

Surface Complexation of Colloidal Semiconductors Strongly Enhances Interfacial Electron-Transfer Rates

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Surface complexation of colloidal titanium dioxide by monodentate and bidentate benzene derivatives, i.e., benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, salicylic acid, and catechol was investigated and was found to obey the Langmuir isotherm. The adsorption constants in water/methanol mixtures (90/10 v/v) at pH 3.6 decrease from 2×10^5 for terephthalate to 2×10^3 for benzoate. Electrophoretic measurements show the adsorption to be accompanied by a decrease of the point of zero ζ potential (PZZP), the shift observed for salicylate being 0.5 pH unit. At pH 3.6, the influence of the adsorbate on the ζ potential of the TiO_2 particles is relatively small. The largest effect is observed with isophthalate, which decreases ζ from 78 to 51 mV. Laser photolysis experiments indicate that surface complexation of TiO_2 by these benzene derivatives drastically accelerates the electron transfer from the conduction band of the colloidal oxide to acceptors in solution, i.e., methylviologen (MV^{2+}) and oxygen. The rate enhancement depends greatly on the structure and chemical nature of the adsorbate. At monolayer coverage, isophthalate enhances the rate of interfacial electron transfer to MV^{2+} 1700 times while terephthalate gives a 133-fold rate increase. Monodentate benzoate accelerates the interfacial electron transfer only by a factor of 3. Similar effects were observed for oxygen as electron acceptor. Trapping of electrons by Ti(IV) surface states and the removal of such traps by complexation with the benzene derivatives is invoked to rationalize these observations.

Introduction

We have recently discovered that the adsorption of complexants such as cobaltoceniumdicarboxylate¹ and phenylfluorone² at the surface of titanium dioxide sharply enhances the rate of electron transfer from the conduction band to electron acceptors in solution. It was suggested that the interfacial electron transfer occurs via Ti(IV) cations on the surface which due to partial coordination to solvent molecules constitute trapping sites for the conduction band electrons. Replacing the solvent by coordinating ligands changes the energetic position of such surface states, affecting in this way their intervention in the charge-transfer events. For example, complexation of titanium surface ions may sweep the redox level of the Ti(IV)/Ti(III) electronic state from the band gap into the conduction band, in which case trapping of electrons can no longer occur. In such a case the interfacial charge transfer involves free conduction band electrons whose rate of reaction with acceptors could differ by many orders of magnitude from that of the trapped species.

Given the importance of surface states for a large number of electronic, electrochemical, and photoelectrochemical processes,³ we have initiated investigations to explore in a systematic fashion the effect of complexants on the dynamics of interfacial redox reactions. Here we present intriguing observations made with colloidal titanium dioxide in the presence of benzene derivatives that are adsorbed at the particle surface.

Experimental Section

Materials. The benzene derivatives benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, and salicylic acid were obtained from Fluka (Buchs, Switzerland) and were used as supplied. Catechol from the same source was purified by vacuum sublimation. Distilled water was filtered through Millipore columns for further purification. All other chemicals were at least reagent grade and were used as received.

Colloidal TiO_2 was prepared according to a published procedure.⁴ The properties of the sol are summarized in Table I. Most of the laser photolysis studies were conducted in the presence of poly(vinyl alcohol) (Moviol 10-98, Hoechst, Germany), purified as previously described,⁵ as a protective agent. The TiO_2 /PVA weight ratio employed was between 1 and 2.

Apparatus. Laser photolysis experiments employed a Q-switched, frequency-doubled ruby laser (JK-2000) having a pulse width of ca. 15 ns. The detector signal (photomultiplier tube or photodiode) was digitized by a Tektronix 7612D programmable digitizer equipped with two 7A16P vertical amplifiers. The fastest sampling rate available was 200 MHz, while the bandwidth of this instrument was 80 MHz to dc. The programmable sampling time switching ability of this instrument allowed all pertinent information for a time-scale range extending from 10^{-8} to 1 s to be obtained with a single laser pulse. The signal incoming prior to the laser pulse was digitized on a linear time scale allowing for the acquisition of a satisfactory base line. The signal following the laser pulse was digitized with variable sampling rate to obtain a satisfactory representation on a logarithmic time scale with less than 3000 data points. The data, when of interest, were stored on diskette for subsequent analysis. Nonlinear least-squares fitting to appropriate expressions allowed the extraction of pertinent kinetic parameters, and eventually base-line parameters.

Electrophoretic measurements employed a Rank Bros. Mark II instrument equipped with a He-Ne laser and a cylindrical cell configuration. The laser beam was focused to a narrow volume of $90 \mu\text{m}^3$ and the field of observation displayed on a TV monitor. Particle migration was observed over a distance of $105 \mu\text{m}$. The mean electrophoretic velocity was determined by measuring the rate of migration at various distances from the cell wall (x). The rates were fit to a polynomial in x , which by integration over the whole tube radius gave the mean particle velocity. Division of the mean velocity by the field strength yields the mobility (u), which under our conditions of particle radius and ionic strength, is related to the ζ potential via Henry's law:

$$\zeta = 6\pi\eta u / \epsilon \quad (1)$$

where η is the solvent viscosity and ϵ its static dielectric constant.

(1) Kölle, U.; Moser, J.; Grätzel, M. *Inorg. Chem.* 1985, 24, 2253.

(2) Frei, H.; Fitzmaurice, D. J.; Grätzel, M. *Langmuir* 1990, 6, 198.

(3) Gerischer, H. *Electrochim. Acta* 1991, 36, 133.

(4) Moser, J.; Grätzel, M. *J. Am. Chem. Soc.* 1983, 105, 6547.

(5) Moser, J.; Grätzel, M. *Helv. Chim. Acta* 1982, 65, 1436.

Table I. Properties of the TiO₂ Colloidal Dispersion Used

mean hydrodynamic particle diameter, nm	13.0
particle concn, mol part.g ⁻¹	3.6×10^{-7}
specific surface area, m ² g ⁻¹	122
Ti ^{IV} s sites concn, mol g ⁻¹	8.6×10^{-4}
Ti ^{IV} s sites per particle	2400

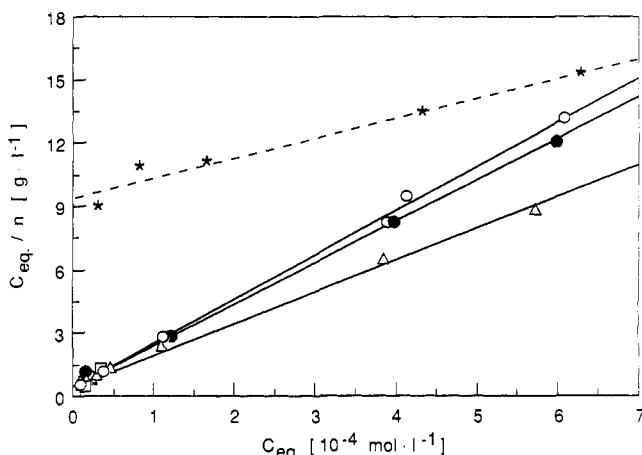


Figure 1. Langmuir adsorption isotherms of phthalate (○), isophthalate (△), terephthalate (□), salicylate (●), and benzoate (★) on TiO₂ (P-25) powders dispersed in water/methanol (90/10 v/v) mixtures at pH 3.6.

Results

Adsorption Isotherms. Adsorption measurements employed solutions of adsorbate in a water/methanol mixture (90/10 v/v) adjusted to pH 3.6 containing 0.25 g/L TiO₂ powder (Degussa P-25, specific surface area 55 m²/g, mainly anatase). The solution concentration of the adsorbate after reaching the adsorption equilibrium (c_{eq}) was determined by UV spectrophotometry. The TiO₂ particles were removed by centrifugation and subsequent filtration and the supernatant was subjected to spectral analysis. The amount of adsorbed complexant [n (mol)] was calculated from the difference in the optical density prior and after equilibration with the TiO₂. Results are shown in Figure 1, where the data are plotted according to the Langmuir isotherm:

$$c_{eq}/n = ac_{eq} + b \quad (2)$$

Here, $a = 1/n_{max}$ is the reciprocal amount of adsorbate at monolayer coverage and $K = a/b$ is the equilibrium constant for surface adsorption. Table III lists values of these constants for the six compounds investigated as well as their surface concentrations at monolayer coverage. The latter values were obtained by dividing n_{max} by the surface area of the TiO₂ dispersed in the solution. Γ_{max} values obtained for three of the adsorbates are close to 1 μ mol/m², indicating that the average surface occupied by one adsorbate molecule is ~ 160 Å² at monolayer coverage. The value of the binding constants for four of the six compounds is between 2×10^4 and 8×10^4 . For terephthalate the binding constant looks significantly higher, i.e., 2×10^5 , while Γ_{max} is lower by a factor of ~ 2 compared to the other adsorbates. The opposite trend is observed for benzoate, whose binding constant is much smaller and the Γ_{max} value somewhat higher than that of the other surface complexants.

Electrophoretic Measurements. Electrophoretic experiments employed again the 90% water/10% methanol solvent mixture containing, apart from the adsorbate and 0.04 g/L TiO₂, 2×10^{-3} M KNO₃. The pH of the solution was adjusted by addition of HNO₃ or KOH. The TiO₂ (P-25, Degussa) was purified by repeated dialysis carried

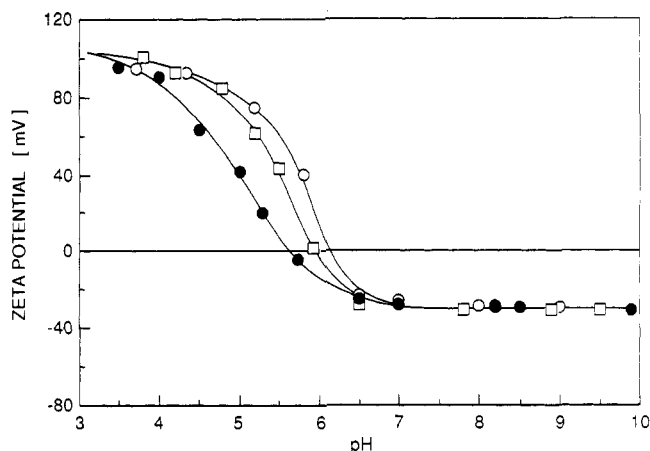


Figure 2. Electrophoretic measurements of ζ potentials of TiO₂ (P-25) particles as a function of pH ($[TiO_2] = 0.04$ g/L, KNO₃ 2×10^{-3} M).

out over a period of 3 months. ζ potentials derived from the mobility values of the purified powders are shown as a function of pH in Figure 2. The point zero ζ potential (PZZP) value for the TiO₂ particles in the absence of adsorbate is 6.2, in excellent agreement with literature values.⁶ In the presence of adsorbate, the PZZP is shifted to lower pH values. The shift is less than 0.2 pH unit for benzoate and 0.5 pH unit for salicylate. Between pH 4 and 6 the ζ potential of TiO₂ coated with salicylic acid is significantly smaller than that of the bare particles. However, below pH 4 all three curves converge toward a ζ potential of 100 mV.

Table II lists mobilities, ζ potentials, the charge densities in the shear plane (σ), the increment $\Delta\sigma$ produced during adsorption of the benzene derivatives and the surface concentration of adsorbate. The data confirm that at pH 3.6 the effect of the adsorbate on the ζ potential of TiO₂ colloids is relatively small. A decrease is observed with all the compounds investigated apart from benzoic acid, which induces a slight increase of ζ . When these data are compared with the results plotted in Figure 2, it should be noted that the experiments reported in the figure employed solutions containing inert electrolyte, i.e., 3×10^{-3} M NaNO₃. The measurements reported in Table II were carried out in the absence of any electrolyte other than a small amount of HClO₄ used to adjust the pH to 3.6. This explains the difference in the ζ potentials obtained in these two series of experiments.

Spectral Analysis of Surface-Complexed TiO₂ Colloids. Figure 3 shows the absorption spectra of colloidal TiO₂ alone and in the presence of salicylate or catechol. The spectrum of the bare colloid is typical for anatase, whose fundamental absorption edge is at 380 nm, corresponding to a band gap of 3.2 eV. Surface complexation of the particles by catechol or salicylate produces a red shift in their absorption. This effect is particularly pronounced for catechol, where the tail of the band reaches far into the visible, the onset being at 600 nm and a shoulder appearing around 430 nm. In contrast, benzoic acid or the phthalic acids fail to produce a noticeable change in the absorption feature of the colloidal TiO₂ above 330 nm. This indicates that the band in the visible observed in the presence of salicylate or catechol corresponds to a charge-transfer transition. Light promotes electron transfer from the surface complexant to the conduction band of TiO₂. Such a band should red shift with decreasing ionization

(6) (a) Parfitt, G. D. *Prog. Surf. Membr. Sci.* 1976, 11, 181. (b) Furlong, D. N.; Parfitt, G. D. *J. Colloid Interface Sci.* 1978, 65, 548. (c) Dunn, W. W.; Aikawa, Y.; Bard, A. J. *J. Am. Chem. Soc.* 1981, 103, 3456. (d) Barringer, E. A.; Bowen, H. K. *Langmuir* 1985, 1, 420.

Table II. Dependence of Electrophoretic Data for TiO₂ (P-25) Particles on the Presence of Adsorbates^a

adsorbate	C, M	u , m ² V ⁻¹ s ⁻¹	ζ , mV	σ , e m ⁻²	$\Delta\sigma$, e m ⁻²	n_{ads} , m ⁻²
blank		3.6×10^{-8}	78.4	3.13×10^{16}	0	0
phthalate	10^{-5}	3.8×10^{-8}	81.8	3.38×10^{16}	$+2.5 \times 10^{15}$	7.2×10^{16}
	10^{-4}	3.1×10^{-8}	66.9	2.50×10^{16}	-6.3×10^{15}	3.9×10^{17}
	4×10^{-4}	2.5×10^{-8}	54.6	1.88×10^{16}	-1.3×10^{16}	5.8×10^{17}
isophthalate	10^{-5}	3.3×10^{-8}	71.7	2.75×10^{16}	-3.8×10^{15}	7.8×10^{16}
	10^{-4}	2.9×10^{-8}	50.8	1.69×10^{16}	-1.4×10^{16}	3.6×10^{17}
	4×10^{-4}	2.4×10^{-8}	51.6	1.75×10^{16}	-1.4×10^{16}	4.8×10^{17}
terephthalate	10^{-5}	3.6×10^{-8}	78.4	3.19×10^{16}	$+0.6 \times 10^{15}$	6.0×10^{16}
	10^{-4}	3.3×10^{-8}	71.7	2.75×10^{16}	-3.8×10^{15}	3.7×10^{17}
	4×10^{-4}	3.4×10^{-8}	72.6	2.75×10^{16}	-3.8×10^{15}	
salicylate	10^{-5}	3.3×10^{-8}	71.5	2.75×10^{16}	-3.8×10^{15}	8.4×10^{16}
	10^{-4}	3.3×10^{-8}	72.1	2.75×10^{16}	-3.8×10^{15}	4.1×10^{17}
	4×10^{-4}	3.3×10^{-8}	71.1	2.69×10^{16}	-4.4×10^{15}	5.8×10^{17}
benzoate	10^{-5}	3.9×10^{-8}	84.7	3.69×10^{16}	$+5.6 \times 10^{15}$	2.4×10^{16}
	10^{-4}	4.0×10^{-8}	85.3	3.69×10^{16}	$+5.6 \times 10^{15}$	9.0×10^{16}
	4×10^{-4}	3.9×10^{-8}	83.6	3.63×10^{16}	$+5.0 \times 10^{15}$	3.1×10^{17}

^a Mobilities (u) are measured in the absence of inert electrolyte other than HClO₄, added to adjust pH at 3.6. ζ potentials are derived by the Henry equation (1). The particle charge within the shear surface is estimated by the Debye-Hückel relation to yield the charge densities σ and their increments $\Delta\sigma$. The amount n_{ads} of complexant molecules adsorbed per surface area unit, determined by the adsorption isotherms, is tabulated for direct comparison.

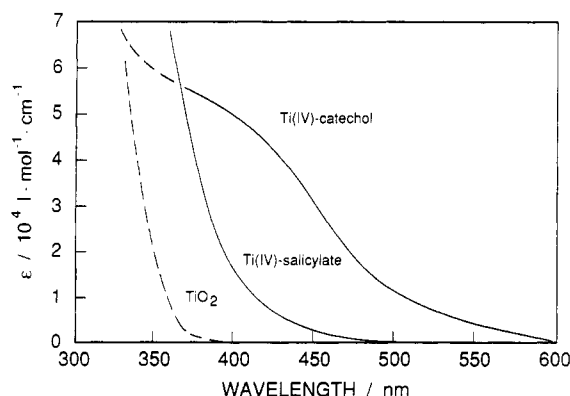


Figure 3. UV-vis absorption spectra of TiO₂ transparent sols (0.5 g/L, pH 3.6). Addition of salicylic acid and catechol (2×10^{-4} M) produces a red shift of the absorption onset to 500 and 600 nm, respectively.

potential of the electron donor as is observed in Figure 3. The absence of any charge-transfer absorption noted when phthalic and benzoic acids are used as surface complexants is due to their high ionization potential shifting the energy of the charge-transfer transition beyond the fundamental absorption edge of TiO₂.

Effect of Surface Complexation on the Dynamics of Reduction of Methylviologen by Conduction Band Electrons. The effect of surface complexation of colloidal titania on the rate of electron transfer from the conduction band to acceptors in solution was investigated with solutions containing, apart from 0.5 g/L TiO₂ and 10^{-3} M MV²⁺, various concentrations of adsorbate. The solutions were deaerated by bubbling with argon. Figure 4 shows oscillograms obtained from the 347.1-nm photolysis of a sol having a pH of 3.6. The temporal evolution of the 600-nm absorption of the MV⁺ radical is shown following band gap excitation of the particles by the laser pulse. In the absence of adsorbate the kinetics of 600-nm absorbance growth are in agreement with the rate constant of $30 \text{ M}^{-1} \text{ s}^{-1}$ determined earlier for the reduction of MV²⁺ by TiO₂ conduction band electrons.⁴ Addition of 10^{-3} M benzoate accelerates the interfacial electron transfer 3-fold. The enhancement is much more pronounced with the bidentate benzene derivatives than with benzoic acid. The largest effect is observed with isophthalate, which increases the rate by a factor of 1760.

The effect of adsorbate concentration on the rate of interfacial electron transfer is summarized in Table III and plotted in a semilogarithmic fashion in Figure 5a. The

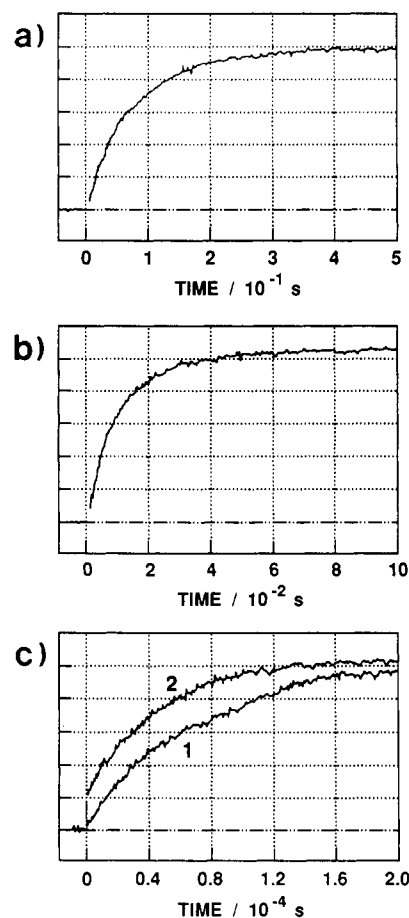


Figure 4. Effect of surface complexation on the kinetics of electron transfer from the conduction band of TiO₂ to methylviologen. Oscillograms showing the temporal behavior of the 600-nm absorbance after laser excitation of water/methanol (90/10, v/v) degassed solutions containing colloidal TiO₂ (0.5 g/L), PVA (0.5 g/L), and 10^{-3} M MV²⁺ at pH 3.6: (a) bare TiO₂ particles; (b) 10^{-3} M benzoic acid added; (c) 10^{-3} M isophthalic acid (1) and 10^{-3} M salicylic acid (2), added respectively.

curves obtained are similar to the adsorption diagrams included for comparison in Figure 5b. The electron-transfer rate accelerates sharply at low adsorbate concentration, reaching a limit in a concentration domain where complete monolayer coverage of the colloidal TiO₂ particles by the adsorbate is approached. The similarity between the adsorption isotherms and the rate enhance-

Table III. Dependence of Rate Constants for Interfacial Electron-Transfer Reactions to Methylviologen on TiO₂ Surface Complexation^a

adsorbate	C, M	$\Phi(\text{MV}^+)$	$k_{\text{et}}, \text{s}^{-1}$	$\log(k_a/k_0)$	$\Gamma_{\text{max}}, \mu\text{mol m}^{-2}$	K, M^{-1}
blank		0.36	3×10^1	0		
phthalate	10^{-4}	0.36	3×10^2	1.0		
	2×10^{-4}		8×10^2	1.4		
	4×10^{-4}	0.14	6×10^3	2.3	1.1	5×10^4
	10^{-3}	0.12	2×10^4	2.8		
isophthalate	10^{-4}		3×10^2	1.0		
	2×10^{-4}		7×10^2	1.4		
	4×10^{-4}		4×10^3	2.1	1.1	2×10^4
	10^{-3}		5×10^4	3.2		
terephthalate	10^{-4}		4×10^2	1.1	0.6	2×10^5
	4×10^{-4}		4×10^3	2.1		
salicylate	10^{-4}	0.20	5×10^2	1.2		
	2×10^{-4}		2×10^3	1.8	1.0	7×10^4
	4×10^{-4}	0.08	7×10^3	2.4		
	10^{-3}	0.02	4×10^4	3.1		
catechol	2×10^{-4}	0.06	8×10^2	1.4	1.0	8×10^4
	10^{-3}	0.01	5×10^3	2.2		
benzoate	4×10^{-4}		5×10^1	0.2	1.4	2×10^3
	10^{-3}	0.35	10^2	0.5		

^a Pseudo-first-order rate constants k_{et} are fitted to the results of flash photolysis experiments carried out in water/methanol (90/10 v/v) degassed solutions, containing 0.5 g/L colloidal TiO₂, 0.5 g/L PVA, 10^{-3} M MV²⁺, and various complexant concentrations (C, M) at pH 3.6. The acceleration factor (k_a/k_0) relates to the rate constant determined for a sol without added adsorbate. Radical-cation production quantum yield Φ is derived from the final MV⁺ concentration reached after each laser pulse and the photon concentration absorbed by the semiconductor. Surface concentration of adsorbates at monolayer coverage (Γ_{max}) and equilibrium constants (K) are extracted from the Langmuir plots of Figure 1.

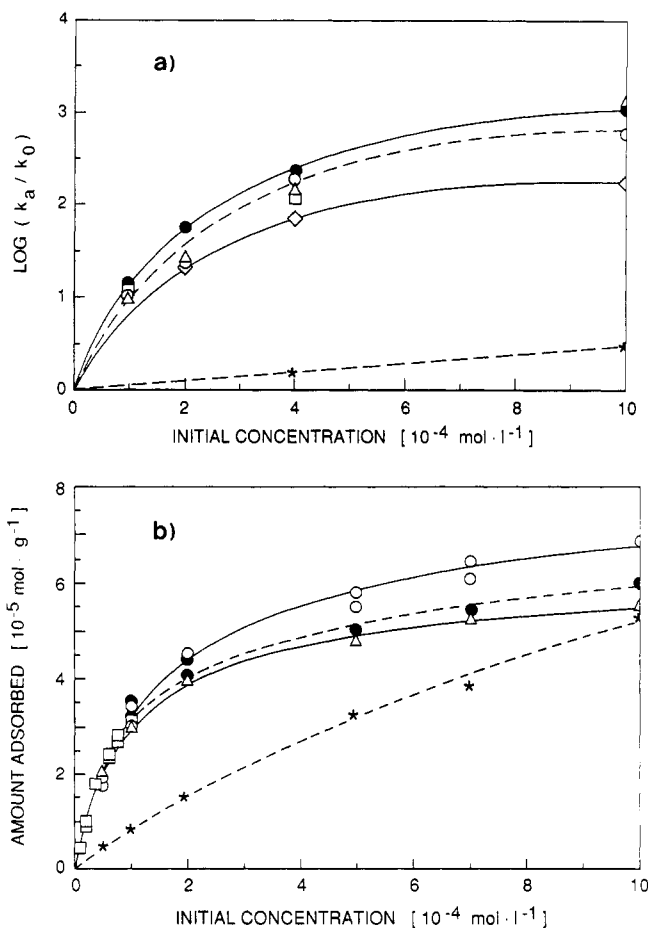


Figure 5. (a) Effect of adsorbate concentration on the rate of interfacial electron transfer to methylviologen. The acceleration factor (k_a/k_0) relatively to the rate of MV⁺ formation on bare TiO₂ particles is plotted on a semilogarithmic scale: (○) phthalate, (△) isophthalate, (□) terephthalate, (●) salicylate, (◇) catechol, (*) benzoate. (b) Adsorption isotherms of the same compounds are shown for comparison.

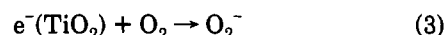
ment curves indicates that the adsorbate present at the surface of the semiconductor catalyses interfacial electron transfer.

It should be noted that the data reported in Table III

and Figure 5a were obtained with colloidal solutions in the presence of poly(vinyl alcohol) (PVA) as protective agent. Experiments carried out with unprotected TiO₂ gave higher acceleration factors than those observed with protected colloids. For example at 2×10^{-4} M salicylate, the rate enhancements were 63 and 567 in the presence and absence of PVA, respectively. This can be rationalized in terms of adsorption of the protective agent at the surface of the colloid competing with that of the benzene derivatives and hence blocking their access to Ti(IV) surface sites that mediate interfacial electron transfer.

The effect of pH on the rate enhancement of electron transfer from the conduction band of TiO₂ to methylviologen was also examined and the results are summarized in Table IV. The acceleration factor was determined at pH 3.6, 4.5, and 6. The results show that the rate enhancement produced by the adsorbate increases with pH except for isophthalate, for which the acceleration of electron transfer is maximal at pH 4.5. For example, in the presence of 4×10^{-4} M salicylate, the reduction of MV²⁺ is accelerated 707 and 166 times at pH 6.3 and 3.6, respectively. Electrostatic effects have to be considered in order to rationalize this finding. It is apparent from Figure 2, that the ζ potentials of salicylate loaded and bare TiO₂ particles are similar at pH 3.6 while at pH 6 they differ by ca. 27 mV. Using this ζ -potential difference to calculate the electrostatic contribution to the free energy of activation, one would predict an increase in the acceleration factor by a factor of 9 between pH 3.6 and 6. Given the uncertainty of the value of $\Delta\zeta$ at pH 6, the agreement with the experimental result is reasonable.

Effect of Surface Complexation on the Dynamics of Oxygen Reduction by Conduction Band Electrons. The one-electron reduction of dioxygen by conduction band electron



is kinetically sluggish in water.⁷ Therefore, it was of interest to explore whether the rate accelerations observed with methylviologen in the presence of surface complexants could be confirmed with this simple and uncharged

(7) Brown, G. T.; Darwent, J. R. *J. Chem. Soc., Faraday Trans. 1* 1984, 80, 1631.

Table IV. Dependence of Interfacial Electron-Transfer Rate Constants k_{et} on pH^a

adsorbate	10 ⁴ C, M	pH	pK _{a1}	pK _{a2}	k_{et} , s ⁻¹	log (k_a/k_0)
blank		3.6			3×10^1	0
		4.5			7×10^1	0
		6.0			10^3	0
phthalate	4	3.6	2.89	5.51	6×10^3	2.3
		4.5			10^4	2.2
		6.0			3×10^5	2.5
isophthalate	4	3.6	3.54	4.60	4×10^3	2.1
		4.5			2×10^4	2.5
		6.0			10^5	2.0
terephthalate	4	3.6	3.51	4.82	4×10^3	2.12
		4.5			2×10^4	2.46
		6.0				
salicylate	4	3.6	2.97		5×10^3	2.22
		4.5			3×10^4	2.63
		6.0			7×10^5	2.85

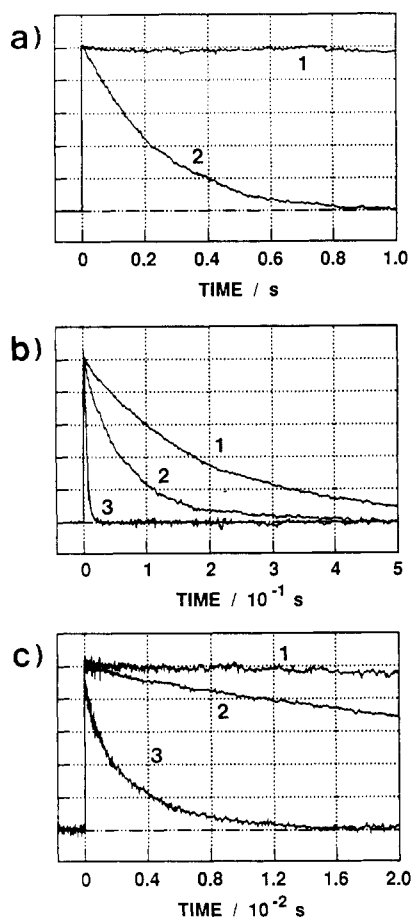
^a Conditions are the same as in Table III.

Figure 6. Effect of surface complexation on the kinetics of reduction of dioxygen on irradiated TiO₂. Oscilloscope traces showing the temporal behavior of the 900-nm absorbance of conduction band electrons after 347.1-nm laser excitation of water/methanol solutions containing colloidal titania (1.0 g/L) and PVA (0.5 g/L) at pH 3.6: (a) bare TiO₂ particles in degassed (1) and air-saturated (2) solutions; (b) air-saturated colloid complexed by addition of 4×10^{-4} M benzoic acid (1), 4×10^{-4} M isophthalic acid (2), and 4×10^{-4} M salicylic acid (3), respectively; (c) curves 2 and 3 of (b) replotted on a shorter time scale; curve 1 is for a deaerated salicylate-complexed TiO₂ sol.

acceptor. Experiments employed the same conditions as before except that MV²⁺ was replaced by oxygen. The kinetics of O₂ reduction were followed by monitoring the time course of the optical absorption of TiO₂ conduction band electrons at 900 nm¹ with use of a tungsten-halogen lamp as analyzing light source and a SH100 silicon diode as detector.

Figure 6 shows oscillograms illustrating the temporal behavior of the optical absorption of conduction band

Table V. Dependence of Interfacial Electron-Transfer Rate Constants k_{et} for Reduction of O₂ by TiO₂ Conduction Band Electrons on Surface Complexation^a

adsorbate	10 ⁴ C, M	k_{et} , s ⁻¹	log (k_a/k_0)
blank		5.0×10^0	0
benzoate	4	5.0×10^0	0
isophthalate	4	1.5×10^1	0.48
salicylate	4	3.7×10^2	1.87

^a Conditions are similar to those of Table III, except that this time solutions are air-saturated and no viologen is added.

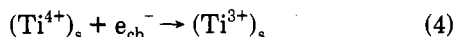
electrons produced at time zero by 347.1-nm pulsed laser excitation of the colloidal TiO₂ at pH 3.6. Traces 1 and 2 in Figure 6a were obtained in the absence of surface complexants with deaerated and aerated solutions, respectively. Under anaerobic conditions, the electron signal is stable⁸ while in the presence of air it decays with a half-lifetime of ca. 0.17 s. Figures 6b illustrates the effect of adding 4×10^{-4} M benzoate (1), isophthalate (2), or salicylate (3) on the O₂ reduction rate. Clearly, there is a sharp acceleration of the electron decay in the presence of the bidentate ligands salicylate and phthalate while the monodentate complexant benzoate exhibits practically no effect on the 900-nm absorption decay. For ease of inspection curves 2 and 3 are replotted on a shorter time scale in Figure 6c. It may be argued that the acceleration of the 900-nm decay is due to the reaction of the electrons with the adsorbate itself. However, this possibility can be excluded on the basis of blank experiments illustrated by trace 1 in Figure 6c. This oscillogram shows the temporal behavior of the 900-nm absorption observed with salicylate-loaded TiO₂ colloids in deaerated solution. There is very little decay of the electron absorption on the time scale of observation, indicating that the fast decay observed in aerated solution is due to the reaction of conduction band electrons with oxygen. A summary of the rate constants and acceleration factors derived from these experiments is given in Table V.

Discussion

The present results demonstrate the dramatic enhancement of interfacial electron transfer by bidentate benzene

(8) A major fraction of the electrons produced by band gap excitation of the colloidal TiO₂ particles recombines with valence band holes. This explains the finding in Table III that the quantum yield for MV⁺ formation is significantly smaller than 1. The sharp decrease in yield observed upon adsorption of salicylate and catechol is attributed to the absorption of 347.1-nm laser photons by the charge-transfer complex formed by these agents at the surface of TiO₂. While light absorption by these surface complexes could lead to electron injection in the conduction band, the yield for this process may be smaller than 1. Also, rapid recombination of electrons with the parent cations is expected to follow the charge injection. If TiO₂ particles are directly excited by light, the quantum yield for electron formation is 1 and the recombination with valence band holes is partially intercepted by reaction of the latter with the PVA protective polymer.

derivatives that are adsorbed on the surface of the TiO_2 particles. These findings are rationalized in terms of removal of surface states by complexation with the adsorbate. From the physical point of view, a surface state is an intraband gap electronic level that arises from incomplete coordination of the atoms present at the interface by other lattice atoms giving rise to dangling bonds or coordinatively unsaturated sites. Chemically, such surface states may be identified with titanium(IV) ions present at the TiO_2 /solution interface that are partially coordinated to water molecules. These sites act as electron traps:

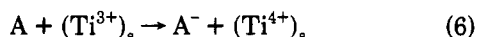


Direct evidence for the trapping process has been obtained from recent EPR studies with colloidal TiO_2 .⁹ In acidic solution, all the trapped electrons were identified with $(\text{Ti}^{3+})_s$ surface species. Siripala and Tomkiewicz have determined the energy of these states to be 0.8 eV below conduction band edge using impedance measurements and *n*-type single-crystal rutile electrodes.¹⁰ For polycrystalline TiO_2 , the trap depth varies with the Lewis acidity of the different titanium surface sites.¹¹ For example, Ti (IV) ions in the (110) plane are better electron acceptors than those located on the (101) or (100) surface. For $(\text{Ti}^{4+})_s$ located in the latter plane, Fan and Bard have derived a trap depth of 0.3 eV using scanning tunneling microscopy¹² in agreement with theoretical predictions.¹³ For colloidal TiO_2 particles, one expects the energy of the surface states to be distributed over a whole range corresponding to different lattice plane orientations.

The surface trapping of conduction band electrons according to eq 4 is a very rapid event. Picosecond time-resolved measurements have shown this process to occur within a few picoseconds.¹⁴ Competing with trapping is the interfacial electron transfer to the acceptor:



The rate constant for this process, k_e , should attain 10^{12} s^{-1} to make this competition effective. Few interfacial redox reactions have such high rates and surface trapping is, therefore, expected to be the dominant pathway. Once trapped, the electron can still be transferred to the acceptor in solution:



However, the rate of this process is expected to be greatly different from that of free carriers. For more detailed analysis, the rate constant for interfacial electron transfer is expressed^{15,16} in terms of a nuclear frequency parameter ν_n , an electronic factor κ_{el} , and a nuclear factor κ_n :

$$k = \nu_n \kappa_{el} \kappa_n \quad (7)$$

For the electronic factor, we apply the Landau-Zener approximation¹⁷ yielding

$$\kappa_{el} = \frac{2[1 - \exp(-\nu_{el}/2\nu_n)]}{2 - \exp(-\nu_{el}/2\nu_n)} \quad (8)$$

where ν_{el} is the frequency of electron transfer

$$\nu_{el} = \frac{2|\mathbf{H}_{if}|^2}{h} (\pi/4\lambda kT)^{1/2} \quad (9)$$

which depends on the electronic coupling matrix element \mathbf{H}_{if} and the reorganization energy λ . By use of classical transition-state theory the nuclear factor is expressed by eq 10, where ΔG^* is the standard free energy for the

$$\kappa_n = \exp\{-(\Delta G^* + \lambda)^2/4\lambda kT\} \quad (10)$$

interfacial electron-transfer reaction. If free conduction band electrons are involved in the charge transfer, the latter corresponds¹⁸ to the difference between the standard potential of the redox couple in solution and the potential of the conduction band edge of the TiO_2 colloids:

$$\Delta G^* = E^\circ(A/A^-) - E_{cb}(\text{TiO}_2) \quad (11)$$

If, on the other hand, the electron transfer involves trapped charge carriers the free energy for electron transfer becomes

$$\Delta G^* = E^\circ(A/A^-) - E_{cb}(\text{TiO}_2) + E_t \quad (12)$$

where $E_t > 0.3 \text{ eV}$ is the trap depth. For colloidal TiO_2 the conduction band potential expressed with respect to the normal hydrogen electrode varies with pH according to¹⁹

$$E_{cb}(\text{TiO}_2) = -0.1 - 0.059\text{pH (NHE)} \quad (13)$$

Using pH 3.6 and $E^\circ = -0.44 \text{ V (NHE)}$ for MV^{2+} as acceptor, one obtains $\Delta G^* = 0.13 \text{ eV}$ and $\Delta G^* > 0.43 \text{ eV}$ for free and trapped conduction band electrons, respectively. Inserting these values into eq 10 and assuming $\lambda = 0.5 \text{ eV}$ for both reactions, one calculates that the nuclear factor for free electrons is at least 10^4 times larger than κ_n for trapped carriers.

The assumption that the reorganization energy λ is the same for the reaction of free and trapped electrons is hardly justifiable in the present case. It is based on the notion that for heterogeneous electron-transfer reactions involving conductors or semiconductors the overall reorganization energy is equal to that of the redox couple in solution.²⁰ Contributions from the solid to the reorganization energy are usually neglected apart from image charge effects. This assumption is untenable for the reaction of electrons trapped at the surface of TiO_2 , during which the valency of surface titanium ions changes from III to IV. Associated with the increase in oxidation state is a shortening of the bond between the titanium ions and coordinated water requiring a significant inner-sphere reorganization. The price to be paid for such nuclear rearrangements is an increase in the reorganization energy resulting in a smaller value for the nuclear factor. (The λ value that should be used for trapped electrons in eq 9 is the average of the reorganization energies for the solution redox couple and the surface titanium ions. This is higher than the λ value for the free electron reaction.)

Apart from κ_n , the rate constant for interfacial electron depends on the electronic factor κ_e . The value of the latter is determined by the magnitude of the electronic matrix coupling element \mathbf{H}_{if} , i.e., the spatial overlap of the donor and acceptor wave functions. Because \mathbf{H}_{if} decreases exponentially with distance, it is possible that due to the close proximity of the surface-trapped electron to the interface its wave function has a better spatial overlap

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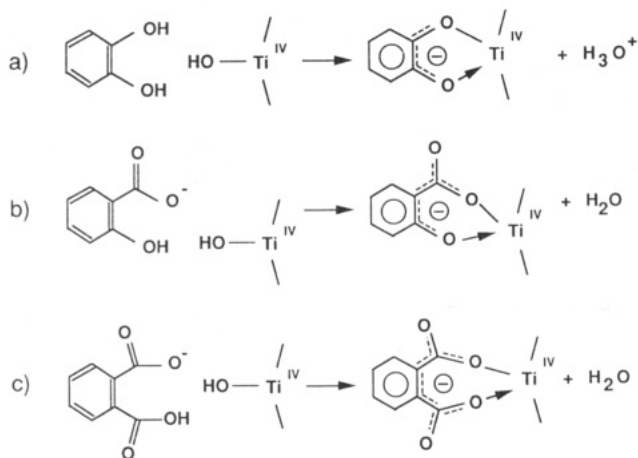


Figure 7. Schematic illustration of the complexation reaction of the hydroxylated TiO₂ surface by (a) catechol, (b) salicylate, and (c) phthalate.

with the acceptor orbital than that of the free electron. However, the opposite trend is predicted from the fact that the wave function for a trapped electron is more localized than that of the free charge carriers. Therefore, the large decrease in the nuclear factor for trapped as compared to free conduction band electron transfer is not likely to be compensated for by a corresponding increase in the electronic factor. As a consequence, the rate constant for reaction 6 involving surface-trapped electrons is expected to have a much smaller value than that for the interfacial transfer of free conduction band electrons, reaction 5.

For these considerations one derives as a plausible explanation for the striking rate enhancements observed in the presence of surface complexants that these agents alter the nature of the surface states of TiO₂ particles. The chelation of Ti(IV) by benzene derivatives, such as catechol, in aqueous solution is a well-known phenomenon.²¹ The very stable nature of these chelates makes the complexation of titanium ions located at the surface of TiO₂ feasible. This reaction involves the replacement of a surface hydroxyl group by deprotonated ligand, as shown for catechol, salicylic acid, and phthalic acid in Figures 7 and 8A–C. Figure 8D and E illustrates the adsorption behavior of iso- and terephthalate, where steric reasons require that the two carboxylate groups of the adsorbate interact with two different surface Ti(IV) sites. For terephthalate, this type of complexation results in a flat adsorption geometry while the other adsorbates are aligned in such a fashion that the plane of the benzene molecule is tilted with regard to the surface. This model is in agreement with the experimental observation in Table II that terephthalate requires practically twice as much surface area at monolayer coverage as the other benzene derivatives.

As a consequence of the replacement of water coordinated to Ti(IV) by the adsorbates, the trap depth of the surface state is expected to decrease. If the Lewis basicity of the ligand is strong enough, the electronic level of the surface state will be swept into the conduction band implying that its trapping action will vanish, Figure 9. Apart from changing the trap depth, complexation of Ti(IV) surface sites is also expected to influence the

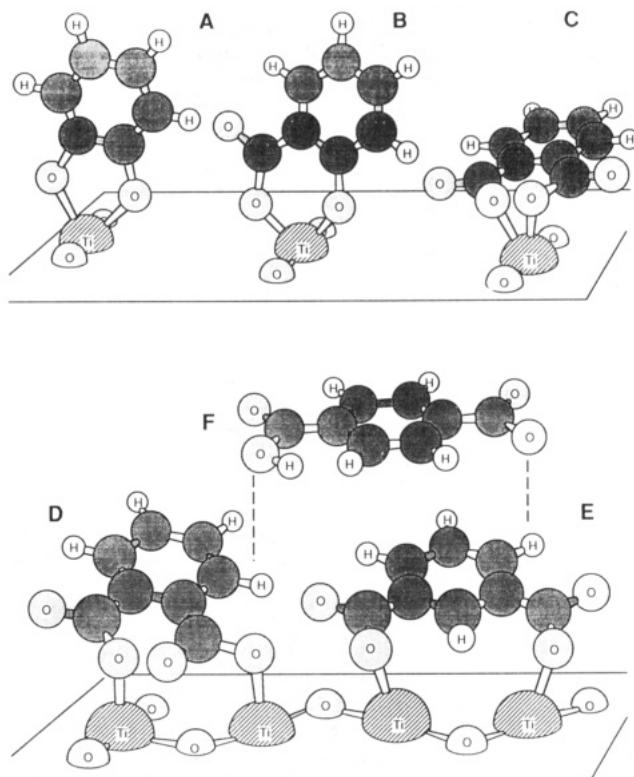


Figure 8. Ball and stick three-dimensional molecular models for Ti(IV)_s complexation by benzene derivatives. While catechol (A) and salicylate (B) could chelate individual titanium sites, standing perpendicular to the oxide surface, phthalic acid isomers are more likely to interact with two different surface Ti(IV) sites.

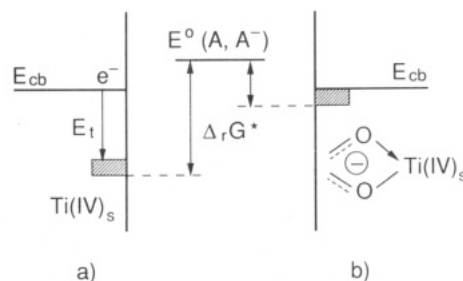


Figure 9. Schematic illustration of the energetics of interfacial electron transfer from the semiconductor to a redox couple in solution. (a) Conduction band electrons are trapped in surface sites which energy lies lower than the band edge. (b) Surface complexation of those Ti(IV)_s sites by electron-donating groups of benzene derivatives raises their energy, decreasing the corresponding standard free energy of reaction.

reorganization energy for electron transfer. Thus, replacing Ti(IV) coordinated water by the phthalate or salicylate may reduce the inner-sphere reorganization energy for reaction 6, increasing the nuclear factor κ_n . These two effects are suggested to play the key role in the striking rate enhancements for interfacial electron transfer observed here in the presence of Ti(IV) complexing adsorbates.

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Registry No. TiO₂, 13463-67-7; O₂, 7782-44-7; benzoic acid, 65-85-0; phthalic acid, 88-99-3; isophthalic acid, 121-91-5; terephthalic acid, 100-21-0; salicylic acid, 69-72-7; catechol, 120-80-9; methylviologen, 4685-14-7.

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