

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 H₂ 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 H₂ 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)₃²⁺, 15158-62-0; EDTA, 60-00-4; Pt, 7440-06-4; H₂, 1333-74-0; H₂O, 7732-18-5.

(19) The quantum yields reported for these reactions vary considerably between different investigators. The present values ($\Phi_{H_2} = 0.02$, corrected for quenching) is lower than the highest reported value ($\Phi = 0.13$) 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 H₂-formation mechanisms occur at the colloid and at bulk electrodes (G. McLendon, submitted for publication). Meisel²¹ has independently reported isotope effect studies of H₂ 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).

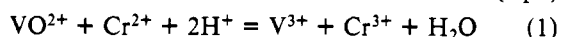
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Rate Constant for the Reaction of Chromium(II) with Vanadium(IV). A Competition Study

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Previous studies of the reaction of VO²⁺ with Cr²⁺ (eq 1)



have shown that the reaction is too fast to be measured by the stopped-flow technique. Espenson¹ reported that the major

Table I. Results of the Competition Experiments^a

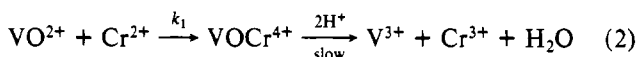
$10^2 \times$ [VO ²⁺] ₀ , M	$10^2 \times$ [Co(NH ₃) ₅ X ²⁺] ₀ , M	$10^4 \times$ [CrCH ₂ OH ²⁺] ₀ , ^b M	$10^4 \times$ [Co ²⁺] _∞ , M
X = F			
1.00	1.80	9.0	4.84
1.00	1.32	9.85 ^c	4.63
1.00	1.00	9.0	3.45
1.50	1.00	9.3	2.96
2.00	1.32	9.85 ^c	3.16
2.00	1.00	9.5	2.52
2.00	0.89	9.85 ^c	2.31
2.50	1.00	9.6	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 HClO₄, 1.0 M ionic strength, 1 M CH₃OH, ~24 °C.

^b A correction was applied for the amount of CrCH₂OH²⁺ that underwent acidolysis.³ ^c The experiment was done in the absence of methanol by direct mixing of Cr²⁺ with the oxidants.

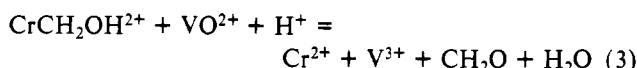
^d 0.50 M HClO₄.

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

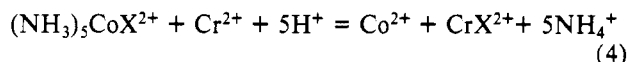


reaction occurs with the rate constant $k_{VO} > 8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 5 °C. Ekstrom and Farrar² later reported that k_{VO} exceeds 10^4 - $10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 14.5 °C, where $k_{VO} = k_1 + k_{\text{direct}}$.

We have recently found³ that VO²⁺ reacts with the hydroxymethylchromium(III) complex CrCH₂OH²⁺ according to eq 3. The chromium(II) produced reacts rapidly with the



second mole of VO²⁺ (eq 1), but it can be partially or completely scavenged in the form of CrX²⁺ if the reaction is done in the presence of an excess of (NH₃)₅CoX²⁺ (X = F, Cl, Br). This indicated to us that the rate constants for reactions 1 and



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 CrCH₂OH²⁺-VO²⁺ reaction to generate Cr²⁺ has the advantage over the direct mixing of Cr²⁺ with the oxidants. The slow formation of small amounts of Cr²⁺ 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 Cr²⁺. A few ex-

(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.

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

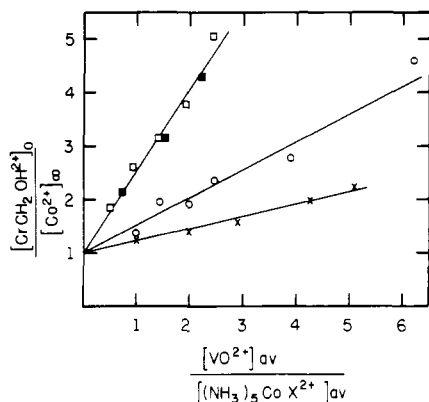


Figure 1. Plots according to eq 5: \square , $X = F$; \circ , $X = Cl$; \times , $X = Br$ ($CrCH_2OH^{2+}$ - VO^{2+} reaction used as a source of Cr^{2+}); \blacksquare , $X = F$ (Cr^{2+} mixed directly with the oxidants; see text).

Table II. Summary of the Kinetic Data for the Oxidation of Cr^{2+} by $(NH_3)_5CoX^{2+}$ and VO^{2+} at 25 °C and 1.0 M Ionic Strength

oxidant	k , $M^{-1} s^{-1}$	ref
$(NH_3)_5CoF^{2+}$	$(9 \pm 1) \times 10^5$	4
$(NH_3)_5CoCl^{2+}$	$(2.6 \pm 0.5) \times 10^6$	4
$(NH_3)_5CoBr^{2+}$	$(6.0 \pm 1.0) \times 10^6$	this work
VO^{2+}	$(1.4 \pm 0.3) \times 10^6$	this work

periments using Cr^{2+} directly were also done to check the method.

Experimental Section

Reagents. The stock solution of vanadium(IV) perchlorate was prepared by ion exchange (Dowex 50W-X8) of the sulfate. Vanadium(IV) was eluted with 1 M perchloric acid and standardized spectrophotometrically (λ_{max} 760 nm, $\epsilon = 17.2 M^{-1} cm^{-1}$). The solutions of chromium(III) perchlorate and $CrCH_2OH^{2+}$ were prepared as previously described.^{3,5} Solutions of $(NH_3)_5CoX^{2+}$ ($X = F, Cl, Br$) were freshly prepared from the solid perchlorate salts before use.

Procedures. Two types of competition experiments were done. In one set of experiments a solution of $(NH_3)_5CoX^{2+}$ was added with a syringe to a freshly prepared solution of $\sim 1 \times 10^{-3} M CrCH_2OH^{2+}$ in 0.1 M $HClO_4$. This was followed immediately by the addition of VO^{2+} which sets off the production of Cr^{2+} . The concentrations of $(NH_3)_5CoX^{2+}$ and VO^{2+} were always in large excess over $[CrCH_2OH^{2+}]$ so that they changed only slightly during the reaction. When the reaction was over (usually 5–20 min) the solution was directly analyzed for Co^{2+} by the thiocyanate method (λ_{max} 623 nm, $\epsilon = 1.842 \times 10^3 M^{-1} cm^{-1}$ in 1:1 acetone–water). Appropriate corrections were made for the absorbance of vanadium(III), vanadium(IV), and $(NH_3)_5CoX^{2+}$ under the conditions of the analyses. On the average $\sim 50\%$ of the measured absorbance corresponded to $Co(NCS)_4^{2-}$. In the second set of experiments a diluted solution of Cr^{2+} ($8.2 \times 10^{-3} M$) was added dropwise to a well-stirred solution of a mixture of the two oxidants. The analyses were done as described above.

Results and Discussion

All the experimental data are shown in Table I. It can

easily be shown that eq 5 holds under the conditions of this

$$\frac{[Cr^{2+}]_0}{[Co^{2+}]_{\infty}} = 1 + \left(\frac{k_{VO}}{k_{CoX}} \right) \left(\frac{[VO^{2+}]_{av}}{[(NH_3)_5CoX^{2+}]_{av}} \right) \quad (5)$$

study, where k_{VO} denotes the rate constant for reaction 1, k_{CoX} is the rate constant for reaction 4, and $[VO^{2+}]_{av}$ and $[(NH_3)_5CoX^{2+}]_{av}$ represent the average concentrations of the oxidants in the experiment. A plot of the left-hand side of the equation vs. the ratio of the average oxidant concentrations should yield a straight line with a unit intercept and a slope which gives directly the ratio of the rate constants. Plots for all three cobalt complexes are shown in Figure 1. Very good agreement between the two types of experiments is noted, indicating that the presence of small amounts of methanol does not affect the ratio of the reaction rates. A computer fit by a nonlinear least-square method gives the following values for the ratios of the rate constants: for $(NH_3)_5CoF^{2+}$, $k_{VO}/k_{CoF} = 1.52 \pm 0.04$; for $(NH_3)_5CoCl^{2+}$, $k_{VO}/k_{CoCl} = 0.514 \pm 0.034$; for $(NH_3)_5CoBr^{2+}$, $k_{VO}/k_{CoBr} = 0.224 \pm 0.010$. From the known rate constants for the reactions of Cr^{2+} with $(NH_3)_5CoF^{2+}$ and $(NH_3)_5CoCl^{2+}$ at 1.0 M ionic strength and 0.10 M H^+ (Table II), we calculate the rate constant k_{VO} to be $(1.4 \pm 0.2) \times 10^6 M^{-1} s^{-1}$ (from the competition with $(NH_3)_5CoF^{2+}$) and $(1.3 \pm 0.3) \times 10^6 M^{-1} s^{-1}$ (from the competition with $(NH_3)_5CoCl^{2+}$). Excellent agreement between the values of k_{VO} obtained in two different competition reactions further substantiates this approach. Note also that in several of the experiments Cr^{2+} was used directly and that these agree with results from the indirect method.

The rate constant for the reaction of $(NH_3)_5CoBr^{2+}$ with Cr^{2+} at 1.0 M ionic strength proved to be too large for direct measurement.⁴ From the ratio k_{VO}/k_{CoBr} and the rate constant k_{VO} determined in this work, we can now calculate $k_{((NH_3)_5CoBr^{2+}-Cr^{2+})} = (6.0 \pm 1.0) \times 10^6 M^{-1} s^{-1}$ at $\mu = 1.0 M$ (25 °C).⁶

The acid dependence of the reaction of VO^{2+} with Cr^{2+} was not studied in great detail. All experiments except one were done at 0.1 M $HClO_4$. The one experiment at 0.50 M $HClO_4$ gave the same result, which indicates that the rate of reaction 1 does not significantly depend on acidity. This is not surprising in view of the similar findings in the closely related V^{2+} - VO^{2+} ⁷ and Cr^{2+} - UO_2^{2+} ² reactions. The protonation of the vanadium(III) product apparently occurs after the rate-determining step, and the formation of the reaction intermediate formulated as $VOCr^{4+}$ is as given in eq 2. If reaction 1 occurs by a "direct" pathway¹ as well as by the mechanism of eq 2, then the value of k_{VO} reported here is the sum of all the pathways contributing to reaction of Cr^{2+} and VO^{2+} .

Registry No. VO^{2+} , 20644-97-7; Cr^{2+} , 22541-79-3; $(NH_3)_5CoBr^{2+}$, 14970-15-1; $(H_2O)_5CrCH_2OH^{2+}$, 32108-95-5.

(5) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

(6) The reliability of this value is further indicated by comparison to the directly determined value⁴ at 0.1 M ionic strength, the ratio of the k_{CoBr} values being 4.3. In comparison, directly determined values⁴ of k_{CoF} and k_{CoCl} at these two ionic strengths are in ratios of 3.6 and 4.3, respectively.

(7) Newton, T. W.; Baker, F. B. *J. Phys. Chem.* **1964**, *68*, 228.