

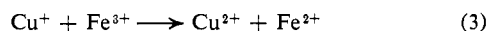
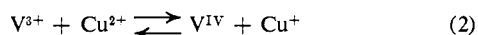
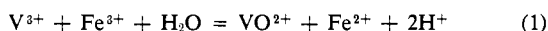
Reactions of Copper(I) in Perchlorate Solution. Kinetics and Mechanism of the Oxidation-Reduction Reaction between Vanadium(IV) and Copper(I)¹

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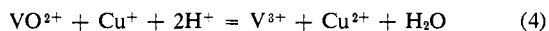
Abstract: The reduction of oxovanadium(IV) by copper(I) in perchloric acid solution produces vanadium(III) and copper(II) at a rate $k_f[\text{VO}^{2+}][\text{Cu}^+][\text{H}^+]$. The values are $k_f = 153$ and $384 \text{ M}^{-2} \text{ sec}^{-1}$ at 25.0° and perchlorate concentrations of 1.00 and 3.00 M , respectively. Activation parameters are $\Delta H^\ddagger = 2.15 \pm 0.08 \text{ kcal mole}^{-1}$ and $\Delta S^\ddagger = -41.3 \pm 0.3 \text{ eu}$ in 1.00 M perchlorate solution. The mechanism of the reaction is discussed in relation to copper(II) catalysis, and with reference to the mechanisms of related processes.

Copper(II) has been found to be an effective catalyst for many different reactions, including certain oxidation-reduction reactions between metal cations. One such instance was the catalysis of the reaction of V^{3+} and Fe^{3+} (eq 1) studied by Higginson and Sykes,² who proposed the first step in the catalytic process was the reaction of V^{3+} and Cu^{2+} to form Cu^+ , shown in eq 2, followed by the rapid reaction of Cu^+ and Fe^{3+} (eq 3).



Our recent success in synthesizing Cu^+ in perchlorate solution by the reaction of an excess of Cu^{2+} with a one-electron reducing agent made possible the preparation of Cu_{aq}^+ in perchlorate solution.^{3,4} Such solutions have proved to be metastable for periods of several hours, depending on reaction conditions. With such solutions available, it has now become possible to study directly reactions of copper(I). These reactions are of interest in their own right since reductions of Cu^+ have not been previously explored. Moreover, they are of particular interest in reference to the catalytic role of $\text{Cu}(\text{II})$. Direct study of $\text{Cu}(\text{I})$ reductions can serve to confirm or refute the processes inferred from $\text{Cu}(\text{II})$ catalysis and may suggest additional processes in which catalysis could be a useful synthetic tool or a useful probe of mechanism.

The net oxidation-reduction reaction occurring between oxovanadium(IV) and copper(I) cations in perchlorate solution is given in eq 4. We have carried out



extensive studies of this process with the view of learning about the detailed reaction mechanism. This reaction is the reverse of that (eq 2) suggested by Higginson and Sykes² as accounting for the catalytic effect of Cu^{2+} on the $\text{V}(\text{III})$ - $\text{Fe}(\text{III})$ reaction which makes a study of its kinetics and mechanism of particular importance.

(1) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2344.

(2) W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 2841 (1962).

(3) J. H. Espenson, K. Shaw, and O. J. Parker, *J. Am. Chem. Soc.*, **89**, 5730 (1967).

(4) K. Shaw and J. H. Espenson, *Inorg. Chem.*, **7**, 1619 (1968).

Experimental Section

Materials. Solutions containing the aquocopper(I) ion were prepared by adding, as solutions of their perchlorate salts in perchloric acid, a deficiency of chromium(II) to copper(II) and allowing adequate time for reaction.⁴ These solutions contained, in addition, chromium(III) and copper(II), each of which was later shown to be without effect on the reaction under study under all the conditions encountered. Such solutions, generally in the range 0.0002 – 0.002 M Cu^+ , were used within 20–40 min of their preparation.

The preparation and analyses of the other ions as their perchlorates, vanadium(IV), chromium(II), and -(III), copper(II), and lithium, have been described in earlier publications.^{4,5} Vanadium(IV) solutions were analyzed by titration with cerium(IV) in acetic acid solution, using ferroin indicator as described by Sriramam and Rao.⁶

Perchloric acid was used without further preparation. All solutions were made up using a double redistillate of laboratory distilled water from alkaline permanganate solution in a tin-lined Barnstead still. The nitrogen used to purge all reaction solutions of oxygen was purified by passage through five frits immersed in scrubbing solutions containing, successively, 0.1 M chromium(II), 0.01 M sodium hydroxide, and water.

Rate Procedures. The progress of reaction was followed by monitoring the absorbance changes at 2700 – 2800 \AA , using either of two methods. At acid concentrations $\geq 0.1 \text{ M}$, rates were measured using the stopped-flow method. The slower reactions with $[\text{H}^+] < 0.1 \text{ M}$ were followed conventionally using a Cary Model 14 spectrophotometer.⁵

In the latter cases solutions containing the requisite amounts of copper(II) perchlorate, lithium perchlorate, and perchloric acid were made up volumetrically. The solution was contained in a quartz cell of 10-cm optical path, fitted with a serum cap through which nitrogen was introduced using a hypodermic needle. Chromium(II) perchlorate was then added from a volumetric syringe, and the solution was allowed to stand until formation of copper(I) was complete as estimated from the previous studies on the reduction of copper(II) by chromium(II). The solutions were thermostated by the customary procedures⁷ and a solution of vanadium(IV) was added from a volumetric syringe.

In the stopped-flow studies copper(I) was prepared by the same method using a low acid concentration, enabling its formation to occur quickly. The concentration of acid was then made up to the required value by addition of a deoxygenated solution of perchloric acid from a buret or a volumetric syringe.

Kinetic Data. The reaction rates were computed from the absorbance values read from the spectrophotometer chart or from the scale of the stopped-flow oscillogram.⁸ The latter values are, in fact, transmittances, but, by working under conditions of concentration and wavelength where the changes were smaller than 0.1 absorbance unit, the readings could be treated as being directly proportional to absorbance and thus to concentration.

(5) J. H. Espenson, *ibid.*, **4**, 1025 (1965).

(6) K. Sriramam and G. G. Rao, *Talanta*, **13**, 1468 (1966).

(7) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

(8) D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

Table I. Rate Constants for the Reaction of Vanadium(IV) and Copper(I) Ions in Perchlorate Solution at 25.0°

Run	$10^3[\text{VO}^{2+}]_0$, <i>M</i>	$10^4[\text{Cu}^+]_0$, <i>M</i>	$10^4[\text{Cu}^{2+}]_0$, <i>M</i>	$[\text{H}^+]$, <i>M</i>	k_t' , M^{-1} sec^{-1}	$k_t (=k_t'/[\text{H}^+])$, $M^{-2} \text{sec}^{-1}$
A. 1.00 <i>M</i> Perchlorate						
1	7.77	7.56	29.9	0.966	147	152
2	3.88	3.40	1.20	0.963	148	153
3	1.94	1.70	0.60	0.963	144	149
4	7.77	6.80	2.41	0.801	123	154
5	7.77	6.05	31.6	0.700	107	152
6	7.77	6.80	2.41	0.701	108	154
7	7.77	6.05	31.6	0.500	78.1	156
8	7.77	6.80	2.41	0.301	46.6	155
B. 3.00 <i>M</i> Perchlorate						
9	7.77	6.80	2.41	2.98	1174	394
10	7.77	6.80	2.41	2.50	1019	408
11	7.77	6.80	2.41	2.00	775	388
12	7.77	6.80	2.41	1.50	580	387
13	7.77	6.80	2.41	1.00	348	348
14	7.77	6.80	2.41	0.50	189	378

The concentration of the limiting reagent, which was Cu(I) in all the experiments, was computed at frequent time intervals from the fractional change in absorbance, D , according to eq 5. In runs

$$[\text{Cu}^+]_t = [\text{Cu}^+]_0(D_t - D_\infty)/(D_0 - D_\infty) \quad (5)$$

where at least a tenfold excess of vanadium(IV) was present, plots of $\log [\text{Cu}^+]$ vs. time proved to be linear to at least 85% completion. A second-order rate constant, defined by eq 6, was computed from

$$-d[\text{Cu}^+]/dt = k_t'[\text{Cu}^+][\text{VO}^{2+}] \quad (6)$$

the slopes of such plots, using the average vanadium(IV) concentration. In those runs with a smaller excess of VO^{2+} , its concentration was computed from the stoichiometry and from the value of $[\text{Cu}^+]$; the data were treated according to the integrated form of eq 6.

In practice, this procedure was generally carried out by a least-squares calculation using a digital computer.⁹ In the cases where a graphical treatment was also carried out, no significant differences in the rate constants were noted.

Results

Two series of rate experiments were performed in different ionic media, in which total perchlorate concentration was maintained at 1.00 and 3.00 *M*, respectively, by the appropriate addition of lithium perchlorate. Since univalent electrolytes predominated, these runs refer, in effect, to ionic strengths 1.00 and 3.00 *M*. In the runs at high $[\text{H}^+]$, ≥ 0.3 *M*, equilibrium in reaction 4 lay effectively far toward the right. The observed rate constants, computed on the assumption that rate eq 6 applied, are tabulated in Table I. In a series of experiments at constant $[\text{H}^+]$ (compare runs 1, 2, and 3), the constancy of k_t' on this basis is good. Copper(II) was present in every solution owing to the method used to prepare Cu^+ solutions. The same data prove that a wide variation of the initial concentration of Cu^{2+} had no discernible effect on k_t' at a particular $[\text{H}^+]$.

In all cases the hydrogen ion concentration was in great excess over copper(I) so that $[\text{H}^+]$ remained effectively constant during the course of an experiment. At both ionic strengths a sizable and regular increase in k_t' was noted as the hydrogen ion concentration was increased in a series of runs, the upper bound on $[\text{H}^+]$ being the limit allowed by total permissible perchlorate concentration. The simplest interpretation consistent

(9) The computer programs were based on the report from Los Alamos Scientific Laboratory, LA 2367+ Addenda, and were generously supplied by Drs. T. W. Newton and R. Moore.

with these data is a direct proportionality of k_t' and $[\text{H}^+]$. The test of this postulate is the observed constancy of the quantity $k_t'/[\text{H}^+]$, the values of which are tabulated for each run in the right-hand column of Table I. Within the precision of the data, we conclude that this quantity is constant and that but a single term in the rate equation is called for. The rate expression applicable under these conditions is that given by eq 7, in which the best values of k_t at 25.0° are 153 ± 2 and 384 ± 14 $M^{-2} \text{sec}^{-1}$ at $\Sigma[\text{ClO}_4^-] = 1.00$ and 3.00 *M*, respectively.

$$-d[\text{Cu}^+]/dt = k_t[\text{Cu}^+][\text{VO}^{2+}][\text{H}^+] \quad (7)$$

Kinetic Data at Low $[\text{H}^+]$. At ionic strength 1.00 *M* the kinetic data at 25.0° were also extended to low $[\text{H}^+]$, down to 0.050 *M*. The values of k_t' and k_t were computed as before, based on the slopes of plots of $\log(D - D_\infty)$ vs. time. The values of k_t computed therefrom did not remain constant but showed a systematic increase as the hydrogen ion concentration was lowered. The data are summarized in Table II.

Table II. Kinetic Studies of the Reaction of Vanadium(IV) and Copper(I) at 25.0° and Low Hydrogen Ion Concentrations

Initial concentrations, <i>M</i>				k_t' , M^{-1} sec^{-1}	$k_t'/[\text{H}^+]$, M^{-2} sec^{-1}
10^4 [VO^{2+}]	10^4 [Cu^+]	10^4 [Cu^{2+}]	[H^+]		
77.7	6.05	31.6	0.100	18.4	183
77.7	6.80	2.41	0.101	17.4	172
12.9	2.02	10.8	0.0800	14.9	187
12.9	2.02	10.8	0.0600	12.4	207
12.9	2.02	10.8	0.0500	12.6	251
12.9	2.02	10.8	0.0500	13.0	260

Although these data could be interpreted in terms of an independent pathway for the reaction that becomes increasingly important as $[\text{H}^+]$ is decreased, this is not the only possible interpretation. As will be shown later, the data provide no evidence for additional reaction paths, even at very low $[\text{H}^+]$.

Effect of Temperature. The reaction was studied at other temperatures under conditions of relatively high acid concentration, $[\text{H}^+] \geq 0.3$ *M*, in a medium of 1.00 *M* perchlorate concentration. The rate constants k_t for these runs are given in Table III.

Table III. Rate Constants for the Reaction of Vanadium(IV) and Copper(I) as a Function of Temperature in 1.00 *M* Perchlorate Solution^a

Temp, °C	10 ⁴ [Cu ²⁺] ₀ , <i>M</i>	[H ⁺], <i>M</i>	<i>k</i> _f ', <i>M</i> ⁻¹ sec ⁻¹	<i>k</i> _t , <i>M</i> ⁻² sec ⁻¹
1.6	31.3	0.977	97.5	100
1.6	2.41	0.701	74.1	106
1.6	31.3	0.501	52.4	105
1.6	2.41	0.301	32.6	108
34.2	31.3	0.977	172	176
34.2	2.41	0.701	129	184
34.2	3.94	0.501	90.3	180
34.2	2.41	0.301	52.1	173

^a Initial concentrations: [VO²⁺] = 7.77 × 10⁻³ *M*, [Cu⁺] = 6.80 × 10⁻⁴ *M*.

Interpretation and Discussion

Equilibrium. The data of Higginson and Sykes² pertained to a reaction of Cu²⁺ and V³⁺ that was claimed to be the reverse of reaction 4. The rate expression of these workers is given by eq 8. The dominant term was

$$-d[V^{3+}]/dt = (g + h[H^+]^{-1})[Cu^{2+}][V^{3+}] \quad (8)$$

that of -1 order with respect to hydrogen ion, the value *h* being 0.3 sec⁻¹ at 25.0° and a perchlorate concentration of 3.00 *M*. The data of Parker and Espenson¹⁰ on a catalytic process involving (presumably) the same process give the expression in eq 9, with *h* = 0.348 sec⁻¹ at

$$-d[V^{3+}]/dt = h[Cu^{2+}][V^{3+}][H^+]^{-1} \quad (9)$$

25.0° and 3.00 *M* perchlorate, and *h* = 0.217 sec⁻¹ at 1.00 *M*. The equating of forward and reverse rates, presuming the process under study here and that¹⁰ involving Cu²⁺ and V³⁺ are so related, leads to an expression for the equilibrium condition for reaction 4 and to values for its equilibrium quotient, as in eq 10.

$$K_{eq} = \frac{[V^{3+}][Cu^{2+}]}{[Cu^+][VO^{2+}][H^+]^2} = \frac{k_f}{h} \quad (10)$$

It should be noted that the expression obtained is that predicted from the form of reaction 4, adding confidence to the presumption that these reactions are the reverse of one another. The values of the equilibrium constant computed from the rate constants at 25.0° are *K*_{eq} = 0.70 × 10³ *M*⁻² at 1.00 *M* perchlorate concentration, and *K*_{eq} = 1.1 × 10³ *M*⁻² at 3.00 *M*. These values can be compared to that computed from the known¹¹ standard potentials; from the *E*⁰ values at 25.0°, corrected to zero ionic strength, *K*_{eq} is 1 × 10³ *M*⁻².

Data at Low [H⁺]. An increase in *k*_f'/[H⁺] at [H⁺] ≤ 0.1 *M* was noted, as shown by the data presented in Table II. We attribute this increase in the apparent rate constant to the failure of our assumption that the reaction proceeded to completion at equilibrium. Under conditions of low [H⁺], especially with Cu²⁺ added along with the reactants, considerable concentrations of Cu⁺ remained in the equilibrium solution, as reflected in the steadily increasing values of *k*_f'/[H⁺] with decreasing [H⁺].

It was assumed that the only pathway of importance for the reaction in the forward direction was that rep-

resented by eq 7; by necessity, then, eq 9 represents the pathway operating in the reverse direction. On this basis the net rate of loss of Cu⁺ is given by eq 11. In

$$-d[Cu^+]/dt = k_f[Cu^+][VO^{2+}][H^+] - h[Cu^{2+}][V^{3+}][H^+]^{-1} \quad (11)$$

all the experiments at low [H⁺], VO²⁺ was in sufficient excess that its concentration could be considered constant to a first approximation. (In the evaluation of *k*_f' at [H⁺] = 0.1 *M*, the decrease of [VO²⁺] in a run was treated precisely in accord with eq 6; for the purposes at hand, however, it is convenient to regard [VO²⁺] as constant during the course of each run, or nearly so.) Likewise, [Cu²⁺] remained reasonably constant during the course of each run in Table II, except the second. As noted earlier, hydrogen ion concentration is effectively constant as well. To the extent that these three species remained constant, the concentrations of Cu⁺ and V³⁺ were the only variables, and the kinetic behavior was simply that of two opposing first-order reactions.

The kinetic data were interpreted in terms of the experimental absorbance readings at equilibrium. These values measured the rate of approach to equilibrium, which is governed by the pseudo-first-order rate constant given by eq 12. The procedure used to treat the

$$k_{obsd} = k_f[VO^{2+}]_{av}[H^+] + h[Cu^{2+}]_{av}[H^+]^{-1} \quad (12)$$

data was this. It was first assumed that eq 7 correctly described the reaction kinetics and the data were treated accordingly, using the best *observed* value of *D*_∞. The value of *k*_f' so obtained, given in Table II, was then considered to follow the relation given by eq 12, which is only approximate owing to the use of average concentrations in a situation where moderate changes did, in fact, occur. The resulting expression is shown in eq 13. This relation should be a close approximation to

$$\frac{k_f'}{[H^+]} = \frac{k_{obsd}}{[VO^{2+}][H^+]} = k_f + \frac{h[Cu^{2+}]_{av}}{[VO^{2+}]_{av}[H^+]^2} \quad (13)$$

the actual kinetics despite its approximate nature since in all circumstances the contribution of *k*_f dominated the sum.

The data were tested for their consistency with eq 13 by a plot of *k*_f'/[H⁺] vs. [Cu²⁺]_{av}/[VO²⁺]_{av}[H⁺]², as suggested by this equation. The data are shown in Figure 1. The slope of such a plot should be *h*, which is related to *K*_{eq} and is known independently. The straight line drawn in Figure 1 has the theoretical slope of *h* = 0.217 sec⁻¹ at 25.0° with 1.00 *M* perchlorate concentration.

The agreement of the data at low [H⁺] with this interpretation is considered to be satisfactory and in keeping with the assumptions employed in the treatment. We conclude that, within experimental error, all the data in the entire range of acidity covered, 0.05 ≤ [H⁺] ≤ 3.0 *M*, are consistent with a single pathway, and that the kinetics are consistent with this, provided the failure of the reaction to proceed to equilibrium at low [H⁺] is properly accounted for.

Comparisons with the Reverse Reaction. We shall now consider the question of the disagreement between the published² rate expression for the reaction of V³⁺ and Cu²⁺ and the expression required on the basis of

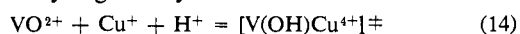
(10) O. J. Parker and J. H. Espenson, submitted for publication.

(11) L. G. Sillen, "Stability Constants," Special Publication No. 17, The Chemical Society, London, pp 4, 17.

microscopic reversibility and the rate law obtained in this study, eq 6. The term $g[\text{Cu}^{2+}][\text{V}^{3+}]$ in eq 8 reported by Higginson and Sykes² would require a second term in eq 6 of the present work of the form $k_f''[\text{VO}^{2+}][\text{Cu}^{2+}][\text{H}^+]^2$. No evidence was obtained for the contribution of such a term, the value of k_f remaining quite constant even at 3.00 M H^+ (see Table I). Invoking the principle of microscopic reversibility, the computed value of k_f'' would be $k_f g/h = 85 \text{ M}^{-3} \text{ sec}^{-1}$ at 3.00 M perchlorate. This would lead to a value of $k_f'/[\text{H}^+]$ (Table I) that increased 55% in going from 0.5 to 3.00 M H^+ . We conclude that either the earlier catalytic rate data² were interpreted incorrectly, or that the term $g[\text{Cu}^{2+}][\text{V}^{3+}]$ corresponds to a process that is not the reverse of reaction 1, or that a relatively minor medium effect became important in their reaction upon exchanging H^+ for Na^+ at constant ionic concentration. This matter will be considered in detail in a subsequent publication dealing directly with the reaction of V^{3+} and Cu^{2+} .¹⁰

Activation Parameters. The individual rate constants that comprise the averages given in Tables I and III were fit to the Eyring relation by a least-squares computer program with the weighting of each value $1/k_f^2$. The activation parameters and their standard deviations are $\Delta H^\ddagger = 2.15 \pm 0.08 \text{ kcal mole}^{-1}$ and $\Delta S^\ddagger (\kappa = 1) = -41.3 \pm 0.3 \text{ cal mole}^{-1} \text{ deg}^{-1}$ in 1.00 M perchlorate solution.

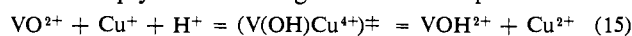
The net activation process¹² corresponding to the process under study is given by



The molar entropy of the transition state may be computed from the relation $S^\ddagger = \Delta S^\ddagger + \sum S^0$ (other reactants). The values¹³ are $S^0(\text{VO}^{2+}) = -26 \text{ eu}$ and $S^0(\text{Cu}^{2+}) = -6.3 \text{ eu}$, each on the scale $S^0(\text{H}^+) = 0$, leading to $S^\ddagger = -73 \text{ eu}$, with an estimated uncertainty of $\pm 3 \text{ eu}$.

Newton and Baker¹⁴ have recently tabulated values of S^\ddagger for many transition states of this general type and have pointed out the close correlation of entropy and ionic charge on the transition state. The value in the present instance lies at the midpoint of the range of -60 to -80 eu in which 90% of their examples of this charge type lie. A general limitation of this procedure is that all of the entropies in question will show some dependence on medium; in treatments such as the present this source of variation has been ignored.

Reaction Mechanism. The results obtained for the kinetics imply the following net activation process



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

(13) Entropy values for VO^{2+} were given by M. J. LaSalle and J. W. Cobble, *ibid.*, **59**, 519 (1955).

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

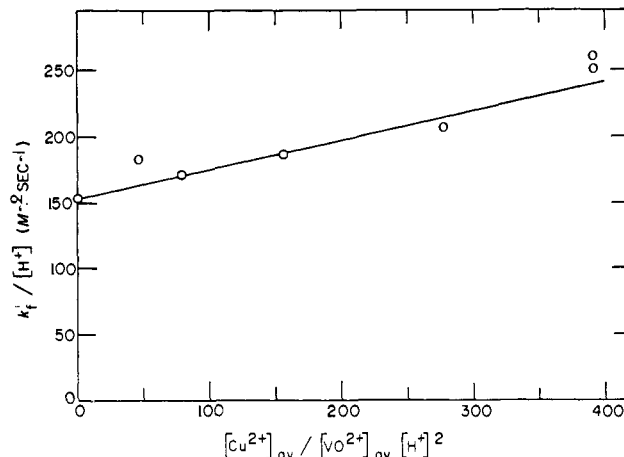
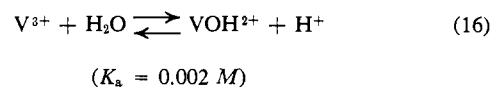


Figure 1. A plot of $k_f'/[\text{H}^+]$ vs. $[\text{Cu}^{2+}]_{\text{av}}/[\text{VO}^{2+}]_{\text{av}}[\text{H}^+]^2$, as suggested by eq 13. The data are from Table II. The line is the theoretical line calculated from $k_f = 153 \text{ M}^{-2} \text{ sec}^{-1}$ and $h = 0.217 \text{ sec}^{-1}$.

where the V^{3+} ion is involved in a rapidly established protolytic equilibrium, eq 16. The implication is that



the transition state contains a bridging hydroxide ion and is thus to be placed in the category of inner-sphere electron-transfer reactions. We advance the following arguments in support of this contention. First, we consider the structural changes accompanying oxidation-reduction, whose main feature is the interconversion of an oxo cation and an aquo cation. The role assigned to H^+ in this mechanism consists of such a conversion through a configuration resembling a hydroxo ligand, structurally between O^{2-} and H_2O . Secondly, the reverse reaction follows the pattern expected for an inner-sphere hydroxide-bridged mechanism, in that the high effectiveness of OH^- as a bridging ligand compared to H_2O is well documented.¹⁵

A comparison of other reduction reactions of VO^{2+} , for example, the reactions with V^{2+} ,¹⁶ Cr^{2+} ,¹⁷ and Fe^{2+} (the latter data computed from the study² of $\text{Fe}^{3+} + \text{V}^{3+}$), brings out the importance of dinuclear hydroxo-bridged species as intermediates. In the present system the high substitution lability of copper(II) precludes detection of such an intermediate.

(15) J. H. Espenson and O. J. Parker, *J. Am. Chem. Soc.*, **90**, 3689 (1968).

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

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