Volume 8
Number 2
February 1969

Inorganic Chemistry

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE INSTITUTE FOR ATOMIC RESEARCH,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Reactions Involving Copper(I) in Perchlorate Solution. Kinetics of the Reduction of Copper(II) by Vanadium(II)[1]

BY O. JERRY PARKER AND JAMES H. ESPENSON

Received August 20, 1968

Copper(II) is reduced to copper(I) by vanadium(II) in acidic perchlorate solution according to the rate law $-d[V^{2+}]/dt = k[V^{2+}][Cu^{2+}]$. At 25.0° and 1.00 M ionic strength (maintained with lithium perchlorate) the value of k is 26.6 M^{-1} sec^{-1}, and the associated activation parameters are $\Delta H^{\ddagger} = 11.4 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -13.8 \pm 0.4$ eu. Under the conditions of the experiment Cu^+ is the only significant product; its disproportionation and the second stage of its reduction by V^{2+} during the run are unimportant. The proposed mechanism is a 1-equiv electron-transfer reaction between the hydrated cations. The question of whether the reaction proceeds by an outer-sphere or an inner-sphere transition state is also considered.

Introduction

Copper(II) is reduced to Cu(I) by reaction with vanadium(II) in dilute perchloric acid.[2] Provided an insufficient amount of vanadium(II) is added, the stoichiometry of the reaction corresponds to the simple 1-equiv reduction

$$V^{2+} + Cu^{2+} = V^{3+} + Cu^+ \qquad (1)$$

In perchlorate solution, where Cu^+ is not stabilized by complexing anions, disproportionation is a favorable reaction. The equilibrium quotient[3] for reaction 2 is $1.3 \times 10^6\ M^{-1}$ at 25.0° and $\mu = 0.02\ M$. Provided a metallic surface is not present, this reaction occurs quite slowly, however, and over a period of several hours $10^{-3}\ M$ solutions of Cu^+ remain virtually unchanged provided oxygen is excluded.

$$2Cu^+ = Cu^0(s) + Cu^{2+} \qquad (2)$$

The beginning of disproportionation generally brings about complete decomposition within a short time. Some runs having a barely sufficient excess of Cu(II) produced metallic copper, especially if the concentrations were high ($\sim$0.01 M). In this case, the production of metal presumably arose from a second stage of reduction, eq 3, that was able to compete with the first stage, owing to the low rate of the latter as the copper(II) concentration became small.

$$V^{2+} + Cu^+ = Cu^0 + V^{3+} \qquad (3)$$

Aside from the interest in a reaction producing a hydrated Cu(I) cation in perchlorate solution, our interest in this reaction arose from two features. First, the study of the production and stability of Cu^+ enables subsequent studies on the mechanism of its reoxidation by a variety of reagents. Particularly, studies using metal complexes as oxidizing agents promise to shed further light on electron-transfer mechanisms. Second, Cu(II) plays a catalytic role in many important and interesting processes. Since it appears that Cu(I) may be involved as an intermediate in such processes, it appeared useful to study a system in which Cu(I) was produced in good yield.

A related reaction[4] is the reduction of Cu(II) by Cr(II), eq 4. A comparison of the results of the present

$$Cu^{2+} + Cr^{2+} = Cu^+ + Cr^{3+} \qquad (4)$$

study with those for eq 4 enables some interesting interpretations concerning the mechanism to be drawn.

Experimental Section

Materials.—Triply distilled water, obtained from the double redistillation of laboratory distilled water from alkaline permanganate solution in a tin-lined Barnstead still, was used in all of the preparations and solutions. Lithium perchlorate was

---

[1] Work performed under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2414. Based on the Ph.D. Thesis of O. J. P., Iowa State University, Aug 1968.

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

[3] J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

[4] K. Shaw and J. H. Espenson, *ibid.*, **7**, 1619 (1968).

prepared from reagent grade lithium carbonate and perchloric acid and was recrystallized twice before use. Solutions of vanadium(II) perchlorate were prepared by two independent procedures. In the first instance a solution of vanadyl perchlorate was prepared from the reagent grade sulfate and a very slight excess of recrystallized barium perchlorate, having removed the precipitated barium sulfate by centrifugation. Perchloric acid was added, and the solution was reduced with amalgamated zinc. A second procedure, used in only a few instances, was the electrolytic reduction at a mercury cathode of a suspension of vanadium pentoxide in perchloric acid at 0°. Vanadium(II) solutions were prepared and stored under nitrogen according to the general techniques earlier described.[5] To prevent appreciable oxidation of vanadium(II) by perchlorate ion,[6] the stock solutions were stored in a refrigerator at −10°. The solutions were periodically tested for chloride ion by adding excess iron(III) and then silver(I); negative tests ($\leq 10^{-3}$ *M* Cl^-) were obtained. Copper(II) perchlorate was also obtained from two independent sources: the reagent grade compound (G. F. Smith) and our preparation from the carbonate and perchloric acid followed by recrystallization. Perchloric acid and other materials were reagent grade chemicals used without further purification.

Stock solutions of copper(II) were analyzed by an ion-exchange procedure, titrating the hydrogen ion released from a column of Dowex 50W-X8 upon passage of a sample of the copper(II) solution, and thorough rinsing of the column with water. This procedure was checked by the standard iodometric titration; the results agreed to within 1%.

Rate Procedures.—The reaction kinetics were followed spectrophotometrically by observing the increase in absorbance in the ultraviolet region (225–235 nm) corresponding to the formation of Cu^+. In all cases the reactions were carried out in a medium in which perchlorate ion was the only anion present, with perchloric acid and lithium perchlorate added to maintain ionic strength at 1.00 *M*.

The reactions were carried out in cylindrical quartz cells of 5-cm optical path, using the customary syringe techniques.[5] The reaction solutions were made up in the cell, except for V^{2+}, and were purged for at least 20 min with a stream of nitrogen. The cell was brought to the reaction temperature in a thermostated water bath, which during the run remained immersed in a small water bath positioned in the sample compartment of the spectrophotometer. The bath was held at constant temperature by water circulating through its walls from a thermostated reservoir.[7] Absorbance values were read from the recording chart of a Cary Model 14 spectrophotometer, the chart drive serving as the timing device for the reactions.

Results

Rate Equation and Stoichiometry.—Kinetic measurements were carried out over a wide range of starting concentrations, $8 \times 10^{-5} \leq [Cu^{2+}]_0 \leq 9 \times 10^{-3}$ *M* and $1.4 \times 10^{-5} \leq [V^{2+}]_0 \leq 1 \times 10^{-3}$ *M*. In experiments where $[Cu^{2+}]$ was in large excess over $[V^{2+}]$ the appropriate pseudo-first-order absorbance plots, according to eq 5, were linear for at least 3 half-lives. In

$$\log (D - D_\infty) = \log (D_0 - D_\infty) - \frac{k'}{2.303}t \qquad (5)$$

several such experiments at varying $[Cu^{2+}]$, values of $k'/[Cu^{2+}]_{av}$ were found to be constant, suggesting the rate equation

$$-d[V^{2+}]/dt = k_1[V^{2+}][Cu^{2+}] \qquad (6)$$

Table I

Kintic Data for the Reaction of Cu(II) and V(II)[k]

10^4 $[V^{2+}]_0$, *M*	10^4 $[Cu^{2+}]_0$, *M*	λ, nm	k_1, M^{-1} sec^{-1}	10^4 $[V^{2+}]_0$, *M*	10^4 $[Cu^{2+}]_0$, *M*	λ, nm	k_1, M^{-1} sec^{-1}
0.630	0.802	225	29.0	1.536	10.0	230	27.8[i]
0.630	2.01	225	28.1	1.725	19.9	231	26.5[b]
0.630	5.02	225	(29.9)[a]	1.725	20.1	231	25.1
1.24	5.02	230	26.7[c]	2.00	10.3	231	(31.1)[a,e]
1.26	5.02	235	26.1	2.00	10.3	235	25.1[e]
1.26	5.02	230	26.9	2.32	10.0	235	27.6[f]
1.26	5.02	225	27.1	2.32	10.0	235	28.3[f]
1.26	5.02	230	26.8	2.32	10.0	235	25.7[f]
1.26	10.0	230	27.6	2.51	5.02	230	25.5
1.27	10.0	230	26.5[c]	2.49	10.0	230	24.1[c]
1.26	20.1	235	25.0	2.51	20.1	235	26.7
1.35	20.0	235	25.9	2.51	50.1	240	27.0
1.35	20.0	231	26.6[b]	3.02	35.1	238	26.3
1.35	20.0	231	25.0	3.76	7.62	750	26.8
1.35	20.0	231	25.9[d]	3.76	7.62	750	28.9
1.35	20.0	230	26.1[d]	3.76	7.62	750	29.2
1.35	20.0	231	26.3[b]	4.71	5.02	230	(32.3)[a]
1.536	10.0	230	26.5[g]			Av	26.6 ± 1.2[j]
1.536	10.0	230	25.0[h]				

[a] Omitted from average; value exceeded three standard deviations. [b] Cu^{2+} prepared from $CuCO_3$. [c] V^{2+} prepared by electrolysis. [d] $[Cr^{3+}] = 2 \times 10^{-3}$ *M*. [e] $[Cu^+]_0 = 4.7 \times 10^{-4}$ *M*; $[Cr^{3+}] = 4.7 \times 10^{-4}$ *M*. [f] $[V^{3+}]_0 = 5.8 \times 10^{-4}$ *M*. [g] $[H^+] = 0.500$ *M*. [h] $[H^+] = 0.100$ *M*. [i] $[H^+] = 0.0400$ *M*. [j] Uncertainty represents the standard deviation. [k] Conditions: 25.0°, $[H^+] = 0.993 \pm 0.005$ *M*, except as noted; $\mu = 1.00$ *M* ($LiClO_4$).

In experiments where the excess of copper(II) was smaller, vanadium(II) concentrations were computed from the fractional change in absorbance, *D*

$$[V^{2+}]_t = [V^{2+}]_0(D_t - D_\infty)/(D_0 - D_\infty) \qquad (7)$$

Concentrations of copper(II) were then computed from the initial concentrations, assuming the stoichiometry given in eq 1

$$[Cu^{2+}]_t = [Cu^{2+}]_0 - [V^{2+}]_0 + [V^{2+}]_t \qquad (8)$$

The appropriate rate plots were then made according to the equation

$$\log [Cu^{2+}]/[V^{2+}] = \log [Cu^{2+}]_0/[V^{2+}]_0 + \frac{k_1([Cu^{2+}]_0 - [V^{2+}]_0)}{2.303}t \qquad (9)$$

These plots were consistently linear, and the values of k_1 so obtained were in excellent agreement with the values from the pseudo-first-order runs. In practice, all runs regardless of the $[Cu^{2+}]_0/[V^{2+}]_0$ ratio were fit to the integrated second-order rate equation using a nonlinear least-squares computer program.[8] The rate constants so obtained generally reproduced the absorbance values during each run to within ±0.002 absorbance unit; the standard deviation of each rate constant, based on the internal fit of each run, was usually ≤2%. The standard deviation of the unweighted mean rate constant at 25.0° was 3%. The rate constants for the individual runs at 25.0° are summarized in Table I.

It can be seen from the tabulated data that the rate

---

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

(6) W. R. King, Jr., and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

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

(8) Based on the report LA 2367 + Addenda from Los Alamos Scientific Laboratory. We are grateful to Drs. R. H. Moore and T. W. Newton for copies of these programs.

TABLE II

KINETIC DATA FOR THE REACTION OF Cu(II) AND V(II)[a]

10^4 $[V^{2+}]_0$, M	10^4 $[Cu^{2+}]_0$, M	λ, nm	k_1, M^{-1} sec^{-1}	10^4 $[V^{2+}]_0$, M	10^4 $[Cu^{2+}]_0$, M	λ, nm	k_1, M^{-1} sec^{-1}
0.507	5.04	222	12.8	2.00	30.1	235	12.6
0.760	5.04	222	12.7	2.00	30.1	233	12.9
0.902	20.1	230	13.0	2.00	30.1	235	13.0
0.902	20.1	228	13.5	2.51	50.1	235	12.7
1.725	5.04	222	13.0	3.92	20.1	232	(14.2)[c]
1.725	20.1	231	12.3[b]	9.95	50.1	248	13.7
1.725	20.1	230	12.6	9.95	90.3	248	13.6
1.725	20.1	230	13.0				
						Av	13.0 ± 0.45[d]

[a] Conditions: 15.0°, $[H^+] = 0.993 \pm 0.005$ M, except as noted; $\mu = 1.00$ M ($LiClO_4$). [b] $[H^+] = 0.100$ M. [c] Omitted from average; value exceeded three standard deviations. [d] Uncertainty represents the standard deviation.

TABLE III

KINETIC DATA FOR THE REACTION OF Cu(II) AND V(II)[a]

10^4 $[V^{2+}]_0$, M	10^4 $[Cu^{2+}]_0$, M	λ, nm	k_1, M^{-1} sec^{-1}	10^4 $[V^{2+}]_0$, M	10^4 $[Cu^{2+}]_0$, M	λ, nm	k_1, M^{-1} sec^{-1}
0.143	2.51	218	53.7	0.862	10.0	224	48.7[d]
0.253	2.51	211	51.3	0.862	10.0	227	48.9
0.253	5.04	218	49.6	0.862	10.0	224	49.1[c]
0.507	5.04	227	51.4	0.862	10.0	224	51.1
0.507	5.04	221	52.7	0.862	10.0	225	51.2[c]
0.760	5.04	222	50.9	0.862	10.0	225	51.3[d]
0.862	10.0	218	(46.2)[b,c]	1.255	25.1	232	47.3
0.862	10.0	227	48.4	1.725	5.04	222	52.2
						Av	50.5 ± 1.8[e]

[a] Conditions: 35.0°, $[H^+] = 0.993 \pm 0.005$ M, except as noted; $\mu = 1.00$ M ($LiClO_4$). [b] Omitted from average; value exceeded three standard deviations. [c] $[H^+] = 0.100$ M. [d] $[H^+] = 0.0400$ M. [e] Uncertainty represents the standard deviation.

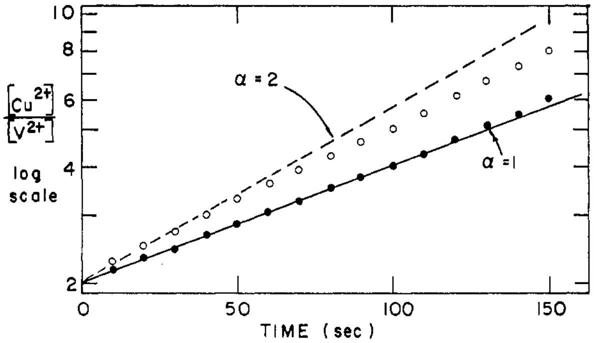

Figure 1.—Second-order rate plots computed assuming the reaction followed the stoichiometry $Cu^{2+} + \alpha V^{2+}$. Plots shown for $\alpha = 1$ and $\alpha = 2$ for run 2 of Table I.

constant is not a function of which source of Cu^{2+} or V^{2+} was used, proving the reaction is independent of Zn^{2+}, which was introduced with V^{2+} in most of the runs. The lack of variation in values of k_1 with different reagents indicates that catalytic impurities were probably not present. The apparent lack of variation of k_1 with added Cu^+ or V^{3+} establishes that the products are not exerting an influence on the rate that escaped detection in runs where they were not added at the start. Finally, the variation of wavelength had no effect on the rate constant.

Hydrogen Ion and Temperature Dependences.—The greatest number of runs was carried out at high $[H^+]$, ~1 M. Variation of $[H^+]$ down to 0.04 M was made in several experiments. This variation was, in all instances, without discernible effect on the value of the second-order rate constant.

Experiments were also carried out at 15.0 and 35.0°. At each of these temperatures the same second-order rate expression was found to hold, and the precision of k_1 at each temperature was quite high. These experiments are summarized in Tables II and III.

Reaction Stoichiometry.—Close agreement of rate constants at high ratios of $[Cu^{2+}]_0/[V^{2+}]_0$ with those in experiments where the ratio was ≤ 2 was noted. In the latter cases the appropriate rate plots according to eq 9 were linear to at least 85%, thus establishing that eq 1 correctly represents the net reaction occurring when Cu^{2+} is in excess. When, for example, we assumed that the reaction produced quantitative yields of Cu^0 (aq), the rate plots at low $[Cu^{2+}]_0/[V^{2+}]_0$ ratios were most noticeably nonlinear, as shown in Figure 1. The extent to which the production of minor amounts of Cu^0 (aq) or Cu^0 (s) would have been evident is not apparent, but it has been clearly established that they are not major products.

Further evidence concerning the stoichiometry came from the runs performed at a wavelength of 750 nm, where Cu(II) made the main contribution to the absorbance. In a set of triplicate runs at 750 nm cited in Table I, the observed absorbance change was 0.039 ± 0.001 absorbance unit (measured on an expanded-scale 0–0.1 slide wire), compared with an expected value of 0.041 for the reaction producing Cu^+ in quantitative yield. The close agreement of calculated and observed absorbance changes substantiates the stoichiometry given in eq 1. Had Cu^0 been produced, the intensity would have decreased by 0.021 absorbance unit; the observed change was clearly much greater. The observed change was reproducible, but it was 5% smaller than the calculated change; the discrepancy probably reflects the uncertainties associated with the molar absorptivity rather than a 10% contribution of a side reaction producing copper(0). In particular, were metal formed, the disproportionation of Cu^+ would have occurred in the time of observation, and that was shown not to have occurred on three accounts: (1) the observed absorbance change was not consistent with the presence of the additional Cu(II), (2) no metals were observed coating the surface of the cell, the process always being quite noticeable in those instances where it did occur, and (3) the solution so produced exhibited the reducing properties of Cu^+.

Interpretation and Discussion

Activation Parameters.—The rate constants were fit to the Eyring relation using the computer program to find values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ that best fit the observed rate constants. In this computation each of the individual rate constants was weighted as the reciprocal of the square of its value, which is the appropriate weighting for a quantity whose per cent error is presumably constant. The values of the activation parameters so obtained are $\Delta H^{\ddagger} = 11.4 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -13.8 \pm 0.4$ cal $\text{mol}^{-1}\ \text{deg}^{-1}$. With these parameters the observations are reproduced to an average deviation of 3.3%; the calculated values of k_1 are 13.0, 26.4, and 50.8 $M^{-1}\ \text{sec}^{-1}$ at the three temperatures studied.

Following the procedure of Newton and Rabideau,[9] one can write the following equation for the net activation process

$$Cu^{2+} + V^{2+} = [CuV^{4+}]^{\ddagger} \qquad (10)$$

Based on known[10] molar entropy $\bar{S}° = -23.6$ eu for Cu^{2+} and the estimated value[11] $\bar{S}° = -23$ eu for V^{2+}, the molar entropy of the transition state is -62 ± 5 eu. Newton and Baker[12] have pointed out the close correlation of the over-all charge on a transition state and its entropy for a variety of reactions covering many different metal ions and a considerable range of observed $\Delta S^{\ddagger}$ values. The entropy computed here, -62 eu, lies in the range -60 to -80 eu in which almost all of the entropies of transition states with 4+ charges lie.[12,13]

In this regard, we note that the typical values[12,13] of $\bar{S}^{\ddagger}$ are generally less negative than one would expect[10] for a monatomic metal cation of the same charge. Considering, however, that a transition state has a radius larger than a single hydrated cation, the lessened ability of the former to create order in the solvent is not surprising.

Reaction Mechanism.—The rate constant for the V^{2+}–Cu^{2+} reaction, 26.6 $M^{-1}\ \text{sec}^{-1}$ at 25.0°, lies in the range of values found for other reactions[14–21] in which V(II) substitution or oxidation is involved (Table IV). Its activation enthalpy, 11.4 kcal, is also in agreement with the other studies. This list includes cases of oxidation–reduction reactions for which inner-sphere mechanisms have been established. The rates all lie quite close to the rate of V(II)–H_2O exchange, and the rates of electron transfer and of substitution are remarkably similar, suggesting that substitution into the primary coordination sphere of $V(H_2O)_6^{2+}$ limits the rate of formation of inner-sphere transition states.[16]

TABLE IV

RATE CONSTANTS FOR REACTIONS OF VANADIUM(II)

Reaction	k,[a] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	Mechanism[e]	Ref
$V^{2+} + NCS^-$ (substitution)	28[b]	13.0	...	17
$V^{2+} + cis\text{-}Co(en)_2N_3^{2+}$	33	...	Inner sphere	18
$V^{2+} + CrSCN^{2+}$	7.1	13.0	Inner sphere	16
$V^{2+} + Co(NH_3)_5C_2O_4^+$	45	...	Inner sphere	19
$V^{2+} + VO^{2+}$	1.6[c]	12.3	Inner sphere[f]	20
$V^{2+} + Cu^{2+}$	26.6	11.4	?	This work
$V^{2+} + Fe^{3+}$	1.8×10^4	...	Outer sphere	16
$V^{2+} + UO_2^{2+}$	47	7.1	?	21
$V^{2+} + Co(NH_3)_5OH_2^{3+}$	0.5	8.2	?	14
$V^{2+} + Co(NH_3)_6^{3+}$	3.7×10^{-3} [d]	9.1	Outer sphere	15

[a] Rate constants at 25.0° and $\mu = 1.00\ M$, except as noted. [b] $\mu = 0.84\ M$. [c] $\mu = 2.0\ M$. [d] $\mu = 0.4\ M$. [e] Cited for oxidation–reduction reactions where the "product criterion" was used to establish inner-sphere mechanisms, and the substitution rates, outer-sphere mechanisms. [f] Only a part of the reaction is inner sphere.

Although, as is often the case,[14,22–25] the question of whether electron transfer proceeds by an inner- or outer-sphere mechanism cannot be settled directly, the rate constant observed for $V^{2+} + Cu^{2+}$ suggests an inner-sphere mechanism in which, as in the other cases, substitution on $V(H_2O)_6^{2+}$ is rate determining. The immediate difficulty faced is why the proposed inner-sphere transition state cannot be made by substitution on the labile Cu^{2+} ion. (That cases of "reverse ligand transfer," such as Cu^{2+} substitution in the present reaction, have not been encountered may refer to the fact that the customary substitution rates of the oxidizing and reducing agents operate strongly against them, rather than to any inherent disadvantage such as being claimed here.) In the usual pattern of reaction, a bridging ligand moves from oxidant to reductant, opposite to the motion of the electron. In fact, the ligand may be intimately involved in the electron-transfer process and not just transferred owing to features of the substitution rates, leading to the so-called "atom-transfer" mechanism, for which some evidence has been obtained recently in the case of appropriate ligands.[26] Whether this point is applicable to reactions such as this remains to be proved. Its use in the present explanation provides a reasonable rationale for the present kinetic data.

It should be noted that in systems[3–5,13,27,28] involving inner-sphere mechanisms a high reactivity of OH^- compared to H_2O as a bridging ligand has been noted. The failure to find an appreciable rate term varying as $1/[H^+]$ in the present system is not significant in this context, however, owing to the rates of V^{2+} with Cu^{2+} and with $CuOH^+$ being leveled to nearly the same value by the $V(H_2O)_6^{2+}$ exchange rate. Based on the acid dissociation constant of Cu^{2+} the expected rate coefficient of the term varying as $[Cu^{2+}][V^{2+}]/[H^+]$ would be ca. $10^{-5}\ \text{sec}^{-1}$, clearly

---

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

(10) 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.

(11) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **69**, 176 (1965).

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

(13) D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2272 (1968).

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

(15) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

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

(17) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968).

(18) J. H. Espenson, *J. Am. Chem. Soc.*, **89**, 1276 (1967).

(19) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(20) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964); *Inorg. Chem.*, **3**, 569 (1964).

(21) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **69**, 176 (1965).

(22) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(23) P. Benson and A. Haim, *ibid.*, **87**, 3826 (1965).

(24) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

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

(26) F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).

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

(28) T. W. Newton, G. E. NcCrary, and W. G. Clark, *J. Phys. Chem.*, **72**, 4333 (1968).

negligible for $[H^+] \geq 0.04$ *M* compared to 26.6 M^{-1} sec^{-1}, the coefficient of the rate term $[Cu^{2+}][V^{2+}]$. According to this point of view the lack of a dominant k_{OH}/k_{H_2O} value does *not*, in this instance, constitute an indication of an outer-sphere mechanism, but rather the inverse $[H^+]$ term is negligible owing to the concentration of $CuOH^+$ being very small compared to Cu^{2+} with both metal ions having nearly the same reactivity. Another example of this effect is the reaction of $Co(NH_3)_5OH_2^{3+}$ with V^{2+},[14] where the lack of dependence of rate on $[H^+]$ also does not constitute evidence for an outer-sphere mechanism, for an inner-sphere reaction of $Co(NH_3)_5OH^{2+}$ and V^{2+} could not possibly compete with the acid-independent term, owing to the limiting effect of $V(H_2O)_6^{2+}$ substitution.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SWARTHMORE COLLEGE, SWARTHMORE, PENNSYLVANIA, AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Kinetics and Mechanism of the Reduction of Molybdenum(V) by Tin(II) in Concentrated Hydrochloric Acid Solutions[1,2]

BY A. A. BERGH AND G. P. HAIGHT, JR.[3]

Received July 24, 1968

The kinetics and mechanism of the reduction of Mo(V) by Sn(II) have been investigated in 9 and 12 *M* hydrochloric acid solutions. The reaction is stoichiometrically a simple 2-equiv process in both reagents: Sn(II) + Mo(V) → Mo(III) + Sn(IV). The complicated kinetics are best fit by the law

$$\frac{-d[Sn(II)]}{dt} = \frac{-d[Mo(V)]}{dt} = \frac{k_1[Mo(V)][Sn(II)]}{k_2 + k_3[Mo(V)] + k_4[Sn(II)] + k_5[Mo(III)]} \tag{1}$$

No significant intermediates are detectable in visible and uv absorption spectra or with esr during the reaction. A mechanism is postulated involving reaction of the predominant Sn(II) and Mo(V) species with solvent-activated forms of each other. Data are consistent with the attack of $SnCl_3^-$ on $MoOCl_5^{2-}$ and the attack of $SnCl_4^{2-}$ on the open position *trans* to the Mo≡O bond in $MoOCl_4^-$ to form Cl^--bridged intermediates. The activation energy for the reaction is about 10 kcal.

Introduction

Potentiometric titrations of Sn(II) with Mo(VI) in hydrochloric acid[4] led to the discovery of a slow reaction between Mo(V) and Sn(II) to give Mo(III) and Sn(IV) in hydrochloric acid of acid concentration >9 *M*. Shaffer[5,6] has remarked that many complementary 2-equiv redox reactions are fast. However this reaction is slow enough to study without employing special mixing techniques.

Experimental Procedure

Reagent grade chemicals were used without further purification. Mo(III) solutions were prepared by reduction of Mo(VI) with mercury and were stored over mercury. Hg_2Cl_2 produced by the oxidation of mercury was removed by filtration. No effect on the reaction under study due to mercury or its ions could be detected. Mo(V) solutions produced by reduction of Mo(VI) with Sn(II) gave the same kinetics as those prepared using reduction by Hg. Mo(V) was prepared by oxidation of Mo(III) with Mo(VI), stock solutions retaining about 6% Mo(III). $SnCl_2$ was dissolved in 12.3 *M* HCl and standardized before and after each series of runs. Hydrochloric acid was standardized acidimetrically using sodium bicarbonate.

All spectrophotometric and kinetic measurements were carried out using a Beckman Model DU spectrophotometer, with 10.0-mm cells. The reagents were mixed in the cell before each measurement, and the cell compartment was kept at a constant temperature of 25 ± 0.05°, unless otherwise stated.

The absorption spectra of Mo(V) and Mo(III) in 12.0 *N* hydrochloric acid are shown in Figure 1. The spectrum of Mo(V) has two and the spectrum of Mo(III) three maxima in the visible region.

The rate of the reaction Mo(V) + Sn(II) ⇄ Mo(III) + Sn(IV) was followed either at 720 mμ by the disappearance of Mo(V) or at 528 mμ by the formation of Mo(III). The same rate was found at both wavelengths, indicating the absence of an intermediate of different spectrum in detectable quantities during the run.

Kinetics Results

The rate law for this reaction was determined in 9 and 12 *M* hydrochloric acid. It is rather complex, so that analysis of the experimental data will be given in some detail, that its derivation may be clear.

Results in 9 *M* HCl. Kinetics with [Sn(II)] = [Mo(V)] = *a*.—All runs with equimolar Sn(II) and Mo(V) in this medium started out with good first-order dependence on either reagent but not on both. There appeared to be a slight indication that the first-order constant was low during the first minute or two,

---

(1) Research was supported by U. S. Army through a grant to Swarthmore College from the Office of Ordnance Research, Durham, N. C., and by a grant from the U. S. Public Health Service to the University of Illinois.

(2) The data on which this paper is based were taken mainly from the doctoral thesis submitted in 1959 by A. A. Bergh to the Graduate School of the University of Pennsylvania.

(3) To whom correspondence should be addressed at the University of Illinois, Urbana, Ill.

(4) G. P. Haight, Jr., and A. A. Bergh, *Inorg. Chem.*, **1**, 688 (1962).

(5) P. A. Shaffer, *J. Phys. Chem.*, **40**, 1021 (1936).

(6) P. A. Shaffer, *Cold Spring Harbor Symp. Quant. Biol.*, **7**, 50 (1939).