nm, is less than that of the lower energy band, 470 nm. The same intensity distribution is also observed for the spectra of acidic MAP solutions of pH = 2.6 and 3.6. As the solution pH decreases from 2.6 to 1.6, the increase in acidity causes more of the chemically transformed new species to be produced. This results in an inversion of the emission intensity of two separated bands shown in Figure 3D. This comparison indicates that the surface pH value of the Vycor glass calcined at 600 °C is ~ 2.6 . The inversion in the emission intensity of 367- and 470-nm bands observed in spectrum a demonstrates that the surface pH value of the Vycor glass calcined at 900 °C is lower than 2.6.

B. Chemical Transformation of Adsorbates Possessing a Low-Lying ${}^{3}\pi,\pi^{*}$ State. Both MAP and 9,10-dp molecules display a low-lying ${}^{3}\pi,\pi^{*}$ state and tend to promote chemical transformation and generation of new species as these molecules were embedded in the calcined Vycor glass or dissolved in sulfuric acid solutions. In 0.5 N H_2SO_4 solution, the photochemical reaction of 9,10-dp produces a new species, i.e., the protonated carbazole,⁸ which is the same species generated by the surface-induced transformation of 9,10-dp embedded in Vycor glass sintered at 900 °C. Likewise, the chemical transformation of MAP in the calcined Vycor glass also formed the same new species as those in the 0.5 N H_2SO_4 solution. However, we have performed a prolonged irradiation experiment for MAP dissolved in acidic solution and also for MAP embedded in Vycor glass, and no photochemical reaction was observed. This is consistent with the general observation that compounds with a low-lying ${}^{3}\pi,\pi^{*}$ state undergo photoreactivity with difficulty.^{11,13}

Since the protonation of carbonyls are reversible under acid conditions,²⁰ the pH value of acidic MAP solutions will cause a change in the equilibrium of carbonyl and protonated carbonyl (i.e., a type of alcohol-like compound). For Figure 3F-C, a lower pH value leads to a higher emission intensity of the peak maximum at 367 nm and a diminishing peak maximum at 470 nm. This suggests that the 367-nm band originates from the alcohol-like compound which is produced by the protonation of MAP species.

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For MAP embedded in Vycor glass, the surface-induced transformation of MAP due to the Brønsted acidity of the surface yields the same alcohol-like compound as MAP dissolved in H_2SO_4 solution. The inverted emission intensity of Figure 3a,b might result from the changes of equilibrium conditions due to the different degree of Brønsted acidity of the Vycor glass at different sintering temperatures (600 and 900 °C).

The interaction of the aromatic benzene ring with the surface hdyroxyl groups was observed for a study of methylbenzene adsorbed on a silica surface.²¹ A similar type of interaction involving the π -electron system of the non-nitrogen-containing aromatic ring and the surface hydroxyl groups was also detected for quinoline adsorbed on the calcined Mo/Al₂O₃ catalyst.²² It is noted that only MAP and 9,10-dp (i.e., molecules with $T_1(\pi,\pi^*)$ in nature) embedded in the calcined Vycor glass undergo a surface-induced reaction. The importance of the ${}^{3}\pi,\pi^{*}$ as T₁ state infers that the surface-induced transformations of 9,10-dp (i.e., a catalytic hydrodenitrogenation reaction) may proceed via the protonation of the N-heterocyclic ring together with the specific interactions between the non-nitrogen-containing aromatic ring and the surface hydroxyl groups. The later interaction leads to a deconjugative effect and allows the hydrodenitrogenation reaction to occur on catalytic surfaces. Similarly, the deconjugative effect would also allow the weakening of the C==O bond and formation of an alcohol-like compount for embedded MAP in the calcined Vycor glass. An analogous surface-induced reaction has also been proposed 23,24 previously.

Acknowledgment. Financial support from the Research Corp., the Northern Illinois University Graduate School, and the Northern Illinois University College of Liberal Arts and Sciences is acknowledged.

Registry No. BP, 119-61-9; AP, 98-86-2; MAP, 100-06-1.

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Selective Photoreduction of CO₂/HCO₃⁻ to Formate by Aqueous Suspensions and Colloids of Pd-TiO₂

Z. Goren, I. Willner,*

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

A. J. Nelson, and A. J. Frank*

Solar Energy Research Institute, Golden, Colorado 80401 (Received: November 9, 1989)

Immobilization of Pd onto TiO_2 powders and colloids results in active photocatalysts for the selective reduction of CO_2/HCO_3^{-1} to formate. The active photocatalysts are prepared by adsorption of either aqueous Pd- β -cyclodextrin colloids (Pd(β -CD)), synthesized at 60 °C, or aqueous Pd(citrate) colloids onto TiO₂ powders or colloids. Illuminated Pd-free TiO₂ suspensions, in the presence of CO_2/HCO_3^- and the electron donor oxalate, generate H_2 and a small amount of formate; formate is formed at a rate of $3.7 \times 10^{-3} \,\mu\text{mol min}^{-1}$. With Pd(β -CD,60 °C)-TiO₂ and Pd(citrate)-TiO₂ suspensions, the photoconversion of CO₂/HCO₃⁻ to formate occurs at rates of 2.3×10^{-2} and $3.7 \times 10^{-2} \,\mu$ mol min⁻¹, respectively. The photocatalytic reduction of CO₂/HCO₃⁻ to HCO₂⁻ is inhibited by mercaptoethanol. Concomitant with the decline in formate production, the rate of H₂ production increases. The inhibition of CO₂/HCO₃⁻ reduction is attributed to the binding of mercaptoethanol to the HCO_3^- -activation sites of Pd. The Pd(β -Cd,60 °C)-TiO₂ particles also catalyze the dark hydrogenation of CO₂/HCO₃by H_2 and the oxidation of formate by methyl viologen. A mechanism is invoked in which the photogenerated conduction-band electrons of TiO₂ either directly reduce protons to H₂ on the semiconductor surface or else reduce protons on the Pd surface to produce palladium hydride. The latter species reduces the Pd-activated HCO3⁻ to formate.

The photoreduction of carbon dioxide and its hydrated form, carbonic acid, or its dissociated ions, bicarbonate (HCO₃⁻) and carbonate (CO_3^{2-}), (eq 1) is a subject of much research.¹⁻³ The standard redox potentials^{4,5} for reducing CO_2 to C_1 products at Photoreduction of CO₂/HCO₃⁻ to Formate

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$
 (1)

pH 7 are given in eqs 2-6; the reduction of water to H_2 is shown in eq 7. The redox potentials show that the reduction of aqueous

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
 $E^\circ = -0.52 V$ (2)

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \qquad E^\circ = -0.42 \text{ V}$$
 (3)

$$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O \qquad E^\circ = -0.48 \text{ V} \qquad (4)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$
 $E^\circ = -0.38 \text{ V}$ (5)

 $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ $E^{\circ} = -0.24 \text{ V}$ (6)

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^\circ = -0.41 \text{ V}$$
(7)

 CO_2 to the C_1 products is favored thermodynamically over H_2 evolution. The kinetics for CO₂ reduction is unfavorable, however, and H₂ evolution generally predominates when thermodynamic conditions for both processes are met. Consequently, much effort has been directed toward the activation of CO₂, bicarbonate, and carbonate with various transition metals^{6,7} and transition-metal complexes.8,9

The reduction of carbon dioxide or bicarbonate can occur by hydrogenation,¹⁰ CO₂ insertion into metal hydride or metal alkyl complexes,¹¹ carbanion nucleophilic attack,¹² and electron transfer followed by protonation.¹³ Electrocatalyzed reduction of CO₂ by transition-metal complexes, such as Ni2+-cyclams and Co²⁺-cyclams,¹⁴ metal porphyrins and phthalocyanines,¹⁵ iron-sulfur clusters,¹⁶ and transition metals, such as Ru, Pd, and Cu, has been observed.¹⁷ The photosensitized reduction of CO_2 to CO by $Ru(bpy)_3^{2+}$ has been accomplished with Co(II)-bipyridine and Re^I(bpy)(CO)₃X catalysts.^{18,19} The photoreduction of CO₂

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to formate with the photosensitizer $Ru(bpy)_3^{2+}$ and either Ru- $(bpy)_2L_2^{2+20,21}$ or a Pd colloid catalyst has been reported.²² Also, CO₂ has been converted photochemically to formate in a system involving the enzyme formate dehydrogenase.²³ The photoconversion of CO₂ to methane in aqueous solutions containing the photosensitizer $Ru(bpy)_3^{2+}$ or $Ru(bpz)_3^{2+}$ and catalytic Ru or Os colloids has been observed.24

The photoelectrochemical reduction of CO₂ occurs at semiconductor electrodes,²⁵ such as GaP and GaAs, and in semiconductor suspensions and colloids,^{26,27} such as SrTiO₃ and CdS. The semiconductors generate a distribution of C_1 products, such as formic acid, formaldehyde, methane, and methanol, as well as C₂ products, such as acetic acid, oxalic acid, and glyoxylic acid. In these systems, the reduction of CO_2 is inefficient and the production of H₂ predominates. The selective photoelectrochemical reduction of CO_2 to formate at a GaP electrode in the presence of the electron relay methyl viologen and the biocatalyst formate dehydrogenase has been demonstrated.²⁸

Here we report on the selective reduction of CO_2/HCO_3^- to formate by photocatalytic Pd-TiO2 powdered suspensions and colloids. Immobilization of Pd onto TiO₂ suppresses H₂ evolution and promotes the selective reduction of CO_2/HCO_3^- to formate. This reaction proceeds, without an electron mediator, by direct coupling of conduction-band electrons of TiO₂ to the Pd surface catalyst.

Experimental Section

UV-visible absorption spectra were recorded on a Uvikon-860 (Kontron) spectrophotometer, equipped with a thermostated cell holder and a magnetic stirring motor. The amount of palladium deposited on the various particles was determined by atomic absorption measurements with a Perkin Elmer Model 403 spectrophotometer. The various methods employed for deposition produced similar Pd loadings (9-11 mg of Pd per gram of TiO₂ or 0.9-1.1% w/w). Hydrogen was analyzed on an HP 5890 gas chromatograph, equipped with a thermal conductivity detector, a 5-Å molecular sieve column, and argon carrier gas. Formate was analyzed by ion chromatography with an LKB HPLC unit, equipped with an anion-exclusion column (Wescan) and a conductivity detector (Knauer).

Illuminations were performed with a 450-W Xe short arc lamp, equipped with a 360-nm cutoff filter. The solution (3 mL) was contained in a serum stoppered 4-mL Pyrex glass cuvette and stirred continuously by a magnetic stirring bar. The temperature of the solution was controlled thermostatically. The quantum yields for the formation of H_2 and formate were determined with the knowledge of the amount of light absorbed by the system. This was estimated from the difference in light intensity that was transmitted through the solution in the absence and the presence of the semiconductor particles. The reported quantum yields should thus be considered as lower limits since scattered light was not taken into account.

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All chemicals were obtained from Aldrich or Sigma except for TiO_2 (Degussa), which was purchased from Fluka.

 $Pd(\beta - CD, 60 \circ C) - TiO_2$ powder was prepared as follows: $PdCl_2$ (15 mg) and 40 mg of NaCl were dissolved in 50 mL of an aqueous solution of β -CD (β -CD = β -cyclodextrin [1% (w/w)]) and stirred for 2 h at 60 °C. The resulting $Pd(\beta$ -CD,60 °C) colloidal solution was centrifuged at 3500 rpm for 10 min to exclude palladium precipitates and then deionized on a 300-mg Amberlite MB-1 column to remove $PdCl_4^{2-}$ (the presence of $PdCl_4^{2-}$ was followed spectrophotometrically before and after deionization). TiO₂ powder (0.4 g) was added to the Pd(β -Cd,60 °C) colloidal solution, which was then stirred for 2 h. The water was removed by evaporating the stirred solution to dryness on a 60 °C water bath. The procedure produced a gray powder, which was washed repeatedly with triple-distilled water, dialyzed, and then dried in vacuo. Elemental analysis showed that the powder did not contain any organic material, i.e., β -cyclodextrin. X-ray photoelectron spectroscopy showed that the Pd adsorbed on the TiO₂ surface was in the 0 and +2 valence states $(Pd^0/Pd^{2+} =$ 1.85); the Pd^{2+} is assumed to arise from the presence of surface PdO species.

 $Pd(\beta$ -CD,90 °C)- TiO_2 powder was prepared by a similar procedure, except that the Pd(β -CD) colloidal solution was synthesized at 90 °C.

 $Pd(citrate)-TiO_2$ powder was also prepared in a similar manner, but the Pd colloid was synthesized as follows: Pd(NO₃)₂ (90 mg) and 400 mg of sodium citrate were dissolved in 350 mL of boiling water, refluxed for 18 h, and then dialyzed for 2 days. TiO₂ powder (0.4 g) was added to 50 mL of the Pd(citrate) colloid.

 $Pd(h\nu)-TiO_2$ powder was prepared by irradiating ($\lambda > 360$ nm) a stirred dispersion of 1 g of TiO₂ powder for 2 h in 35 mL of triple-distilled water containing 102 mg of Na₂PdCl₆. The resulting powder was filtered, washed repeatedly with water, and then dried in vacuo.

 $TiO_2-(PVA)$ colloid (2 g L⁻¹) was prepared by hydrolysis of 0.28 mL of TiCl₄ in a cold aqueous solution (100 mL) of poly(vinyl alcohol) (1%, MW 86 000). The solution was then dialyzed at pH 3; the final pH was adjusted by adding NaOH.

Photoreduction of CO_2/HCO_3^- with $Pd-TiO_2$ Powders. TiO_2 powder (8 mg) was dispersed in aqueous solution containing 0.05 M NaHCO₃ and 0.05 M sodium oxalate as an electron donor. A sample (3 mL) of the solution was transferred to a cuvette, deaerated by repeated evacuation, and then bubbled with oxygen-free CO₂; the resulting pH was 6.8-7.0. Aliquots of the solution were removed during the illumination ($\lambda > 360$ nm) and analyzed for formate. The headspace above the solution was analyzed for H₂.

The kinetics of HCO_2^- production was studied as a function of the HCO_3^- concentration in an aqueous solution (3 mL) containing 0.1 M sodium oxalate and 8 mg of $Pd(\beta$ -CD,60 °C)-TiO₂ powder; the system was dearated by bubbling with Ar. Varying amounts of NaHCO₃ stock solution (5 × 10⁻¹ M) were added to the system and the pH was adjusted to 6.8 with dilute HCl before illumination. Formate production was inhibited by adding mercaptoethanol (HOCH₂CH₂SH) to the solution prior to photolysis.

Dark Hydrogenation of CO_2/HCO_3^- . Water (20 mL) containing 53 mg of Pd(β -CD,60 °C)-TiO₂ powder and 0.05 M NaHCO₃ was deaerated by bubbling with oxygen-free CO₂ (the resulting pH was 6.8-7.0) in a 50-mL pressure-tolerant vessel connected to H₂ and CO₂ cyclinders. Both CO₂ and H₂ were maintained at 1 atm in the vessel. The solution was stirred vigorously during the reaction and aliquots were taken to analyze for formate production. In some studies, mercaptoethanol was added to the solution prior to the introduction of H₂.

Oxidation of HCO_2^{-1} to Bicarbonate by MV^{2+} . The kinetics of HCO_2 oxidation was followed spectrophotometrically by monitoring the formation of the methyl viologen radical cation (MV^{*+}) at 602 nm ($\epsilon = 12400 \text{ M}^{-1} \text{ cm}^{-1}$) in a cuvette. The cuvette, which was maintained at 26 °C, contained a deaerated aqueous solution (3 mL, pH 6.8) of $1.7 \times 10^{-4} \text{ M MV}^{2+}$ and 40 mg L⁻¹ Pd(β -CD,60 °C) colloids. A sodium formate stock solution



Figure 1. Dependence of formate production on irradiation time ($\lambda_{ex} > 360 \text{ nm}$) for deaerated aqueous 0.05 M NaHCO₃ solutions (3 mL; pH 6.8) containing powdered suspensions of (a) Pd(β -CD,60 °C)-TiO₂ and (b) TiO₂.



Figure 2. Dependence of H₂ on irradiation time ($\lambda_{ex} > 360$ nm) for deaerated aqueous 0.05 M NaHCO₃ solutions (3 mL; pH 6.8) containing powdered suspensions of (a) Pd(β -CD,60 °C)-TiO₂, (b) TiO₂, (c) Pd-(β -CD,60 °C)-TiO₂ without NaHCO₃.

 $(100 \ \mu L)$ was then added to obtain a final concentration of 0.1 M sodium formate. To inhibit the oxidation reaction, mercaptoethanol was introduced to the solution before the sodium formate was added.

Results

Photocatalyzed Reduction of CO_2/HCO_3^- with TiO_2-Pd Powders. Illumination of aqueous $Pd(\beta-CD)-TiO_2$ suspensions (pH 6.8) containing 5×10^{-2} M bicarbonate and the sacrificial electron donor oxalate produced formate (Figure 1a) and H₂ (Figure 2a). In the absence of bicarbonate, only H_2 evolution took place, implying that the formate originates from the reduction of CO_2/HCO_3^- . The initial rates of HCO_2^- and H_2 formation were 2.3×10^{-2} and $5.2 \times 10^{-2} \mu \text{mol min}^{-1}$, respectively. Figure 2b shows that H₂ was the major product when a TiO₂ suspension without the Pd catalyst was illuminated in the presence of CO_2/HCO_3^{-} . In this system, only a small amount of formate was formed and its initial rate of production was $3.7 \times 10^{-3} \,\mu\text{mol min}^{-1}$ (Figure 1b). Figure 2c shows the production of H_2 when $Pd(\beta$ -CD,60 °C)-TiO₂ was illuminated in the absence of CO_2/HCO_3^- . The implication of Figure 1b is that illuminated TiO₂ particles without the Pd catalyst can reduce CO_2/HCO_3^- to formate. The addition of the catalyst, however, improved the activity of the TiO₂ particles by a factor of 6.2 compared to the Pd-free semiconductor system. The rate of H₂ evolution in the Pd(β -CD,60 °C)-TiO₂ system without CO_2/HCO_3^- was comparable to that in the Pd-free TiO_2 system, implying that Pd did not significantly catalyze H₂ production.

The activity of Pd toward CO_2/HCO_3^- reduction depends on the method by which the metal is prepared.²⁹ For example, an aqueous Pd colloid prepared with β -CD at 60 °C exhibited much higher catalytic activity toward CO_2/HCO_3^- reduction than one prepared with β -CD at 90 °C. To further investigate the effect of Pd preparation on the TiO₂ activity, several Pd-derivatized TiO₂ powders were synthesized. These included Pd(β -CD,60 °C)-TiO₂, Pd(β -CD,90 °C)-TiO₂, Pd(citrate)-TiO₂, and Pd($h\nu$)-TiO₂;³⁰ in

⁽²⁹⁾ Willner, I.; Mandler, D. J. Am. Chem. Soc. 1989, 111, 1330.

TABLE I: Initial Rates and Quantum Yields for H₂ Evolution and Formate Generation in Various Aqueous Suspensions of Pd-TiO2 and TiO2ª,b

semiconductor	υ _{H2} , μmol min ⁻¹	$\phi_{ m H_2}$	υ _{HCO2} -, μmol min ⁻¹	<i>ф</i> нсо₂-	SF
TiO,	17×10^{-2}	1.3×10^{-1}	3.7×10^{-3}	2.9×10^{-3}	46
Pd(β-CD,60 °C)-TiO ₂	5.2×10^{-2}	4×10^{-2}	2.3×10^{-2}	1.8×10^{-2}	2.3
Pd(citrate- TiO ₂	8.5×10^{-2}	6.8×10^{-2}	3.7×10^{-2}	2.9×10^{-2}	2.3
$Pd(hv) - TiO_2$	15×10^{-2}	1.1×10^{-1}	1.2×10^{-2}	9.2×10^{-3}	12
Pd(β-CD,90 °C)TiO ₂	17.9×10^{-2}	1.4×10^{-1}	1.4×10^{-2}	1.1×10^{-2}	12.8

^a In 3 mL solution containing 8 mg of catalyst, 5×10^{-2} M sodium oxalate, and 5×10^{-2} M HCO₃⁻ under a CO₂ atmosphere; $\lambda > 320$ nm. ^bLight intensity = 1.7×10^{-3} einstein min⁻¹ L⁻¹. ^c Selectivity factor SF = v_{H_3} / VHCO2-



Figure 3. (a) Initial rates (v_0) of HCO₂⁻ photogeneration ($\lambda_{ex} > 360 \text{ nm}$) as a function of HCO_3^- concentrations in deaerated aqueous solutions (3) mL; pH 6.8) containing a powdered suspension of 2.7 mg mL⁻¹ Pd(β -CD,60 °C)-TiO₂. (b) Reciprocals of the initial rates of HCO_2^- formation $(1/v_0)$ as a function of reciprocals of HCO₃⁻ concentrations, 1/[HCO₃⁻⁻].

the study of each semiconductor, oxalate was used as an electron donor. Table I summarizes the initial rates, v_0 , and quantum yields, ϕ , of both H₂ and formate production in these systems and compares their activities to that of Pd(β -CD,60 °C)-TiO₂. Table I also lists the selectivity factor, SF, which is defined as the ratio of the rate of H₂ evolution to the rate of formate production (SF = $v_{\rm H_2}/v_{\rm HCO_2}$). It can be seen that the initial rates of H₂ and HCO_2^- formation with Pd(citrate)-TiO₂ are comparable to those with Pd(β -CD,60 °C)-TiO₂; the selectivity factors of these semiconductors are essentially the same, 2.3. The $Pd(\beta$ -CD,90 °C)-TiO₂ and Pd($h\nu$)-TiO₂ suspensions exhibit, on the other hand, relatively low activity toward \dot{CO}_2/HCO_3^- reduction and higher activity toward H₂ evolution; their selectivity factors are 12.8 and 12, respectively.

Figure 3a shows the photoproduction of formate increases with the bicarbonate concentration in an aqueous suspension of Pd-(β -CD,60 °C). After a concentration of 0.1 M HCO₃, however, the rate of formate production levels off, reaching a maximum value of $3.3 \times 10^{-2} \ \mu \text{mol min}^{-1}$. The plateauing of formate production at high bicarbonate concentrations suggests the existence of specific Pd sites, where both activation and reduction of HCO_3^- take place. The leveling off of HCO_2^- production is thus attributed to the saturation of these active sites by HCO3-. By analogy with substrate activation by enzymes,³¹ the rate-limiting step in the production of formate is presumed to involve the



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Figure 4. Dependence of (a) formate and (b) H_2 production on irradiation time (λ_{ex} > 360 nm) for deaerated aqueous 0.05 M NaHCO₃ solutions (3 mL; pH 6.8) containing a powdered suspension of $Pd(\beta$ -CD,60 °C)-TiO₂ at different concentrations of mercaptoethanol.

TABLE II:	Initial Rates	of Formate	e and H ₂ Pi	roduction in	the
Presence of	Pd(β-CD, 60	°C)-TiO ₂	and Merca	ptoethanol	

mercaptoethanol, M	υ _{H2} , μmol min ⁻¹	^υ нсо₂⁻, µmol min⁻¹	SF ^b
0	5.2×10^{-2}	2.3×10^{-2}	2.3
1×10^{-6}	7.5×10^{-2}	2.2×10^{-2}	3.4
1×10^{-5}	10.2×10^{-2}	1.5×10^{-2}	6.8
5×10^{-5}	13.9×10^{-2}	1.1×10^{-2}	12.6
1×10^{-4}	14.7×10^{-2}	8.2×10^{-3}	17.9

^a In 3 mL solution containing 8 mg of catalyst, 5×10^{-2} M sodium oxalate, and 5×10^{-2} M HCO₃⁻ under a CO₂ atmosphere; $\lambda > 320$ nm. ^bSelectivity factor SF = $v_{\rm H_2}/v_{\rm HCO_2^{-1}}$

formation of a complex between HCO3⁻ and specific Pd sites (eq 8). The applicability of the active-site kinetics model of enzymes³¹

$$Pd + HCO_3^{-} \rightleftharpoons [Pd - HCO_3^{-}]$$
(8)

to formate production in the Pd(β -CD,60 °C)-TiO₂ system was investigated by applying eq 9, which correlates the initial rate of formate production, v_0 , with the concentration of bicarbonate

$$v_0 = \frac{V_{\max}[\text{HCO}_3^-]}{K_m + [\text{HCO}_3^-]}$$
(9a)

$$1/v_0 = \frac{1}{V_{\text{max}}} + \frac{K_{\text{m}}}{V_{\text{max}}} \frac{1}{[\text{HCO}_3^-]}$$
 (9b)

where V_{max} is the maximum rate of formate production at the specific concentration of Pd and K_m is the bicarbonate concentration at which the rate is half-maximal.³² Figure 3b shows the predicted linear relationship between $1/v_0$ and $1/\text{HCO}_3^-$ near the plateau in Figure 3a. From the plot, $K_{\rm m}$ and $V_{\rm max}$ were evaluated to be 4.3×10^{-2} M and $4.2 \times 10^{-2} \,\mu{\rm mol\ min^{-1}}$, respectively. Inhibition of CO_2/HCO_3^- Reduction. The photocatalyzed

reduction of CO_2/HCO_3^- by Pd-TiO₂ is inhibited by amines,

(31) Segel, I. H., Ed. Enzyme Kinetics; Wiley: New York, 1975. (32

) The definition of
$$K_m$$
 (Michaelis–Menten constant) is

$$K_{\rm m} = \frac{k_2 + k_3}{k_1}$$

where the rate constants k_1 , k_2 , and k_3 are for the reactions

These reactions correspond to eqs 16 and 17.

$$H-Pd-H + HCO_3^{-} \xrightarrow{k_1} H-Pd-HCO_3^{-} \xrightarrow{k_3} Pd + HCO_3^{-} + H_2O$$

(30) Kraeutler, B.; Bard, A. J. J. Am. Chem. Soc. 1978, 100, 2239.



Figure 5. Dependence of formate production on both time and the mercaptoethanol concentration in the dark hydrogenation of bicarbonate in deaerated aqueous 0.05 M NaHCO₃ solutions (3 mL; pH 6.8) under H₂ ($P_{H_2} = 1 \text{ atm}$) and CO₂ ($P_{CO_2} = 1 \text{ atm}$). (a) Pd(β -CD,60 °C)-TiO₂ suspension without mercaptoethanol, (b) Pd(β -CD,60 °C) colloid without TiO₂ and mercaptoethanol, (c) Pd(β -CD,60 °C)-TiO₂ suspension, 10⁻³ M mercaptoethanol, (d) Pd(β -CD,60 °C)-TiO₂ suspension, 10⁻³ M mercaptoethanol, (e) Pd(β -CD,60 °C)-TiO₂ suspension, 10⁻² M mercaptoethanol.

aldehydes, or thiols. Figure 4a shows the inhibition effect of mercaptoethanol (HOCH₂CH₂SH) on the photoproduction of formate in aqueous $Pd(\beta-CD,60 \circ C)$ -TiO₂ suspensions. Figure 4b displays the concentration effect of mercaptoethanol on the photoproduction of H_2 in the same system. It can be seen that, with increasing concentration of mercaptoethanol, the rate of formate formation declines. Concomitant with the inhibition of formate production, the rate of H₂ evolution increases. Table II lists the initial rates of H₂ and formate production and the corresponding selectivity factors at different mercaptoethanol concentrations. At 10⁻⁴ M mercaptoethanol, the activity of the system toward CO_2/HCO_3^- reduction approaches that of the Pd-free TiO₂ powder (see Table I). The major photoproduct of the reaction is H₂. Similarly, in Pd(citrate)-TiO₂ suspensions, mercaptoethanol inhibits the photoreduction of CO_2/HCO_3 . The inhibition of CO_2/HCO_3^{-} reduction is attributed to the binding of mercapoethanol to HCO₃-activation sites on Pd (eq 10).

$$[Pd-HCO_3^-] + RS^- \rightleftharpoons [Pd-SR^-] + HCO_3^- \qquad (10)$$

Dark Hydrogenation of CO_2/HCO_3^- to Formate. The dark hydrogenation of bicarbonate to formate in the presence of Pd/C and Pd/Al₂O₃ catalysts has been investigated.³³ These studies suggest that H₂ dissociates on the palladium surface to form Pd hydrides or surface-bound hydrogen atoms that subsequently hydrogenate Pd-activated bicarbonate. We have examined the dark hydrogenation of CO₂/HCO₃⁻ by Pd(\beta-CD,60 °C)-TiO₂ suspensions. Figure 5 shows the production of formate in a Pd- $(\beta$ -CD,60 °C)-TiO₂ suspension was 5 × 10⁻² M HCO₃⁻ under an atmosphere of CO₂ and H₂ at various concentrations of mercaptoethanol. It can be seen that the rate of formate production declines with increasing concentrations of the mercaptoethanol; at 10⁻² M HOCH₂CH₂SH, the hydrogenation of bicarbonate is blocked completely. Thus, the activity of the Pd catalyst toward hydrogenation of bicarbonate in the dark is lowered by mercaptoethanol in analogy to the thiol effect observed in the photocatalyzed reduction of CO_2/HCO_3^- (Figure 4a).

Reversible Activity of $Pd(\beta$ -CD,60 °C). The addition of the Pd(β -CD,60 °C)–TiO₂ powder to an aqueous 5 × 10⁻² M formate solution resulted in the slow oxidation of formate to bicarbonate and concomitant H₂ evolution (eq 11). When the electron mediator methyl viologen, MV²⁺, was added to the system, the blue MV⁺⁺ radical cation was formed rapidly (eq 12). Because of light

$$HCO_2^- + H_2O \xrightarrow{Pd(\beta-CD,60 \circ C)-TiO_2} HCO_3^- + H_2 \quad (11)$$

$$HCO_3^- + 2MV^{+} + 2H^+$$
 (12)

scattering by the powdered suspension, the reduction of MV²⁺

 $HCO_{2}^{-} + 2MV^{2+} + H_{2}O$





Figure 6. Absorption-time profiles of the dark reduction of MV^{2+} by HCO_2^- with $Pd(\beta$ -CD,60 °C) colloid in deaerated aqueous solutions (3 mL; pH 6.8) containing $1.7 \times 10^{-4} MV^{2+}$, 0.1 M NaHCO₂, and 40 mg L⁻¹ $Pd(\beta$ -CD,60 °C) colloids at different concentrations of mercaptoethanol. (a) 0 M, (b) 10^{-5} M, (c) 2.5×10^{-5} M, (d) 10^{-4} M, (e) 2×10^{-4} M.

by formate could not be followed spectrophotometrically. To circumvent this problem, transparent colloidal solutions of Pd- $(\beta$ -CD,60 °C) were examined in the absence of TiO₂ particles. Figure 6a shows the absorbance-time profile of MV*+ formation in the Pd(β -CD,60 °C) system. It can be seen that, following an induction period, MV⁺⁺ concentration builds up rapidly, passes through a maximum, and then declines. Figure 6b-e shows the reduction of MV²⁺ by formate in the presence of varying concentrations of mercaptoethanol. It can be seen that, as the concentration of mercaptoethanol increases, the induction period becomes longer. The presence of an induction period is attributed to the time required for reduction of Pd⁰ and PdO to Pd hydride during the dehydrogenation of formate; the existence of Pd in the 0 and +2 valence state was indicated by XPS. Presumably, Pd-H reduces MV^{2+} to the MV^{++} radical cation $[E^{\circ}(MV^{2+}/MV^{++}) =$ -0.42 V (NHE)] and mediates H₂ production, which is also observed.

$$2MV^{+} + 2H^{+} \xrightarrow{Pd} 2MV^{2+} + H_{2}$$
(13)

The rate of H₂ production (see eq 11) is slower than that of MV^{*+} formation (see eq 12) in the colloidal Pd(β -CD,60 °C) system. Figure 6b–e shows that the rate and yield of MV^{*+} formation decline with increasing mercaptoethanol concentration, suggesting that the thiol inhibits the dehydrogenation reaction of formate and the consequential formation of Pd hydride. Because mercaptoethanol inhibits both the dehydrogenation of formate and the hydrogenation of carbon dioxide/bicarbonate, we infer that the activation of HCO₂⁻ toward hydrogenation and the activation of CO₂/HCO₃⁻ toward reduction involve the same Pd surface sites. It should be noted that the Pd(β -CD,90 °C)-TiO₂ suspension is a poor catalyst for both the photoreduction of CO₂/HCO₃⁻ and the dehydrogenation of formate and does not catalyze significantly the reduction of MV²⁺ by formate.

Photoreduction of CO_2/HCO_3^- by $Pd-TiO_2$ Colloids. The photoreduction of CO_2/HCO_3^- by TiO₂ colloids stabilized by poly(vinyl alcohol), TiO₂-PVA, in the absence and the presence of Pd(β -CD,60 °C) colloids was examined. The experimental results of this study were similar to those found in the investigation of the suspensions (Figures 1, 2, and 4). Illumination of aqueous TiO₂-PVA colloids with CO₂/HCO₃⁻ in the absence of Pd(β -CD,60 °C) colloids generated H₂ and a small amount of formate, which was formed at an initial rate of 2.1 × 10⁻³ µmol min⁻¹. When the Pd(β -CD,60 °C) catalyst was also present in the TiO₂-PVA system, the yield of formate was augmented. Also, the initial rate of formate production (3.9 × 10⁻² µmol min⁻¹; ϕ = 1.4 × 10⁻²) was improved by a factor of 18.5 compared to the colloidal solution with the catalyst. Along with the enhanced

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 HCO_2^- production, H_2 evolution decreased. The selectivity factors for bicarbnate reduction by TiO₂-PVA and Pd(β -CD,60 °C)-(TiO₂-PVA) colloids were 71.4 and 3.1, respectively. Thus, even though TiO₂-PVA was in the colloidal state, good contact between the semiconductor and the Pd(β -CD,60 °C) catalyst took place to effect the reduction of CO₂/HCO₃⁻ to formate.

Discussion

The reduction of CO_2/HCO_3^- by semiconductor particles, such as TiO₂, SrTiO₃, and CdS, is usually inefficient and nonselective, yielding a mixture of C1- and C2-organic products, such as formic acid, glyoxylic acid, oxalic acid, formaldehyde, and methanol.^{26,27} The one-electron reduction of free CO_2 ($E^{\circ}(CO_2^{\bullet-}/CO_2) = -2.1$ V) by conduction-band electrons of these semiconductors is thermodynamically unfavorable. The low quantum yields for CO₂ reduction in these systems are attributed to the kinetic limitation inherent in multielectron transfer.^{27a} The complex mixture of C₁ and C2 products was believed to arise from the photocatalyzed oxidation and reduction of singly reduced CO2/HCO3-. Solid-gas spectroscopic studies^{8a,34} have shown that CO₂ reduction is activated by metal oxides, such as TiO2. The results of our study suggest that Pd-TiO₂ particles promote the selective two-electron reduction of CO₂/HCO₃⁻ to formate. This reduction is thermodynamically favorable since the redox potential of conduction-band electrons of TiO₂ [$E^{\circ'}_{CB}(e^{-}) = (0.11-0.06 \text{ pH}) V =$ -0.53 V]³⁵ is negative of the redox potential for converting CO_2/HCO_3^- to formate ($E^\circ = -0.42$ V, pH 7 vs NHE).^{4,5} The low yield of HCO₂⁻ in the Pd-free TiO₂ system is thus attributed to the unfavorable kinetics because of the high activation energy for reduction of CO_2/HCO_3^- on the semiconductor surface. The Pd catalysts, immobilized on the TiO₂ particle surface by adsorption of Pd(β-CD,60 °C) or Pd(citrate) colloids, greatly promote the light-driven reduction of CO_2/HCO_3^- to formate. The $Pd(\beta$ -CD,60 °C)-TiO₂ and Pd(citrate)-TiO₂ systems showed a respective 6.2- and 10-fold enhancement in the reduction of bicarbonate to HCO2⁻ compared to the Pd-free TiO2 system. On the time scales of the photolysis experiments, the only organic product found was formate. Although the Pd-TiO₂ particles exhibit relatively high activity towards CO₂/HCO₃⁻ reduction, they displayed only a small degree of activity toward the photoreduction of water to H₂ as evidenced by the comparable rates of H₂ evolution in the TiO₂ and the Pd(β -CD,60 °C)-TiO₂ systems without CO_2/HCO_3^- . In the presence of CO_2/HCO_3^- , the yield of H_2 in the Pd-TiO₂ system is 3 times lower than that in the catalyst-free TiO₂ system, indicating that the Pd catalyst enhances HCO_2^- production with respect to H₂ evolution. The selectivity factor of the Pd(β -CD,60 °C)–(TiO₂–PVA) colloids (SF = 3.1) for formate and H₂ production is similar to that of the powdered $Pd(\beta$ -CD,60 °C)-TiO₂ suspensions (SF = 2.3). The observation that Pd deposits on TiO_2 do not effectively catalyze H₂ evolution is of special interest since other noble metals, such as Pt and Rh, are very active water-reduction catalysts. Other studies³⁶ have also shown that Pd is a poor H2-evolution catalyst compared to Pt and Rh. The rationale for this behavior is that hydrogen atoms or hydrides bind tightly to Pd, disfavoring H₂ production. The poor activity of Pd to evolve H₂ from water was also consistent with the results of the experiments on the oxidation of formate to bicarbonate (eq 11 and eq 12). Formate reduces water to H₂ more slowly than it reduces MV²⁺ to MV⁺⁺. Since these two processes probably proceed through a common Pd-H intermediate (see below), we infer that the rate of H₂ formation from the dimerization of adsorbed hydrogen atoms is relatively slow.

The method of preparing the Pd catalysts significantly affects their activity toward CO_2/HCO_3^- reduction. Both Pd(citrate)-TiO₂ and Pd(β -CD,60 °C)-TiO₂ suspensions are active



Figure 7. Representation of the photocatalyzed reduction of HCO_3^- to formate by $Pd(\beta$ -CD)-TiO₂.

toward CO_2/HCO_3^- reduction, whereas both $Pd(\beta$ -CD,90 °C)-TiO₂ and $Pd(h\nu)$ -TiO₂ exhibit poor activity. The difference in activity between $Pd(\beta$ -CD,60 °C) and $Pd(\beta$ -CD,90 °C) colloids is probably due to their surface morphology. Preliminary high-resolution electron microscopy studies indicate that, although $Pd(\beta$ -CD) colloids prepared at 60 and 90 °C have a similar size distribution (30-200 Å), $Pd(\beta$ -CD,60 °C) is composed of smaller aggregates, which presumably have more exposed edges.

The electron carrier MV^{*} has been shown to mediate the dark reduction of CO_2/HCO_3^- to formate in the presence of the Pd-(β -CD,60 °C) colloid.²⁹ The present study demonstrates that the photoreduction of CO_2/HCO_3^- also takes place in aqueous powdered suspensions and colloids of Pd-TiO₂. The mechanism of CO_2/HCO_3^- reduction on Pd has been the subject of several reports.^{10c,29,33}

$$Pd + H_2 \xrightarrow{H} Pd - H$$
(14)

$$Pd + 2MV^{+} + 2H_2^{+} = Pd_{-}H + 2MV^{2+}$$
 (15)

$$[HCO_3^--Pd_-H] \longrightarrow Pd + HCO_2^- + H_2O$$
 (17)

Hydrogen atoms (or hydrides) are formed by dissociation of H₂ on the Pd surface (eq 14) or by proton reduction on electronically charged Pd (eq 15). Bicarbonate is activated on specific Pd sites (eq 16) followed by its hydrogenation to formate (eq 17). Both the dark and the light-activated hydrogenation of CO₂/HCO₃ in the presence of Pd(\beta-CD,60 °C)-TiO2 also appear to proceed via eqs 14, 16, and 17. The photoreduction of CO₂/HCO₃probably entails electronic charging of Pd sites by conduction-band electrons of TiO₂ followed by proton reduction at the metal surface and then hydrogenation of CO₂/HCO₃-, as portrayed in Figure 7. The reverse process (eqs 17-14) in which formate is oxidized by MV^{2+} is also observed. In the reverse reaction, however, H_2 evolution (eq 14) was found to be relatively inefficient. This observation supports the inference that Pd is a poor H2-evolution catalyst because of the relatively unfavorable energetics for H-atom recombination on the Pd surface. Both the photoreduction and dark hydrogenation of CO₂/HCO₃⁻ and the oxidation of formate are inhibited by mercaptoethanol, implying that the thiol binds to specific HCO3⁻ and HCO2⁻ activation sites of Pd. Furthermore, since illuminated Pd(\beta-CD,60 °C)-TiO2 suspensions in the presence of mercaptoethanol augment the relative yield of H_2 with respect to CO₂/HCO₃⁻ reduction, the thiol probably does not interfere directly with the mechanism of H₂ production. Pre-

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sumably, mercaptoethanol selectively blocks Pd surface sites for activating bicarbonate, thus favoring the transfer of conductionband electrons to H_2 -evolving sites.

A comparison of the selectivity factor can be made between the Pd-TiO₂ systems and the previously examined photosystem²⁹ consisting of the photosensitizer deazariboflavin, dRFl, the electron mediator MV2+, the electron donor oxalate, and the catalyst Pd(β -CD,60 °C) colloids. The best selectivity factor of the Pd- TiO_2 systems (SF = 2.3; see Table I) is larger than that of $dRFl/MV^{2+}/oxalate/Pd(\beta-CD,60 \ ^{\circ}C)$ (SF = 0.013), indicating that the former exhibits lower selectivity for HCO₃⁻ reduction with respect to H₂ evolution than the latter. The basis for this difference in selectivity remains to be established, however.

In conclusion, electron transfer from TiO₂ to properly prepared catalytic Pd surface sites promotes the reduction of CO_2/HCO_3^{-1}

to formate. The selectivity exhibited by the Pd-TiO₂ particle systems is quite noteworthy in relation to other semiconductorbased systems, which generate a broad distribution of products. Specific sites on the Pd surface favor CO₂/HCO₃⁻ reduction over H_2 evolution. The experimental results reported here as well as those of others^{24a} suggest that other metals might exhibit selectivity in catalyzing the reduction of CO₂ to other desirable organic photoproducts.

Acknowledgment. This work was supported by the Kernforschung Anlage, Juelich, W. Germany, and the Gas Research Institute (Contract No. 5083-260-0796).

Registry No. Pd, 7440-05-3; Pd(citrate), 73276-33-2; TiO₂, 13463-67-7; CO₂, 124-38-9; HCO₃⁻, 71-52-3; HCO₂⁻, 71-47-6; C₂O₄²⁻, 62-76-0; HOCH₂CH₂SH, 60-24-2; H₂, 1333-74-0; methyl viologen, 1910-42-5.

Free Energy of a Charge Distribution in a Spheroidal Cavity Surrounded by Concentric **Dielectric Continua**

Juan S. Gomez-Jeria*

Department of Chemistry, Faculty of Sciences, University of Chile, P.O. Box 653, Santiago, Chile

and Demian Morales-Lagos*

Institute of Chemistry, Faculty of Sciences, Austral University of Chile, P.O. Box 567, Valdivia, Chile (Received: December 27, 1988; In Final Form: September 28, 1989)

We present a theoretical treatment for the Helmholtz free energy of an arbitrary discrete charge distribution in a central prolate or oblate spheroidal cavity surrounded by two and three concentric dielectric continua of the same symmetry. The electrostatic interaction is accounted for by a multipolar expansion. This model permits us to consider in a simple way nonlinear dielectric effects and the nonsphericity of solute molecules. The results are presented in a suitable form to discuss them in terms of a virtual polarization charge distribution. Also, we give an explicit expression for the contributions coming from the zeroth-order multipole moments for any number of shells.

I. Introduction

Solvent effects can be modeled in three ways. The first, referred to as the continuum approach,¹⁻³ considers the solute localized in an empty cavity embedded in a structureless polarizable dielectric continuous medium. The electrostatic solute-solvent interactions are accounted for by means of reaction field theory⁴ and then incorporated into quantum mechanical formalisms. The second is the supermolecule approach in which the medium is explicitly represented by a finite number of solvent molecules.⁵ The last is a combination of the other two approaches and it is called the "continuum-supermolecule" approach.^{6,7} In the following, we shall center our attention on the continuum models because they give solvation energies with good accuracy maintaining the simplicity of their mathematical formulation and numerical applications.⁷

Continuum models are rooted in the fact that, at larger solute-solvent distances, it is possible to replace the discrete summations of the intermolecular interactions over the solvent molecules with continuous integrals.⁸ On the other hand, they allow the incorporation of temperature-dependent effects.⁹

The earliest analysis was presented in the now classical paper of Born.¹ His work considered a point charge located in the center of a spherical cavity surrounded by a homogeneous continuous medium characterized by the macroscopic dielectric permitivity of the solvent.

This model can be improved in three principal ways. First, the interaction of the homogeneous dielectric continuum with higher

electric moments can be considered. Within this scheme we have the Onsager model in which the solute molecule carries a permanent dipole moment that can be enhanced by the reaction field through an isotropic harmonic polarizability,² and the Kirkwood analysis of the case of discrete point charges inside a spherical cavity employing a multipolar expansion of the charge distribution in the cavity center.⁹ The general case of a polarizable charge distribution was studied later.¹⁰ Quantum mechanical schemes have been derived from these approaches.11-13

The second improvement takes into account the shape of the cavity. Clearly, spherical cavity models are restricted to physical systems possessing the same symmetry, i.e., spherical ions and molecules. This consideration led to the analysis of spheroidal

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