

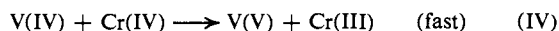
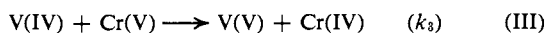
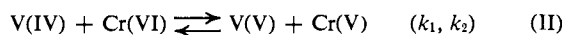
A Kinetic Study of the First Step of the Oxidation of Vanadium(IV) by Chromium(VI)^{1a}

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Abstract: Use has been made of V(III) to scavenge the V(V) product of the reaction of V(IV) by Cr(VI). This study permits the study of the kinetics of the V(IV)-Cr(VI) reaction under conditions of very small [V(V)], thereby allowing evaluation of the otherwise unmeasurable rate constant for the first step of the V(IV)-Cr(VI) reaction. The rate expression is $-d[\text{Cr(VI)}]/dt = k[\text{VO}^{2+}][\text{HCrO}_4^-]$ with $k = 1.8 \pm 0.1 \times 10^2 M^{-1} \text{sec}^{-1}$ at 25.0° and $\mu = 1.00 M$, independent of $[\text{H}^+]$. The implication of these findings with regard to some other Cr-V reactions is discussed.

An earlier kinetic study² on the oxidation of VO^{2+} by HCrO_4^- , reaction I, established that the reaction occurred by a succession of three one-equivalent $3\text{VO}^{2+} + \text{HCrO}_4^- + \text{H}^+ = 3\text{VO}_2^+ + \text{Cr}^{3+} + \text{H}_2\text{O}$ (I) steps, that the second step was rate determining under the conditions employed, and that the observed composite rate constant was independent of $[\text{H}^+]$ in the range $0.005 \leq [\text{H}^+] \leq 0.04 M$.³ The proposed reaction sequence was the following.



If the reverse of II occurs at a much higher rate than the forward of III, the following rate expression results.

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{k_1 k_3 [\text{V(IV)}]^2 [\text{Cr(VI)}]}{k_2 [\text{V(V)}]} \quad (1)$$

The rate law in eq 1 correctly describes the rate behavior under all the conditions employed earlier,² with $k_1 k_3 / k_2 = 0.56 M^{-1} \text{sec}^{-1}$. The individual rate parameters associated with reaction steps II and III were not evaluated. Also the lack of an $[\text{H}^+]$ rate dependence established that the composite $k_1 k_3 / k_2$ did not depend on $[\text{H}^+]$, but it did not reveal whether each of the individual rate constants was independent of $[\text{H}^+]$, or whether this was a consequence of cancelling $[\text{H}^+]$ dependences.

In principle the situation might be resolved by a study under conditions of very low $[\text{V(V)}]$. The complete expression applicable to the proposed mechanism is

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{k_1 k_3 [\text{V(IV)}]^2 [\text{Cr(VI)}]}{k_3 [\text{V(IV)}] + k_2 [\text{V(V)}]} \quad (2)$$

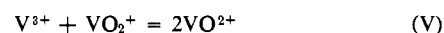
It was found, however, that even when V(V) is not added initially, the concentrations produced very early in the reaction sufficed to make the second denominator term predominate, reducing eq 2 to eq 1.

(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2637; (b) Fellow of the Alfred P. Sloan Foundation, 1968-1970.

(2) (a) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 1883 (1964); (b) *ibid.*, **86**, 5101 (1964).

(3) The discussion here is limited to the path with a first-order dependence upon $[\text{HCrO}_4^-]$. The less important path (see ref 2), proportional to $[\text{Cr}_2\text{O}_7^{2-}] \times [\text{H}^+]$, carries a quite small fraction of the overall reaction under the conditions employed here and is thus being neglected.

In the course of a study⁴ of the oxidation of V(III) by Cr(VI), it was noted that addition of V(IV) considerably increased the rate of reduction of Cr(VI) at low $[\text{H}^+]$, $\leq 0.04 M$. The same concentration of V(IV) by itself would have reacted very slowly with Cr(VI). The interpretation offered for this effect is based on eq 2: the scavenging effect of V(III) toward V(V), reaction V,⁵ keeps the denominator term $k_2[\text{V(V)}]$ insignifi-



cant with respect to the value of $k_3[\text{V(IV)}]$. Consequently the rate of the first step, reaction II, controls the rate of Cr(VI) reduction under the circumstances, in contrast to the earlier work in which the second step was rate determining. In effect, the present study is that of a sequence in which VO^{2+} acts as a catalyst for the V(III)-Cr(VI) reaction.

This paper reports on experiments to confirm this interpretation through quantitative studies of the effect of VO^{2+} in the V^{3+} - HCrO_4^- reaction. Such results can allow a value to be calculated for the previously unknown rate constant k_1 and can also permit a study of the effect of $[\text{H}^+]$ on the individual rate constants in reactions II-IV.

Experimental Section

The materials and experimental methods used in this study are identical with those used in the earlier work.⁴ The concentration of Cr(VI) was always much smaller than that of V(III) so that the latter remained effectively constant in the course of an experiment. As in the earlier work,⁴ all the kinetic data were taken for solutions of constant ionic strength, 1.00 M, maintained by lithium perchlorate. The rate data were read from the stopped-flow oscillograms, and the customary pseudo-first-order rate plots were constructed.⁶

Results

The rate of oxidation of V^{3+} by Cr(VI) shows a first-order dependence upon $[\text{HCrO}_4^-]$,⁴ which is also maintained in the presence of VO^{2+} (at least at the low concentrations of HCrO_4^- in the present experiments).³

(4) K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, **92**, 1884 (1970).

(5) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **68**, 612 (1964). Values of the apparent second-order rate constants ($M^{-1} \text{sec}^{-1}$) at 25.0°, $\mu = 2.0 M$ for reaction V at several hydrogen-ion concentrations are $k = 240$ ($[\text{H}^+] 1.0$), 280 (0.80), 2300 (0.10). Values extrapolated from other temperatures give also 1.6×10^4 (0.020) and 3.8×10^4 (0.010).

(6) O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 1968 (1969).

Table I. Experimental Rate Constants for the Oxidation of V^{3+} - VO^{2+} Mixtures by $HCrO_4^-$ ^a

Initial concn, <i>M</i>				k_{exp}, sec^{-1}	$k_{exp}/[V^{3+}]_{av}^b$		$[VO^{2+}]/[V^{3+}]_{av}^b$
$10^3[VO^{2+}]$	$10^3[V(III)]$	$10^4[HCrO_4^-]$	$[H^+]$		Obsd	Calcd	
2.02	5.19	1.00	0.020	2.19	465	457	0.429
1.94	2.62	1.00	0.020	1.10	477	531	0.840
4.07	5.06	0.20	0.0051	2.55	646	565	1.03
3.60	2.55	1.00	0.020	1.48	660	670	1.61
3.10	1.96	0.20	0.0076	1.31	805	722	1.90
1.94	0.99	0.20	0.040	0.698	753	756	2.09
6.01	2.50	1.00	0.020	1.88	856	873	2.74
6.01	1.83	0.20	0.010	1.85	1159	1066	3.81
3.88	0.985	0.20	0.040	1.02	1106	1140	4.21
9.90	2.54	1.00	0.020	2.55	1142	1180	4.43
9.84	1.79	0.20	0.0050	2.56	1862	1670	7.16
17.4	2.69	1.00	0.020	3.65	1538	1700	7.33
7.56	1.14	0.20	0.010	1.88	1931	1780	7.76
14.0	1.73	0.20	0.020	3.05	1920	1965	8.81
24.9	2.45	1.00	0.020	4.81	2238	2470	11.6

^a Temp = 25.0°, $\mu = 1.00 M$. The estimated precision of the k_{exp} values is $\pm 3-8\%$ average deviation. ^b $[V^{3+}]$ computed from $[V(III)]$ using the acid dissociation quotient $1.4 \times 10^{-3} M$: L. Pajdowski, *J. Inorg. Nucl. Chem.*, **28**, 443 (1966).

With increasing concentrations of VO^{2+} the observed rate of disappearance of $HCrO_4^-$ becomes progressively higher.

Figure 1 illustrates typical linear pseudo-first-order rate plots, confirming the first-order $HCrO_4^-$ dependence. The rate runs depicted in Figure 1 refer to a

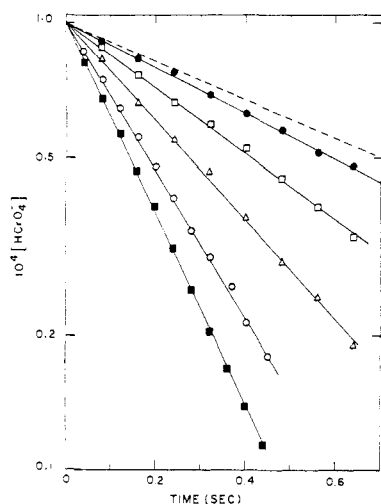


Figure 1. Pseudo-first-order rate plots of $[HCrO_4^-]$ (log scale) vs. time, illustrating the effect of added concentrations of VO^{2+} . The dashed line refers to an experiment having no added VO^{2+} , the slope interpolated from the average of such runs.⁴ The VO^{2+} concentrations ($M \times 10^3$) in the other runs are 1.94, 6.01, 9.90, 17.4, and 24.9. All the runs refer to $[V^{3+}] = ca. 2.56 \times 10^{-3}$, $[H^+] = 0.020$, $\mu = 1.00 M$ at 25.0°.

series having approximately constant $[V^{3+}]$ and variable concentrations of VO^{2+} . The V^{3+} concentrations in the various runs are all within 7% of the value $2.56 \times 10^{-3} M$, and the VO^{2+} concentrations are ($M \times 10^3$) 0.0, 1.94, 6.01, 9.90, 17.4, and 24.9. The following pseudo-first-order rate constants (k_{exp}) were evaluated from the slopes of these lines: 0.93, 1.10, 1.88, 2.55, 3.65, and 4.81 sec^{-1} . The increase in rate was linear in $[VO^{2+}]$, as shown by a plot of these rate constants vs. $[VO^{2+}]$ in Figure 2.

The treatment of all the experimental results is simplified by a prior consideration of the interpretation

arrived at to explain the observations. Under the assumption that both V^{3+} and VO^{2+} react with $HCrO_4^-$, the following expression for the rate of disappearance of $HCrO_4^-$ is applicable.

$$-d[HCrO_4^-]/dt = (k[V^{3+}] + k_1[VO^{2+}])(HCrO_4^-) \quad (3)$$

The implication of the equation is that the two reducing agents react in parallel and independent processes. Employing the definition $k_{exp} = -d \ln [HCrO_4^-]/dt$,

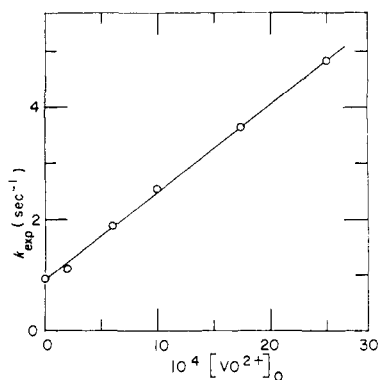


Figure 2. Linear dependence of the pseudo-first-order rate constants upon $[VO^{2+}]$ in a series of runs at constant $[V^{3+}]$.

the following expression is derived from eq 3 when both the concentrations of V^{3+} and VO^{2+} are constant during the run.

$$k_{exp}/[V^{3+}] = k + k_1[VO^{2+}]/[V^{3+}] \quad (4)$$

The form of this equation and the presumed dependence of k_{exp} upon $[V^{3+}]$ and $[VO^{2+}]$ can be checked by appropriate concentration variations. Also in the model k was ascribed to the reaction of V^{3+} and $HCrO_4^-$, for which the value 386 $M^{-1} sec^{-1}$ was established independently.⁴

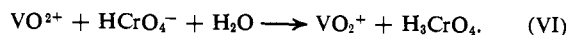
Experiments covering the concentration ranges of $1.0-5.2 \times 10^{-3} M V^{3+}$ and $9-25 \times 10^{-3} M VO^{2+}$ were performed. In addition, in different experiments the hydrogen ion concentration was varied between 0.005 and 0.040 M . Table I summarizes the individual experiments and gives the value of k_{exp} found in each. Figure 3 illustrates the linear relation obtained when

$k_{\text{exp}}/[\text{V}^{3+}]$ was plotted vs. $[\text{VO}^{2+}]/[\text{V}^{3+}]$. The intercept and slope give the values $k = 3.8 \pm 0.3 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$ (in good agreement with the independently known value⁴), and $k_1 = 1.8 \pm 0.1 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$. The rate constant k is known to be independent of $[\text{H}^+]$. Because the rate constants evaluated at different $[\text{H}^+]$ lie along a single line in Figure 3, the rate constant k_1 is also independent of hydrogen ion concentration within the error of the experiments. Because of the necessity of making corrections for the acid dissociation of V^{3+} , the reaction cannot be claimed to be without any H^+ dependence whatever; for example, the points at $[\text{H}^+] = 0.0076$ and 0.01 M all lie slightly above the line in Figure 1.

The reaction of V^{3+} - VO^{2+} mixtures with HCrO_4^- was also studied under conditions of high $[\text{H}^+]$ where V^{3+} does not efficiently scavenge VO_2^+ (V^{3+} and VO_2^+ react with an apparent second-order rate constant⁵ of $280 \text{ M}^{-1} \text{ sec}^{-1}$ at 0.800 M H^+ , $\mu = 2.0 \text{ M}$ and 25.0°). At 0.80 M H^+ the absorbance-time traces did not follow pseudo-first-order kinetics as had been observed at $[\text{H}^+] \leq 0.04 \text{ M}$. The absorbance change accompanying the reaction at the HCrO_4^- maximum ($\lambda 350 \text{ nm}$) was composed of a rapid initial decrease corresponding to HCrO_4^- consumption, followed by a much slower absorbance decrease corresponding to reaction V. Furthermore, at wavelengths where VO_2^+ absorbs strongly (e.g., $\lambda 280 \text{ nm}$) the absorbance change at 0.80 M H^+ was now quite small and the rate apparently much slower than at $[\text{H}^+] \leq 0.04 \text{ M}$ (as if an absorbing species such as VO_2^+ were being formed and destroyed at comparable rates). These observations appear consistent both with the accumulation of VO_2^+ in solution owing to the lower rate of the V^{3+} - VO_2^+ reaction rate at high $[\text{H}^+]$ and with the explanation offered for the effect of VO^{2+} at low $[\text{H}^+]$ wherein V^{3+} scavenges VO_2^+ .

Interpretation and Discussion

Rate Expression and Mechanism of the VO^{2+} - HCrO_4^- Reaction. The rate of the first step of the oxidation of VO^{2+} by HCrO_4^- shows a first-order dependence upon each concentration. These dependencies are consistent with the three-step mechanism proposed on the basis of the earlier studies, reactions II-IV, in which the first step is rate determining. Because k_1 is independent of $[\text{H}^+]$, the composition of the activated complex for reaction II is $[\text{VOHCrO}_4^+ \pm m\text{H}_2\text{O}]^\ddagger$. When the reaction is written in terms of the reactant species, the following form is obtained.



In terms of a detailed mechanism it is not known whether there is a reshuffling of oxygen atoms during this process, or whether the Cr(V) species H_3CrO_4 retains the oxygen atoms originating with HCrO_4^- . If the correlation suggested by earlier work⁷⁻⁹ applies in this instance, however, the transition state in reaction VI would utilize an oxo or hydroxo bridge between V and Cr atoms.

Implications of the Rate Studies—The Role of Cr(V). The formula¹⁰ H_3CrO_4 written for Cr(V) in reaction VI

(7) J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, **85**, 3328 (1963).

(8) J. H. Espenson, *ibid.*, **92**, 1880 (1970).

(9) J. P. Birk, *ibid.*, **91**, 3189 (1969).

(10) The formula is arbitrary to the extent of the number of water molecules; HCrO_3 or H_7CrO_6 are among other possible species. Rate

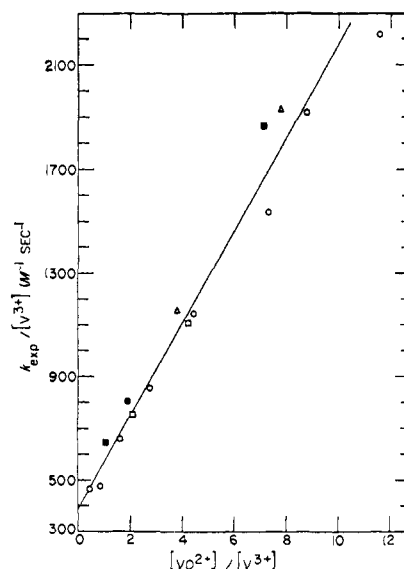


Figure 3. Linear relation of the value of $k_{\text{exp}}/[\text{V}^{3+}]$ with the quotient $[\text{VO}^{2+}]/[\text{V}^{3+}]$ in accord with eq 4. The different symbols refer to varying $[\text{H}^+]$: 0.005 (closed squares), 0.0076 (closed circles), 0.0100 (triangles), 0.0200 (open circles), and 0.0400 (open squares).

was based upon the formula of each of the predominant reactant species and of V(V) under the conditions employed, consistent with the form of the rate law. The same formula for the Cr(V) intermediate was noted in the other reactions, including the reactions of HCrO_4^- with V^{3+} ,⁴ Fe^{2+} ,⁸ and NpO_2^+ .¹¹

The results of this study substantiate the proposal made earlier,^{2b} on indirect evidence, that the first step involved the species shown in reaction VI. Based on the composition of the transition state in that reaction step and on the studies² in which reaction II was a pre-equilibrium preceding a rate-determining reaction III, the composition of the transition state for the latter reaction is $[\text{VOH}_3\text{CrO}_4^{2+} \pm n\text{H}_2\text{O}]^\ddagger$.

The value of k_3/k_2 was computed from the quotient of k_1k_3/k_2 ($0.56 \text{ M}^{-1} \text{ sec}^{-1}$ at 25.0° , $\mu = 1.00 \text{ M}$)⁴ and the value of k_1 found in the present study; the value is $k_3/k_2 = 3.1 \times 10^{-3}$. This value confirms the conclusion drawn in the earlier work² that V(V) oxidizes Cr(V) at a considerably higher rate than V(IV) reduces it. With regard to the particular value of k_3/k_2 found, and with reference to the earlier rate results,² can the failure to observe any deviation from the form of the limiting rate expression (eq 1) toward the more general form (eq 2) be accounted for? According to eq 2 at a ratio of $\text{V(V)}/\text{V(IV)}$ of 0.03, the second denominator term, $k_2[\text{V(V)}]$, exceeds the first by a factor of ca. 10. Thus, after only 3% of the V(IV) has been oxidized, even in the initial absence of V(V) , the complete rate expression applicable to reaction I reduces essentially quantitatively to the simpler form of eq 1.

Chromium(V) is produced at comparable rates by the parallel first-step oxidations of V^{3+} and VO^{2+} . The subsequent fate of Cr(V) is reduction to Cr(III) in two successive single-electron steps such as reactions II and

correlations (J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **82**, 3805 (1960); C. Altman and E. L. King, *ibid.*, **83**, 2825 (1961)) suggest, however, that the most likely coordination number of chromium(V) is four. Furthermore, the species written as H_3CrO_4 might just as well be $\text{H}_2\text{CrO}_4^- + \text{H}^+$; alternatives such as this are indistinguishable.

(11) J. C. Sullivan, *ibid.*, **87**, 1495 (1965).

IV or their analogs⁴ for V³⁺ reduction steps. When both VO²⁺ and V³⁺ are present, the Cr(V) intermediate produced in one of the reactions does not necessarily continue in subsequent reactions with the same vanadium oxidation step. Because the intermediate is common to both sequences, the two mechanisms may interact to some extent. The following paragraph is an attempt to explore the fate of Cr(V) under such conditions.

The rate constants for the reduction of Cr(V) to Cr(IV) by V³⁺ and VO²⁺ are not known. The scavenging effect of iodide ion in each separate system has, however, been studied, affording the ratio of each rate constant, in turn, to that for reduction of Cr(V) by I⁻. Comparison of these results and earlier work¹² gives^{4,8} the rate expression for each, $k_{35}[V^{3+}][H_3CrO_4]/[H^+]$ and $k_{45}[VO^{2+}][H_3CrO_4]$. The quotient k_{35}/k_{45} is 0.76 *M*. At the hydrogen ion concentrations in the present work, 0.005–0.04 *M*, and when V³⁺ and VO²⁺ are present at equal concentrations, the oxidation of V³⁺ by Cr(V) is at least 20 times more important than that of V(IV), reaction III. On the other hand, at higher [H⁺], 0.8 *M*, VO²⁺ and V³⁺ compete for reduction of Cr(V) to an approximately equal extent. Under those conditions, however, the reverse of reaction II is important,

(12) C. Wagner and W. Preiss, *Z. Anorg. Allg. Chem.*, **168**, 265 (1928).

as VO²⁺ has not been removed by its reaction with V³⁺.

The upper limit of useful [H⁺] variation in the present study was set by the necessity of making the rate of the V(III)–V(V) reaction high relative to that of V(V)–Cr(V). Since the former process (reaction V) obeys a rate expression⁵ in which the major term varies as 1/[H⁺], the limitation of relatively low acidity (≤ 0.04 *M*) is needed in order to promote the scavenging effect of V(III).

The finding that k_1 is not dependent on [H⁺] confirms the inference drawn earlier, and it thereby affirms the conclusion² that the reaction of Cr(V) and I⁻ occurs according to a rate expression which is first-order in [H⁺]: $k_{15}[H_3CrO_4][I^-][H^+]$.

Finally, whether the catalytic effect of VO²⁺ on the V³⁺–HCrO₄⁻ reaction⁴ exerted an appreciable effect on the results of the V³⁺–HCrO₄⁻ rate study should be considered. In those runs the quotients [VO²⁺]/[V³⁺] at 50% completion were between 0.003 and 0.15, averaging 0.065 in 17 experiments. The error so introduced in interpreting⁴ the resulting rate as solely that of the V³⁺–HCrO₄⁻ reaction was, according to eq 4, between 0.14 and 7.0%, averaging 3.1%. The small systematic trend of the rate constants with V³⁺ and HCrO₄⁻ concentration,⁴ which was perhaps not even outside the expected experimental uncertainty, may possibly be attributed to this cause.

The Kinetics and Mechanism of the Reaction of Chromium(II)–Cyanide Complexes with Hydrogen Peroxide in Aqueous Solution¹

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Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973. Received October 2, 1969

Abstract: The stoichiometry and kinetics of the oxidation of chromium(II) by hydrogen peroxide have been investigated in alkaline cyanide solutions. The standard potential of the chromium(II)/chromium(III) couple, $E^\circ = -(1.39 \pm 0.01)$ V vs. sce, has been measured polarographically. The stoichiometry of the reaction was found to be $2\Delta[H_2O_2] = \Delta[Cr(II)]$ under the experimental conditions used. The kinetics of the reaction were studied by observing the disappearance of chromium(II) at wavelengths between 260 and 450 nm under pseudo-first-order conditions at 1.0 *M* ionic strength and 25.0°. The observed rate constants are given by $k_{obsd} = \{2[H_2O_2]_T(k_0K_1[CN^-] + k_1 + k_2K_cK_a/[H^+][CN^-])\}/\{(1 + K_a/[H^+])(1 + K_1[CN^-]) + K_cK_a[H_2O_2]_T/[H^+][CN^-]\}$ with $K_1 = (9.55 \pm 0.03)$ *M*⁻¹, $K_a = 2.15 \times 10^{-12}$ *M*, $k_0 = (3.29 \pm 0.36) \times 10^2$ *M*⁻¹ sec⁻¹, $k_1 = (3.57 \pm 0.16) \times 10^3$ *M*⁻¹ sec⁻¹, $K_c = (2.95 \pm 0.19) \times 10^1$, and $k_2 = (2.13 \pm 0.10) \times 10^1$ sec⁻¹. The equilibrium constants K_1 , K_a , and K_c refer to the reactions $Cr(CN)_5H_2O^{3-} + CN^- \rightleftharpoons Cr(CN)_6^{4-} + H_2O$, $H_2O_2 \rightleftharpoons H^+ + HO_2^-$, and $Cr(CN)_5H_2O^{3-} + HO_2^- \rightleftharpoons [complex]^{3-} + CN^-$; and the rate constants k_0 , k_1 , and k_2 are defined by the reactions $Cr(CN)_6^{4-} + H_2O_2 \rightarrow Cr(CN)_6^{3-} + OH + OH^-$, $Cr(CN)_5H_2O^{3-} + H_2O_2 \rightarrow Cr(CN)_5OH^{3-} + OH + H_2O$, and $[complex]^{3-} \rightarrow$ products, respectively. The mechanisms of the reactions are discussed.

The very strong reducing properties of Cr(CN)₆⁴⁻ have limited the number of investigations involving aqueous cyanide solutions of chromium(II).^{3–9}

Haim and Wilmarth⁹ have prepared K₃Cr(CN)₆ in 78% yield by rapidly oxidizing a concentrated solution of chromium(II) in 5 *M* potassium cyanide with oxygen or hydrogen peroxide. Since the main chromium(III)

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) On sabbatical leave from Adams State College, Alamosa, Colo.

(3) D. N. Hume and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **65**, 1897 (1943).

(4) R. Samuel and A. R. R. Deshpande, *Z. Phys.*, **80**, 395 (1933).

(5) W. Traube and W. Lange, *Chem. Ber.*, **58**, 2773 (1925).

(6) E. Fisherova and O. Fischer, *Collect. Czech. Chem. Commun.*, **30**, 675 (1965).

(7) D. N. Hume and H. W. Stone, *J. Amer. Chem. Soc.*, **63**, 1200 (1941).

(8) A. G. MacDiarmid and N. F. Hall, *ibid.*, **76**, 4222 (1954).

(9) A. Haim and W. K. Wilmarth, *ibid.*, **83**, 509 (1961).