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]

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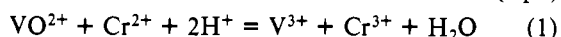(23) G. McLendon and D. Miller, *J. Chem. Soc., Chem. Commun.*, 533 (1980).

Contribution from the Ames Laboratory
and Department of Chemistry,
Iowa State University, Ames, Iowa 50011

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

Andreja Bakač and James H. Espenson*

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

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

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+}]$_\infty$, 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$_3$OH, ~24 °C. [b] A correction was applied for the amount of CrCH$_2$OH^{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$_4$.

portion of the reaction (>90%) occurs directly, while a small fraction proceeds through the dinuclear intermediate VO-$(OH)_n Cr^{(4-n)+}$, as in reaction 2 (written for $n = 0$). The

$$VO^{2+} + Cr^{2+} \xrightarrow{k_1} VOCr^{4+} \xrightarrow[\text{slow}]{2H^+} V^{3+} + Cr^{3+} + H_2O \qquad (2)$$
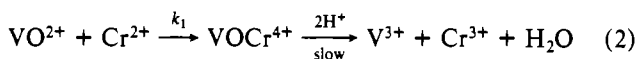
reaction occurs with the rate constant $k_{VO} > 8 \times 10^3$ M^{-1} s^{-1} at 5 °C. Ekstrom and Farrar[2] later reported that k_{VO} exceeds 10^4–10^5 M^{-1} s^{-1} at 14.5 °C, where $k_{VO} = k_1 + k_{\text{direct}}$.

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

$$CrCH_2OH^{2+} + VO^{2+} + H^+ =$$
$$Cr^{2+} + V^{3+} + CH_2O + H_2O \qquad (3)$$
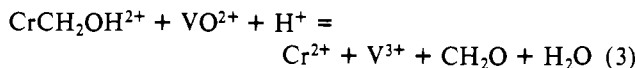
second mole of VO^{2+} (eq 1), but it can be partially or completely scavenged in the form of CrX^{2+} if the reaction is done in the presence of an excess of $(NH_3)_5CoX^{2+}$ (X = F, Cl, Br). This indicated to us that the rate constants for reactions 1 and

$$(NH_3)_5CoX^{2+} + Cr^{2+} + 5H^+ = Co^{2+} + CrX^{2+} + 5NH_4^+ \qquad (4)$$
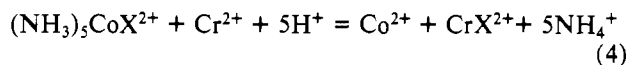
4 are of comparable magnitude. This system seemed to be well suited for the determination of the rate constant k_{VO} by the competition method, since k_4 is known for a number of groups X.[4] Using the $CrCH_2OH^{2+}$–VO^{2+} reaction to generate Cr^{2+} has the advantage over the direct mixing of Cr^{2+} 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-

(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.
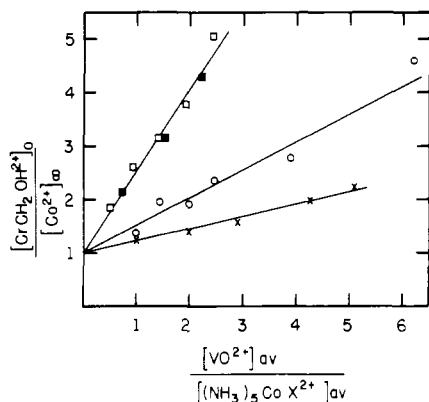
Figure 1. Plots according to eq 5: □, X = F; O, X = Cl; ×, X = Br (CrCH$_2$OH^{2+}–VO^{2+} reaction used as a source of Cr^{2+}); ■, X = F (Cr^{2+} mixed directly with the oxidants; see text).

Table II. Summary of the Kinetic Data for the Oxidation of Cr^{2+} by (NH$_3$)$_5$CoX^{2+} and VO^{2+} at 25 °C and 1.0 M Ionic Strength

oxidant	k, M^{-1} s^{-1}	ref
(NH$_3$)$_5$CoF^{2+}	$(9 \pm 1) \times 10^5$	4
(NH$_3$)$_5$CoCl^{2+}	$(2.6 \pm 0.5) \times 10^6$	4
(NH$_3$)$_5$CoBr^{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, ϵ = 17.2 M^{-1} cm^{-1}). The solutions of chromium(III) perchlorate and CrCH$_2$OH^{2+} were prepared as previously described.[3,5] Solutions of (NH$_3$)$_5$CoX^{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$_3$)$_5$CoX^{2+} was added with a syringe to a freshly prepared solution of ~1 × 10^{-3} M CrCH$_2$OH^{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$_3$)$_5$CoX^{2+} and VO^{2+} were always in large excess over [CrCH$_2$OH^{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, ϵ = 1.842 × 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$_3$)$_5$CoX^{2+} under the conditions of the analyses. On the average ~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 × 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

$$\frac{[\text{Cr}^{2+}]_0}{[\text{Co}^{2+}]_\infty} = 1 + \left(\frac{k_{\text{VO}}}{k_{\text{CoX}}}\right)\left(\frac{[\text{VO}^{2+}]_{av}}{[(\text{NH}_3)_5\text{CoX}^{2+}]_{av}}\right) \quad (5)$$

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$_3$)$_5$CoX^{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$_3$)$_5$CoF^{2+}, $k_{\text{VO}}/k_{\text{CoF}}$ = 1.52 ± 0.04; for (NH$_3$)$_5$CoCl^{2+}, $k_{\text{VO}}/k_{\text{CoCl}}$ = 0.514 ± 0.034; for (NH$_3$)$_5$CoBr^{2+}, $k_{\text{VO}}/k_{\text{CoBr}}$ = 0.224 ± 0.010. From the known rate constants for the reactions of Cr^{2+} with (NH$_3$)$_5$CoF^{2+} and (NH$_3$)$_5$CoCl^{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 ± 0.2) × 10^6 M^{-1} s^{-1} (from the competition with (NH$_3$)$_5$CoF^{2+}) and (1.3 ± 0.3) × 10^6 M^{-1} s^{-1} (from the competition with (NH$_3$)$_5$CoCl^{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$_3$)$_5$CoBr^{2+} with Cr^{2+} at 1.0 M ionic strength proved to be too large for direct measurement.[4] From the ratio $k_{\text{VO}}/k_{\text{CoBr}}$ and the rate constant k_{VO} determined in this work, we can now calculate k-((NH$_3$)$_5$CoBr^{2+}–Cr^{2+}) = (6.0 ± 1.0) × 10^6 M^{-1} s^{-1} at μ = 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" pathway[1] 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$_3$)$_5$CoBr^{2+}, 14970-15-1; (H$_2$O)$_5$CrCH$_2$OH^{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 value[4] at 0.1 M ionic strength, the ratio of the k_{CoBr} values being 4.3. In comparison, directly determined values[4] 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.