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ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · OCTOBER 1983

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Light-Induced Electron Transfer in Colloidal Semiconductor Dispersions: Single vs. Dielectronic Reduction of Acceptors by Conduction-Band Electrons

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Contribution from the Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland. Received March 28, 1983

Abstract: Colloidal particles of TiO_2 (anatase, 50-Å radius) were produced via hydrolysis of TiCl_4 in aqueous solutions and characterized by electron microscopy, light scattering, and absorption and electrophoresis techniques. Laser photolysis and continuous illumination techniques were applied to investigate the reaction of conduction-band electrons (e^-_{CB}) with various acceptor molecules. The rate of reduction of methyl viologen is diffusion controlled in alkaline solution (pH > 10) but becomes limited by interfacial electron transfer at lower pH. No diffusion limit is observed with the functionalized viologen $\text{C}_{14}\text{MV}^{2+}$ which is adsorbed at the surface of the TiO_2 particles. Preirradiated samples produce hydrated electrons owing to photoionization of C_{14}MV^+ . A cofacial dimeric viologen (DV^{4+}) is reduced by e^-_{CB} via a simultaneous two-electron-transfer step. In contrast, $\text{Rh}(\text{bpy})_3^{3+}$ undergoes one-electron reduction to $\text{Rh}(\text{bpy})_3^{2+}$ by e^-_{CB} . Subsequent dark reactions produce $\text{Rh}(\text{bpy})_2^+$. Heterogeneous rate constants and transfer coefficients for these interfacial redox processes are derived and implications for artificial photosynthetic systems discussed.

Introduction

In the field of artificial photosynthesis, attempts are presently made to design functional molecular assemblies that achieve the task of fuel formation by visible light. Colloidal semiconductors exhibit several advantageous features that make them attractive candidates as light-harvesting units in such devices. These particles combine a number of desirable properties, such as high extinction coefficients, fast carrier diffusion to the interface, and suitable positioning of their valence and conduction band, to accomplish high efficiencies in the light-energy-conversion process. Particularly attractive is, furthermore, the possibility of modifying the surface of the semiconductor particle by chemisorption, chemical derivatization, and/or catalyst deposition assisting light-induced charge separation and subsequent fuel-generating dark reaction.

Following our initial water cleavage investigations with colloidal dispersions of TiO_2 ¹ and CdS ,² we carried out laser photolysis and luminescence³ experiments to probe light-induced electron-hole separation and interfacial electron-transfer events involving ultrafine semiconductor particles.^{4,5} Recently, a number of related investigations have appeared in the literature. Apart from flash photolysis⁶⁻⁸ and luminescence^{3,9} studies, the elegant work of Brus¹⁰ and Hester¹¹ using resonance Raman technique to identify intermediates should be mentioned. The preparation of TiO_2 sols in organic solvents and investigation of electron and hole transfer to species in solution have also been recently reported.¹²

The present report deals with interfacial electron transfer involving colloidal TiO_2 dispersions in aqueous medium. An important aspect of the work is related to the achievement of

multielectron transfer from the conduction band to suitable acceptors present at the surface of the semiconductor particle.

Experimental Section

Preparation and Characterization of Colloidal TiO_2 . TiCl_4 (Fluka purissimum) was further purified by vacuum distillation (40 °C, ca. 25 torr) until a colorless liquid was obtained. The purified material (5 g) was slowly added to water at 0 °C. The final pH of the solution was about 0.5. The solution was subsequently dialyzed until the pH reached a value of ca. 3. Precise determination of the TiO_2 content after dialysis was carried out as described previously.⁵ At pH > 3 poly(vinyl alcohol) (PVA, 0.1%) was used to stabilize the colloidal particles. Commercial PVA (Mowiol, Hoechst, W. Germany) was pretreated by UV light (10–98) to remove impurities.⁵ This method of preparation has the advantage over the one previously employed,^{1,3} i.e., hydrolysis of titanium tetraisopropoxide in that it avoids organic compounds that subsequently would have to be removed from the system.

Transmission electron microscopy applied to TiO_2 sols obtained in this manner showed that the particles have a roughly spherical shape and are polydisperse. Direct measurement of the size of all the particles and averaging yielded a mean particle radius of 46 Å. These aggregates consist of both amorphous phase and anatase as shown by application of dark field electron microscopy and electron diffraction techniques.

Independent confirmation of the particle dimensions was obtained by applying a quasi-elastic light-scattering technique to aqueous dispersions of the TiO_2 sol.¹³ The temporal decay of the correlation function was evaluated by computer analysis. Optimal fit was obtained for a diffusion coefficient $D = 4.43 \times 10^{-7} \text{ cm}^2/\text{s}$ of the particles. Application of the Stokes-Einstein equation yields for the hydrodynamic radius a mean value of 56 Å. Data analysis below will be based on an average radius of 50 Å for the colloidal TiO_2 particles.

The point of zero ζ potential (ZZP) of the particles was determined by electrophoretic measurements using a Rank Bros. Mark II instrument equipped with an He-Ne laser.¹ Electrophoretic mobilities are plotted as a function of pH in Figure 1. The intersection of the curve with the abscissa corresponds to ZZP = 4.7. This value is higher than that observed for the TiO_2 colloid prepared from titanium tetraisopropoxide (ZZP = 3.2) but still lower than that reported in the literature¹⁴ for very pure anatase (ZZP \approx 6). Presumably, the presence of Cl^- on the particle surface produces a decrease in the ZZP with respect to samples that are free of anionic impurities.

The optical absorption spectrum of the TiO_2 sol is shown in Figure 2. The absorption rises sharply toward the UV below 380–390 nm. The onset agrees well with the 3.2-eV band gap of anatase and amorphous

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(10) R. Rossetti, S. M. Beck, and L. E. Brus, *J. Am. Chem. Soc.*, **104**, 7321 (1982).

(11) K. Metcalfe and R. E. Hester, *J. Chem. Soc., Chem. Commun.*, 133 (1983).

(12) M. A. Fox, B. Lindig, and C. C. Chen, *J. Am. Chem. Soc.*, **104**, 5828 (1982).

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(14) (a) H. P. Boehm, *Discuss. Faraday Soc.*, **52**, 264 (1971); (b) G. D. Parfitt, *Prog. Surf. Membr. Sci.*, **11**, 181 (1976); (c) Dunn et al. report ZZP = 5.35 for TiO_2 (anatase) particles; c.f. W. W. Dunn; Y. Aikawa, and A. J. Bard, *J. Am. Chem. Soc.*, **103**, 3456 (1981).

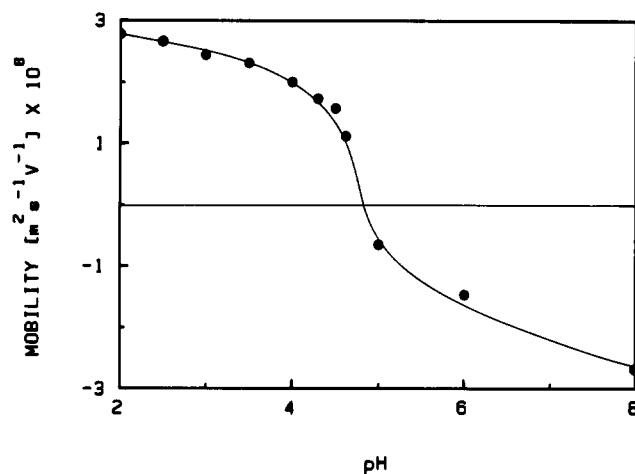


Figure 1. Electrophoretic measurements of the mobility of colloidal TiO_2 particles as a function of pH ($[\text{TiO}_2] = 20 \text{ mg/L}$, ionic strength $= 2 \times 10^{-1} \text{ M}$).

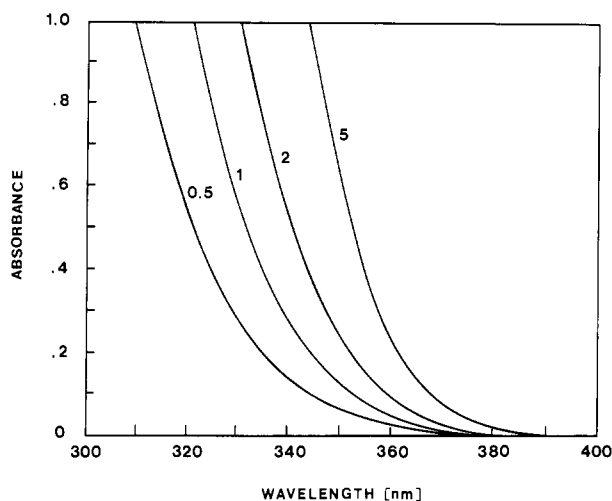
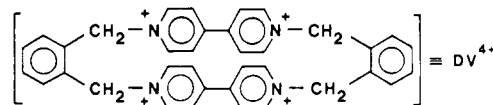


Figure 2. UV absorption spectra of TiO_2 sols: 0.5 g of TiO_2/L , 1 g of TiO_2/L , 2 g of TiO_2/L , 5 g of TiO_2/L . These curves represent true absorption data. Solutions were transparent, scattering effects being eliminated by use of an integrating sphere. Lambert-Beers law is observed within this concentration range and the extinction coefficient at $\lambda 347 \text{ nm}$ evaluated as $\epsilon = 0.785 \text{ g}^{-1} \text{ L cm}^{-1}$, optical pathlength 2 mm.

titania.¹⁵ (The optical absorption coefficient near the band edge may be expressed¹⁶ by $\alpha = A(h\nu - E_g)^2/h\nu$ for an indirect band gap material such as TiO_2 .¹⁷)

Apparatus. Laser photolysis experiments employed a frequency-doubled JK 2000 ruby laser combined with fast kinetic spectroscopy technique to detect transient species.¹⁸ Continuous illumination was carried out with an XBO 450-W Xe lamp (Osram) equipped with a 15-cm water jacket to remove IR radiation. UV-visible absorption spectra were recorded on a Cary 219 (Varian) spectrophotometer. The absorption spectrum of the TiO_2 sol was measured with a Perkin-Elmer/Hitachi 340 spectrophotometer using an integrating sphere attachment to correct for light scattering. A Philips E.M. 300 instrument was used to perform transmission electron microscopy. The equipment employed for quasi-elastic light scattering has been previously described.⁵

Materials. *N*-Tetradecyl-*N'*-methyl-4,4'-bipyridinium ($\text{C}_{14}\text{MV}^{2+}$) was synthesized by Dr. A. M. Braun in our laboratory.¹⁹ The *o*-xylene bridged viologen dimer was a kind gift of Professor Sigfried Hünig, Institute of Organic Chemistry, University of Würzburg, W. Germany. $\text{Rh}(\text{bpy})_3^{3+}$ trichloride salt was synthesized in our laboratory by Dr. K.



Kalyanasundaram. Deionized water was refluxed over KMnO_4 and subsequently distilled three times. All other compounds were at least reagent grade and used as supplied by the vendor.

Results and Discussion

i. Dynamics of Light-Induced Reduction of Surfactant and Simple Viologen by $e^-_{\text{CB}}(\text{TiO}_2)$. In two previous investigations^{3,4} we examined the dynamics of methyl viologen (MV^{2+}) reduction by conduction-band electrons (e^-_{CB}) of colloidal TiO_2 .



The kinetics of this reaction were found to be controlled by the diffusion of MV^{2+} to the particle surface as well as the rate of interfacial electron transfer. The pseudo-first-order rate constant k_1 (s^{-1}) was found to increase linearly with MV^{2+} concentration, $k_1 = k_2[\text{MV}^{2+}]$, where k_2 [$\text{M}^{-1} \text{s}^{-1}$] is the second-order rate constant for MV^{2+} formation. The value of the latter rate constant, expressed in units of $\text{cm}^3 \text{s}^{-1}$, $k_2' = k_2 \times 1000/N_A$ (N_A = Avogadro's number), was shown⁴ to be given by

$$\frac{1}{k_2'} = \frac{1}{4\pi r^2} \left(\frac{1}{k_{\text{et}}} + \frac{r}{D} \right) \quad (2)$$

where r is the reaction radius corresponding to the sum of the radii of semiconductor particle and relay and D is the sum of their respective diffusion coefficients. The parameter k_{et} (cm/s) is the rate constant for interfacial electron transfer²⁰ which changes with overvoltage ($E - E^\circ$) according to the Tafel equation ($T = 298 \text{ K}$)

$$k_{\text{et}} = k_{\text{et}}^0 \exp\left(-\frac{\alpha}{0.059}(E - E^\circ)\right) \quad (3)$$

where α is the transfer coefficient and k_{et}^0 the value of the rate constant for $E - E^\circ = 0$. The overvoltage can be expressed in terms of the standard redox potential of the $\text{MV}^{2+}/^+$ couple and the potential of the TiO_2 conduction band.

$$E - E^\circ = E_{\text{CB}}(\text{TiO}_2) - E^\circ(\text{MV}^{2+}/^+) \quad (4)$$

where $E_{\text{CB}}(\text{TiO}_2)$ depends on pH according to²¹

$$E_{\text{CB}} = -0.11 - 0.059(\text{pH}) \quad (5)$$

From eq 2 to 5 one obtains finally

$$\frac{1}{k_2'} = \frac{1}{4\pi r^2} \left(\frac{1}{k_{\text{et}}^0 \exp[\alpha(\text{pH}) - \alpha(5.54)]} \right) + \frac{r}{D} \quad (6)$$

In the following section, we shall apply eq 6 to analyze MV^{2+} reduction by $e^-_{\text{CB}}(\text{TiO}_2)$. We attempt to obtain information on the effect of TiO_2 particle preparation (i.e., hydrolysis of TiCl_4 viz. titanium isopropoxide) on the kinetic parameters k_{et}^0 and α . Furthermore, the behavior of the surfactant viologen $\text{C}_{14}\text{MV}^{2+}$ is analyzed.

Figure 3 shows data obtained from the laser photolysis of colloidal TiO_2 (500 mg/L) in the presence of $2 \times 10^{-4} \text{ M}$ viologen. The logarithm of the observed rate constant (k_1) for the reduction of viologens MV^{2+} and $\text{C}_{14}\text{MV}^{2+}$ is plotted as a function of solution pH. The k_1 values were determined by monitoring the growth

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(19) M.-P. Pileni, A. M. Braun, and M. Grätzel, *Photochem. Photobiol.*, **31**, 423 (1980).

(20) The rate parameter k_{et} is defined as the interfacial electron flux due to MV^{2+} reduction (flux $= d\text{M}(\text{MV}^+)/S \text{ dt}$) at unit bulk concentration of MV^{2+} (mol/cm^3): $k_{\text{et}} = \text{flux}/[\text{MV}^{2+}]$ and is therefore expressed in units of cm/s .

(21) The conduction-band potential (Fermi level) of the TiO_2 particles employed in this study was determined as $E_{\text{CB}} = -0.11 - 0.059(\times \text{pH})$ against NHE by using the same method as described in ref 3. This is slightly more positive than the value $E_{\text{CB}} = -0.13 - 0.059(\times \text{pH})$ derived for TiO_2 particles produced via hydrolysis of titanium isopropoxide.³ Note that a similar value, i.e., $E_{\text{CB}} = -0.05 - 0.059(\text{pH})$, has been estimated recently for the Fermi level of anatase particles from photoelectrochemical measurements with slurry electrodes [M. D. Ward, J. R. White, and A. J. Bard, *J. Am. Chem. Soc.*, **105**, 27 (1983)].

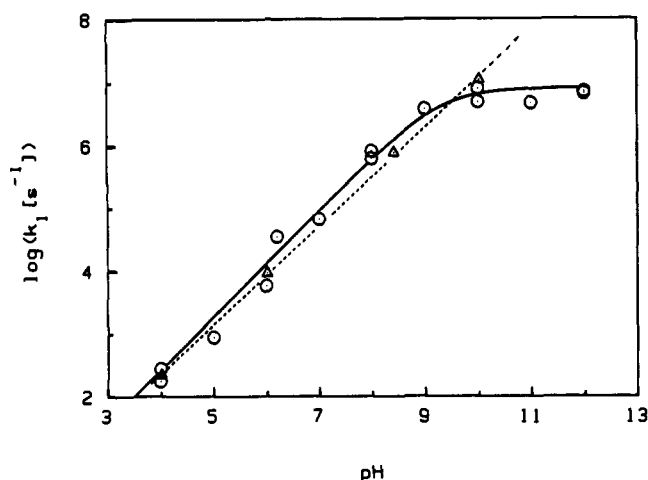


Figure 3. Reduction of MV^{2+} (\circ , 2×10^{-4} M) and $C_{14}MV^{2+}$ (Δ , 2×10^{-4} M) by $e^-_{CB}(TiO_2)$. The observed rate constant for MV^{2+} and $C_{14}MV^{2+}$ formation is plotted as a function of pH. The solid line represents a computer fit for MV^{2+} reduction using $\alpha = 0.84$ and $k_{et}^0 = 10^{-2}$ cm/s. A dashed line with a slope of 0.78 was drawn through the $C_{14}MV^{2+}$ points. $[TiO_2] = 0.5$ g/L protected by 1 g/L PVA.

of the 602-nm absorption of the viologen cation radicals after excitation of the TiO_2 colloid by the 20-ns laser pulse. For $C_{14}MV^{2+}$ a precisely linear relation is obtained between $\log k_1$ and pH over a domain of at least 7 units,²² the slope of the line being 0.78. A straight line with similar slope is also obtained when MV^{2+} is used as an electron acceptor. However, in this case linearity of the $\log k_1$ (pH) function is restricted to pH < 10. At higher alkalinity the curve bends sharply, k_1 attaining a limit of $\sim 10^7$ s⁻¹. Another noteworthy difference between the kinetic behavior of MV^{2+} and $C_{14}MV^{2+}$ concerns the effect of concentration on k_1 . While k_1 increases with MV^{2+} concentration, it is not affected when $[C_{14}MV^{2+}]$ is varied from 2×10^{-4} to 10^{-3} M. The solid line in Figure 3 is a computer plot of eq 6 using the experimentally available parameters²³ $r = 55$ Å and $D = 10^{-5}$ cm²/s. The results obtained for MV^{2+} are in excellent agreement with the predictions of eq 6, supporting the validity of the kinetic model applied. From this curve α is evaluated as 0.85 ± 0.05 and $k_{et}^0 = (1 \pm 0.5) \times 10^{-2}$ cm/s.

In the case of TiO_2 sols prepared via hydrolysis of titanium isopropoxide,^{3,4} the kinetic parameters for MV^{2+} reduction by e^-_{CB} were $k_{et}^0 = 5 \times 10^{-3}$ cm/s and $\alpha = 0.48$. Thus, while the heterogeneous rate constants for the two preparations are approximately equal, the α values differ significantly. A transfer coefficient of 0.5 is predicted²⁴ from a Marcus-type free-energy relation, i.e.

$$\Delta G^* = \lambda \left(1 + \frac{\Delta G^0}{4\lambda} \right)^2 \quad (7)$$

where ΔG^* , ΔG^0 ($\approx E - E^0$), and λ are the free energy of activation, the free energy of reaction, and the reorganization energy. In the region where $|\Delta G^0| < 4\lambda$, $d\Delta G^*/d\Delta G^0 = 0.5$, such a relation seems to apply to TiO_2 particles prepared from isopropoxide but not for those produced via hydrolysis of $TiCl_4$. The relatively large α value found for the latter is, however, compatible with other free-energy relations derived empirically.²⁵ For simple one-electron-transfer processes $\alpha > 0.5$ indicates an unsymmetrical transition state implying that a large fraction of the overvoltage contributes to the decrease of the free energy of activation of the

reaction. Alternatively, anomalously large Tafel slopes can result from a multistep reaction mechanism.

Previous investigations of the reduction of a variety of electron acceptors on TiO_2 electrodes have obtained α values exceeding unity²⁶ which have been attributed to the participation of surface states in the electron-transfer events. More recently,²⁷ these surface states have been identified with OH groups coordinated to one lattice Ti^{4+} ion.²⁸ By analogy, it is reasonable to assume that the same type of surface hydroxyl function also mediates electron-transfer processes involving the conduction band of TiO_2 particles. Indeed, it has been shown by infrared studies²⁹ that TiO_2 powders prepared from the propoxide and $TiCl_4$ differ in the nature and density of surface hydroxyl groups. This may explain the difference in the transfer coefficients for the reduction of MV^{2+} by e^-_{CB} of these two types of TiO_2 particles.

The transfer coefficient for the reaction of TiO_2 conduction band electrons with $C_{14}MV^{2+}$ is 0.78 ± 0.05 and hence almost identical with that obtained for MV^{2+} . However, the kinetic behavior of the surfactant viologen differs from simple MV^{2+} in two important aspects: (1) k_1 continues to increase and does not attain a diffusion-limited value at pH > 10; (2) within the range $2 \times 10^{-4} \leq 10^{-3}$ M, k_1 is independent of viologen concentration. One infers from this behavior that the reduction of $C_{14}MV^{2+}$ by e^-_{CB} involves mainly surface-bound acceptor molecules. This contrasts with the behavior of MV^{2+} which is predominantly present in the solution bulk. Apparently, the amphiphilic nature of $C_{14}MV^{2+}$ enhances adhesion to the TiO_2 particles.

The case of charge transfer from a semiconductor particle to a surface-adsorbed species cannot be treated by eq 6. The correct interpretation of the k_1 values obtained for $C_{14}MV^{2+}$ is that of a reciprocal average time for electron transfer from the conduction band of the particle to the adsorbed acceptor molecule. Moreover, since for a 50-Å-radius TiO_2 particle the average transit time of e^-_{CB} from the particle interior to the surface is only ~ 2 ps⁴, k_1 reflects properly the rate of the heterogeneous electron-transfer step. A simple consideration shows that k_1 is related to the electrochemical rate constant k_{et} via

$$k_{et} = k_1 d \quad (8)$$

where d is the average distance over which the electron jump occurs. Assuming that the C_{14} chain of $C_{14}MV^{2+}$ extends radially away from the TiO_2 surface, the viologen moiety facing the aqueous phase, the upper limit for d is calculated as approximately 25 Å. If it is further assumed that the redox potential of the $C_{14}MV^{2+/+}$ couple is not affected by adsorption to the TiO_2 particles, the pH value for which $E - E^0 = 0$ is 5.54, as in the case of MV^{2+} , and the k_1 value of this pH obtained from Figure 3 is 4×10^3 s⁻¹. Application of eq 8 yields finally $k_{et}^0 = 10^{-3}$ cm/s which is smaller by a factor of ~ 10 than the corresponding value for methyl viologen. This difference is likely to arise from the closer contact of the latter acceptor to the TiO_2 surface.

ii. Generation of Hydrated Electrons in Preirradiated $C_{14}MV^{2+}/TiO_2$ Dispersions. Continuous irradiation of colloidal TiO_2 in the presence of $C_{14}MV^{2+}$ leads to the formation of a violet color³⁰ which is due to the buildup of $C_{14}MV^+$ and its dimeric form in solution. Exposure of such a preirradiated solution to the 347.1-nm laser flash results in the generation of a short-lived

(26) (a) E. L. Dutoit, F. Cardon, and W. P. Gomes, *Ber. Bunsenges. Phys. Chem.*, **76**, 475 (1972); (b) R. N. Noufi, P. A. Kohl, S. N. Frank, and A. J. Bard, *J. Electrochem. Soc.*, **125**, 246 (1978); (c) J. Vanderminden, W. P. Gomes, and F. Cardon, *ibid.*, **127**, 324 (1980).

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(28) Two different types of hydroxyl groups exist at the surface of TiO_2 .^{14a} The first bridges two adjacent Ti^{4+} sites and is acidic in character (pK = 2.9). The second, basic type OH^- is associated with only Ti^{4+} site (pK = 12.7). The latter hydroxyls constitute the surface states that play a decisive role in electron-transfer processes involving the conduction band of TiO_2 .^{25b}

(29) P. Jones and J. A. Hockey, *Trans. Faraday Soc.*, **67**, 2669 (1971).

(30) At pH > 9.5 the violet color changes to yellow under continuing illumination owing to formation⁸ of doubly reduced viologen $C_{14}MV^0$. Laser photolysis studies have shown⁸ that the generation of $C_{14}MV^0$ occurs via two sequential and time-separated electron-transfer reactions involving $e^-_{CB}(TiO_2)$.

(22) In contrast to MV^{2+} where k_1 attains the diffusion-controlled limit at pH ≥ 10 , the $\log k_1$ value for $C_{14}MV^{2+}$ reduction continues to increase linearly with pH in alkaline solution. Thus $k_1(C_{14}MV^{2+}) \approx 10^8$ s⁻¹ at pH 11. Rates at pH > 11 are too high to be measurable with our equipment.

(23) The diffusion coefficient for MV^{2+} is 9.2×10^{-6} cm²/s and that for the TiO_2 particles 4×10^{-7} cm²/s. A value of $r = 5$ Å was used for the reaction radius of MV^{2+} .

(24) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

(25) (a) D. Rehm and A. Weller, *Ber. Bunsenges Phys. Chem.*, **73**, 834 (1969); (b) R. D. Levine and N. Agonon, *Chem. Phys. Lett.*, **52**, 197 (1977).

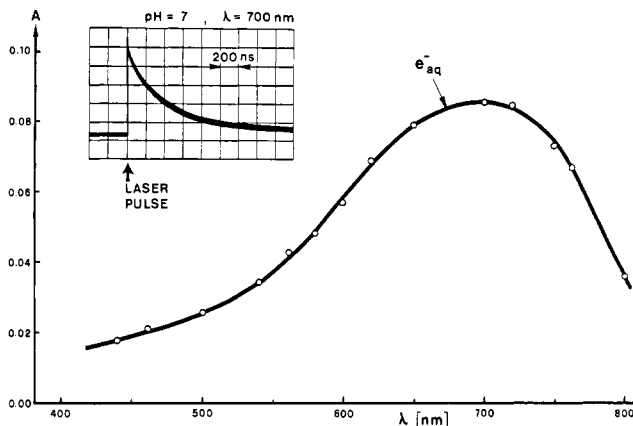
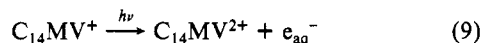


Figure 4. Hydrated electron production from $C_{14}MV^+$ adsorbed to the surface of colloidal TiO_2 . A preirradiated solution was exposed to 347.1-nm laser pulses; transient spectrum obtained at the end of the laser pulse. Insert: temporal behavior of the hydrated electron absorption at 700 nm. Solution composition: 500 mg/L of TiO_2 , 2×10^{-4} M $C_{14}MV^{2+}$, pH 7.

transient with maximum absorption around 715 nm (Figure 4). As shown by the oscilloscope trace inserted in the figure, the lifetime of the transient is ca. 300 ns. In the presence of N_2O , a typical electron scavenger, the lifetime is shortened drastically. From this observation and the features of the spectrum in Figure 4, the transient species can be identified unambiguously with the hydrated electron³¹ (λ_{max} 715 nm, ϵ_{max} $18\,500\text{ M}^{-1}\text{ cm}^{-1}$). The yield of e_{aq}^- was found to be linearly dependent on the laser light intensity, indicating that a monophotonic process was operative. The explanation of this effect is as follows. In preirradiated $C_{14}MV^{2+}/TiO_2$ dispersions the 347.1-nm laser light is not only absorbed by the semiconductor particles but also by $C_{14}MV^+$. Excitation of the latter leads to hydrated electron formation



and concomitant reoxidation of the viologen radical. Since the redox potentials for e_{aq}^- and the $C_{14}MV^{2+/+}$ couple are -2.7 and -0.44 V, respectively, the minimum free-energy input required to drive reaction 9 is 2.26 eV corresponding to a photoionization threshold of 550 nm. Blank experiments carried out with TiO_2 dispersions alone and in the presence of $C_{14}MV^{2+}$ showed no formation of e_{aq}^- by laser light, confirming that reduced viologen³² is the source of hydrated electrons in preirradiated TiO_2 solutions.

To elucidate the role of the TiO_2 semiconductor particle in the photoionization process, we produced $C_{14}MV^+$ in aqueous micellar solution of triton X100 via thermal reduction of $C_{14}MV^{2+}$ by dithionite ions. In this case no formation of e_{aq}^- by 347.1-nm laser light was observed. This would indicate that the photoionization of $C_{14}MV^+$ is assisted by the local environment present at the TiO_2 surface. The detailed reasons for this behavior are unclear. The negative surface charge of the TiO_2 particle could enhance escape of the photoejected electron from its parent ion into the bulk aqueous phase. Alternatively, since $C_{14}MV^+$, because its hydrophobic character,³³ is strongly adsorbed to the TiO_2 surface, it may be considered as a filled surface state of the semiconductor. Light could promote electrons from these surface states to the continuum in the conduction band from where emission into water and hydration would occur. A similar mechanism may be op-

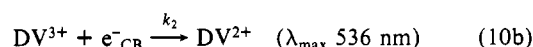
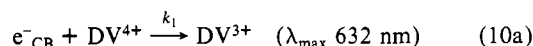
erative in the photogeneration of hydrated electrons in colloidal CdS solutions.³⁴ Several reports on electron injection processes from p-type semiconductor electrodes (GaAs, Si) into liquid ammonia have appeared recently.³⁵

iii. Reduction of the Dimeric Viologen DV^{4+} by Conduction-Band Electrons: Simultaneous Two-Electron Transfer Induced by Light. DV^{4+} is a potential four-electron acceptor³⁶ whose redox behavior in aqueous solution has not been investigated so far. Aqueous solutions of DV^{4+} (0.2 M KCl, phosphate buffer pH 7) were therefore examined by cyclic voltammetry using a basal plane pyrolytic graphite electrode.³⁷ A first reversible wave corresponding to reduction of DV^{4+} to DV^{3+} appears at $E_1^\circ = 0$ V (NHE). It is followed by a second one-electron reduction step³⁸ $E_2^\circ(DV^{3+/2+}) \approx -0.07$ V (NHE). DV^{2+} can be further reduced at potentials more negative than ca. -800 mV. This reduction wave is irreversible and leads to a product, probably DV^+ , which precipitates from the electrolyte solution.

From this study two noteworthy differences in the redox behavior of MV^{2+} and DV^{4+} emerge. (1) The dimer is more readily reduced than the monomer (E_1° shifted positively by 440 mV). (2) The difference between the first and second reduction potential of DV^{4+} is very small (ca. 70 mV), making it an excellent candidate for participation in simultaneous two-electron-transfer processes.

Figure 5 shows UV-visible absorption spectra resulting from illumination of 10^{-4} M DV^{4+} in deaerated solutions of colloidal TiO_2 (500 mg/L) at pH 1 in a 1-cm pathlength optical cell. Under light exposure the initially colorless solution very rapidly develops an intensively blue color. The spectrum present after 10-s irradiation exhibits a pronounced peak at 632 nm, weaker maxima being located at 700, 398, and 359 nm and shoulders at 585, 536, and 410 nm. Under continuing exposure to light the color changes rapidly from blue to pink. Within 40 s the absorptions at 632 and 398 nm have almost completely disappeared with concomitant growth of the 536- and 359-nm peaks.³⁹ Distinct isosbestic points located at 714, 517, 447, 380, and 325 nm are associated with this transition, indicating sequential photogeneration of only two light-absorbing species.

These results are interpreted in terms of band-gap excitation of TiO_2 particles producing conduction band electrons and valence band holes. The former reduce DV^{4+} according to the sequence

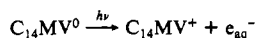


The absorption maxima at 632 and 398 nm are attributed to DV^{3+} and those at 536 and 359 nm to DV^{2+} , respectively. Extinction coefficients for these species can also be derived from experimental data such as shown in Figure 5. Since the assumption is made that during photolysis, DV^{4+} is first quantitatively converted to DV^{3+} , which subsequently is transformed completely into DV^{2+} , these values represent only lower limits. One obtains for DV^{3+} (λ_{max} 632 nm) $\epsilon \geq 14\,800\text{ M}^{-1}\text{ cm}^{-1}$ and for DV^{2+} (λ_{max} 536 nm) $\epsilon \geq 13\,000\text{ M}^{-1}\text{ cm}^{-1}$.

Note that the spectroscopic features of DV^{3+} and DV^{2+} distinguish themselves from those of the methyl viologen radical⁴⁰

(31) E. J. Hart and M. Anbar, "The Hydrated Electron", Wiley-Interscience, New York, 1970.

(32) At pH >9.5 the final product obtained from illuminating $TiO_2/C_{14}MV^{2+}$ dispersions is $C_{14}MV^0$. The latter was found to ionize also monophotonically after 347.1-nm laser excitation:



(33) (a) P. A. Brügger and M. Grätzel, *J. Am. Chem. Soc.*, **102**, 2461 (1980); (b) P. A. Brügger, P. P. Infelta, A. M. Braun, and M. Grätzel, *ibid.*, **103**, 320 (1981).

(34) Z. Alfassi, D. Bahnemann, and A. Henglein, *J. Phys. Chem.*, **86**, 4656 (1982).

(35) (a) J. Belloni, G. V. Amerongen, R. Heindl, M. Herlem, and J. L. Sculfort, *C. R. Acad. Sci., Ser. B*, **288**, 295 (1979). (b) R. E. Malpas, K. Itaya, and A. J. Bard, *J. Am. Chem. Soc.*, **101**, 2535 (1979). (c) R. E. Malpas, K. Itaya, and A. J. Bard, *J. Am. Chem. Soc.*, **103**, 1622 (1981).

(36) S. Hünig, International Farbenzsymposium, Baden-Baden, FRG, Sept 1982, abstract.

(37) Cyclic voltammetric measurements have been performed by Dr. T. Geiger in our institute using a Pine Co. instrument.

(38) A distinct sharpening of the anodic return peak after cyclic voltammetric reduction of DV^{3+} to DV^{2+} indicates that the latter adheres at least partially to the surface of the graphite electrode.

(39) The extinction coefficient of DV^{2+} at 359 nm is 2.3 times larger than at 535 nm. Thus, after 40-s irradiation the absorbance at 359 nm in Figure 7 has increased to ca. 2.8.

(40) T. Watanabe and K. Honda, *J. Phys. Chem.*, **86**, 2617 (1982), and references cited therein.

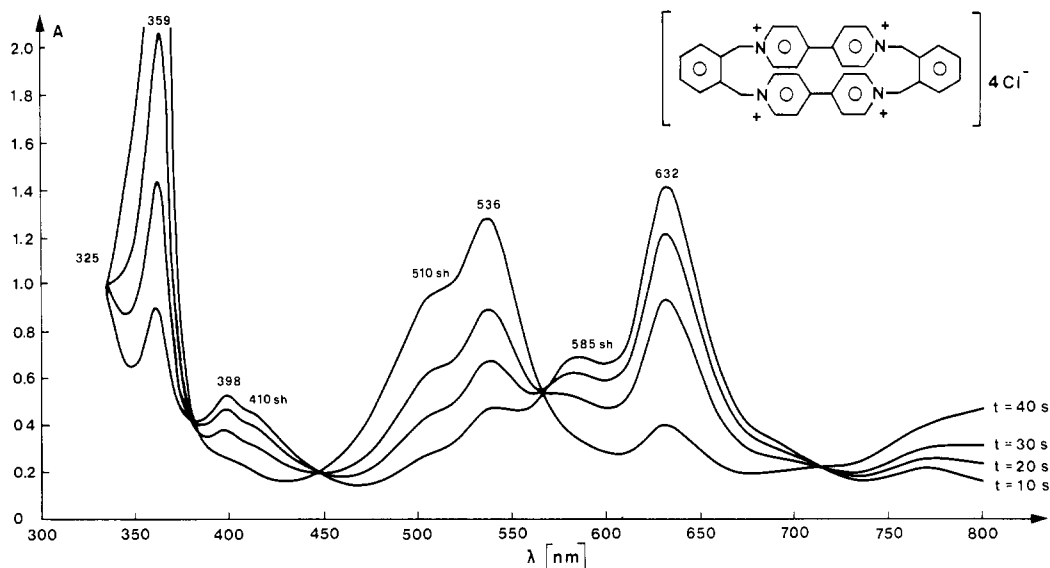


Figure 5. Spectral changes observed under irradiation of deaerated TiO_2 solutions (500 mg/L) by $\lambda > 330$ nm light in the presence of 2×10^{-4} M DV^{4+} . Spectra of the products were recorded after 10, 20, 30 and 40 s of irradiation time. The spectra were measured against colloidal TiO_2 (500 mg/L) as reference solution; optical pathlength 1 cm. Note the clean isosbestic points at 714, 517, 447, 380, and 325 nm.

or its dimeric form⁴¹ $(\text{MV}^+)_2$. MV^+ has a strong electronic transition at 396 nm ($\epsilon 4.2 \times 10^4$) which is almost totally absent in DV^{3+} . Furthermore, the 606-nm band of MV^+ ($\epsilon 1.3 \times 10^4$) is significantly red-shifted and enhanced in DV^{3+} . In the case of DV^{2+} , both the visible and UV absorptions are much stronger than the corresponding transitions of $(\text{MV}^+)_2$. Interestingly, there is close similarity between the spectrum of DV^{2+} and that of the intramolecular dimer cation-radical $^+\text{MVCH}_2\text{CH}_2\text{CH}_2\text{MV}^+$ which is produced via photoreduction of bisviologen compounds in alcohols.⁴² In the latter case, formation of a sandwich-type complex is sterically favored by the propylene linkage between the two MV^+ moieties.

The time course of the two consecutive electron-transfer steps leading to DV^{2+} formation in irradiated TiO_2 dispersions was monitored individually using the laser photolysis technique. Figure 6 shows oscilloscope traces obtained from experiments with 10^{-4} M DV^{4+} in colloidal TiO_2 (500 mg/L) dispersions. Excitation of the semiconductor particles by the laser pulse is followed by a pronounced growth of the 635-nm absorption of DV^{3+} which occurs on a millisecond time scale and reaches a plateau value. Kinetic evaluation of these data yields $k_1 = 35 \text{ s}^{-1}$ for the pseudo-first-order rate constant of DV^{3+} formation. The DV^{3+} concentration after completion of the e^-_{CB} transfer is calculated as 3.7×10^{-5} and corresponds to a quantum yield of 1.2 for DV^{3+} formation. (This value is based on the same assumptions as made in deriving the extinction coefficient of DV^{3+} .) In order to determine the rate parameter k_2 for the second electron-transfer step from the TiO_2 conduction band to DV^{3+} , DV^{4+} was converted into DV^{3+} by preirradiating the solution. The blue DV^{3+} -containing dispersion of TiO_2 was subsequently exposed to the laser flash. Figure 6b shows the time course of the 535-nm absorption of DV^{2+} after excitation of the semiconductor particle. A smooth growth of the signal is again observed which attains a plateau in the millisecond time domain. Kinetic evaluation yields for the specific rate of the second electron-transfer step $k_2 = 20 \text{ s}^{-1}$.

Dividing k_1 and k_2 by the DV^{4+} concentration gives for the second-order rate constants the values $k_1' = 3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2' = 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. One concludes that the two consecutive electron-transfer events from the TiO_2 conduction band to the

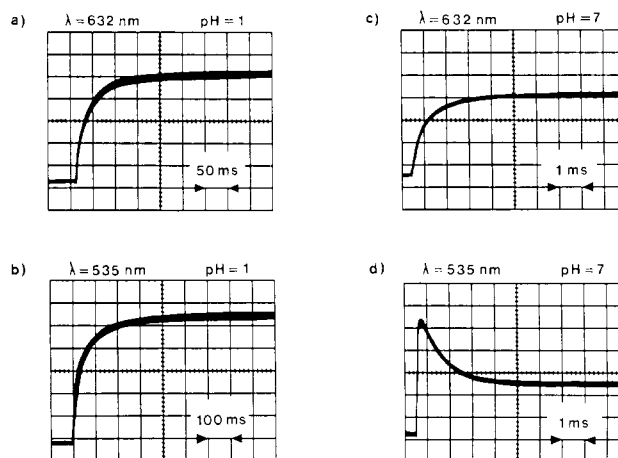


Figure 6. Visible absorption spectrum of the product obtained from irradiation of colloidal TiO_2 (500 mg/L) solutions in the presence of $\text{Rh}(\text{bpy})_3^{3+}$ (2×10^{-4} M) and 2,2'-bipyridine (2×10^{-3} M) by $\lambda > 335$ nm light; pH 10 solution deaerated with Ar; irradiation time; 5 min. The spectrum was measured against a reference solution containing 500 mg/L of colloidal TiO_2 ; optical pathlength 1 cm.

viologen dimer occur at a similar rate which is significantly below the diffusion-imposed limit. Apparently these processes are controlled by the rate of heterogeneous electron transfer at the semiconductor surface, i.e., the parameter k_{et} in eq 6. This is not surprising since at pH 1 the overvoltages available to drive the first and second reduction of DV^{4+} are only 170 and 100 mV, respectively. Furthermore, since the TiO_2 particles are positively charged at pH 1 they repel the DV^{4+} and DV^{3+} ions, decreasing the frequency of diffusional encounter between the reactants.

Included in Figure 6 are oscilloscope traces obtained from the laser photolysis of $\text{TiO}_2/\text{DV}^{4+}$ solutions at pH 7. Care was taken to protect samples from exposure to light prior to performing flash irradiations. Only one laser pulse was applied to each sample. The temporal behavior of the transient absorption is distinguished by an immediate increase of the absorption signals followed by a slower growth at 632 nm which is matched by a decay at 535 nm. A plateau is reached within several milliseconds.

The transitory spectrum present at the end of the fast absorbance rise is essentially the same as that displayed for DV^{2+} in Figure 5, the maximum in the visible being located at 536 nm. After completion of the slower process when the transient absorption has reached a plateau, the species present has the spectral characteristics of DV^{3+} with a maximum at 636 nm. From this

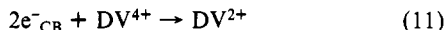
(41) E. M. Kosower and J. L. Letter, *J. Am. Chem. Soc.*, **86**, 5524 (1964).

(42) (a) M. Furue and S. Nozakura, *Bull. Chem. Soc. Jpn.*, **55**, 513 (1982); *Chem. Lett.*, 821 (1980). (b) A. Deronzier, B. Galland, and M. Vieira, *Nouv. J. Chim.*, **6**, 97 (1982).

(43) From the fact that DV^{2+} is formed within the laser pulse, the time required for interfacial two-electron transfer is $< 10^{-8}$ s. Using an electron-transfer distance of $d \approx 5$ Å, one calculates from eq 8 $k_{\text{et}} > 0.2 \text{ cm}^2/\text{s}$ as the rate constant for reaction 11 at pH 7.

behavior one infers that the transient produced *first* after laser excitation of the TiO₂ particles is the *doubly reduced* viologen dimer, the *monoreduced* species being formed in a *subsequent* process that occurs on a millisecond time scale.

These observations may be rationalized in terms of simultaneous transfer of two electrons from the conduction band of the TiO₂ particle to DV⁴⁺:



followed by coproportionation of DV²⁺ with excess DV⁴⁺ to form the monoreduced radical DV³⁺:



In the presence of DV⁴⁺ the monoreduced viologen is thermodynamically favored over the doubly reduced form since the equilibrium constant for reaction 12 calculated from the first two reduction potentials of DV⁴⁺ is 16. Its formation reflects therefore relaxation of the redox system into equilibrium following light-driven, two-electron transfer. In principle, it is possible to determine directly the value of the equilibrium constant K_{12} from transient absorption data such as displayed in Figure 6c,d, which could then be compared with the value derived from the electrochemical measurements. Lack of precise knowledge of the extinction coefficients for DV³⁺ and DV²⁺ prevents us from performing this evaluation at present.

It was mentioned already above that the two-electron reduction of DV⁴⁺ by TiO₂ conduction-band electrons is a very rapid process. Experiments with nanosecond-time resolution showed that even at DV⁴⁺ concentrations as small as 2×10^{-5} M, a major fraction of DV²⁺ is already produced within the 20-ns duration of the laser pulse.⁴³ This rapid reaction must involve surface-adsorbed acceptor molecules since there is insufficient time for bulk diffusion. Adsorption of DV⁴⁺ is favored by coulombic interactions with the TiO₂ particles which are negatively charged at pH 7. The remaining part of DV²⁺ grows in within a few microseconds after the laser pulse. We attribute this second component to reaction of e^-_{CB} with DV⁴⁺ present in the solution bulk, which is supported by the fact that its rate increases with DV⁴⁺ concentration. Further studies employing picosecond-time resolution are required to obtain a more quantitative picture of these rapid electron-transfer events. This should clarify whether there is truly concerted two-electron transfer or whether sequential electron transfer occurs within the laser pulse. Experiments with low laser fluence might appear as an alternative way to discern these alternatives. However, particle concentrations are so small that populations of only a few electron-hole pairs/particle would lead to undetectable quantities of DV³⁺ or DV²⁺.

With regards to the formation of DV³⁺ via coproportionation of DV⁴⁺ and DV²⁺, it was illustrated in Figure 6c,d that this is a relatively slow process occurring on a millisecond time scale. In accordance with the predictions of eq 12, the rate of DV³⁺ formation was found to increase with DV⁴⁺ concentration. Evaluation of the data in Figure 7c,d gives $k_{12} = 1.5 \pm 0.5 \times 10^7$ M⁻¹ s⁻¹.

iv. Light-Induced Reduction of Rh(bpy)₃³⁺ by TiO₂ Conduction Band Electrons. In the search for transition metal complexes that could function as multielectron acceptors for conduction-band electrons in colloidal semiconductor dispersions, we selected Rh(bpy)₃³⁺ as a suitable model compound. The redox behavior of Rh(bpy)₃³⁺ has been very thoroughly investigated⁴⁴⁻⁵² because

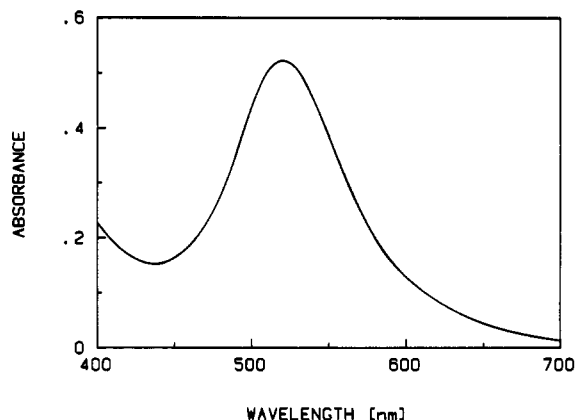
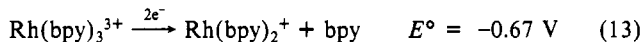
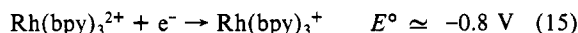
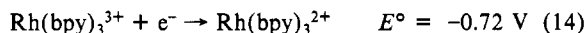


Figure 7. Oscillograms from the laser photolysis of deaerated aqueous colloidal dispersions of TiO₂ (0.5 g/L) in the presence of 2×10^{-4} M DV⁴⁺. The 632-nm absorbance indicates the temporal behavior of DV³⁺ while that at 535 nm reflects the temporal behavior of DV²⁺. The oscillogram in the lower left corner was obtained with preirradiated solutions where most of the DV⁴⁺ had been converted to DV³⁺ prior to laser exposure.

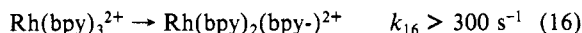
of its prominence as an electron relay in sacrificial photochemical hydrogen-producing systems.⁴⁶⁻⁵¹ From polarographic and coulometric studies of aqueous solutions (pH 10), Kirsch et al.⁴⁸ concluded that Rh(bpy)₃³⁺ undergoes *dielectronic reduction*:



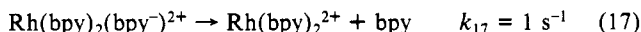
The product Rh(bpy)₂²⁺ was found to have an absorption maximum at 520 nm and the extinction coefficient was determined at 4800 M⁻¹ cm⁻¹. By contrast, Chan et al.⁵⁰ inferred from cyclic voltammetric measurements that the Rh(bpy)₃³⁺ reduction in aqueous alkaline solution (0.05 M NaOH), similarly to the case where acetonitrile was used as a solvent,^{44,45} occurs via two subsequent single electron-transfer steps



From the lack of anodic reoxidation of Rh(bpy)₃²⁺ even at high scan speeds, they concluded that Rh(bpy)₃²⁺ undergoes a rapid chemical reaction, suggested to consist of ligand labilization:



to give a monodentate species. The latter loses a ligand



which is followed by electronic dismutation



$$k_{18} = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

The final reduction product was found to be again the red-colored Rh(bpy)₂²⁺ complex (λ_{max} 520 nm, ϵ 1.1×10^4 M⁻¹ cm⁻¹). Using pulse radiolysis technique, Mulazzani et al.⁵¹ have determined the UV-visible absorption spectrum of Rh(bpy)₃²⁺ and that of Rh(bpy)₂²⁺ (λ_{max} 518, ϵ 9.8×10^3 M⁻¹ cm⁻¹) and derived for the rate parameters k_{16} and k_{17} the values 10^4 and 0.9 s^{-1} , respectively.

Continuous illumination of alkaline (pH > 8) aqueous solutions containing Rh(bpy)₃³⁺ and colloidal TiO₂ with $\lambda > 335$ -nm light⁵³ leads within a few minutes to appearance of an intense pink red color, Figure 7. The spectrum is readily identified with that of Rh(bpy)₂²⁺. Based on $\epsilon_{520} = 10^4$, ca. 25% of the Rh(bpy)₃³⁺ has been reduced to Rh(bpy)₂²⁺ after 5 min of photolysis. When the

(44) G. Kew, K. DeArmond, and K. Hanck, *J. Phys. Chem.*, **78**, 727 (1974).

(45) G. Kew, K. Hanck, and K. DeArmond, *J. Phys. Chem.*, **79**, 1829 (1975).

(46) J.-M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, **1**, 449 (1977).

(47) G. M. Brown, J. F. Chan, C. Creutz, and H. A. Schwarz, and N. J. Sutin, *J. Am. Chem. Soc.*, **101**, 7639 (1979).

(48) M. Kirch, J. M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, **62**, 1345 (1979).

(49) K. Kalyanasundaram, *Nouv. J. Chim.*, **3**, 511 (1979).

(50) S. F. Chan, M. Chu, C. Creutz, T. Matsubara, and N. Sutin, *J. Am. Chem. Soc.*, **103**, 369 (1981).

(51) D. G. Mulazzani, S. Emmi, M. Z. Hoffman, and M. Venturi, *J. Am. Chem. Soc.*, **103**, 3362 (1981).

(52) O. Enea, *Nouv. J. Chim.*, **6**, 423 (1982).

(53) This filter prevents any direct excitation of Rh(bpy)₃³⁺ by UV light, which in the presence of organic donors such as triethanolamine has been shown to yield Rh(bpy)₂²⁺, ref 49.

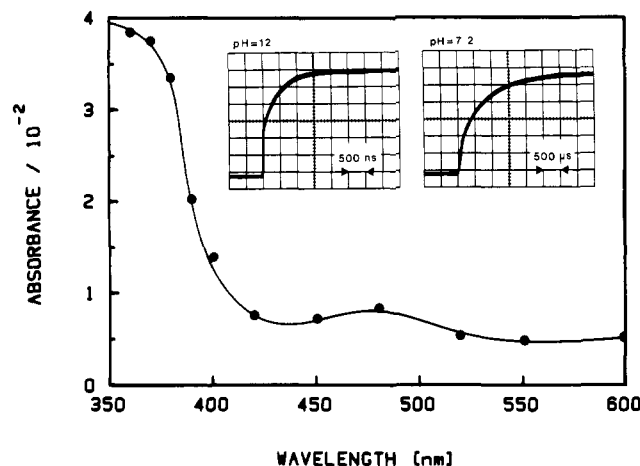
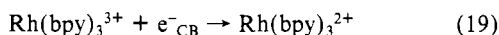


Figure 8. Transient spectrum obtained 5 μ s after laser excitation of colloidal TiO_2 in the presence of 2×10^{-4} M $\text{Rh}(\text{bpy})_3^{3+}$ and 2×10^{-3} M 2,2'-bipyridine: pH 12 (NaOH), λ_{exc} 347.1 nm, $[\text{TiO}_2] = 500$ mg/L protected by PVA (1 g/L); optical pathlength 0.5 cm. Solution was deaerated with Ar. Inserts: Oscillograms showing the growth of the $\text{Rh}(\text{bpy})_3^{2+}$ absorption at 360 nm at two different pH values. Conditions used are the same as in continuous photolysis. Note the 1000-fold difference in time scale between the two pH values.

photolysis is carried out in the pH range 6–8, a pink-brown solution is obtained. It exhibits a broad absorption rising continuously below 500 nm into the UV which has been attributed⁵⁴ to dimeric Rh(I) complexes, e.g., $[\text{Rh}(\text{bpy})_2]_2^{2+}$ and the hydride $[\text{Rh}(\text{bpy})_2]\text{H}^{3+}$, the monomer hydride $\text{Rh}(\text{bpy})_2\text{H}^{2+}$ being colorless.

Laser photolysis technique was applied to investigate the mechanism of Rh(I) formation. Figure 8 shows the transient spectrum obtained 5 μ s after laser excitation of colloidal TiO_2 in the presence of 2×10^{-4} M $\text{Rh}(\text{bpy})_3^{3+}$ at pH 12. One notices a rather weak absorption in the visible centered around 480 nm. Below 400 nm the spectrum rises sharply toward the UV, a maximum being attained at 350 nm. These features match exactly the absorption characteristics of the divalent $\text{Rh}(\text{bpy})_3^{2+}$ complex.⁵¹ Therefore, it is concluded that the conduction-band process involves single electron transfer from the colloidal TiO_2 particles to $\text{Rh}(\text{bpy})_3^{3+}$. Inserted in Figure 8 are oscillograms illustrating the kinetics of $\text{Rh}(\text{bpy})_3^{2+}$ formation at two different pH values. In alkaline solution (pH 12) the growth of the 360-nm absorption of $\text{Rh}(\text{bpy})_3^{2+}$ occurs in two distinct phases. A fast rise immediately after the laser pulse accounts for 40% of the total transient absorbance and is followed by a slower increase which is completed within 2 μ s. The fast component is not observed in neutral solution (pH 7.2). Here, the rate of $\text{Rh}(\text{bpy})_3^{2+}$ formation is drastically decreased, the buildup of the 360-nm absorption occurring on a 2000 times (!) longer time scale than at pH 12. The effect of pH on the rate of e_{CB}^- reaction with $\text{Rh}(\text{bpy})_3^{3+}$



is illustrated in Figure 9 in more detail. A logarithmic plot of k_{19} (s^{-1}), the observed rate constant for $\text{Rh}(\text{bpy})_3^{2+}$ formation, against pH gives within the pH range of 7–12 a straight line with a slope of 0.64. In acid solution the points show increasingly negative deviation from this line.

To rationalize this behavior we recall that the conduction-band position of the TiO_2 particles changes with pH according to eq 5, while the redox potential of the $\text{Rh}(\text{bpy})_3^{3+}/\text{Rh}(\text{bpy})_3^{2+}$ couple is essentially pH independent. Hence, decreasing the pH by one unit leads to a 59-mV decrease of the driving force (or overvoltage) for reaction 19. This, in turn, decreases the value of the heterogeneous rate constant, k_{et} , for electron transfer from the TiO_2 conduction band to $\text{Rh}(\text{bpy})_3^{3+}$ at the particle surface, eq 3. It can be readily shown by applying eq 2 to the data displayed in Figure 9 that it is the interfacial electron transfer and not diffusion

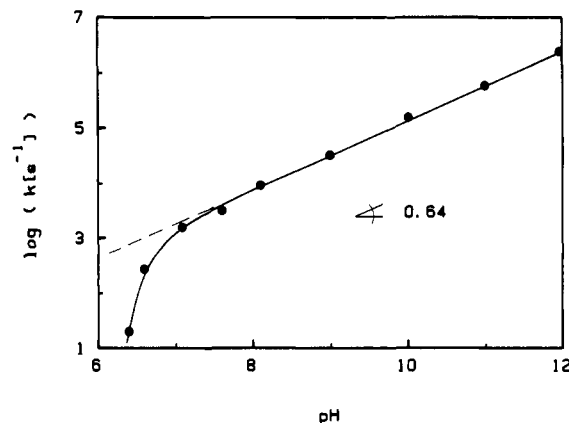


Figure 9. Effect of pH on the observed rate constant of $\text{Rh}(\text{bpy})_3^{2+}$ reduction by $e_{\text{CB}}^-(\text{TiO}_2)$. Conditions as in Figure 8. Data obtained from laser photolysis experiments (λ_{exc} 347.1 nm, λ_{obs} 360 nm).

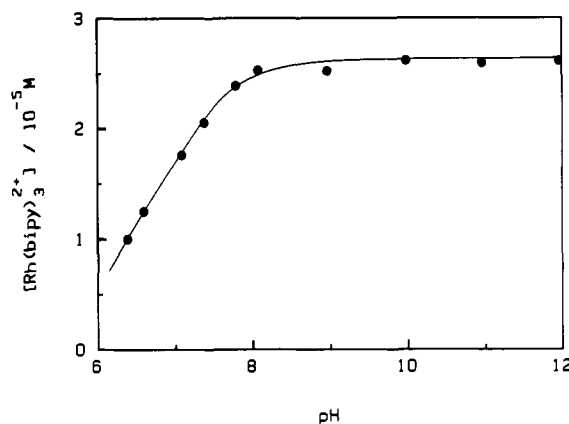


Figure 10. Effect of pH on the yield of $\text{Rh}(\text{bpy})_3^{2+}$ measured after completion of electron transfer from the conduction band of colloidal TiO_2 to $\text{Rh}(\text{bpy})_3^{3+}$. Laser photolysis technique was applied: conditions as in Figure 8.

that controls the rate of $\text{Rh}(\text{bpy})_3^{2+}$ formation. (Even at pH 12 where k_{et} is calculated as 7 cm/s, the condition $1/k_{\text{et}} \gg r/D$ is still fulfilled.) A simplified version of eq 2, i.e., $k_{19}' = k_{19} \times 1000/N_A \times [\text{Rh}(\text{bpy})_3^{3+}] \approx 4\pi r^2 k_{\text{et}}$, may therefore be applied to evaluate the data displayed in Figure 9. Hence, the slope of the straight line can be identified with α , the transfer coefficient for reduction of $\text{Rh}(\text{bpy})_3^{3+}$ by TiO_2 conduction-band electrons. The value of 0.64 is distinctively smaller than that obtained for MV^{2+} reduction by e_{CB}^- .

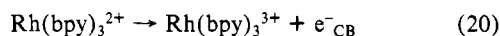
Another electrokinetic parameter which can be derived from Figure 9 is k_{et}^0 , the heterogeneous rate constant for electron transfer at zero driving force. Using -0.7 V for the first reduction potential of $\text{Rh}(\text{bpy})_3^{3+}$, the pH⁵⁵ where $E_{\text{CB}}(\text{TiO}_2) = E^\circ(\text{Rh}(\text{bpy})_3^{3+}/\text{Rh}(\text{bpy})_3^{2+})$ is 10. At this pH, $k_{19} = 1.7 \times 10^5 \text{ s}^{-1}$ and from eq 2 k_{et}^0 is calculated as 0.4 cm/s. This value is 40 times larger than the heterogeneous rate constant for MV^{2+} reduction by conduction band electrons of TiO_2 . It reflects a low intrinsic barrier for electron transfer from TiO_2 particles to $\text{Rh}(\text{bpy})_3^{3+}$ and hence a small reorganization energy associated with the $\text{Rh}(\text{III}) \rightarrow \text{Rh}(\text{II})$ transition.

Apart from the electron-transfer rate, the pH influences also strongly the yield of $\text{Rh}(\text{bpy})_3^{2+}$ formation. Figure 10 illustrates the effect of pH on the concentration of $\text{Rh}(\text{bpy})_3^{2+}$ determined

(54) M. Chou, C. Creutz, D. Mahajan, N. Sutin, and A. P. Zipp, *Inorg. Chem.*, **21**, 3989 (1982).

(55) The concentration of $\text{Rh}(\text{bpy})_3^{2+}$ after completion of e_{CB}^- transfer is about 2.6×10^{-5} M at pH 7 and an initial $\text{Rh}(\text{bpy})_3^{3+}$ concentration of 2×10^{-4} M. The redox potential of the solution is therefore 48 mV more positive than the standard potential $E^\circ(\text{Rh}(\text{bpy})_3^{3+}/\text{Rh}(\text{bpy})_3^{2+}) = -0.7$ V. Strictly speaking, the pH of zero overvoltage is therefore 9.2 instead of 10. This should be kept in mind when interpreting k_{et}^0 , the rate constant of e_{CB}^- transfer under conditions where the Fermi level of the particle equals the standard redox potential E° . The rate constant for $\text{Rh}(\text{bpy})_3^{3+}$ reduction at free zero driving force is 0.13 cm/s.

after completion of the $\text{Rh}(\text{bpy})_3^{3+}$ reduction by $e^-_{\text{CB}}(\text{TiO}_2)$, i.e., from the plateau region of oscillograms such as shown in Figure 8. In alkaline solution the quantum yield of $\text{Rh}(\text{bpy})_3^{2+}$ formation is practically unity.⁵⁶ It decreases, however, sharply at $\text{pH} < 7.5$. Note that this decrease occurs in the same domain where the points in Figure 9 start to deviate from the Tafel line. Apparently, in this pH range only a fraction of the conduction-band electrons, generated initially by the laser flash, leave the TiO_2 particle, equilibrium with the solution redox system being established through simultaneous occurrence of charge ejection (eq 19) and injection via



The fact that reoxidation of $\text{Rh}(\text{bpy})_3^{2+}$ becomes noticeable only at pH values several units below 10 where $E_{\text{CB}}(\text{TiO}_2) = E^\circ(\text{Rh}(\text{bpy})_3^{3+}/\text{Rh}(\text{bpy})_3^{2+})$ can be explained by the occurrence of the competing ligand destabilization process, eq 16. The latter takes place very rapidly ($k_{16} \approx 10^4 \text{ s}^{-1}$) and produces an electroinactive species as shown by the lack of an anodic reoxidation wave in cyclic voltammetry. Therefore, in order to be able to compete with ligand destabilization, charge injection from $\text{Rh}(\text{bpy})_3^{2+}$ into the TiO_2 particle must occur on a microsecond time scale. At $\text{pH} < 7$ the overvoltage for the anodic reaction is at least $\sim 180 \text{ mV}$ which appears to be sufficient to reach such high charge injection rates.

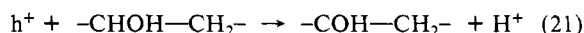
In summary, the reduction of $\text{Rh}(\text{bpy})_3^{3+}$ by $e^-_{\text{CB}}(\text{TiO}_2)$ in colloidal semiconductor dispersions consists of single electron transfer to form the transient $\text{Rh}(\text{bpy})_3^{2+}$. This reaction is characterized by a high electrochemical exchange rate constant k_{et}^0 . The reduction is rendered irreversible over a large pH domain by rapid consumption of $\text{Rh}(\text{bpy})_3^{2+}$ due to destabilization and loss of a bpy ligand. This is confirmed by the finding that purple-colored $\text{Rh}(\text{bpy})_2^+$ is the end product produced by continuous band-gap irradiation of colloidal TiO_2 in the presence of $\text{Rh}(\text{bpy})_3^{3+}$. Although the mechanistic details of the conversion of $\text{Rh}(\text{bpy})_3^{2+}$ into $\text{Rh}(\text{bpy})_2^+$ have not been investigated here, it can be assumed that this follows the sequence outlined by eq 16 to 18 which has been established through earlier work with homogeneous $\text{Rh}(\text{bpy})_3^{3+}$ solutions.⁴⁶⁻⁵²

It should be pointed out in this context that while the reduction of $\text{Rh}(\text{bpy})_3^{3+}$ to $\text{Rh}(\text{bpy})_3^{2+}$ involves single electron-transfer steps, reoxidation of the latter could occur via simultaneous transfer of two electrons to a suitable acceptor. Very recently⁵⁷ Wienkamp and Steckhan have obtained evidence that such a mechanism is operative in the electrocatalytic reduction of NAD^+ on a graphite electrode in the presence of $\text{Rh}(\text{bpy})_3^{3+}$. From the fact that NADH , and not the NAD dimer, was formed as a product, it was inferred that $\text{Rh}(\text{bpy})_2^+$ generated at the cathode acted as a true two-electron donor in this process. Note that this concept could be readily applied to the colloidal TiO_2 particles investigated here, which in the presence of $\text{Rh}(\text{bpy})_3^{3+}$ as a two-electron relay should achieve photochemical generation of NADH from NAD^+ . Work in this direction is in progress and will be reported in a subsequent paper.

v. Valence-Band Processes. So far, the discussion has centered on reactions of conduction-band electrons which have been the main interest of the present study. For completeness we wish to deal here briefly with the fate of the valence-band holes (h^+) generated concomitantly with e^-_{CB} by band-gap excitation of the TiO_2 particles. It has been known since the earlier work by Honda et al.⁵⁸ that holes in illuminated TiO_2 crystals react efficiently with water under formation of oxygen. This reaction can, however, be intercepted by a variety of hole scavengers,⁵⁹ in particular,

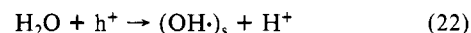
organic molecules such as alcohols or reducing inorganic species such as sulfite or halide ions. Holes produced in colloidal TiO_2 particles undergo similar redox processes. Using laser photolysis technique, we^{3,5} and others⁶ have shown hole transfer from the valence band of these particles to adsorbed halide ions (X^-) resulting in radical ion (X_2^-) formation. For the latter to compete efficiently with water oxidation, low pH and high halide concentrations were required.

A further process competing with water oxidation by valence-band holes is h^+ scavenging by the polymeric agent, i.e., PVA, used to stabilize the TiO_2 sol. The latter reaction is believed to occur also in the present system, where PVA polymer was always employed to protect the TiO_2 particles from coagulation. Very likely, the product is an α -alcohol-type radical:

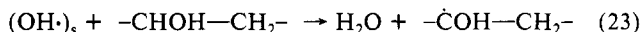


which due to its reducing properties could inject an electron in the conduction band of the TiO_2 particles, producing a "current-doubling" effect.⁵⁸ However, recombination and/or dismutation constitute alternative and very efficient pathways for reactions of α -alcohol-type radicals. At present, the contribution of these different processes cannot be quantitatively assessed.

Instead of the direct generation of polymer radicals via reaction 21, one might envisage a sequence involving first hole scavenging by water (or OH^-) to product surface-bound OH^- radicals

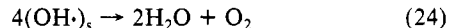


followed by hydrogen abstraction from the protective agent to produce again an α -alcohol-type radical



A similar mechanism has been evoked to explain the chalking of TiO_2 -based paints⁶⁰ in sunlight.

It is also feasible that at least part of the OH radicals produced via reaction 22 yield oxygen as a final product:



One might argue that such a mechanism is incompatible with the simultaneous generation of air-sensitive species such as $\text{Rh}(\text{bpy})_2^+$ via the conduction-band process. As has been shown above, significant quantities of reduced acceptor accumulate in solution which in the presence of oxygen would be rapidly reoxidized. However, numerous studies in the literature⁶¹ including our own observations⁶² have shown that TiO_2 particles, in particular, highly hydroxylated anatase, can function as oxygen carriers. The role of surface hydroxyl groups in the chemisorption of O_2 and subsequent reduction to O_2^- has recently been elucidated.^{27b} The adsorbed O_2 appears to be much less reactive than free oxygen in solution as indicated by the fact that it can coexist with reducing agents such as H_2 .

Conclusions

This study is part of our continuing effort to explore the behavior of photoinduced charge carriers in ultrafine semiconductor particle dispersion: 50-Å-sized particles of TiO_2 were produced via hydrolysis of TiCl_4 in aqueous solution and carefully characterized. The subsequent laser and continuous photolysis investigations centered on conduction-band processes involving various one- and two-electron acceptors in aqueous solution. The important results emerging from this study are summarized as follows. (1) The salient features of the interfacial electron transfer are adequately described by the electrokinetic parameters k_{et}^0 and α , which can

(56) Calculated from the optical density of the solution at 347 nm and the incident laser photon fluence. Uncertainty in the irradiated volume introduces a ca. 25% error in this determination. The concentration of absorbed light quanta is $\sim 3 \times 10^{-5} \text{ einstein/L}$. Since at 500 mg of TiO_2/L the particle concentration is $4 \times 10^{-7} \text{ M}$, there are on the average 75 electron-hole pairs produced per particle corresponding to a carrier density of $1.5 \times 10^{20} \text{ cm}^{-3}$.

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be derived from the experimental data by applying a kinetic model developed earlier.^{4,63} The transfer coefficient α for MV^{2+} reduction is much larger for particles prepared from $TiCl_4$ than those obtained from the hydrolysis of titanium isopropoxide, indicating participation of surface states (OH groups) in the electron-transfer event. (2) Drastic pH effects on the rate of MV^{2+} reduction by conduction-band electrons observed earlier³ are confirmed for other acceptors and arise from the cathodic shift of the Fermi level of the particles with increasing pH. (3) A particularly favorable configuration for rapid electron transfer is achieved with acceptors which through suitable functionalities adhere to the semiconductor surface. Thus in the case of the amphiphilic viologen $C_{14}MV^{2+}$

the conduction-band process occurs on a subnanosecond time scale at high pH. Preirradiated samples give rise to hydrated electron generation via photoionization of $C_{14}MV^{+}$. (4) Simultaneous two-electron transfer from the conduction band of colloidal TiO_2 to cofacial dimeric viologen has been unambiguously demonstrated. By contrast, $Rh(bpy)_3^{3+}$, a potential two-electron acceptor, undergoes mono-electronic reduction by e^-_{CB} . These results should be of importance for the application of ultrafine semiconductor particles in artificial photosynthesis.

Acknowledgment. This work was supported by the Schweizerische National Fonds zur Förderung der Wissenschaft. We are grateful to Professor S. Hünig, University of Würzburg, West Germany, for a gift of the cofacial viologen and to Dr. Kalyanasundaram for a gift of $Rh(bpy)_3^{3+}$.

Registry No. TiO_2 , 13463-67-7; $TiCl_4$, 7550-45-0; MV^{2+} , 4685-14-7; $C_{14}MV^{2+}$, 79039-57-9; DV^{4+} , 87174-68-3; $Rh(bpy)_3^{3+}$, 47780-17-6.

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Chain-Length Dependence of Electronic and Electrochemical Properties of Conjugated Systems: Polyacetylene, Polyphenylene, Polythiophene, and Polypyrrole

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Received April 8, 1983

Abstract: The valence effective Hamiltonian (VEH) technique is used to compute ionization potentials, optical transition energies, and electron affinities of oligomers and polymers in four conjugated systems: polyacetylene, poly(*p*-phenylene), polythiophene, and polypyrrole. The theoretical results compare very favorably with experimental data on gas-phase ionization potentials, optical absorption, and electrochemical redox potentials. The latter case is especially important, and the calculated oxidation and reduction potentials are in remarkably good agreement with experiment. For polyacetylene the predicted oxidation potential is 0.4 V vs. SCE, and the predicted reduction potential is -1.1 V, both of which are in good agreement with experimentally observed oxidation and reduction onsets. In these systems, the electronic and electrochemical properties predicted by VEH theory for the oligomers extrapolate to those of the polymer with an inverse chain-length dependence.

Introduction

A number of organic polymers become electrically conducting on addition of electron donors or acceptors.¹⁻⁵ Thus far, the highest conductivities ($\sim 1000 \Omega^{-1} \text{ cm}^{-1}$) have been obtained for acceptor doped poly(*p*-phenylene)² and acceptor doped polyacetylene.³ Despite the enormous interest in these conducting polymer systems, many theoretical aspects of the problem remain poorly understood, especially the electronic properties of the "doped" (partially ionized) polymers. Progress is being made, however, in understanding the undoped polymer precursors. In a series of recent papers, we have demonstrated the utility of the valence effective Hamiltonian (VEH) method in understanding the ground-state properties of conjugated polymers, in particular, those which become highly conducting upon doping.⁶⁻⁸ The VEH method employs atomic potentials derived from double-zeta (ζ) quality ab initio computations on small molecules⁹ in calculations on large molecules. With this method, X-ray photoelectron spectra (X-ray PES), ionization potentials, and optical band gaps have been computed for polyacetylene, poly(*p*-phenylene), poly(*p*-

phenylene sulfide), and poly(dibenzothiophene).¹⁰ The theoretical X-ray PES spectra and ionization potentials are all in good agreement with experiment, as are the theoretical band gaps for the planar systems.^{6-8,10}

A fundamental question in this area is the extent to which polymer properties can be predicted based on extrapolation from oligomer data.¹¹⁻¹³ This is fundamental, for example, in the

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