwitterionic intermediate $T^{\pm}$ is involved. However, a recent theoretical study[2] suggests that the structure corresponding to $T^{\pm}$ does not exist as a bound chemical species in the gas phase. In this case, PT cannot occur before $T^{\pm}$ dissociates to reactants, and thus the stepwise mechanism is not feasible. Instead, the HAR and PT processes must occur concertedly: the mechanism is enforced[3] as concerted.

In aqueous solution the situation differs from this simple gas-phase scheme as the result of interactions between the reacting system and its environment. Within a transition-state theoretical framework, the effect of solvation upon the mechanism of carbonyl addition may be studied by consideration of the environmental influences acting upon the reactant, intermediate, product, and transition-state structures involved in the gas-phase mechanistic scheme. However, the possible existence of new intermediate or transition-state structures involving solvent molecules, which may open new channels for reaction, ought also to be admitted. A complete treatment of solvation effects upon mechanism should include the influence not only of the cybotactic region of the solvent, whose structure is modified by the presence of the solute, but also of the bulk solvent. Such a project is, however, currently beyond the scope of this work. In the present theoretical study, *specific interactions of small numbers of ancillary solvent water molecules* have been considered with regard to the mechanism of formaldehyde hydration. In particular, a dramatic reduction of the energy barrier to concerted addition, effected by a *single* ancillary water molecule, and stabilization of the zwitterionic intermediate $T^{\pm}$ by four or six solvent water molecules, are reported herein.

Scheme I



Computational Methods and Results

Ab initio SCF-MO calculations with the STO-3G basis[4] were employed throughout this work. Preliminary calculations were

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0002-7863/83/1505-0031$01.50/0