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Quantitative Electrochemical Kinetics Studies of "Microelectrodes": Catalytic Water Reduction by Methyl Viologen/Colloidal Platinum

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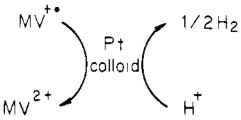
Abstract: The reduction of water by methyl viologen, catalyzed by colloidal platinum, has been extensively studied as a function of pH, radical concentration, and platinum concentration by several independent techniques. The data present a comparative test of a homogeneous kinetic approach and a novel electrochemical approach. Two techniques were used to monitor the platinum-catalyzed oxidation of methyl viologen radical: conventional and stopped flow mixing experiments, and a novel application of electrocatalytic cyclic voltammetry. Conventional kinetic analysis for homogeneous reactions provides conditional rate constants which are greater than first order in platinum. At $[\mathrm{Pt}] = 10^{-6}$ M and pH 3.0, the conditional rate constant is $k = 1.2 \times 10^4$ L mol^{-1} s^{-1}. In addition, steady state catalysis of hydrogen production analogous to photochemical systems was monitored in a nonphotochemical system, using electrochemically reduced mediators. The methods are critically compared as mechanistic tools. Only data obtained with use of steady state techniques can be quantitatively analyzed by using simple electrochemical theory. The principle findings include the following: (1) a surprising apparent second order rate dependence on colloid concentration is accounted for by electrochemical theory, but *not* by homogeneous theory; (2) the electrochemical model quantitatively accounts for the shift in $\mathrm{pH}_{1/2}$ with mediator concentration; and (3) with use of an electrogenerated mediator an experimental value for $\log j_{\mathrm{H}_2}{}^0 = -3.4$ is obtained for colloidal platinum, in good agreement with the bulk electrode.

While redox catalysis at metal colloids has long been of interest,[1-6] this interest has been heightened by the use of metal colloids in (solar) photoreduction of water. In these reactions, a (photoreduced) mediator, e.g., methyl viologen radical, ($\mathrm{MV}^{+\cdot}$), reacts with protons at the metal colloid to produce hydrogen as in eq 1. This catalytic step can ultimately determine the efficiency of such photochemical schemes (by competing with unproductive back reaction of the photoproducts).[7-9] Therefore, a number of kinetic studies of this colloid catalysis have appeared.[2,4,8-12] A developing consensus of this work is that the metal colloids function like dispersed electrodes (or "microelectrodes"). However, most kinetic studies to date have been analyzed by using microscopic kinetic models which apply to homogeneous reactions. For example, Meisel,[2] Heinglein,[3] and others have analyzed data on colloid catalyzed H_2 production in terms of a series of linked, homogeneous reactions:



(1)

$$\mathrm{D}^- + \mathrm{M}_{\mathrm{colloid}} \rightarrow \mathrm{D} + \mathrm{M}_{\mathrm{colloid}}{}^-$$

$$\mathrm{D}^- + \mathrm{M}_{\mathrm{colloid}}{}^{n-} \rightarrow \mathrm{D} + \mathrm{M}_{\mathrm{colloid}}{}^{(n+1)-}$$

$$\mathrm{M}^{n-} + \mathrm{H}^+ \rightarrow \tfrac{1}{2}\mathrm{H}_2 + \mathrm{M}^{(n-1)-}$$

While these experiments have yielded much useful insight, the homogeneous kinetic models provide only conditional rate constants which lack simple predictive power. If the colloidal catalysts indeed function like bulk electrodes, then kinetic modeling should be based on the fundamental theories of heterogeneous, electrode kinetics. Quite recently, such a theory, with preliminary supporting data, has been presented by Miller, Bard, et al.[12] These homo-

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[11] Kalyanasundaram, K.; Micic, O.; Pramauro, E.; Grätzel, M. *Helv. Chim. Acta* **1979**, *62*, 2432–41.

[12] Miller, D.; Bard, A.; McLendon, G.; Ferguson, J. *J. Am. Chem. Soc.* **1981** *103*, 5336–5341.

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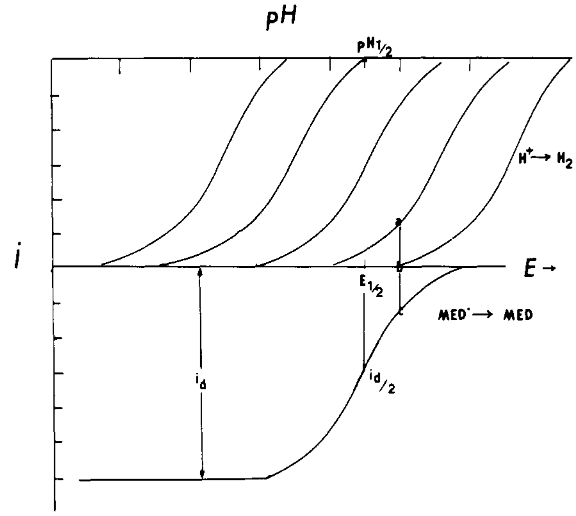

Figure 1. Current-voltage curves for the potential matching of an anodic reaction (mediator· → mediator) with a cathodic reaction ($H^+ \rightarrow {}^1/_2H_2$). The current, or rate of H_2 formation and rate of mediator· disappearance, at each pH is predicted by the vertical displacement between the zero current line and the anodic (mediator) curve (line bc). At low pH, the rate i_{H_2} is assumed to be limited by mediator mass transport. The rate at half-maximal velocity $i/2$ defines the "Nernst" potential for the hydrogen reaction ($E_{1/2}$ or $pH_{1/2}$).

geneous kinetics yield only conditional rate constants which lack simple predictive power. In addition, many photochemical studies have been complicated by the presence of extraneous reactions involving the photoacceptor. Thus, new, simple experimental techniques combined with an appropriate electrochemical rate theory are needed to obtain clear (predictive) understanding of this catalysis.

Quite recently, an appropriate electrochemical theory and preliminary supporting data were presented by Miller, Bard, et al.[12] This treatment is based on the corrosion theory of Wagner and Traud,[21] as modified by Spiro.[6] In essence, if the colloid functions like a bulk electrode, the individual current-potential (i–E) curves for both half-reactions hold, as shown in a simplified representation in Figure 1. At a steady state the individual anodic and cathodic currents (i.e., the net oxidation and reduction rates at the surface) must be equal. Thus the particle attains a mixed potential, E_m, at which the rate of reaction is v_m and the partial currents are i_m. This overall process affords a means of matching the donor and acceptor redox potentials and electron-transfer rates. These kinetics have been quantitatively described elsewhere.[12] The final equations thus obtained are included in the Experimental Section IIC. However, insufficient quantitative data were previously available to test this theory in detail. Furthermore, many previous studies have been complicated by the presence of extraneous reactions involving the electron-transfer (photo) catalyst.

Thus, the present work was developed with three goals in mind. First, it is necessary to develop a range of techniques to study microelectrode catalysis. In particular, steady state catalysis measurements in the absence of extraneous, (photochemical) reactions are desirable. Second, the data thus made available should provide a rigorous test of the applicability of electrochemical theory to colloid catalysis. Finally, we hope to provide a logical nexus between previous homogeneous kinetic treatments and the current electrochemical approach. The fundamental electrochemical parameters (e.g., exchange current density) obtained in this work should allow prediction of the observed "homogeneous" rates. Furthermore, it should be possible to compare the electrokinetic parameters for microelectrodes with those for bulk electrodes.

Experimental Section

I. Materials. The poly(vinyl alcohol) stabilized platinum colloid was prepared following the method of Kiwi and Grätzel.[4a] Poly(vinyl alcohol) (Aldrich, 100% hydrolyzed, average mol wt. 86 000) and K_2PtCl_6 (Alfa) were used without further purification. After preparation, the colloid solution was centrifuged at 12 000 rpm at 20 °C for 2 h and the transparent yellow supernatant solution was used. The platinum concentration after centrifugation was determined by atomic absorption (Perkin-Elmer 305 Atomic Absorption Spectrophotometer) to be 0.85 mM [Pt]. The particle size was characterized by electron microscopy. The *total* particle radius (Pt + polymer) is approximately 360 Å by light scattering.[4a] The radius of the Pt component alone was determined by electron microscopy, since only the dense Pt will strongly scatter electrons. The average radius thus was 300 ± 20 Å. Methyl viologen (Aldrich) was recrystallized twice from ethanol. Water was doubly distilled.

II. Methods. A. Mixing Kinetics. Stopped flow and manual mixing experiments were used to determine the methyl viologen radical oxidation rate dependence on pH (1.0 to 9.0) and platinum concentration (1.0 to 30.0 μM). The initial concentrations of $MV^{+}\cdot$ were independently determined for each run, but were approximately 0.1 mM. Buffered (pH 1.0–2.5:0.05 M KCl/0.1 M KNO_3; pH 3.0–5.8:0.05 M phthalate/0.1 M KNO_3; pH 5.8–7.0:0.05 M phosphate/0.1 M KNO_3; pH 9.0:0.05 M borax/0.1 M KNO_3), electrochemically generated radical was mixed with platinum and radical disappearance was monitored with use of a Dionex Stopped Flow System or a Gilford Spectrophotometer (manual mixing).

B. Cyclic Voltammetry. The cyclic voltammetric procedure of Nicholson and Shain (Case VII)[13a] was used to determine radical oxidation rate constants at pH 3.0 and 4.3. This method eliminates handling of the air-sensitive radical. Two experimental constraints exist in this system: platinum concentrations <24 μM are necessary to prevent aggregation, and low pH must be used, as explained below. In order to use the electrocatalytic CV technique, the rate of radical oxidation during the anodic sweep must equal or exceed the rate of water reduction by the radical. At pH 4.3, the methyl viologen concentration needed to attain the appropriate kinetic range was sufficiently low (0.5 mM) that a small mercury pool working electrode was needed to measure a detectable peak current. At pH 3.0, a higher methyl viologen concentration was needed (2.5 mM) and a glassy carbon working electrode was used. Platinum wire auxiliary and saturated calomel reference electrodes were used with a PAR Model 175 Universal Programmer in conjunction with a PAR Model 173 Potentiostat to obtain cyclic voltammograms for solutions with and without platinum (24 μM) over a scan rate range of 500–20 mV s^{-1}.

C. Electrogenerated Reductant. Steady state kinetics were monitored with use of an electrogenerated reductant to measure reduction rate dependence on pH (2.5 to 7.0) and reductant concentration. The methyl viologen and methyl viologen radical concentrations were varied by using a methyl viologen concentration range of 2.0–8.0 mM. The procedure involved electrolytic reduction of methyl viologen. The radical subsequently reduces water to hydrogen in the presence of colloidal platinum. Deaerated, buffered solutions (pH 2.5–5.8:0.05 M phthalate/0.1 M KNO_3; pH 5.8–7.0:0.05 M phosphate/0.1 M KNO_3) containing 2.0, 4.0, and 8.0 mM methyl viologen and centrifuged platinum catalyst (approximate concentration 8.5×10^{-6} M Pt) were electrolyzed at −1.0 V (vs. SCE) in a specially designed gas tight electrochemical cell, using a PAR Model 173 Potentiostat. Appropriate controls showed no H_2 production in the absence of methyl viologen and trace amounts in the absence of platinum. The cell was cleaned frequently with aqua regia to remove adsorbed platinum. A mercury pool working electrode, an isolated platinum auxiliary electrode, and a saturated calomel reference electrode were used. The nitrogen atmosphere above the solution was frequently sampled and hydrogen measured by gas chromatography (43 °C, Porapak Q column, nitrogen carrier gas). The solution pH was checked before and after electrolysis.

The $MV^{+}\cdot$ concentration was measured in two ways. With use of 10 mL of 2.0 mM methyl viologen, $[MV^{+}\cdot]$ was measured by following the current at the mercury pool.[14]

$$[MV^{+}\cdot] = [MV^{2+}]^0 - (i/i_0)[MV^{2+}]^0$$

Bulk $[MV^{+}\cdot]$ was also measured, using 25 mL of 2.0, 4.0, and 8.0 mM methyl viologen, by attachment of a flow-through spectrophotometric cell to the electrolysis cell. ($\epsilon_{MV^{+}\cdot} = 11\,300$ M^{-1} cm^{-1} at 600 nm.)[8a] A peristaltic pump was used to maintain continuous solution flow through the cell during electrolysis. Appropriate controls showed no significant hydrogen leakage through the pump tubing.

Results

I. Oxidation Rates. The oxidation rate dependence on pH was determined with use of mixing and cyclic voltammetry experi-

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(13) (a) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–23. (b) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; John Wiley: New York, 1980; p 458.

(14) Reference 13b, pp 378–9.

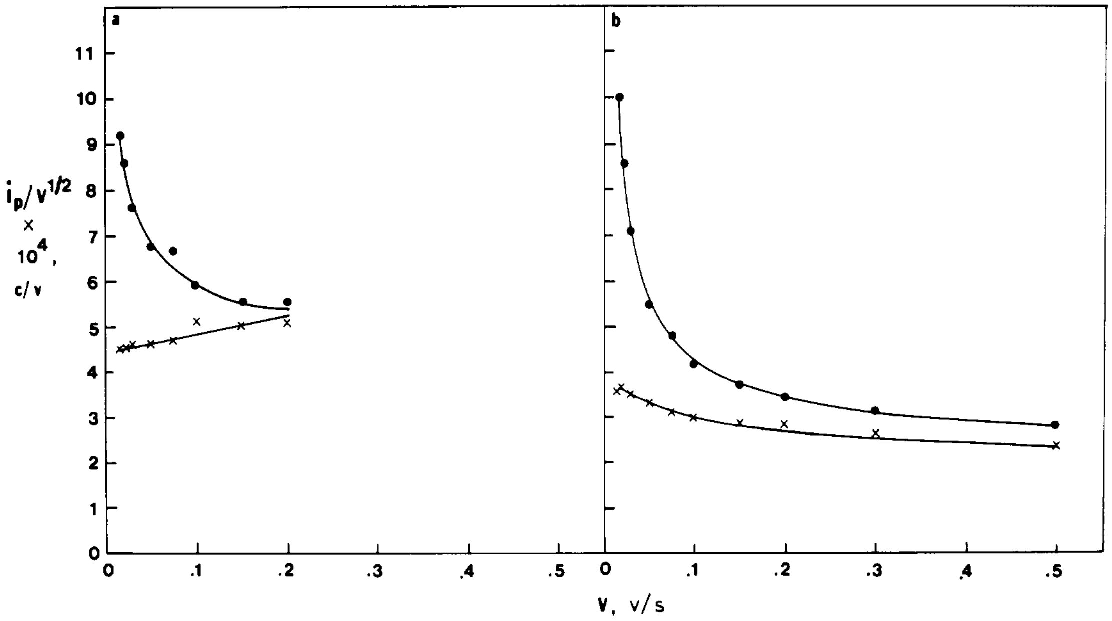

Figure 2. Demonstration of catalytic $\epsilon C'$ behavior for the $MV^{+}\cdot/Pt/H^{+}$ system (●: with Pt, ×: without pt): (a) pH 4.3, (b) pH 3.0.

ments. The effect of platinum concentration was investigated with use of only mixing experiments. Since the radical decayed exponentially in mixing experiments, homogeneous pseudo-first-order kinetics ([Pt] constant) were used for data analysis. The following homogeneous reactions were assumed, analogous to previous reports.[2b,4a]

$$MV^{+}\cdot + Pt \xrightarrow{k_1} MV^{2+} + Pt^{-}$$

$$Pt^{-} + H^{+} \xrightarrow{k_2} Pt + {}^{1}/{}_{2}H_2$$

In the mixing experiments, the radical disappearance rate, $-d[MV^{+}\cdot]/dt$, equals $k_1[Pt][MV^{+}\cdot]$, where [Pt] is assumed essentially constant. Values of $k_1[Pt]$ and k_1 were determined from the slope of an ln Abs ($MV^{+}\cdot$) versus time plot.

Catalytic, homogeneous, pseudo-first-order kinetics were also assumed for interpretation of the cyclic voltammetry data. The catalytic behavior of the system was demonstrated by plotting $i_p/v^{1/2}$ vs. v,[15,16] (v = scan rate in V s^{-1}). The expected appearance of both normal (no Pt) and catalytic curves (with Pt) was observed at pH 3.0 and 4.3, as shown in Figure 2. The rate constant, k_1, was determined from the scan rate dependence of the cathodic peak ratios with platinum (i.e., kinetic current) and without platinum (i.e., diffusion current), using the following relationship[13a]

$$i^{k}/i^{d} \propto \psi^{1/2}$$

where $\psi = k_1[Pt]RT/nFv$ (v = scan rate in V s^{-1}). Theoretical values of ψ were used as numerically calculated by Nicholson and Shain.[13a] Rate constants were also determined for the limiting kinetic case, using the following equation[13]

$$i = \frac{nFAC_{MV^{2+}}{*}(Dk_1C_{Pt}{*})^{1/2}}{1 + \exp\left[\frac{nF}{RT}(E - E_{1/2})\right]}$$

where the following values were used: A = electrode area = 0.12 cm^2 (pH 3.0), ~1 cm^2 (pH 4.3); F = 96 487 C mol^{-1}; $D = 10^{-5}$ cm^2 s^{-1}; nF/RT = 38.9 V^{-1}; $C_{MV^{2+}}{*}$ = bulk concentration, mol mL^{-1}; and $C_{Pt}{*}$ = bulk concentration, mol L^{-1}.

A. pH Dependence. As the electrochemical model predicts,[12] a definite oxidation rate dependence of pH was observed in the mixing and cyclic voltammetry data. The pH dependence of pseudo-first-order rate constants is shown in Figure 3 for stopped flow data and Figure 4 for manual mixing data. Cyclic voltammetry yielded rate constants of 1.1 × 10^5 L mol^{-1} s^{-1} at pH 3.0 and 3.0 × 10^4 L mol^{-1} s^{-1} at pH 4.3. The pH dependence of oxidation rate constants is summarized for all methods in Table I and depicted graphically as k/k_1 (limiting) in Figure 5.

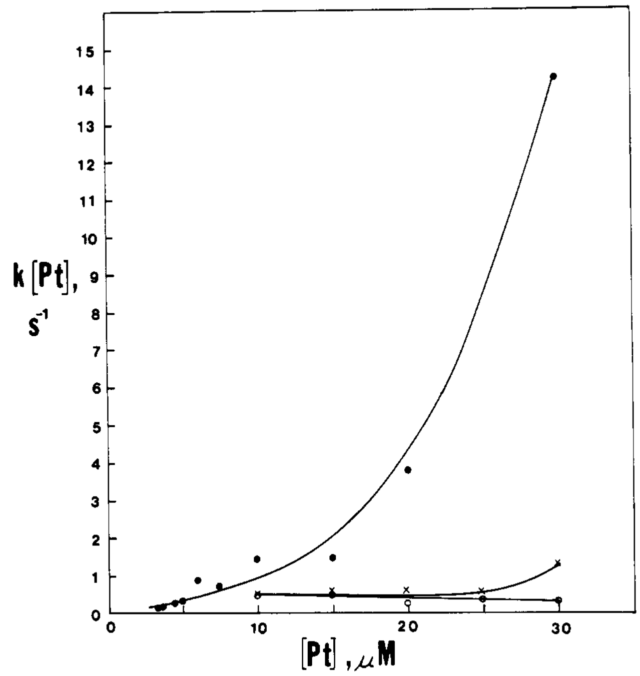

Figure 3. Dependence of pseudo-first-order oxidation rate constants, k[Pt], on [Pt] and pH as determined with use of stopped-flow experiments ((●) pH 3.25, (×) pH 4.0, (○) pH 9.0).

Table I. Homogeneous Oxidation Rate Constants

pH	(10^{-4}) average k, L mol^{-1} s^{-1}	k/k_1 (pH 1.0)
1.00	20.0	1.00
3.00	12.0, 11.0	0.60, 0.55
3.25	13.0	0.65
4.00	2.3, 3.7	0.12, 0.19
4.30	3.0	0.15
5.00	1.3	0.07
6.00	0.7	0.03
7.00	0.3	0.02
9.00	2.4	0.12

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(15) Reference 13b, pp 217–8.
(16) Reference 13b, p 459.

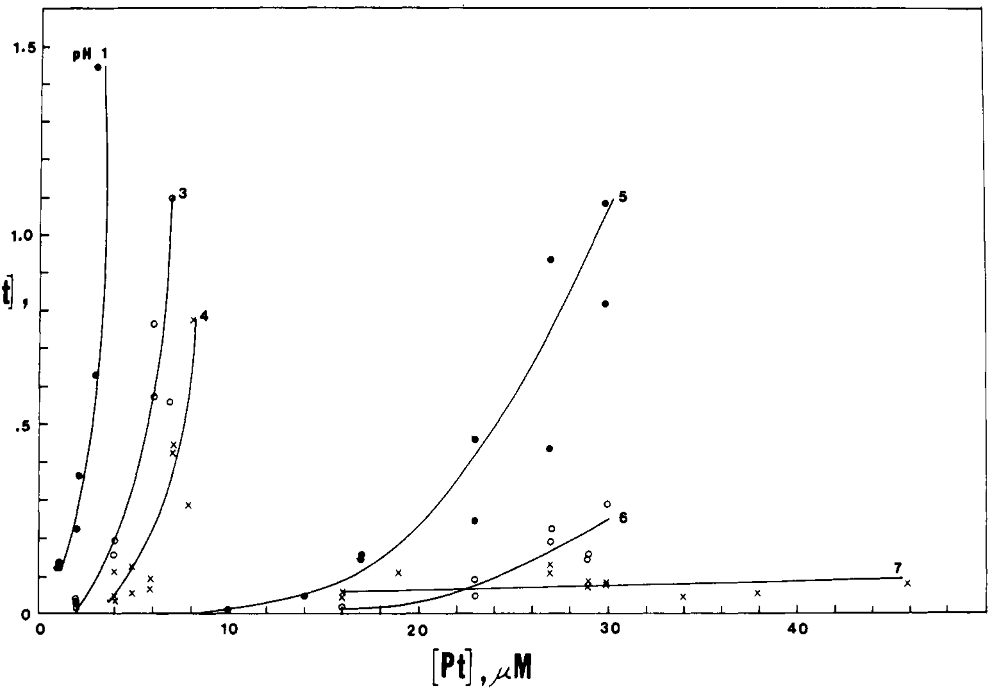

Figure 4. Dependence of pseudo-first-order oxidation rate constants, k[Pt], on [Pt] and pH as determined with use of mixing experiments.

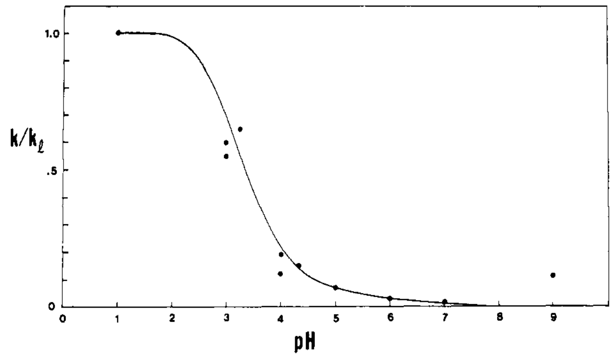

Figure 5. Summary of all mixing data (oxidation rate constants) plotted as k/k_l, where k_l is the limiting rate.

Table II. Values of [MV$^{+}\cdot$] Measured at Hg Pool and Spectrophotometrically (Bulk), Using [MV^{2+}]^0 = 0.002 M

	pH	v/v_l	[MV$^{+}\cdot$], mM		solution volume, mL
			Hg	bulk	
(a)	3.00	1.00	0.5		10
	3.30	0.98	0.9		10
	3.75	0.93	0.8		10
	4.00	0.83	0.7		10
	4.30	0.78	0.8		10
	4.70	0.72	0.5		10
	5.00	0.80	0.8		10
	6.00	0.24	1.8		10
	7.00	0.08	1.4		10
(b)	3.00	1.00	1.2	<0.001	25
	4.00	0.81	1.4	0.005	25
	5.00	0.38	2.0	0.100	25
	5.20	0.31	2.0	0.140	25
	5.50	0.15	2.0	0.200	25
	6.00	0.04	2.0	0.300	25

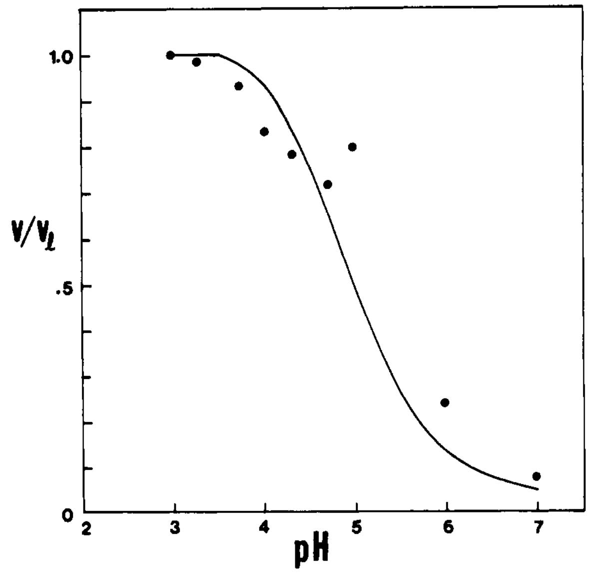

Figure 6. pH dependence of reduction rate determined with use of the electrogenerated reductant method ([MV^{2+}]^0 = 2.0 mM, solution volume = 10 mL).

Table III. Experimentally Determined pH$_{1/2}$

[MV^{2+}]^0, M	10^3 × [MV$^{+}\cdot$], M	pH$_{1/2}$
0.002	0.8[a]	5.0
0.002	~0.14	4.7
0.004	~0.30	4.4
0.008	~0.60	4.2

[a] Measured at Hg.

B. Platinum Concentration Dependence. The oxidation rate dependence on platinum concentration, determined in mixing experiments, is shown in Figures 3 and 4. In agreement with recent results using different techniques,[2b,4b] a reaction order >1 is found for Pt.

II. Reduction Rates. The dependences of the rate of reduction of water to H_2 on pH, [MV^{2+}], and [MV$^{+}\cdot$] were determined by using the steady state electrogenerated reductant method. These data were used, in conjunction with the electrochemical model of Miller et al.,[12] to calculate an exchange current density for the colloidal platinum catalyst. Note that under our electrolysis conditions, a maximum of 8% of doubly reduced [MV]^0 could be formed. This should not greatly affect our results.

A. pH Dependence. The pH dependence of reduction rate, over a range of methyl viologen concentrations, is shown in Figures 6 and 7. The data from Figures 6 and 7a are listed with corresponding methyl viologen radical concentrations in Table II.

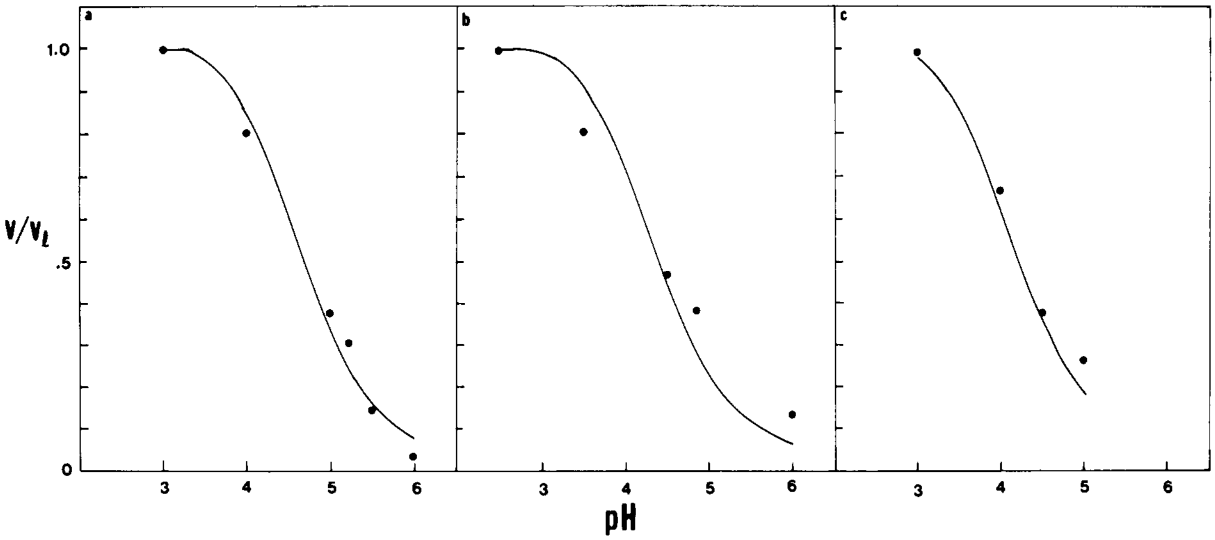

Figure 7. pH dependence of reduction rate determined with use of the electrogenerated reductant method (solution volume = 25 mL): (a) $[MV^{2+}]^0$ = 2.0 mM, (b) $[MV^{2+}]^0$ = 4.0 mM, (c) $[MV^{2+}]^0$ = 8.0 mM.

B. $[MV^{+}\cdot]$ and $[MV^{2+}]$ Dependence. The rate vs. pH curve is shifted about −0.3 pH units for each concurrent twofold increase in $[MV^{+}\cdot]$ and $[MV^{2+}]$, ($[MV^{+}\cdot]/[MV^{2+}]$ constant) as shown in Table III for $pH_{1/2}$ (vertical midpoint of the curve).

C. Exchange Current Density. It is clear, from Table II, that the bulk $[MV^{+}\cdot]$ measured at the mercury pool is greater than that measured spectrophotometrically. This discrepancy decreases with increasing pH. This experimental artifact is due to inefficient mass transport (i.e., stirring) of the radical relative to the radical oxidation rate. Under limiting conditions of small volume and high pH, mass transport becomes efficient compared to the slower radical oxidation reaction. Therefore, exchange current densities were only calculated with use of the highest pH data, where the artifact is negligible.

With use of equations derived by Miller et al.,[12] the mixed potential, E_m, and the rate constant, k_1^0, were calculated by using pH 7.0 data (Table IIa).

$$\left(\frac{2}{A}\right)\frac{d[H_2]}{dt} = v_1 = \frac{i_1}{nFA} = k_1^0 C_{H^+}{}^* \exp\{-\alpha f E_m\}$$

$$-\left(\frac{1}{A}\right)\frac{d[MV^{+}\cdot]}{dt} = -v_2 = -\frac{i_2}{nFA} = \frac{-C_{MV^{2+}}{}^* \exp\{-\alpha f(E_m - E_2{}^0)\} + C_{MV^{+}\cdot}{}^* \exp\{(1-\alpha)f(E_m - E_2{}^0)\}}{\dfrac{\exp\{-\alpha f(E_m - E_2{}^0)\}}{m_{MV^{2+}}} + \dfrac{\exp\{(1-\alpha)f(E_m - E_2{}^0)\}}{m_{MV^{+}\cdot}}}$$

At steady state,

$$v_1 = -v_2 = v_m = i_m/nFA$$

and

$$\frac{v_m}{v_{m,l}} = \frac{2\left[\dfrac{d[H_2]}{dt}\right]_{pH\ 7}}{[m_{MV^{+}\cdot}][C_{MV^{+}\cdot}{}^*](A)} = \frac{\left[\dfrac{d[H_2]}{dt}\right]_{pH\ 7}}{\left[\dfrac{d[H_2]}{dt}\right]_l}$$

where: $\alpha = 0.5$; $f = F/RT = 38.9\ V^{-1}$; $m_{MV^{2+}} = m_{MV^{+}\cdot} = 10^{-3}$ cm s^{-1}; $E_2{}^0 = -0.44$ V; C^* = bulk concentration, mol mL^{-1}; k_1^0 = rate constant, cm s^{-1}; $d[H_2]/dt$ = H_2 production rate, mol s^{-1}; and A = surface area of colloidal metal, cm^2. Exchange current densities, j^0, were calculated using k_1^0 and the following equation[12,17a,18]

$$j^0 = k_1^0 F(C_{H^+}{}^*)^{1/2}(C_{H_2}{}^*)^{1/2}$$

where $C_{H^+}{}^* = 10^{-3}$ mol mL^{-1} and $C_{H_2}{}^* = 7.7 \times 10^{-7}$ mol mL^{-1}. Values of E_m, k_1^0, and $\log j^0$ are listed in Table IV.

Table IV. Calculated Values of E_m, k_1^0, and $\log j^0$

$[MV^{2+}]^0$, mM	$[MV^{+}\cdot]$, mM	pH	E_m, V	k_1^0, cm s^{-1}	$-\log j^0$
2.0	1.4	7.0	−0.456	1.4×10^{-4}	3.4

Discussion

I. pH Dependence. The electrochemical kinetic interpretation predicts that at high pH, a pH dependence should be observed. At low pH, the rate should be constant and limited by mass transfer of radical to platinum. The oxidation and reduction rate dependences on pH agree, within experimental error, with this theoretically predicted dependence. The data in Figures 5, 6, and 7 are fit to the theoretical heterogeneous curve shape (solid line).[12]

II. $[MV^{+}\cdot]$ and $[MV^{2+}]$ Dependence. The heterogeneous theory of Miller, Bard, et al.[12] predicts a $pH_{1/2}$ shift of −0.3 pH units for each concurrent twofold increase in $[MV^{+}\cdot]$ and $[MV^{2+}]$ (constant $[MV^{+}\cdot]/[MV^{2+}]$). As shown in Table III, this predicted dependence is indeed observed in the electrogenerated mediator experiments under conditions of minimal artifact. The experimental artifact (arising from inefficient stirring as discussed above) is responsible for the discrepancy in $pH_{1/2}$ values for $[MV^{2+}]^0$ = 2.0 mM. The value $pH_{1/2}$ = 5.0 is more accurate than $pH_{1/2}$ = 4.7 since it was obtained by using a smaller solution volume where this artifact is reduced. Even when the artifact cannot be ignored, the observed shift in $pH_{1/2}$ with increasing concentration of methyl viologen is reliable, since the values of $pH_{1/2}$ = 4.7, 4.4, and 4.2 were obtained under identical experimental conditions. The curve in Figure 4, obtained from oxidation rate constants, has a much lower $pH_{1/2}$ of 3.3 reflecting higher initial $[MV^{+}\cdot]/[MV^{2+}]$ concentration ratios than were used for the water reduction rate measurements. The $pH_{1/2}$ is shifted in the predicted direction. We note that a simple homogeneous pseudo-first-order kinetic treatment does not predict any simple shift in $pH_{1/2}$ with radical concentration.

III. Exchange Current Density. The rate constants and exchange current densities for colloidal Pt behaving as a "microelectrode" are of considerable interest. These were calculated with use of data at pH 7 where any experimental artifacts are negligible. We find that the exchange current density of the colloid, $\log j^0 = -3.4$, agrees remarkably well with known values, −2.6 to −3.6,[17] for bulk platinum electrodes.

IV. Comparison of Oxidation and Reduction Rates. From simple electrochemical charge balance, the oxidation rate, $-d[MV^{+}\cdot]/dt$, should equal twice the reduction rate, $d[H_2]/dt$. As

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(17) (a) Bockris, J. O'M. *Mod. Aspects Electrochem.* **1954**, *1*, 180–276. (b) Kita, H.; Kurisu, T. *J. Res. Inst. Catal. Hokkaido Univ.* **1973**, *21*, 200.

(18) Reference 13b, pp 100–1.

shown in Figures 4–7, the qualitative behavior for oxidation and reduction rates is consistent. Quantitative comparison is hampered by the experimentally mandated unequal concentrations of MV^{2+} and $MV^{+}\cdot$ during measurement of oxidation and reduction rates and by differences in theoretically expected limiting rates, as discussed below.

The oxidation rate constant at pH 5.0 of $k = 1.3 \times 10^4$ L mol^{-1} s^{-1} ([Pt] = 6 μM) compares to $k = 1.4 \times 10^6$ L mol^{-1} s^{-1} ([Pt] = 100 μM) and $k = 5.0 \times 10^7$ L mol^{-1} s^{-1} ([Pt] = 1250 μM) obtained by Grätzel, using flash photolysis.[4a] However, the dependence of oxidation rate constants on platinum concentration makes meaningful rate constant comparisons and quantitative kinetic predictions impossible. Furthermore, rates obtained by using different experimental techniques (i.e., electrogenerated reductant, mixing, cyclic voltammetry, and flash photolysis) should not necessarily agree due to differences in limiting mass transfer rates. Specifically, mass transfer for rapid kinetic, non-steady state techniques (e.g., flash photolysis, cyclic voltammetry) will depend on the spherical diffusion rate to the colloid (and thus on colloid size). Mass transfer in the electrogenerated reductant experiments (as well as in steady state photochemical experiments) is independent of particle shape.[12] Non-steady state mixing experiments occur over a farily long time period (seconds to minutes) and mass transfer is not clearly defined. Since the steady state electrogenerated reductant experiment most accurately duplicates the actual photochemical systems in which the catalysts are used, this technique seems the most appropriate for kinetic investigations. Furthermore, the electrogenerated reductant system is not complicated by extraneous reactions of the photoacceptor or ultimate electron donor (e.g., water or a sacrifical organic donor such as EDTA).

V. Platinum Concentration Dependence. Surprisingly, the rate of methyl viologen decay in the mixing studies is greater than first order in [Pt] (particle number/cm^3).[4a] Similar studies of viologen radical reacting with Au also showed a second order dependence.[2b] For a homogeneous reaction, the second-order kinetics were explained by collision of two metal particles to liberate H_2.[2b] This explanation seems unlikely in light of the electrochemical model presented here. Indeed, the present stopped flow data cannot be explained in this way. For the Pt particles, $D^0 \simeq 0.67 \times 10^{-7}$ cm^{-2}/s.[4a] In a typical stopped flow experiment, the platinum concentration (by atomic absorption) was 8.5 μM. Taking a Pt radius of 300 Å (by electron microscopy) gives a particle "concentration" of 1×10^{-12} M, corresponding to an average particle separation, $d = 10^5$ Å. However, under these conditions, the flow reactions were complete in ca. 0.5 s, thus the particle diffusion distance, R, equals 2.5×10^4 Å. Thus during the reaction time, few Pt particles could collide. Previous literature data[4a] may be similarly interpreted. By using the following reported values, Pt radius $\simeq$ 80 Å (assuming $r_{\mathrm{Pt}} \ll r_{\mathrm{total}}$), $D^0 \sim 2 \times 10^{-7}$ cm^2/s, $\tau \simeq 1 \times 10^{-3}$ s, the particle separation exceeds the average diffusion length as calculated above by 30-fold. Clearly, collisions between platinum particles by analogy to homogeneous kinetics cannot explain the present data. By contrast, a thin layer electrochemical model may predict a dependence on [Pt] greater than first order. The mixing experiments can be viewed as a potential step in a multielectrode (i.e., multiple working electrodes) cell, with the electrodes separated by a short distance l. Although the diffusion equation is complex for this three-dimensional ensemble average, the basic predicted behavior of the system can be illustrated by the simpler one-dimensional case: electrolysis in a twin working electrode, thin-layer cell.[19] For this case $i(t) \simeq i(0)\exp(-\chi t)$ where $\chi = m_0/l$, $i(0) = 4nFAC_0{}^*m_0/\pi^2$, and $m_0 = \pi^2 D_0/l$. The area, A, scales with [Pt], as already discussed.[12] Furthermore, the distance between electrodes, l, scales inversely with [Pt]; $l \propto [\mathrm{Pt}]^{-1/3}$. Since m_0 is inversely proportional to l, m_0 becomes directly proportional to [Pt]. The $i(0)$ term will scale as $(A)(m_0) \sim [\mathrm{Pt}][\mathrm{Pt}]^{1/3}$ and the exponential will also show a [Pt] dependence. Overall, this simple electrochemical model predicts that the instantaneous rate $i(t)$ will be greater than first order in [Pt], as observed. Clearly, the precise form of this dependence requires an analytical solution for the spherical ensemble. Thus, the observed [Pt] order may simply reflect the small diffusion layer of [$MV^{+}\cdot$], rather than particle–particle interactions. Further work will be necessary to test this idea.

Conclusions

In summary, the primary findings of the present report are listed below.

(1) Although a number of "clean" systems (i.e., without extraneous photochemical components) may be used to study the mediator-microelectrode reaction, only the steady state experiments with electrogenerated mediator can presently be interpreted with use of the simple heterogeneous electrochemical theory. Other techniques (e.g., stopped flow, pulse radiolysis) produce a potential step response which is complicated by the radial dependence of diffusion.

(2) In rapid mixing (potential step) experiments a roughly second-order dependence on Pt concentration (particle number) was observed. This dependence cannot be explained with use of classical homogeneous reaction theory, but is expected for a diffusion-controlled reaction at multiple spherical electrodes.

(3) The steady state experiments are in quantitative agreement with the previous predictions of electrochemical theory: (A) The pH of $^1/_2$ maximum rate, $\mathrm{pH}_{1/2}$, shifts by −0.3 pH units for each simultaneous twofold increase in methyl viologen radical and oxidized methyl viologen concentrations.

(B) Spectroscopically determined concentrations of methyl viologen radical in a spectroelectrochemical experiment were used to derive a precise value for log j^0 for H_2 reduction at the Pt colloids. The value log $j^0 = -3.4$ agrees well with a previous rough estimate[12] and with the value for bulk Pt electrodes (log $j^0 = -2.6$ to −3.6).

Thus the present manuscript has experimentally established the validity of an electrochemical approach to the colloidal catalysis of water reduction. Furthermore, the electrochemical approach makes predictions which are not amenable by using the homogeneous reaction rate theory.

The techniques and concepts presented here should be applicable to a wide range of metal-catalyzed electron-transfer reactions, as noted by Spiro. We are presently applying these concepts to photocatalytic water oxidation.

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(19) Reference 13b, pp 406–8.

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