$$COF_2 \xrightarrow{F^-} CF_3O^- \begin{cases} \overset{\delta+}{Cl}-\overset{\delta-}{O}-Cl \longrightarrow CF_3OCl + OCl^- \\ \overset{\delta-}{F}-\overset{\delta+}{O}-\overset{\delta-}{F} \longrightarrow CF_3OOF + F^- \end{cases}$$

We expect to explore further the differences between fluorinations and chlorofluorinations and to compare the new hypochlorites chemically with the fluoroxy compounds.

Caution: While we have experienced no explosive decomposition of the simple hypochlorites, an explosion did occur during attempts to isolate the products from the chlorofluorination of oxalyl fluoride. All the hypochlorites are powerful oxidizing agents and may react violently with certain reducing agents. In addition, all the new hypochlorites are expected to be quite toxic. Adequate safety shielding and ventilation should be used at all times when handling these compounds.

Reactions Involving Copper(I) in Perchlorate Solution. Kinetics and Mechanism of the Copper(II) Catalysis of Vanadium(III) Reductions of Cobalt(III) Complexes[1a-c]
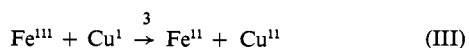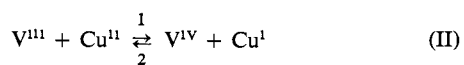
O. Jerry Parker and James H. Espenson[1d]

Contribution from the Department of Chemistry and the Institute for Atomic Research, Iowa State University, Ames, Iowa 50010. Received October 3, 1968

Abstract: Copper(II) catalyzes the oxidation of V^{3+} to VO^{2+} by the cobalt(III) complexes $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5Cl^{2+}$, and *trans*-$Co(en)_2Cl_2^+$. The rate equation is $-d[V^{3+}]/dt = (g + h/[H^+])[Cu^{2+}][V^{3+}]$, independent of [Co(III)]. At 25.0° and $\mu = 3.00 M$ (LiClO$_4$), the values are $g = 0.018 \pm 0.002 M^{-1}sec^{-1}$ and $h = 0.336 \pm 0.001 sec^{-1}$. The activation parameters for h are $\Delta H^\ddagger = 19.4 \pm 0.1$ kcal mole^{-1} and $\Delta S^\ddagger = 4.4 \pm 0.4$ eu. The rate was also studied with NaClO$_4$ as the added electrolyte and at $\mu = 1.00 M$ (LiClO$_4$). The rate-determining step is proposed to be the rapid reaction of V^{3+} and Cu^{2+}, followed by the rapid reoxidation of the Cu^+ so formed by Co(III). The role of Cu(I) in the catalytic cycle is discussed, and some "direct" measurements of the $V^{3+} + Cu^{2+}$ rate are presented. The relation of the present results to those on the reverse reaction, $VO^{2+} + Cu^+$, is considered. Arguments are advanced for a mechanism in which the inner-sphere reaction of VOH^{2+} and Cu^{2+} is the main rate-determining step.

The oxidation–reduction reaction between hydrated V^{3+} and Cu^{2+} cations in dilute perchloric acid solution is given by reaction I. This process has been considered in three previous studies.[2-4] One of these was

$$V^{3+} + Cu^{2+} + H_2O = VO^{2+} + Cu^+ + 2H^+ \tag{I}$$
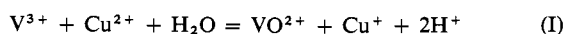
the study of the reaction of Fe(III) and V(III), for which Higginson and Sykes[2] proposed the following two-step mechanism[5] to account for the catalytic effect of Cu^{2+}.

$$V^{III} + Cu^{II} \underset{2}{\overset{1}{\rightleftarrows}} V^{IV} + Cu^{I} \tag{II}$$

$$Fe^{III} + Cu^{I} \overset{3}{\rightarrow} Fe^{II} + Cu^{II} \tag{III}$$

Since the rate expression for catalysis was first order with respect to V(III) and Cu(II), the first step of the sequence

was presumed to be rate determining and the catalytic rate constant thereby identified as k_1. In addition, the reaction of VO^{2+} and Cu^+, the reverse of the process presumed responsible for the catalysis, has been studied.[3] The work of Ramsey, *et al.*,[4] established the catalytic effect of Cu^{2+} on the oxidation of V^{3+} by molecular oxygen in perchloric acid solution. They proposed the rate-determining step was reaction II, followed by the rapid reaction of Cu(I) with O_2.

In the present study we have considered further the reaction of V^{3+} and Cu^{2+} to study its kinetics and mechanism in the absence of the complications present in the earlier work, where substantial corrections had to be made for the uncatalyzed reaction. Since equilibrium in reaction I lies largely toward the left, a direct study of $Cu^{2+} + V^{3+}$ is not possible except under a very special and limited set of circumstances.

We have used a procedure similar to the earlier catalytic work,[2] except that used as an oxidizing substrate in place of Fe^{3+} or O_2 was a substance for which the spontaneous oxidation of V^{3+} in the absence of Cu^{2+} does not occur to an appreciable extent. The materials used have been Co(III) complexes, which are known[6] to react rapidly with Cu(I). The three complexes $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5Cl^{2+}$, and *trans*-$Co(en)_2Cl_2^+$ were studied in

(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission, Contribution No. 2427; (b) based on the Ph.D. Thesis of O. J. Parker, Iowa State University, Aug 1968; (c) presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; (d) Fellow of the Alfred P. Sloan Foundation.

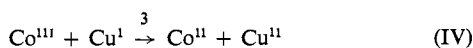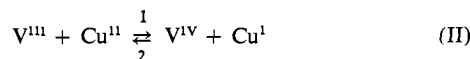(2) W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 2841 (1965).

(3) K. Shaw and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 6622 (1968).

(4) J. B. Ramsey, R. Sugimoto, and H. DeVorkin, *ibid.*, **63**, 3480 (1941).

(5) The mechanism is deliberately written showing only the over-all pattern of oxidation–reduction. The question of the reacting species and the role of protolytic equilibria will be considered separately.

(6) O. J. Parker and J. H. Espenson, *J. Am. Chem. Soc.*, in press.

detail. The proposed sequence of reactions is the following.

$$V^{III} + Cu^{II} \underset{2}{\overset{1}{\rightleftharpoons}} V^{IV} + Cu^{I} \qquad (II)$$

$$Co^{III} + Cu^{I} \xrightarrow{3} Co^{II} + Cu^{II} \qquad (IV)$$

These lead to the following net reactions using $Co(NH_3)_5Br^{2+}$ as an example.

$$V^{3+} + Co(NH_3)_5Br^{2+} + 3H^+ + H_2O =$$
$$VO^{2+} + Co^{2+} + 5NH_4^+ + Br^- \qquad (V)$$
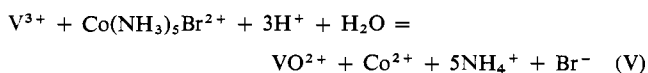
Experimental Section

Materials. Solutions of copper(II), vanadium(III), oxovanadium(IV), sodium, and lithium perchlorates were prepared and analyzed as before.[3,7,8] Conductivity water was used for all experiments. The cobalt(III) complexes were prepared by published procedures: $[Co(NH_3)_5Br]Br_2$ by the method of Diehl, et al.,[9] $[Co(NH_3)_5Cl]Cl_2$ according to Basolo and Murmann,[10] and trans-$[Co(en)_2Cl_2]Cl$ by the procedure of Bailar.[11] The first two complexes were converted to their perchlorates by adding $LiClO_4$ or $HClO_4$ to saturated solutions of the halides. The complexes were analyzed for Co by reduction with a small excess of Cr^{2+} and spectrophotometric determination of the Co^{2+} produced as the thiocyanate complex in 50 vol % acetone. Further identification of the complexes was made on the basis of the ultraviolet–visible spectra. In all cases the values of λ_{max} and ε agreed quite closely with those in the literature.[12-16] The analyses and spectra are summarized in the thesis cited.[1b]

Rate Measurements. The reaction progress was followed using a Cary Model 14 spectrophotometer. The change in absorbance with time was recorded at fixed wavelength, with the Co(III) absorption making the predominant contribution in most experiments. The reactions were carried out in cylindrical fused silica cells of 2–10-cm optical path, immersed in a water-filled thermostating bath[17] during the run. The cell was closed with a rubber serum cap after all the reagents but one had been added, and it was then thoroughly purged with purified nitrogen and brought to the reaction temperature. The kinetic results proved to be independent of the order of mixing the reactants, and in most experiments vanadium(III) was added last through the cell cap using a hypodermic syringe.

Reaction Conditions. Different series of runs were done with $\mu = 1.00$ and 3.00 M using $LiClO_4$ as the added electrolyte and at $\mu = 3.00$ M using $NaClO_4$. The Cu(II) catalysis of the Fe(III)–V(III) reaction[2] was studied in the latter medium, and the Cu(I)–V(IV) reaction was also studied under some of these sets of conditions. In most runs the absorbance was followed at 280 nm ($\varepsilon(RBr^{2+})$ 3430 M^{-1} cm^{-1}), but runs were also carried out at longer and shorter wavelengths, including the low-energy visible maximum. Typical reaction times are 2–40 min, and the aquation reactions of the cobalt(III) complexes were not significant during the times required to make fresh stock solutions and make the rate runs. For a series of consecutive runs, a stock solution of the complex was prepared and stored at 0° between runs.

Results

Stoichiometry. Experiments were performed to demonstrate that the uncatalyzed reactions of V^{3+} and the

(7) (a) K. Shaw and J. H. Espenson, Inorg. Chem., 7, 1619 (1968); (b) O. J. Parker and J. H. Espenson, ibid., 8, 185 (1969).
(8) J. H. Espenson, ibid., 4, 1025 (1965).
(9) H. Diehl, H. Clark, and H. H. Willard, Inorg. Syn., 1, 186 (1939).
(10) F. Basolo and R. K. Murmann, ibid., 4, 171 (1953).
(11) J. C. Bailar, Jr., ibid., 2, 222 (1946).
(12) S. Nakamura, Ph.D. Thesis, University of Chicago, 1964.
(13) A. Haim and H. Taube, J. Am. Chem. Soc., 85, 3110 (1963).
(14) M. Linhard and M. Weigl, Z. Anorg. Allgem. Chem., 271, 101 (1952).
(15) P. Benson and A. Haim, J. Am. Chem. Soc., 87, 3826 (1965).
(16) C. Bifano and R. G. Linck, Inorg. Chem., 7, 910 (1968).
(17) J. H. Espenson, J. Am. Chem. Soc., 86, 5101 (1964).

Table I. Rate Constants (M^{-1} sec^{-1}) for the Reaction of V(III) and Cu(II) at $\mu = 3.00$ M, $LiClO_4$ Medium

$10^2 \times [Cu^{2+}]$	$10^4 \times [V^{3+}]_0$	$10^4 \times [RBr^{2+}]_0$	k
[H⁺]=2.75; T=15.0°			
2.06	0.75	1.5	0.0426
8.32	0.75	1.5	0.0427
8.32	0.75	1.5	0.0431
[H⁺]=2.00, T=15.0°			
3.99	0.75	1.5	0.0570
33.4	0.75	1.5	0.0552
[H⁺]=1.01, T=15.0°			
2.00	0.75	1.5	0.109
9.98	0.75	0.75	0.108
9.98	0.75	0.110	0.110
9.98	0.75	1.5	0.110
9.98	3.0	6.0	0.112
20.1	0.75	1.5	0.107
[H⁺]=0.506, T=15.0°			
1.01	0.75	1.5	0.209
10.1	0.75	1.5	0.209
[H⁺]=0.209, T=15.0°			
0.406	0.75	1.5	0.482
1.60	0.75	1.5	0.475
1.60	0.75	1.5	0.479
4.06	0.75	1.5	0.485
[H⁺]=2.85, T=25.0°			
0.998	0.75	1.5	0.136
4.59	3.6	5.5ᵇ	0.138
4.67	10.0	12.0ᵃ	0.136
4.67	10.0	12.0ᵃ	0.142
4.92	1.1	3.4	0.130
4.92	0.75	2.3	0.134
4.92	0.75	2.3	0.136
4.92	0.75	2.3	0.137
4.92	0.75	2.3	0.138
4.99	0.75	1.5	0.133
4.99	0.75	1.5	0.137
[H⁺]=2.00, T=25.0°			
0.998	0.75	1.5	0.184
4.99	0.75	1.5	0.185
10.1	0.75	1.5	0.186
20.1	0.75	1.5	0.180
[H⁺]=1.01, T=25.0°			
0.299	0.75	1.5	0.356
0.499	0.75	1.5	0.355
1.53	0.75	1.5	0.347
1.60	3.6	5.5ᵇ	0.348
1.60	3.0	5.5ᵇ	0.350
1.60	3.6	11.1ᵇ	0.353
3.19	0.75	2.3	0.348
3.19	0.75	2.3	0.349
3.19	0.75	2.3	0.351
3.19	1.1	3.4	0.355
3.19	0.75	2.3	0.359
4.99	0.75	1.5	0.347
4.99	0.75	1.5	0.349
4.99	0.75	1.5ᵃ	0.352
4.99	0.75	1.5ᵃ	0.352
4.99	0.75	1.5ᵃ	0.361
10.0	0.75	1.5	0.345
[H⁺]=0.506, T=25.0°			
0.299	0.75	1.5	0.670
1.53	0.75	1.5	0.686
2.99	0.75	1.5	0.680
5.07	0.75	1.5	0.662
[H⁺]=0.210, T=25.0°			
0.0100	13.0	21.0	1.70
0.0765	12.0	21.0	1.65
0.0989	10.0	15.0	1.67
0.206	10.0	15.0	1.64
0.319	3.6	5.5ᵇ	1.62
0.752	0.75	1.5	1.58
0.752	0.75	1.5	1.62
0.752	2.0	3.0	1.62
0.752	3.0	2.0	1.69
1.17	1.1	3.4	1.59
1.17	0.75	2.3	1.62
1.53	0.75	1.5	1.59
1.64	0.75	1.5	1.56
1.64	0.75	1.5	1.66
2.99	0.75	1.5	1.56
[H⁺]=2.85, T=35.1°			
0.605	0.75	1.5	0.439
5.06	0.75	1.5	0.408
5.06	0.75	1.5	0.409
[H⁺]=2.00, T=35.1°			
0.406	0.75	1.5	0.575
4.06	0.75	1.5	0.562
[H⁺]=1.01, T=35.1°			
0.206	0.75	1.5	1.10
1.00	0.44	0.75	1.05
1.01	0.75	1.5	1.07
1.01	0.75	1.5	1.08
1.01	3.0	6.0	1.09
2.06	0.75	1.5	1.06
[H⁺]=0.506, T=35.1°			
0.101	0.75	1.5	2.02
1.01	0.75	1.5	2.05
[H⁺]=0.210, T=35.1°			
0.0416	0.75	1.5	4.70
0.181	0.75	1.5	4.60
0.181	0.75	1.5	4.90
0.406	0.75	1.5	4.77

ᵃ RCl^{2+} used in place of RBr^{2+}. ᵇ $Co(en)_2Cl_2^+$ used in place of RBr^{2+}.

Table II. Rate Constants (M^{-1} sec^{-1}) for the Reaction of V(III) and Cu(II) at $\mu = 3.00$ M, $NaClO_4$ Medium

$10^2 \times [Cu^{2+}]$	$10^4 \times [V^{3+}]_0$	$10^4 \times [RBr^{2+}]_0$	k
[H⁺]=2.75, T=15.0°			
2.06	0.75	1.4	0.0423
8.32	0.90	0.80	0.0419
8.32	0.75	1.4	0.0423
[H⁺]=2.00, T=15.0°			
3.99	0.75	1.4	0.0526
33.3	0.75	1.4	0.0547
[H⁺]=1.00, T=15.0°			
2.00	0.75	1.4	0.0948
14.6	0.45	0.69	0.0931
14.6	1.5	2.8	0.0959
14.6	0.75	1.4	0.0969
14.6	0.75	1.4	0.0972
20.0	0.75	1.4	0.0971
[H⁺]=0.498, T=15.0°			
1.01	0.75	1.4	0.178
10.1	0.75	1.4	0.175
[H⁺]=0.201, T=15.0°			
0.406	0.75	1.4	0.438
1.60	0.75	1.4	0.424
1.60	0.75	1.4	0.427
4.06	0.75	1.4	0.427
[H⁺]=2.85, T=25.0°			
1.66	0.75	1.4	0.137
1.66	0.75	1.4	0.140
4.92	0.75	1.4	0.141
[H⁺]=2.00, T=25.0°			
1.33	0.75	1.4	0.176
13.3	0.75	1.4	0.179
[H⁺]=1.00, T=25.0°			
0.319	0.75	1.4	0.316
0.652	0.75	1.4	0.314
3.19	1.5	2.8	0.333
3.19	0.75	1.4	0.335
6.52	0.75	1.4	0.314
[H⁺]=0.498, T=25.0°			
0.319	0.75	1.4	0.633
3.19	0.75	1.4	0.605
[H⁺]=0.201, T=25.0°			
0.133	0.75	1.4	1.49
0.286	0.75	1.4	1.42
0.586	0.75	1.4	1.44
0.586	0.75	1.4	1.45
[H⁺]=2.85, T=35.0°			
0.605	0.90	1.4	0.418
5.06	0.90	1.4	0.398
5.06	0.90	1.4	0.408
[H⁺]=2.00, T=35.0°			
0.406	0.90	1.4	0.527
4.06	0.90	1.4	0.528
[H⁺]=1.00, T=35.0°			
0.206	0.90	1.4	0.983
1.01	0.69	0.45	0.960
1.01	0.90	0.80	0.973
1.01	0.90	1.4	0.979
1.01	1.8	2.8	0.989
2.06	0.90	1.4	0.946
[H⁺]=0.498, T=35.0°			
0.406	0.75	1.4	1.84
1.01	0.90	1.4	1.79
[H⁺]=0.201, T=35.0°			
0.166	0.75	1.4	4.34
0.406	0.75	1.4	4.35
0.725	0.75	1.4	4.32
0.725	0.75	1.4	4.38

cobalt(III) complexes were unimportant. For example, the absorbance of a solution with the composition $[V^{3+}]_0 = 1.30 \times 10^{-3}$, $[RBr^{2+}] = 2.05 \times 10^{-3}$, $[H^+] = 0.210$ M at $\mu = 3.00$ M ($LiClO_4$) and 25.0° was measured at 360 nm. The rate of reaction was quite low, and $\sim 90\%$ of the absorbance change was a result of the aquation of RBR^{2+} to ROH_2^{3+}. After ca. 8 hr (a time much longer than the runs of interest), the yield of Co^{2+} was 0.15×10^{-3} M, and this run had vanadium(III) and cobalt(III) concentrations each 15 times higher than the values in most runs.

In the same experiment with 10^{-4} M Cu^{2+} added, the rate increased markedly, following pseudo-first-order kinetics with a rate constant 1.70×10^{-4} sec^{-1}. The

Table III. Effect of Different Cobalt(III) Complexes on the Cu(II)–V(III) Rate Constant

Complex	k, M^{-1} sec^{-1} (no. of expts)[a]		
	2.85 M H$^+$	1.01 M H$^+$	0.210 M H$^+$
Co(NH$_3$)$_5$Br^{2+}	0.135 ± 0.002 (8)	0.352 ± 0.004 (12)	1.62 ± 0.04 (14)
Co(NH$_3$)$_5$Cl^{2+}	0.140 ± 0.002 (2)	0.356 ± 0.005 (2)	...
trans-Co(en)$_2$Cl$_2$$^+$	0.138 (1)	0.350 ± 0.002 (3)	1.62 (1)

[a] 25.0°, μ = 3.00 M (LiClO$_4$). The uncertainty represents the average deviation from the mean of the rate constants using that complex under the given set of conditions.

yield of Co^{2+} at apparent completion of the run was 1.23×10^{-3} M, essentially the same as the original V^{3+} added. These observations support the assertion that the net process is that in reaction IV. Under the conditions of nearly all the experiments with [Cu^{2+}]$_0$ ≥ 1.10×10^{-3} M, no correction was needed either for aquation of the cobalt complexes or for the uncatalyzed reaction with vanadium(III).

Kinetics. We shall first consider the rate studies with an excess of cobalt(III) over vanadium(III). When this situation was reversed, or when vanadium(IV) was added in large excess, certain complications arose that provided useful information. These cases will be considered separately. Provided the cobalt(III) complex was in excess over vanadium(III), the traces of absorbance vs. time decreased smoothly to a steady value. Plots of log $(D - D_\infty)$ vs. time were linear for at least 85% reaction, indicating a pseudo-first-order dependence of rate on vanadium(III) concentration. The rate expression is that given by eq 1, and the rate constants were obtained by

$$-d[V^{3+}]/dt = k[Cu^{2+}]_0[V^{3+}] \qquad (1)$$

dividing the pseudo-first-order rate constant by the initial concentration of copper(II). Since the copper(II) is replenished by the rapid reaction of Cu$^+$ and RBr^{2+}, the Cu^{2+} concentration does not change to any appreciable extent even in runs where its concentration is lower than that of RBr^{2+}.

The total variation of concentrations under one set of reaction conditions is illustrated by the data at 25.0°, μ = 3.00 M (LiClO$_4$), with [H$^+$] = 0.210 M. The ranges are 10^{-4} ≤ [Cu^{2+}] ≤ 3×10^{-2}; 7.5×10^{-5} ≤ [V^{3+}]$_0$ ≤ 1.3×10^{-3}; 1.5×10^{-4} ≤ [RBr^{2+}] ≤ 2.1×10^{-3}. Tables I and II summarize the second-order rate constants at μ = 3.00 M, with, respectively, LiClO$_4$ and NaClO$_4$ used as supporting electrolytes. These data cover 15.0, 25.0, and 35°, and a range of [H$^+$], 0.2–2.85 M. A much smaller number of runs was carried out at μ = 1.00 M (LiClO$_4$) and refer only to 0.852 M H$^+$, 25.0°; the value of k is 0.258 M^{-1} sec^{-1}, ±0.004 standard deviation in six runs.

The rate constants did not depend on the concentration of cobalt(III) complex. Moreover, the use of other complexes that also reacted rapidly with Cu$^+$ gave identical rate constants. Table I includes a number of experiments in which Co(NH$_3$)$_5$Cl^{2+} and trans-Co(en)$_2$Cl$_2$$^+$ were used in place of Co(NH$_3$)$_5$Br^{2+}. Runs in which the use of Co(NH$_3$)$_5$NCS^{2+} was attempted failed owing to the precipitation of highly insoluble CuSCN(s) during the experiments. The lack of effect of the source of cobalt-(III) complex is illustrated by the summary of Table III.

Runs were performed with added bromide and chloride ions. The point of such rate measurements was to
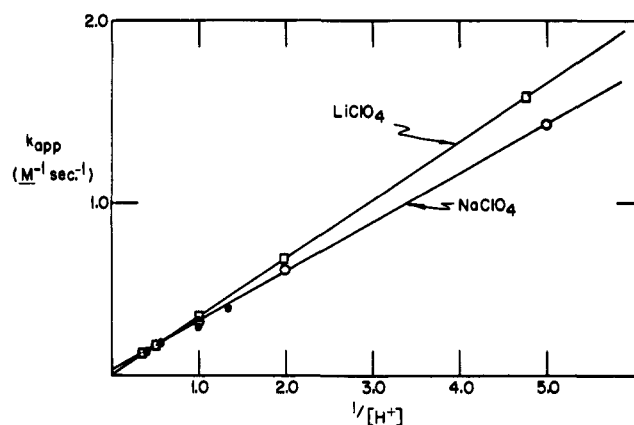

Figure 1. Plots illustrating the dependence of the apparent second-order rate constant with hydrogen ion concentration, as in eq 2. The graph refers to 25.0°, depicting data at μ = 3.00 M, with LiClO$_4$ (open squares) and NaClO$_4$ (open circles) illustrated. The data from ref 2 (25.0°, μ = 3.00 M, NaClO$_4$) are included (solid circles).

demonstrate their lack of effect, since they are released during each run, as shown in reaction V. Low concentrations of Br$^-$ and Cl$^-$ had no effect, including concentrations up to ten times the level at which the ions were generated in runs conducted in their initial absence. Considerably higher halide concentrations did cause an acceleration of rate; these effects are still under investigation.

The rate constants increased with decreasing hydrogen ion concentration, according to the relation given in eq 2.

$$k = g + h/[H^+] \qquad (2)$$

As suggested by this equation, plots of k vs. 1/[H$^+$] are linear, as shown in Figure 1. In both NaClO$_4$ and LiClO$_4$ media the intercepts of such plots are very small, although the best line does not pass through the origin. The values in the two media do not coincide precisely, but the differences are not large. For purposes of comparison, some of the data of Higginson and Sykes[2] are shown in these plots. The agreement is within 10%, which can be considered an adequate demonstration that both studies are controlled by the same rate-determining process. The present values are more reliable, however, owing to the errors introduced by the necessity in the earlier work of correcting for the uncatalyzed reaction, where some difficulties were noted.[2] The study[4] of the effect of Cu^{2+} on the reaction of V^{3+} and O$_2$ gave an identical rate expression, including the inverse dependence on [H$^+$], with h = 0.6 sec^{-1} at 25.0° and μ = 0.4 M. In that work, however, the order with respect to copper(II) fell below unity with progressively increasing concentra-

Table IV. Values[a] of the Parameters g and h at $\mu = 3.00\ M$ and Various Temperatures

Temp, °C	g, M^{-1} sec^{-1}		h, sec^{-1}	
	LiClO$_4$[b]	NaClO$_4$[b]	LiClO$_4$[b]	NaClO$_4$[b]
15.0	0.0076 ± 0.0008	0.0117 ± 0.0006	0.0999 ± 0.0006	0.0837 ± 0.0005
25.0	0.018 ± 0.002	0.038 ± 0.003	0.336 ± 0.001	0.285 ± 0.002
35.0[c]	0.083 ± 0.010	0.111 ± 0.005	0.981 ± 0.008	0.852 ± 0.004

[a] The uncertainties represent the standard deviation. [b] The inert electrolyte used to maintain ionic strength. [c] For LiClO$_4$, 35.1°.

tions above $5 \times 10^{-5}\ M$. Moreover, the apparent activation enthalpy of 16.6 kcal was lower than the value 19.4 kcal found in this study. These observations suggest that other processes than the reaction studied here may be involved in the oxygen reaction.

The data in Tables I and II were fit to eq 2 using a least-squares computer program.[18] The values of the parameters g and h at each temperature are given in Table IV. The contribution of the g term in eq 2 is so small that its precision is quite low. In fact, the question will later be raised as to whether the term represents a genuine pathway for the reaction or a medium effect.

Experiments with Insufficient Co(III) Complex. We shall now consider the situation when the starting concentration of V^{3+} exceeded that of RBr^{2+}. Figure 2 depicts the absorbance at 280 nm vs. time for an experiment with $[Cu^{2+}] = 0.0075$, $[V^{3+}]_0 = 3.0 \times 10^{-4}$, $[RBr^{2+}]_0 = 2.0 \times 10^{-4}\ M$ (25.0°, $\mu = 3.00\ M$, LiClO$_4$, $[H^+] = 0.210\ M$). The striking feature of the plot is the abrupt change in slope occurring after ca. 100 sec of reaction time, followed by a small but reproducible rise in absorbance.

The first stage corresponds to the reduction of RBr^{2+} by reactions II and IV, the former being rate determining. The value for the rate constant determined by the method of Guggenheim[19] was $1.69\ M^{-1}$ sec^{-1}, in agreement with the average value of $1.62\ M^{-1}$ sec^{-1} in experiments where the complication of a second stage did not occur. The second stage represents the absorbance increase from the Cu(I) generated as reaction II approached equilibrium. (Reaction II can establish the equilibrium concentration of Cu$^+$ only after all the Co(III) has been reduced.) Unlike the first stage, its apparent rate constant is not the forward rate constant of II alone, but a combination of the forward and reverse rate constants. Under certain specified conditions the second-stage rate follows the pseudo-first-order expression[20] given in eq 3,

$$k_{app} = k[Cu^{2+}] + k_r[VO^{2+}] \qquad (3)$$

where $k = 1.62\ M^{-1}$ sec^{-1} (Table I) and $k_r = 80.6$ sec^{-1} (calcd from ref 3) at 25.0°, $[H^+] = 0.210\ M$, $\mu = 3.00\ M$, LiClO$_4$.

An experiment was designed to make the second-stage change as significant as possible. The starting composition was $[Cu^{2+}] = 4.99 \times 10^{-2}$, $[V^{3+}] = 3.10 \times 10^{-4}$, $[RBr^{2+}] = 2.70 \times 10^{-4}\ M$. The second-stage rate constant k_{app} was 0.100 sec^{-1}. The theoretical value, using

(18) Based on Report LA 2367 + Addenda from Los Alamos Scientific Laboratory. We are grateful to Drs. T. W. Newton and R. H. Moore for copies of the program.
(19) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 137 (1926).
(20) The concentrations of Cu^{2+} and H$^+$ are effectively constant, as is that of VO^{2+}, since the latter ion was generated at a value (= [RBr^{2+}]$_0$) high compared to subsequent shifts caused by the approach to equilibrium in reaction II. Thus only V^{3+} and Cu$^+$ change concentration significantly during the second stage.
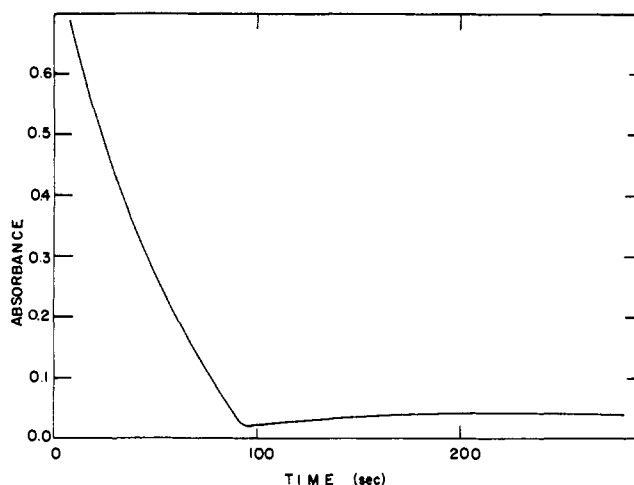

Figure 2. The absorbance–time tracing in an experiment with insufficient cobalt(III). The following were the initial concentrations: $[Cu^{2+}] = 7.5 \times 10^{-3}$, $[V^{3+}] = 3.0 \times 10^{-4}$, $[RBr^{2+}] = 2.0 \times 10^{-4}\ M$ at 25.0°, $\mu = 3.00\ M$, LiClO$_4$, $[H^+] = 0.210\ M$, λ 280 nm, optical path 5.0 cm.

the average $[VO^{2+}]$ during the second stage, from eq 3 was $1.62 \times 0.0499 + 80.6 \times 2.85 \times 10^{-4} = 0.104$ sec^{-1}, in very good agreement.

Direct Study of the V(III)–Cu(II) Reaction. Related to the above experiments were our attempts to measure the rate of the $V^{3+} + Cu^{2+}$ reaction without using a cobalt(III) complex in a catalytic cycle. The low equilibrium constant for reaction II makes a direct evaluation possible only under conditions of low $[H^+]$ and high $[Cu^{2+}]$. The rate of reaction II under these circumstances is given by eq 4, where $k' = k[Cu^{2+}]$ (Table I)

$$d[Cu^+]/dt = k'[V^{3+}] - k_r'[Cu^+][VO^{2+}] \qquad (4)$$

and the value of k_r', 80.6 M^{-1} sec^{-1} at 0.210 M H$^+$, was computed from earlier studies.[3] The data for an experiment with $[Cu^{2+}] = 4.99 \times 10^{-2}$ and $[V^{3+}] = 3.1 \times 10^{-4}\ M$ were treated by a computer program that fit the data to a mixed first- and second-order expression for approach to equilibrium. In duplicate experiments, the values were $k = 1.53$ and $1.71\ M^{-1}$ sec^{-1}, which are considered to be in adequate agreement with $1.62\ M^{-1}$ sec^{-1} from the catalytic experiments (Table I).

Reactions with High Vanadium(IV) Concentrations. The complete steady-state rate expression for the catalytic mechanisms (reactions II and IV) is given by eq 5. Under all the conditions considered before, the second denom-

$$\frac{-d[V^{3+}]}{dt} = \frac{k_1k_3[Cu^{2+}][V^{3+}][Co(III)]}{k_2[VO^{2+}] + k_3[Co(III)]} \qquad (5)$$
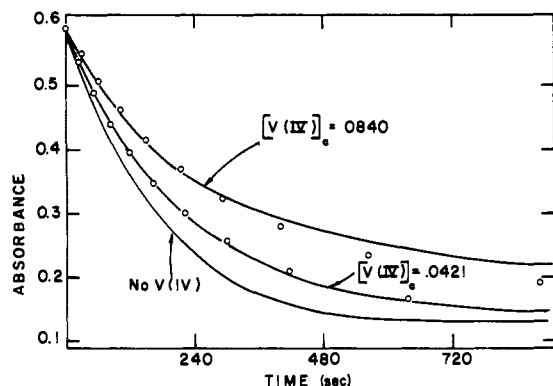
Figure 3. Comparison of observed absorbance traces in runs with added concentrations of vanadium(IV) to the values (points) computed using the integrated expression (eq 6) for the complete two-step process employing the known values of the three rate constants presumed to apply. Initial concentrations, $[Cu^{2+}]$ = 4.01 × 10^{-2}, $[V^{3+}]$ = 9.00 × 10^{-4}, $[RCl^{2+}]_0$ = 1.20 × 10^{-3} M (25.0°, μ = 3.00 M, LiClO₄, $[H^+]$ = 0.210 M, λ 280 nm). The three runs had $[VO^{2+}]_0$ = 0.0, 0.0421, and 0.0840 M.

inator term was far greater than the first, leading to the simple expression of eq 1, with $k = k_1$. The rate of reaction of $Co(NH_3)_5Cl^{2+}$ and Cu^+ is the lowest of the complexes considered, k_3 being[5] 1.13 × 10^5 M^{-1} sec^{-1} (25.0°, μ = 3.00 M, LiClO₄).

Several runs with high concentrations of added VO^{2+} were carried out to test the correctness of eq 5. The addition of VO^{2+} in runs involving RCl^{2+} had a noted retarding effect. The absorbance data from these experiments were compared with the values computed using the known rate constants which at 25.0°, $[H^+]$ = 2.66 M, μ = 3.00 M, are k_1 = 0.147 M^{-1} sec^{-1} (Table I) and k_2 = 1.02 × 10^3 M^{-1} sec^{-1} (computed from ref 3). Integration of eq 5 gives the expression in eq 6. The

$$\{k_3[V^{3+}]_0 - k_3[RCl^{2+}]_0 + k_2[VO^{2+}]_0\} \times$$

$$\ln\{[V^{3+}]_0/([V^{3+}]_0 - [Co^{2+}])\} - k_2[VO^{2+}]_0 \times$$

$$\ln\{([RCl^{2+}]_0 - [Co^{2+}])/[RCl^{2+}]_0\} =$$

$$k_1k_3[Cu^{2+}]_0\{[V^{3+}]_0 - [RCl^{2+}]_0\}t \quad (6)$$

known rate constants and starting conditions were applied to eq 6 and concentrations computed at various time intervals. The molar absorptivity of each species was then used to construct a theoretical curve of total absorbance vs. time. Three experiments will be considered, each of which had $[Cu^{2+}]$ = 4.01 × 10^{-2}, $[V^{3+}]_0$ = 9.00 × 10^{-4}, and $[RCl^{2+}]_0$ = 1.20 × 10^{-3} M. The three runs had $[VO^{2+}]_0$ = 0.0, 0.0421, and 0.0840 M. The computed absorbance–time curves are shown in Figure 3, along with the points from the experiments. The agreement is adequately close considering that three rate constants and various molar absorptivities entered the computation. It remains possible that at high $[VO^{2+}]$ other processes may become important, accounting for the deviation seen in Figure 3 for $[VO^{2+}]_0$ = 0.084 M. The latter possibility was not explored further.

Interpretation and Discussion

Rate Law, Medium Effects, and Activation Parameters.
The rate expression for the reaction of V^{3+} and Cu^{2+} in perchlorate solution is given by eq 7. The second term

carries the major portion of the reaction under all the conditions employed in these studies. The first inter-

$$-d[V^{3+}]/dt = (g + h/[H^+])[V^{3+}][Cu^{2+}] \quad (7)$$

pretation offered is that both parameters represent genuine reaction pathways (i.e., that there are two parallel reaction paths, with transition states $(VCu^{5+})^{\ddagger}$ and $(VOHCu^{4+})^{\ddagger}$, of relative importance $g/h[H^+]$). Activation parameters were computed for each rate constant, assuming the Eyring relation (with κ = 1). This computation employed a nonlinear least-squares computer program[18] to fit values of k to eq 2 considering simultaneously all hydrogen in concentrations and temperatures. The values are summarized in Table V.

Table V. Activation Parameters[a] for the Rate Constants at μ = 1.00 M

Rate parameter	$\Delta H^{\ddagger}$, kcal mole^{-1}		$\Delta S^{\ddagger}$, eu	
	LiClO₄	NaClO₄	LiClO₄	NaClO₄
g	21.3 ± 1.3	19.0 ± 0.7	5.2 ± 4.4	−1.3 ± 2.3
h	19.4 ± 0.1	19.9 ± 0.1	4.4 ± 0.4	5.8 ± 0.4

[a] Uncertainties represent one standard deviation.

Alternatively, the minor rate term may arise from changes in the activity coefficients of substances in the predominant term that occur when H^+ and Li^+ or H^+ and Na^+ are traded at constant ionic strength. This explanation finds support in the small magnitude of the effect, and in the substantial change in the value of g when NaClO₄ was replaced by LiClO₄ (Table IV). In similar situations[21-28] comparable rate effects have been interpreted as arising from medium effects. It is assumed that the activity effects at constant ionic strength are adequately described by Harned's rule.[29,30] The relation becomes

$$k = h°[H^+]^{-1} \exp(\beta[H^+]) \quad (8)$$

where $h°$ is an intrinsic rate constant referring to a medium of ionic strength 3.00 M, where all activity coefficients have the values they do in 3.00 F LiClO₄ (or 3.00 F NaClO₄). For small values of β, the expression in eq 8 is $k = h°[H^+]^{-1}(1 + \beta[H^+] + ...) \cong h°[H^+]^{-1} + h°\beta$. The similarity to eq 2 is obvious, with $g = h°\beta$. The values of β are 0.05–0.08 (LiClO₄) and 0.13–0.14 (NaClO₄).

The present data do not allow one to assert which of the above interpretations of g, a reaction path or a medium effect, is correct. The main rate term does not change appreciably, however, and its detailed mechanism can be

(21) J. H. Espenson and D. E. Binau, Inorg. Chem., 5, 1365 (1966).
(22) (a) T. W. Newton and F. B. Baker, J. Phys. Chem., 67, 1425 (1963); (b) Inorg. Chem., 4, 1166 (1965).
(23) G. Gordon and P. H. Tewari, J. Phys. Chem., 70, 200 (1966).
(24) D. H. Huchital and H. Taube, J. Am. Chem. Soc., 87, 5371 (1965).
(25) J. P. Birk and J. H. Espenson, Inorg. Chem., 7, 991 (1968).
(26) R. C. Thompson and J. C. Sullivan, J. Am. Chem. Soc., 89, 1098 (1967).
(27) D. E. Pennington and A. Haim, Inorg. Chem., 6, 2138 (1967).
(28) D. W. Carlyle and J. H. Espenson, J. Am. Chem. Soc., 91, 599 (1969).
(29) H. S. Harned, ibid., 48, 326 (1926).
(30) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co., Ltd., London, 1955, Chapter 15.
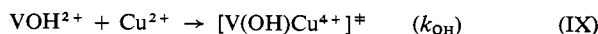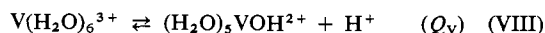
considered independently. The values of β in the second interpretation are reasonable for such a medium effect, and their interpretation in this light seems to us a safer approach than the assertion that g is a true rate constant whose values are to be interpreted in terms of a reaction mechanism.

Reaction Mechanism. The net activation processes for the forward and reverse[3] reactions are

$$V^{3+} + Cu^{2+} + H_2O = (V(OH)Cu^{4+})^{\ddagger} + H^+ \quad (VI))$$

$$VO^{2+} + Cu^+ + H^+ = (V(OH)Cu^{4+})^{\ddagger} \quad (VII)$$
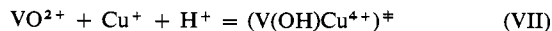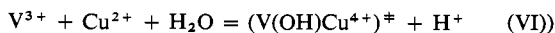
The entropy of the activated complex was computed from kinetic data[3] on the reaction of VO^{2+} and Cu^+ to be $S^{\ddagger} = -73 \pm 3$ eu ($\mu = 1.00\ M$, $LiClO_4$).[3] From the present work, we compute an independent value $S^{\ddagger} = -68 \pm 3$ eu, using the values[31] $S° = -23.6$ eu for Cu^{2+} and 16.7 eu for H_2O, and the estimate[32] -65 eu for V^{3+}. The two values of $S^{\ddagger}$, which presumably refer to the same activated complex, are considered to be in good agreement. As noted earlier,[3] the values of $S^{\ddagger}$ lie in the range expected[33] from the charge on the activated complex.

The mechanism proposed for the rate term inversely dependent on hydrogen ion concentration is the following.

$$V(H_2O)_6^{3+} \rightleftarrows (H_2O)_5VOH^{2+} + H^+ \quad (Q_V) \quad (VIII)$$

$$VOH^{2+} + Cu^{2+} \rightarrow [V(OH)Cu^{4+}]^{\ddagger} \quad (k_{OH}) \quad (IX)$$

According to this mechanism the rate law is given by eq 9.

$$\frac{-d[V(III)]}{dt} = \frac{k_{OH}Q_V[V(III)][Cu^{2+}]}{Q_V + [H^+]} \quad (9)$$

The value of Q_V is ca. $0.002\ M$,[34] which is considerably smaller than $[H^+]$ in all the runs carried out. The relation simplifies to that given in eq 10, from which it is seen

$$-d[V^{3+}]/dt = k_{OH}Q_V[V^{3+}][Cu^{2+}] \quad (10)$$

that the empirical rate constant h is $k_{OH}Q_V$. The thermodynamic quantities for formation of VOH^{2+} are $\Delta H_V° = 10.0 \pm 1.0$ kcal mole^{-1} and $\Delta S_V° \sim +20$ eu,[8] allowing computation of the activation parameters for k_{OH} from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for rate constant h. The activation parameters are $\Delta H_2^{\ddagger} = 9.4 \pm 1.1$ kcal mole^{-1} and $\Delta S_2^{\ddagger} = -16 \pm 5$ eu.

The dominance of the inverse acid term suggests that the transition state contains a bridging OH^- ligand. Ample precedent[6,8,35-42] exists to support the assertion that a

high k_{OH}/k_{H_2O} ratio constitutes evidence for an inner-sphere mechanism. This being the case, the question should be considered of whether the mechanism involves the reaction of VOH^{2+} and Cu^{2+} as shown above, or whether the rate-determining reaction could be that of V^{3+} and $CuOH^+$. The kinetic studies do not distinguish between the alternatives, each leading to a rate expression of the same form. Since the computed[43] second-order rate constant for $V^{3+} + CuOH^+$ exceeds the rate of replacement of H_2O coordinated to $V(H_2O)_6^{3+}$, formation of a bridged transition state for V^{3+} and $CuOH^+$ is prohibited.

In the earlier studies and in this work as well, the results have been interpreted in terms of Cu^+ being a steady-state intermediate. The retarding effect of high concentrations of VO^{2+}, making the reverse reaction important, lends support to the proposed mechanisms, as does the observation that VO^{2+} has an effect only with RCl^{2+} used to react with the presumed intermediate (but not with the faster reacting RBr^{2+} and $Co(en)_2Cl_2^+$).

The reversal of the absorbance–time traces (Figure 2) in runs where the initial V^{3+} concentration exceeded that of the Co(III) complex confirmed the presence of Cu^+ at a steady-state concentration smaller than that produced in the presence of a Co(III) complex. The directly known rate parameters for the reaction[3] of VO^{2+} and Cu^+ verified the observed rate constant for the second-stage process observed after all the Co(III) had been reduced.

The rate constants of this work and from the study[3] of the reaction of Cu^+ and VO^{2+} refer to processes that are the reverse of one another. Their quotient gives the equilibrium quotient for reaction I. Had the medium effects that apparently caused the nonzero intercepts in Figure 1 been of negligible importance, a single value would pertain to a particular ionic strength and temperature. As it stands, the equilibrium quotient for reaction I also shows a nominal medium dependence. Values of $10^3 Q_I$ (M^2), eq 11, are 1.45 at $\mu = 1.00\ M$ ($LiClO_4$) with

$$Q_I = \frac{[VO^{2+}][Cu^+][H^+]^2}{[V^{3+}][Cu^{2+}]} \quad (11)$$

$[H^+] = 0.852\ M$; 1.01, 0.88, and 0.74 each at $\mu = 3.00\ M$, with respective concentrations $3.00\ F\ HClO_4$, $LiClO_4$, and $NaClO_4$.

Likewise the activation parameters from the two rate studies can be combined to yield the thermodynamic parameters $\Delta H°$ and $\Delta S°$ for reaction I. The standard state chosen is the hypothetical solution of $\mu = 3.00\ M$, in which activity coefficients have the value they do in $3.00\ F\ LiClO_4$. Under these conditions $\Delta H°$ is 17.2 ± 0.2 kcal mole^{-1} and $\Delta S°$ 45.7 ± 0.7 eu. The computation based on the values tabulated by Latimer[31] and on other estimates[32] gives $\Delta H = 17.5$ kcal mole^{-1} and $\Delta S = 40$ eu at 25° and in unspecified media. The comparison cannot be expected to be exact, but the agreement is satisfactory confirmation that the two rate processes are related as we have claimed.

(31) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952.

(32) T. W. Newton and S. W. Rabideau, J. Phys. Chem., 63, 365 (1959).

(33) T. W. Newton and F. B. Barker, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 268.

(34) S. C. Furman and C. S. Garner, J. Am. Chem. Soc., 72, 1785 (1950).

(35) D. W. Carlyle and J. H. Espenson, ibid., 90, 2272 (1968).

(36) P. Dodel and H. Taube, Z. Physik Chem. (Frankfurt), 44, 92 (1965).

(37) J. F. Endicott and H. Taube, J. Am. Chem. Soc., 86, 1686 (1964).

(38) J. H. Espenson and O. J. Parker, ibid., 90, 3689 (1968).

(39) B. Baker, M. Orhanovic, and N. Sutin, ibid., 89, 722 (1967).

(40) G. Dulz and N. Sutin, ibid., 86, 829 (1964).

(41) T. W. Newton, G. E. McCrary, and W. G. Clark, J. Phys. Chem., 73, 4333 (1969).

(42) J. H. Espenson and D. W. Carlyle, Inorg. Chem., 5, 586 (1966).

(43) The second-order rate constant for the reaction between $CuOH^+$ and V^{3+} would be h/Q_{Cu}, where Q_{Cu} is the acid ionization constant of Cu_{aq}^{2+}, $-10^{-7}\ M$. The calculated value is $\sim 3 \times 10^6\ M^{-1}\ sec^{-1}$, in great excess over the rate of $V(H_2O)_6^{3+}$ substitution, ca. $10^2\ M^{-1}$ sec^{-1} [B. R. Baker, N. Sutin, and T. J. Welch, ibid., 6, 1948 (1967)].