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Model Systems for Photocatalytic Water Reduction: Role of pH and Metal Colloid Catalysts

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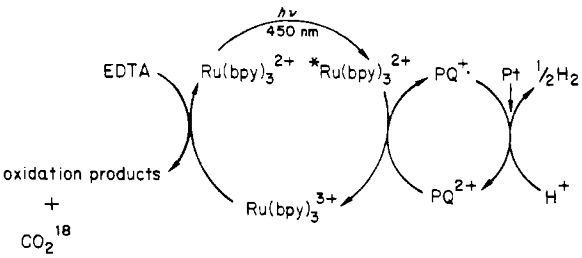
The extensive work directed toward conversion of light energy to chemical energy[1–4] has met with success in several recent schemes using tris(bipyridyl)ruthenium(II) to photocatalyze water reduction.[5,6] These schemes should be viewed as model systems since they require a sacrificial organic electron donor to drive the series of reactions leading to hydrogen production. Recent work has indicated that these organic reagents may utimately be replaced by water, in the presence of an appropriate catalyst (e.g., RuO_2).[7] Since the completion of the studies presented here, Grätzel has published a scheme using $Ru(bpy)_3^{2+}$ as a photocatalyst to split water into hydrogen and oxygen.[8,9]

One important aspect of these model systems is their potential use as assay systems to evaluate the photocatalytic activity of metals other than ruthenium. Use of these systems in this manner requires that they be well characterized. Kagan[6] has reported a water photoreduction system including $Ru(bpy)_3^{2+}$ as the photocatalyst, paraquat (PQ^{2+}) as the electron-transfer mediator (quencher), ethylenediaminetetraacetic acid (EDTA) as the organic electron donor, and a colloidal platinum catalyst necessary for hydrogen production. The proposed mechanism is shown in Scheme I. This catalysis is attenuated by the competitive back-reaction

$$Ru(bpy)_3^{3+} + PQ^{+\cdot} \rightarrow Ru(bpy)_3^{2+} + PQ^{2+}$$

The system is reported to produce hydrogen over a pH range of 4–7. Although the general mechanism of this scheme has been determined, little characterization has been done with regard to the quantitative effect of solution pH on hydrogen quantum yield or to the role of the platinum catalyst.[9] In particular, the colloidal Pt cocatalyst has been suggested to function as a "microelectrode"[9] providing a surface at which the donor potential of the reduced quencher can be matched to the water reduction potential, analogous to the potential matching at a bulk electrode. If this model is correct, the total H_2 yield might well depend on the potential of the photoreduced quencher (and the pH). A second undetermined feature of these systems is the kinetics of reaction between tris(bipyridyl)ruthenium(III) and EDTA, which in part determines the efficiency of H_2 formation. Therefore, we wish to report studies which clarify the roles of pH, mediator potential, and EDTA oxidation rate in these water reduction systems.

Scheme I



pH 4–7

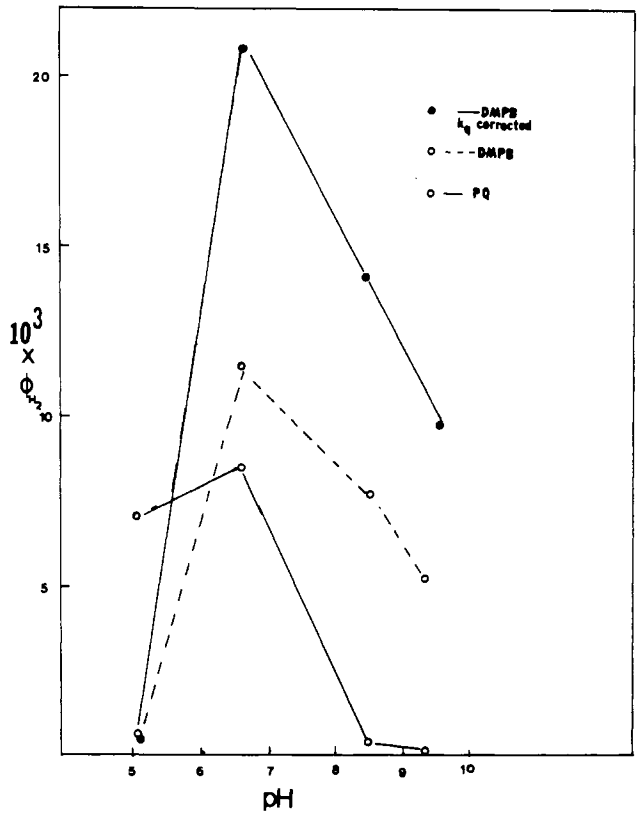


Figure 1. Hydrogen quantum yield as a function of pH.

Experimental Section

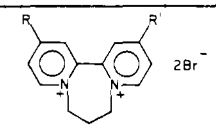
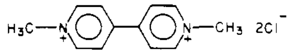
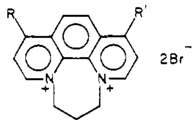
$Ru(bpy)_3Cl_2 \cdot 6H_2O$ (G. Fredrick Smith Co.), paraquat (Aldrich), and Na_2EDTA (Sigma Chemical Co.) were used with no further purification. Hydrogen quantum yields were measured on solutions containing a buffer (phosphate or borate), $Ru(bpy)_3Cl_2$ (2.0×10^{-4} M), Na_2EDTA (2.0×10^{-2} M), an electron-transfer mediator such as paraquat (2.0×10^{-3} M), and polyvinyl alcohol stabilized platinum catalyst.[10] The Pt catalyst was prepared as described in ref 10, except that it was reduced by H_2 gas for 2 h and subsequently centrifuged at 150 000 G for 1 h. A clear yellow solution results which contains a highly active Pt catalyst. A similar preparation has recently been reported by Grätzel.[9] The total concentration of Pt in the experimental runs was ca. 10^{-6} M. The reactions were run at 23 °C under a nitrogen atmosphere. The stirred solutions were irradiated with a 300-W tungsten–halogen lamp filtered to transmit light between 400 and 500 nm. Irradiation was continued until the quantum yield became constant (4–6 h). Light intensities were measured with use of a Reinecke's salt actinometer.[11] Hydrogen was measured by gas chromatography with use of a Poropak Q column at 43 °C and nitrogen as the carrier gas.[12]

The electron-transfer mediators listed in Table I were prepared by refluxing the desired ligand (G. Fredrick Smith Co.) in 1,3-dibromopropane for several hours. The crude product was filtered from the solution, dissolved in hot methanol/charcoal, and then reprecipitated by the addition of methyl ethyl ketone.[13] Elemental analyses

(1) (a) B. V. Koriakin, T. S. Dzabiev, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **233**, 620 (1977); (b) T. Meyer, *Acc. Chem. Res.*, **11**, 94 (1978).
(2) N. Sutin, *J. Photochem.*, **10**, 19 (1979).
(3) N. Sutin and C. Creutz, *Adv. Chem. Ser.*, **No. 168**, 1 (1978).
(4) P. DeLaive, J. Lee, H. Abruña, H. Sprintschnik, T. Meyer, and D. Whitten, *Adv. Chem. Ser.*, **No. 168**, 28 (1978).
(5) (a) J.-M. Lehn and J.-P. Sauvage, *Nouv. J. Chim.*, **1**, 449 (1977); (b) M. Kirch, J.-M. Lehn, and J.-P. Sauvage, *Helv. Chim. Acta*, **62**, 1345 (1979).
(6) A. Moradpour, E. Amouyal, P. Keller, and H. Kagan, *Nouv. J. Chim.*, **2**, 547 (1978).
(7) (a) J.-M. Lehn, J.-P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, **3**, 423 (1979). (b) J. Kiwi and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, **18**, 624 (1979); *Chimica*, **33**, 289 (1979).
(8) K. Kalyanasundaram and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, **18**, 701 (1979).
(9) J. Kiwi and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 7214 (1979).
(10) L. Rampino and F. Nord, *J. Am. Chem. Soc.*, **63**, 2746 (1941).
(11) E. Wegner and A. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
(12) The use of nitrogen as the carrier gas ensures greater sensitivity and a linear calibration curve of hydrogen.

0020-1669/81/1320-0950$01.25/0

Table I. Electron-Transfer Quenchers

compd	R	R′	abbr	$E°$ (vs. SHE), V	K_{sv}
	CH_3	CH_3	DMPB	−0.63	102.6
	H	H	PB	−0.49, −0.608,[13b] −0.548,[13d] −0.556[13a]	163.5
			PQ	−0.449,[13a] −0.418[13b]	186.7
	CH_3	CH_3	DMPP	−0.40	319.2
	C_6H_5	C_6H_5	DPPP	−0.31	584.2
	CH_3	H	MPP	−0.22	295.6
	H	H	PP	−0.18, −0.116[13c]	467.5
	Cl	H	CPP	−0.11	586.5

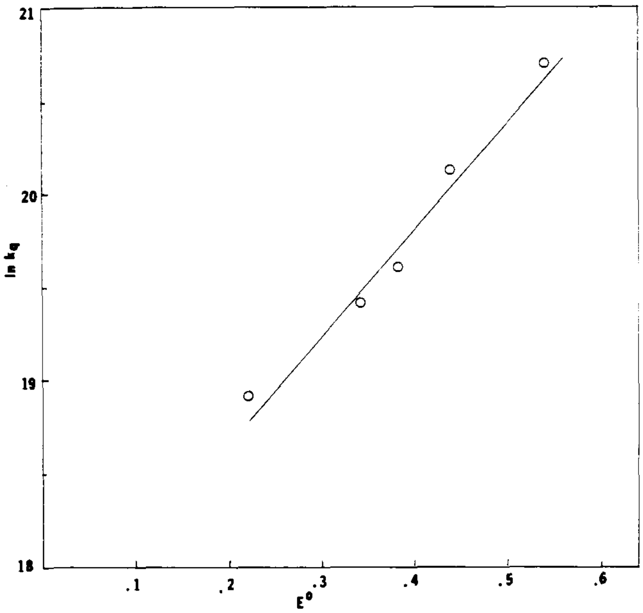


Figure 2. Plot of electron-transfer quenching rate ($k_q = K_{sv}/\tau$) vs. electron-transfer driving force ($E° = E*_{Rubpy^{2+}} - E_{(Ru^{3+}\to Ru^{2+})} + E_{red(Q\to Q\cdot)}$).

confirmed the identity of the products. The $E_{1/2}$ values (vs. SCE) of these mediators were measured in aqueous 0.1 M KNO_3 solutions by differential-pulse polarography and cyclic voltammetry with the use of a Princeton Applied Research Model 174A polarographic analyzer. Stern–Volmer constants for the quenching of $Ru(bpy)_3^{2+}$ luminescence by the electron-transfer mediators were measured with a Perkin-Elmer MPF 44A fluorescence spectrophotometer.

Kinetics of $Ru(bpy)_3^{3+}$ reduction by EDTA were monitored with a Dionex D-110 stopped flow apparatus. Weakly acidic ruthenium solutions (10^{-3} M H^+) were prepared and used within minutes of preparation. EDTA solutions were buffered by addition of excess acid (pH 2) or base (pH 4–6). A 10-fold excess of EDTA insured pseudo-first-order conditions.

Results and Discussion

The pH dependence of the hydrogen quantum yield is shown in Figure 1. In accord with previous results,[6] an optimum pH of 6–7 was observed. Kagan has previously suggested that the rate decrease above pH 7 occurs because the driving force for $PQ^{+\cdot}$ oxidation ($E°_{Ox} = +0.4$ V) is less than the reduction potential for water at pH 7 ($E°_{Red} = -0.45$ V). In a more general form, this explanation suggests that water reduction (rate) is coupled to the driving force for mediator oxidation. So that this general proposal could be tested, a series of ho-

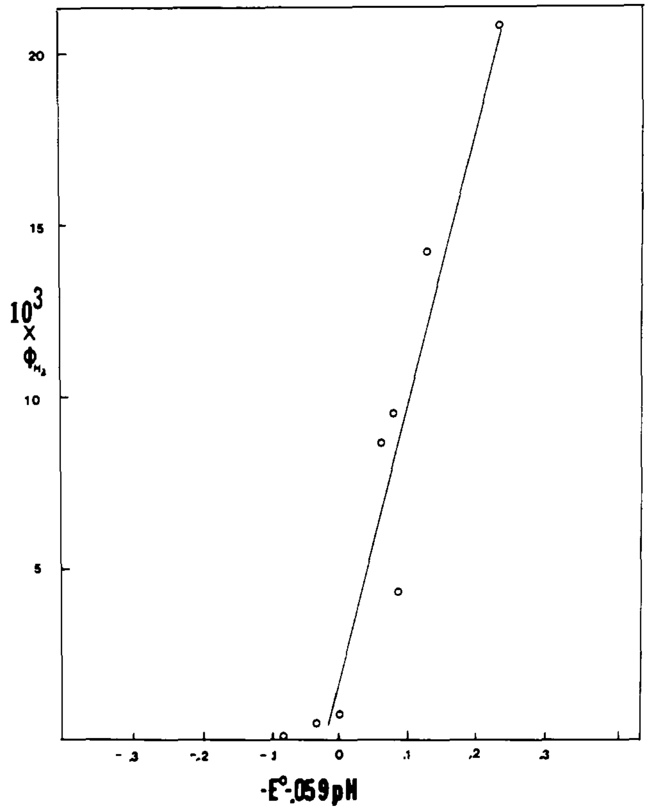


Figure 3. Hydrogen quantum yield as a function electromotive driving force. The points shown were obtained by varying the quencher, or pH, or both. Data using different quenchers have been corrected for differential quench rates.

mologous electron-transfer quencher mediators were synthesized and characterized for use in H_2-generation system. A list of these quenchers is contained in Table I. The reduction potentials of these systems were characterized by cyclic voltammetry and differential-pulse polarography on a hanging-Hg-drop electrode. While PQ^{2+} and $DMPB^{3+}$ showed good electrochemical reversibility (ΔE(peak a − peak c) ≈ 60 mV) the other mediators were only quasi-reversible at lower scan rates. Hünig and co-workers have previously reported polarographic potentials for three of these systems.[13] Their values are also listed in Table I. We believe that the discrepancies observed between the studies are largely due to the poor electrochemical reversibility of several mediators. Given this irreversibility it is likely that the fast scan CV measurements are more reliable than the previous polarographic data. The bipyridyl-based species showed good electrochemical reversibility by CV. As expected, all these mediators efficiently quenched the ruthenium excited state. Stern–Volmer quench constants for these systems are also given in Table I. These values of K_{sv} correspond to quench rate constants of ca. 10^9

(13) (a) E. Steckham and T. Kuwana, *Ber. Bunsenges. Phys. Chem.*, **78**, 253 (1974). (b) S. Hünig, J. Gross, and W. Schenk, *Liebigs Ann. Chem.*, **1973**, 324–338. (c) S. Hünig, J. Gross, E. F. Lier, and H. Quast, *ibid.*, **1973**, 339–358. (d) R. F. Homer and T. E. Tomlinson, *J. Chem. Soc.*, **1960**, 2498.
(14) A. Krasna, *Photochem. Photobiob.*, **29**, 267 (1979).

M^{-1}/s^{-1}. The quench behavior has been previously studied in detail for PQ^{2+} [3] and more recently for PB^{2+}.[18c] The relative quenching rates follow the mediator potentials (Figure 2), as expected for an outer-sphere electron-transfer quenching reaction.[3] After the electron-transfer properties of the mediators had been characterized, the effect of driving force on H_2 yield was studied. The dependence of the H_2 quantum yield on electromotive force is shown in Figure 3. A clear linear relationship between H_2 quantum yield (Φ_{H_2}) (corrected for relative quenching efficiency among different quenchers) and the driving force for water reduction ($E°$) is observed. This relationship holds whether the driving force is altered by changing the mediator potential or by changing the pH. This dependence is consistent with control of H_2 formation by "potential matching" at the Pt colloid surface, consistent with the microelectrode model previously proposed[9] and with Kagan's explanation of the alkaline limit for H_2 formation. However, the control of Φ_{H_2} is potentially complex, involving not only H_2 evolution from the colloids but also the efficiency of separation of photoproduced redox products. In the case of PQ^{2+}, this efficiency is only ca. 30%.[3] Thus, the observed ΦH_2 dependence might be complicated by pH or mediator-dependent differences in initial redox product formation. Factors which affect this efficiency include the rate of quenching (k_q, obtained from the Stern–Volmer constants in Table I), the rate of back reaction, k_b, and the rate of reduction of Ru^{3+} by EDTA, k_{Red}. Differences in the quenching rates of different mediators have been corrected for in Figure 3 by using the observed K_{sv} values in Table I to normalize to identical quenching efficiencies. (Without this correction, significant deviations would be expected and are observed). For any single quencher, varying the pH should not affect k_q but would only affect the driving force for water reduction. The back reaction rate in principle might depend on the driving force for reaction and would increase as the quencher oxidation potential increased. Thus, if k_b changed for different mediators, this change would affect Φ_{H_2} in the *opposite* fashion to that observed. An increase in $E°$ of the mediator should increase k_b and decrease Φ_{H_2}. Instead, as $E°$ increases, Φ_{H_2} increases. This behavior can be rationalized by the fact that the back reaction is essentially diffusion controlled for $PQ^{+\cdot}$ + Ru^{3+} and will proceed at a similar rate for the other mediators. (The self-exchange rates of the mediators, estimated from the quenching rates with use of Marcus theory, vary less than a factor of 3.) Thus although the back-reaction influences the overall quantum efficiency, it does not affect the relative quantum efficiencies observed with the different mediators or pHs used here. (Clearly pH should have little if any effect on k_b.) In independent work,[20] it has been shown that the *same* pH dependence of the rate of H_2 formation is found for a photochemically reduced mediator (as in the present work) as for an electrochemically reduced mediator. In the electrochemical system, only an electrode (C or Hg), the mediator, and Pt colloid are present. The fact that the same pH dependence of H_2 rate is seen for the electrochemical system, in which neither amine nor ruthenium is present, as for the photochemical system strongly supports the above analysis that the H_2 production rate is governed by potential matching at the Pt surface. This control will only hold under conditions where the ancillary reactions (excitation, quenching, and back-recombination) are essentially constant or corrected for, as in the present case. Finally, the effect of pH on Ru^{3+} reduction by EDTA should be addressed. (Changes in mediators should not affect this reaction). This reaction has been studied over a range of pH as summarized in Figure 4. The rate of EDTA reduction decreases over 200 fold between pH 7 (k_{Red}) = 2×10^6 M^{-1}/s^{-1}) and pH 4 (k_{Red} = $8 \times 10^3/M^{-1}/s^{-1}$). This decrease likely explains the previously observed

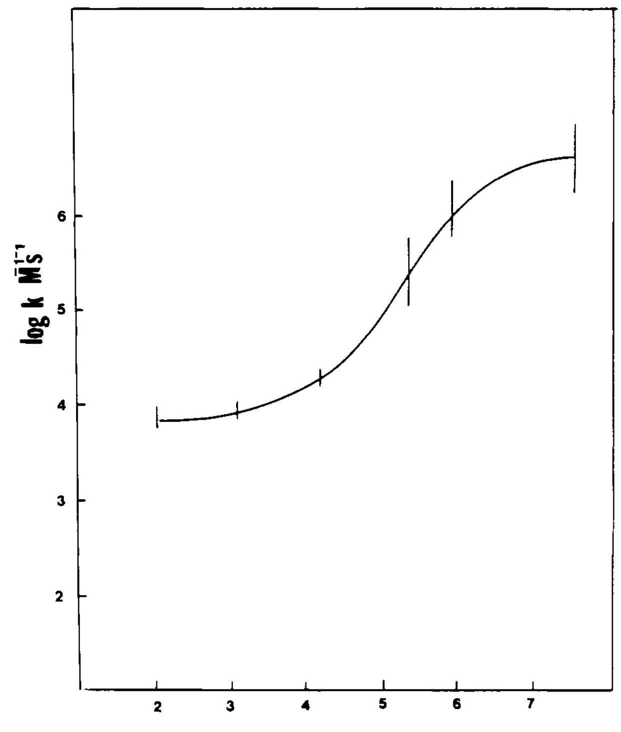


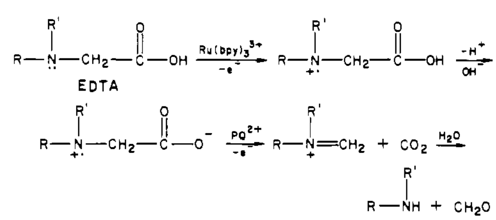
Figure 4. pH dependence of the rate of reaction between $Ru(bpy)_3^{3+}$ and EDTA.

cessation of H_2 production below pH 4. In these sacrificial model systems, redox product separation depends on competition between reduction of Ru^{3+} by EDTA and back-reaction of Ru^{3+} with $PQ^{+\cdot}$. At pH <4, EDTA becomes protonated and might react far less rapidly with Ru^{3+}. This explanation is strongly supported by Figure 4. The rate profile describes a titration curve with an approximate pK = 5.5 corresponding to the first pK for amine deprotonation in EDTA (pK = 6.16).[15] The argument is also supported by the observed anodic shift in EDTA potential with decreasing pH.[16-18] This

(15) A. Martell and R. Smith, "Critical Stability Constants", Vol. 1, Plenum Press, New York, 1974, p 204.

(16) L. Meites and P. Zuman, "Electrochemical Data", Part I, Vol. A, Wiley, New York, 1974, p 454.

(17) An addition contribution to the pH 4 limitation for hydrogen production may be the pH dependence of the reduction potential of the EDTA radical produced by reaction with $Ru(bpy)_3^{3+}$. In acidic solution, protonated EDTA radical may oxidize $PQ^{+\cdot}$ to PQ^{2+}, reducing hydrogen production. However, in alkaline solution, deprotonated EDTA radical could reduce additional PQ^{2+} to $PQ^{+\cdot}$.[18d] This explanation is consistent with the observed CO_2 production based on the mechanism



A precedent for this explanation was demonstrated for an analogous hydrogen-production scheme using triethanolamine rather than EDTA.[18a] A previously proposed mechanism for photochemical oxidation of EDTA is also in close agreement to that postulated here for the thermal oxidation of EDTA by Ru^{3+}.[18b] An alternate decomposition pathway producing glyoxylic acid and the ethylenediamine-*N,N'*-diacetic acid was recently proposed by Keller et al.[18d]

(18) (a) K. Kalyanasundaram, J. Kiwi, and M. Grätzel, *Helv. Chim. Acta*, **61**, 2720 (1978). (b) F. C. Goodspeed, B. L. Scott, and J. G. Burr, *J. Phys. Chem.*, **69**, 1149 (1965). (c) K. Takuma, Y. Shuto, and T. Matsuo, *Chem. Lett.*, 983 (1978). (d) P. Keller, A. Moradpour, and E. Amouyal, H. Kagan, *Nouv. J. Chim.*, **4**, 377 (1980).

potential varies from 0.13 V at pH 9 to 0.56 V at pH 2. Over the pH range (6.5–9) used in the H_2 yield studies, the EDTA reaction rate is already maximized and should not change appreciably.

The simplest explanation for the dependence of Φ_{H_2} on $E°$ which is consistent with all the data obtained both by pH variation and mediator replacement is that the H_2 yield in the system reported here is determined by the matching of the mediator redox potential to the water reduction potential at the Pt surface, analogous to potential matching at an electrode surface. This data thus provides the first direct evidence for the "microelectrode" model of the dispersed Pt catalyst.[9,20] The work reported here, and elsewhere, has sufficiently defined this "sacrificial" water reduction system that it may be confidently used as an assay system to test the photocatalytic activity of metals other than ruthenium. Indeed, with the use of such an assay, preliminary results have demonstrated photocatalytic water reduction by chromium(III)[22] and metalloporphyrins.[23]

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Registry No. PQ, 1910-42-5; DMPB, 5875-57-0; PB, 2895-98-9; DMPP, 19934-07-7; DPPP, 75934-61-1; MPP, 75934-62-2; PP, 15302-99-5; CPP, 75934-63-3; Ru(bpy)$_3^{2+}$, 15158-62-0; EDTA, 60-00-4; Pt, 7440-06-4; H_2, 1333-74-0; H_2O, 7732-18-5.

(19) The quantum yields reported for these reactions vary considerably between different investigators. The present values (Φ_{H_2} = 0.02, corrected for quenching) is lower than the highest reported value (Φ = 0.13) for a similar system. The reasons for this difference are not clear. They may reflect the relatively low Pt concentrations (10^{-6} M) used in these experiments.

(20) Since this paper was submitted, further support for this model has appeared. McLendon has reported kinetic studies which show that similar H_2-formation mechanisms occur at the colloid and at bulk electrodes (G. McLendon, submitted for publication). Meisel[21] has independently reported isotope effect studies of H_2 formation on Au colloids which indicate an electrodic mechanism analogous to that found on Au electrodes.

(21) D. Meisel, K. Kopple, and D. Meyerstein, *J. Phys. Chem.*, **84**, 870 (1980).

(22) G. McLendon and D. Miller, *Chem. Eng. News*, **57** (Sept 24), 44 (1979).

(23) G. McLendon and D. Miller, *J. Chem. Soc., Chem. Commun.*, 533 (1980).

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Rate Constant for the Reaction of Chromium(II) with Vanadium(IV). A Competition Study

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Previous studies of the reaction of VO^{2+} with Cr^{2+} (eq 1)

$$VO^{2+} + Cr^{2+} + 2H^+ = V^{3+} + Cr^{3+} + H_2O \qquad (1)$$

have shown that the reaction is too fast to be measured by the stopped-flow technique. Espenson[1] reported that the major portion of the reaction (>90%) occurs directly, while a small fraction proceeds through the dinuclear intermediate $VO(OH)_nCr^{(4-n)+}$, as in reaction 2 (written for $n = 0$). The

$$VO^{2+} + Cr^{2+} \xrightarrow{k_1} VOCr^{4+} \xrightarrow[\text{slow}]{2H^+} V^{3+} + Cr^{3+} + H_2O \qquad (2)$$

reaction occurs with the rate constant $k_{VO} > 8 \times 10^3$ M^{-1} s^{-1} at 5 °C. Ekstrom and Farrar[2] later reported that k_{VO} exceeds 10^4–10^5 M^{-1} s^{-1} at 14.5 °C, where $k_{VO} = k_1 + k_{direct}$.

We have recently found[3] that VO^{2+} reacts with the hydroxymethylchromium(III) complex $CrCH_2OH^{2+}$ according to eq 3. The chromium(II) produced reacts rapidly with the

$$CrCH_2OH^{2+} + VO^{2+} + H^+ = Cr^{2+} + V^{3+} + CH_2O + H_2O \qquad (3)$$

second mole of VO^{2+} (eq 1), but it can be partially or completely scavenged in the form of CrX^{2+} if the reaction is done in the presence of an excess of $(NH_3)_5CoX^{2+}$ (X = F, Cl, Br). This indicated to us that the rate constants for reactions 1 and

$$(NH_3)_5CoX^{2+} + Cr^{2+} + 5H^+ = Co^{2+} + CrX^{2+} + 5NH_4^+ \qquad (4)$$

4 are of comparable magnitude. This system seemed to be well suited for the determination of the rate constant k_{VO} by the competition method, since k_4 is known for a number of groups X.[4] Using the $CrCH_2OH^{2+}$–VO^{2+} reaction to generate Cr^{2+} has the advantage over the direct mixing of Cr^{2+} with the oxidants. The slow formation of small amounts of Cr^{2+} in a homogeneous solution in the presence of the oxidants affords ideal competition conditions for the reactions which are extremely rapid and could otherwise be affected by the quality of stirring and rate of addition of Cr^{2+}. A few ex-

Table I. Results of the Competition Experiments[a]

$10^2 \times [VO^{2+}]_0$, M	$10^2 \times [Co(NH_3)_5X^{2+}]_0$, M	$10^4 \times [CrCH_2OH^{2+}]_0$,[b] M	$10^4 \times [Co^{2+}]_\infty$, M
	X = F		
1.00	1.80	9.0	4.84
1.00	1.32	9.85[c]	4.63
1.00	1.00	9.0	3.45
1.50	1.00	9.3	2.96
2.00	1.32	9.85[c]	3.16
2.00	1.00	9.5	2.52
2.00	0.89	9.85[c]	2.31
2.50	1.00	9.6	1.90
	X = Cl		
1.50	1.44	9.3	6.68
1.50	1.00	9.3	4.75
2.00	0.98	9.4	4.87
2.50	1.00	9.5	4.02
3.00	0.77	9.6	3.47
3.00	0.48	9.6	2.09
	X = Br		
2.00	2.00	9.4	7.57
2.00	1.00	9.4	6.72
2.00	0.70	9.4	6.00
2.50[d]	0.60	8.7	4.40
3.00	0.60	9.4	4.20

[a] 0.10 M $HClO_4$, 1.0 M ionic strength, 1 M CH_3OH, ~24 °C. [b] A correction was applied for the amount of $CrCH_2OH^{2+}$ that underwent acidolysis.[5] [c] The experiment was done in the absence of methanol by direct mixing of Cr^{2+} with the oxidants. [d] 0.50 M $HClO_4$.

(1) Espenson, J. H. *Inorg. Chem.* **1965**, *4*, 1533.

(2) Ekstrom, A.; Farrar, Y. *Inorg. Chem.* **1972**, *11*, 2610.

(3) Bakač, A.; Espenson, J. H., submitted for publication.

(4) Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 766.