IV or their analogs[4] for V^{3+} reduction steps. When both VO^{2+} and V^{3+} 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 V^{3+} and VO^{2+} 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 work[12] 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 V^{3+} and VO^{2+} are present at equal concentrations, the oxidation of V^{3+} 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, VO^{2+} and V^{3+} compete for reduction of Cr(V) to an approximately equal extent. Under those conditions, however, the reverse of reaction II is important, as VO_2^+ has not been removed by its reaction with V^{3+}.

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 expression[5] 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 conclusion[2] that the reaction of Cr(V) and I^- occurs according to a rate expression which is first-order in $[H^+]$: $k_{I5}[H_3CrO_4][I^-][H^+]$.

Finally, whether the catalytic effect of VO^{2+} on the V^{3+}–$HCrO_4^-$ reaction[4] exerted an appreciable effect on the results of the V^{3+}–$HCrO_4^-$ rate study should be considered. In those runs the quotients $[VO^{2+}]/[V^{3+}]$ at 50% completion were between 0.003 and 0.15, averaging 0.065 in 17 experiments. The error so introduced in interpreting[4] the resulting rate as solely that of the V^{3+}–$HCrO_4^-$ reaction was, according to eq 4, between 0.14 and 7.0%, averaging 3.1%. The small systematic trend of the rate constants with V^{3+} and $HCrO_4^-$ concentration,[4] which was perhaps not even outside the expected experimental uncertainty, may possibly be attributed to this cause.

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The Kinetics and Mechanism of the Reaction of Chromium(II)–Cyanide Complexes with Hydrogen Peroxide in Aqueous Solution[1]

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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, $E° = -(1.39 \pm 0.01)$ 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 $k_{obsd} = \{2[H_2O_2]_T(k_0K_1 \cdot [CN^-] + k_1 + k_2K_cK_a/[H^+][CN^-])\}/\{(1 + K_a/[H^+])(1 + K_1[CN^-]) + K_cK_a[H_2O_2]_T/[H^+][CN^-]\}$ 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 $Cr(CN)_6{}^{4-}$ have limited the number of investigations involving aqueous cyanide solutions of chromium(II).[3-9] Haim and Wilmarth[9] have prepared $K_3Cr(CN)_6$ 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)

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[2] On sabbatical leave from Adams State College, Alamosa, Colo.

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product did not contain a chromium–oxygen bond, these authors suggested that the oxidation of $Cr(CN)_6{}^{4-}$ by oxygen or hydrogen peroxide proceeds by an outer-sphere mechanism. This proposed mechanism is in contrast with the inner-sphere mechanisms found for the oxidation of ammoniacal[10] and aqueous[11] solutions of chromium(II). The evidence for inner-sphere mechanisms in the latter oxidations is that the products of the oxidation, $(NH_3)_5CrOCr(NH_3)_5{}^{4+}$ and $Cr(OH)_2Cr^{4+}$, respectively, contain coordinated oxygen. It seemed somewhat surprising to us that the oxidation of $Cr(CN)_6{}^{4-}$ by hydrogen peroxide should proceed by an outer-sphere mechanism since $Cr(CN)_6{}^{4-}$, in common with the other chromium(II) complexes, is substitution labile, and an inner-sphere mechanism could offer some advantages in reactions in which several equivalents need to be transferred. We decided, therefore, to investigate the kinetics of the reaction of chromium(II) with hydrogen peroxide in alkaline cyanide solutions.

Experimental Section

Materials. Stock solutions approximately 7 M in sodium perchlorate were prepared by neutralizing sodium carbonate with perchloric acid. The stock solutions of chromium(II) for the kinetic and spectrophotometric experiments were 0.2 M and 0.02 M in chromium(II), and 1.0 M and 0.5 M in perchloric acid, respectively, and were prepared by the reduction of perchloric acid solutions of chromium(III) with amalgamated zinc. The chromium(II) solutions were stored under argon. Stock solutions approximately 0.1 M in hydrogen peroxide were prepared by dilution of 30% H_2O_2 (Baker and Adamson). The cyanide stock solution was approximately 5 M in sodium cyanide and 0.1 M in sodium hydroxide. Cerium(IV) sulfate solution and potassium hexacyanochromate(III) (K and K Laboratories, Inc.) were used without further purification. All other chemicals were of analytical grade. Triply distilled water was used throughout.

Analysis of Solutions. Hydrogen peroxide concentrations were calculated from the decrease in absorbance at 320 nm of a standard cerium(IV) sulfate solution resulting from the addition of an aliquot of the hydrogen peroxide solution (ϵ 5580 at 320 nm). Sodium cyanide was estimated by the Liebig method and sodium perchlorate was estimated gravimetrically. Chromium(II) concentrations were determined by adding an aliquot of the chromium(II) solution to a deoxygenated solution of 0.1 M iron(III) in 0.1 M sulfuric acid and titrating the iron(II) formed with standard dichromate solution. Total chromium was determined spectrophotometrically as chromate after oxidation by alkaline peroxide. Concentrations of hexacyanochromate(III) were determined from spectrophotometric measurements at 264 and 377 nm.[12]

Potentiometric Measurements. The electrode potential of the chromium(II)/chromium(III) couple in alkaline cyanide solutions was measured polarographically[3] using a dropping mercury electrode and a standard calomel electrode as reference. The concentration ranges used were $[Cr(CN)_6{}^{3-}] = (0.036–4.71) \times 10^{-3}$ M, $[Cr(II)] = (0.018–2.64) \times 10^{-3}$ M, $[OH^-] = 0.001–0.50$ M, and $[CN^-] = 0.10–1.00$ M at ionic strength 1.0 M and 25°.

Kinetic Measurements. The kinetics of the oxidation of chromium(II)–cyanide solutions by hydrogen peroxide were studied by use of the stopped-flow technique.[13] In the majority of the kinetic experiments a deoxygenated solution containing excess hydrogen peroxide and sodium perchlorate was mixed with a deoxygenated solution containing sodium cyanide, sodium hydroxide, chromium(II) perchlorate, and sodium perchlorate. The ionic strength was kept constant at 1.0 M and the solutions were used within 2 hr of their preparation. The chromium(II)–cyanide solution was prepared by bubbling argon for about 30 min through a solution containing the calculated amount of sodium hydroxide and sodium perchlorate. The appropriate amount of sodium cyanide was then added and the resulting solution was deoxygenated for an additional 5–15 min.[14] The chromium(II) perchlorate solution was then added from a stock solution through a buret and hypodermic needle. Several solutions were analyzed spectrophotometrically to determine the efficiency of transfer (loss of chromium(II) due to oxidation was usually less than 5%) and to determine analytically the loss of cyanide as HCN (always less than 2%). In some experiments, hydrogen peroxide solutions containing sodium hydroxide and sodium perchlorate were used; however, because of the instability of these solutions, hydrogen peroxide solutions of pH ≈5 were used in most of the experiments. The rates of dissociation of H_2O_2 were studied at pH 11 and 13 by mixing a perchloric acid solution of hydrogen peroxide and sodium cyanide. It was found that the equilibrium between H_2O_2 and $HO_2{}^-$ was established in less than 1 msec in all cases. No reaction between cyanide and hydrogen peroxide could be detected under the experimental conditions.

In all kinetic experiments the excess of hydrogen peroxide was such as to ensure pseudo-first-order conditions. The reaction was found to be independent of wavelength in the range 260–450 nm, although the majority of runs were made at 327 nm (an absorbance maximum of chromium(II)–cyanide solutions). Each kinetic experiment was repeated at least six times. The average error of these measurements was ±5%.

Spectra and Stoichiometry of the Reaction. The spectra of chromium(II)–cyanide solutions prepared as described above, as well as the spectra of solutions prepared by reducing alkaline solutions of $Cr(CN)_6{}^{3-}$ with amalgamated zinc in the presence of excess cyanide ions, were measured on a Cary Model 14 spectrophotometer. The chromium(II) concentrations of the solutions were in the range $8 \times 10^{-5}–1 \times 10^{-3}$ M. The stoichiometry of the reaction of excess hydrogen peroxide with the chromium(II)–cyanide solutions was determined by collecting the reaction mixture from the stopped-flow apparatus in an excess of perchloric acid, removing the HCN by bubbling with argon, and estimating the remaining peroxide as the titanium(IV) complex (ϵ 731 at 415 nm).

Results

Spectrophotometric and Potentiometric Measurements. The spectra of the chromium(II) solutions were independent of their method of preparation and also of the ratio of the cyanide to the hydroxide ion concentration of the solution provided this ratio was larger than ~20, and the cyanide ion concentration was larger than 0.5 M. Under these conditions the spectra exhibited maxima at 227, 264, and 327 nm, with molar absorptivities of 9700 ± 200, 5,800 ± 400, and 8,700 ± 700, respectively.

Plots of E_{obsd} *vs.* log [Cr(II)]/[Cr(III)] were linear with a slope corresponding to a one-equivalent change for the chromium(II)/chromium(III) couple. The standard electrode potential at ionic strength 1.0 M determined from these measurements, −(1.39 ± 0.01) V *vs.* sce, is in excellent agreement with the value reported earlier by Hume and Kolthoff.[3]

Oxidation Products. The stoichiometry of the reaction was found to be $2\Delta[H_2O_2] = \Delta[Cr(II)]$ within the experimental error of the measurements (±2%) at $[OH^-] = 0.1, 0.01$, and 0.002 M, and $[CN^-] = 0.4$,

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[14] The equilibrium constant for the reaction $HCN \rightleftharpoons H^+ + CN^-$ is 6.02×10^{-10} M at ionic strength 1.0 M and 25.0°.[15,16] At the highest acidity used the proportion of the total cyanide concentration in the form of HCN is less than 2%. The acid concentration of the solution resulting from the addition of a given amount of cyanide, peroxide, and hydroxide was calulated from the appropriate cubic equation using a computerized Newton–Raphson routine. Working curves were then constructed for different added peroxide concentrations at each cyanide concentration so that a solution of any desired hydrogen ion concentration could be prepared. The equilibrium constant for the reaction $H_2O_2 \rightleftharpoons H^+ + HO_2{}^-$ is 2.15×10^{-12} M at ionic strength 1.0 M and 25.0°.[17]

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Table I. Kinetic Data for the Reaction between Chromium(II) and Hydrogen Peroxide in Alkaline Cyanide Solutions at 25.0° and Ionic Strength 1.0 M[a]

$[CN^-]$, M	$10^3[H_2O_2]_T$, M	$10^{12}[H^+]$, M	k_{obsd}, sec^{-1}	k_{calcd},[b] sec^{-1}
1.00	0.97	1.98	0.72	0.65
1.00	0.98	2.95	0.76	0.77
1.00	1.54	1.56	1.00	0.93
1.00	2.91	1.98	2.29	1.95
1.00	2.94	3.14	2.69	2.36
1.00	4.87	0.531	1.56	1.67
1.00	4.87	0.982	2.19	2.32
1.00	4.87	1.47	2.73	2.84
1.00	4.87	1.99	3.32	3.26
1.00	4.87	2.48	3.94	3.57
1.00	4.87	2.98	4.36	3.82
0.80	4.00	0.0866	0.79	0.90
0.80	8.00	0.0884	1.58	1.78
0.60	1.00	0.0426	0.38	0.33
0.60	2.00	0.0427	0.74	0.66
0.60	4.00	0.0429	1.52	1.31
0.60	8.00	0.0433	2.90	2.55
0.50	0.66	2.51	0.64	0.76
0.50	0.97	2.03	1.05	1.05
0.50	1.32	2.60	1.29	1.54
0.50	4.86	1.97	4.78	5.11
0.50	9.70	0.473	6.54	6.08
0.50	9.70	0.965	8.03	7.73
0.50	9.70	2.92	14.2	11.3
0.50	9.70	3.97	15.6	12.3
0.45	1.12	0.345	0.58	0.79
0.40	0.66	2.64	0.80	0.92
0.40	0.66	3.65	0.94	0.99
0.40	0.91	4.57	1.34	1.42
0.40	1.32	2.73	1.65	1.84
0.40	1.82	4.76	2.80	2.86
0.40	1.98	3.90	2.50	2.98
0.40	3.64	5.14	5.60	5.75
0.40	1.54	0.172	1.00	1.13
0.40	2.37	0.174	1.55	1.72
0.40	4.00	0.0866	2.70	2.66
0.40	4.74	0.178	2.90	3.35
0.40	6.72	0.181	4.00	4.64
0.40	8.00	0.0884	4.90	5.04
0.30	0.66	2.79	1.16	1.17
0.30	0.97	1.98	1.93	1.61
0.30	1.32	2.90	2.10	2.34
0.30	1.54	0.172	1.90	1.75
0.30	1.54	1.70	2.10	2.47
0.30	2.28	0.353	2.22	2.73
0.30	4.78	0.891	6.90	6.38
0.30	4.85	1.98	8.52	7.67
0.30	9.70	1.99	14.3	14.5
0.30	19.4	2.01	30.3	26.1
0.25	2.28	0.353	34.1	34.9
0.20	0.66	0.343	1.56	1.45
0.20	0.66	2.98	1.68	1.68
0.20	0.66	4.51	1.68	1.73
0.20	0.91	6.13	2.30	2.43
0.20	0.95	2.00	2.81	2.33
0.20	1.12	0.346	2.40	2.41
0.20	1.32	3.10	3.70	3.32
0.20	1.54	1.75	3.20	3.67
0.20	1.82	6.42	4.90	4.81
0.20	1.90	2.02	4.95	4.54
0.20	1.98	4.87	4.40	5.12
0.20	2.28	0.174	4.70	4.52
0.20	2.28	0.354	4.70	4.68
0.20	3.64	6.98	9.25	9.47
0.20	3.73	2.93	9.80	8.90
0.20	3.73	3.96	10.4	9.20
0.20	3.73	4.97	10.7	9.41
0.20	3.73	5.83	10.2	9.55
0.20	3.73	6.04	11.3	9.58
0.20	3.80	2.00	9.65	8.67
0.20	4.00	0.0866	8.80	7.31
0.20	4.56	0.368	8.30	8.61
0.20	4.76	1.98	11.1	10.6
0.20	5.71	1.96	12.6	12.4
0.20	6.66	1.96	14.3	14.2
0.20	7.65	1.96	15.1	15.9
0.20	8.00	0.0884	14.2	12.6
0.20	8.56	1.96	16.2	17.5
0.20	9.32	0.951	15.6	16.7
0.20	9.51	1.96	17.0	19.0
0.20	18.8	1.90	32.9	31.2
0.20	28.2	1.88	39.2	39.9
0.10	0.66	3.23	3.80	3.14
0.10	0.91	8.02	4.50	3.97
0.10	1.67	1.81	8.90	7.79
0.10	1.82	8.45	8.20	7.70
0.10	1.98	5.82	8.30	8.49
0.10	2.08	1.67	1.39	1.09
0.10	2.28	0.174	13.9	10.8
0.10	2.28	3.54	12.7	10.7
0.10	2.50	1.89	9.50	11.0
0.10	3.00	1.94	10.3	12.7
0.10	3.57	0.176	15.1	14.8
0.10	3.64	9.29	13.4	14.6
0.10	4.00	0.0429	21.0	16.0
0.10	4.00	0.0866	18.8	16.0
0.10	4.56	0.368	18.1	17.4
0.10	4.82	2.91	21.5	18.5
0.10	4.82	3.85	21.4	18.5
0.10	4.82	6.02	20.0	18.7
0.10	4.82	8.06	21.2	18.8
0.10	4.82	10.00	21.5	18.8
0.10	4.83	1.95	20.2	18.4
0.10	6.24	2.31	18.6	22.1
0.10	7.25	0.182	22.0	22.5
0.10	8.00	0.0884	23.0	23.4
0.10	9.66	1.99	30.4	28.8
0.10	14.3	0.196	26.0	29.8
0.10	19.3	1.95	40.3	40.1
0.10	19.8	6.64	13.6	13.2
0.05	1.98	6.64	13.6	13.2
0.05	2.28	0.174	23.0	19.9
0.05	2.28	0.354	22.0	19.6
0.05	2.94	2.01	22.7	20.5
0.05	4.00	0.0866	25.0	26.0
0.05	4.56	0.368	26.0	27.2
0.05	4.90	1.97	27.3	27.3
0.05	8.00	0.0884	30.0	32.4
0.05	9.80	2.00	34.8	36.3
0.05	19.6	2.00	43.6	43.5
0.025	2.28	0.354	30.0	28.3
0.025	2.28	0.174	28.0	28.7
0.010	1.54	1.85	28.0	30.8

[a] $(Cr(II))_0$ in the range (0.04–1.06) × 10^{-3} M. [b] k_{calcd} from eq 8 using the values of the parameters obtained from a nonlinear least squares fit of the data (see text).

0.5, and 0.1 M, respectively, provided $[H_2O_2]_0 \leq 1 \times 10^{-3}$ M. At much higher hydrogen peroxide concentrations (5×10^{-2} M) and hydroxide ion concentrations of about 0.01 M, chromate is the major product of the oxidation.

When the oxidation was carried out at low hydroxide ($\sim 10^{-3}$ M) and high cyanide (0.04 M) concentrations, the spectrum of the oxidized solution exhibited a maximum at 264 nm, which is also an absorbance maximum of $Cr(CN)_6^{3-}$. The absorbances at this wavelength indicate either that $Cr(CN_6)^{3-}$ is formed in at least 60% yield under these conditions, or that chromium(III) species having spectra very similar to that of $Cr(CN)_6^{3-}$ are formed in high yield. The first interpretation is preferred in view of the results on this system obtained by Haim and Wilmarth,[9] and this interpretation finds further support from the kinetic measurements described below. Absorbance measurements at 263 nm indicate that the yield of $Cr(CN)_6^{3-}$ is less than 50% when the oxidation is carried at high hydroxide (0.4 *M*) and low cyanide (0.1 *M*) concentrations.

Rate Measurements. The observed pseudo-first-order rate constants for the disappearance of chromium(II) are summarized in Table I. The rates increase with decreasing cyanide ion and with increasing hydrogen peroxide concentrations. The kinetic data are consistent with the following mechanism.

$$Cr(CN)_5H_2O^{3-} + CN^- \rightleftharpoons Cr(CN)_6^{4-} + H_2O \qquad K_1 \qquad (1)$$

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad K_a \qquad (2)$$

$$Cr(CN)_6^{4-} + H_2O_2 \xrightarrow{k_0} Cr(CN)_6^{3-} + OH + OH^- \qquad (3)$$

$$Cr(CN)_5H_2O^{3-} + H_2O_2 \xrightarrow{k_1} Cr(CN)_5OH^{3-} + OH + H_2O \qquad (4)$$

$$Cr(CN)_5H_2O^{3-} + HO_2^- \rightleftharpoons [\text{complex}]^{3-} + CN^- \qquad K_c \qquad (5)$$

$$[\text{complex}]^{3-} \xrightarrow{k_2} \text{products} \qquad (6)$$

$$Cr(II) + OH \longrightarrow Cr(III) + OH^- \qquad (7)$$

The above mechanism yields the following expression for the observed pseudo-first-order rate constants.

$$k_{obsd} = \frac{2[H_2O_2]_T(k_0K_1[CN^-] + k_1 + k_2K_cK_a/[H^+][CN^-])}{(1 + K_a/[H^+])(1 + K_1[CN^-]) + K_cK_a[H_2O_2]_T/[H^+][CN^-]} \qquad (8)$$

The kinetic data were fitted to eq 8 using a nonlinear least squares program.[18] The values of the rate constants calculated by the program are included in Table I. Agreement between the observed and calculated rate constants is satisfactory over the very wide concentration range used. The values of the parameters and their standard deviations calculated by the program are $K_1 = (9.55 \pm 0.03)\ M^{-1}$, $k_0 = (3.29 \pm 0.36) \times 10^2\ M^{-1}\ sec^{-1}$, $k_1 = (3.57 \pm 0.16) \times 10^3\ M^{-1}\ sec^{-1}$, $K_c = (2.95 \pm 0.19) \times 10^1$, and $k_2 = (2.13 \pm 0.10) \times 10^1\ sec^{-1}$.

The limiting form of eq 8 at low hydrogen ion concentrations is

$$k_{obsd} = \frac{2k_2K_cK_a[H_2O_2]_T/[H^+][CN^-]}{(1 + K_a/[H^+])(1 + K_1[CN^-]) + K_cK_a[H_2O_2]_T/[H^+][CN^-]} \qquad (9)$$

which can be arranged to give

$$1/k_{obsd} = \alpha/2k_2K_c + 1/2k_2 \qquad (10)$$

where $\alpha = \{[CN^-](1 + K_1[CN^-])(1 + [H^+]/K_a)\}/[H_2O_2]_T$. A plot of $1/k_{obsd}$ *vs.* α is presented in Figure 1. The slope and intercept of this plot yield the values $K_c = (3.3 \pm 0.3) \times 10^1$ and $k_2 = (2.2 \pm 0.2) \times 10^1\ sec^{-1}$, which are in good agreement with the computer-generated values considering the drastically different weighting factors used in the two treatments.

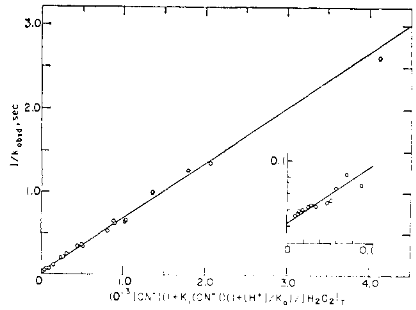

Figure 1. Plot of $1/k_{obsd}$ *vs.* $[CN^-](1 + K_1[CN^-])(1 + [H^+]/K_a)/[H_2O_2]_T$ for the kinetic data satisfying the conditions of eq 10.

The above mechanism predicts that very little $Cr(CN)_6^{3-}$ should be formed when the oxidation is carried out at high hydroxide and low cyanide ion concentrations. Although detailed product analyses were not performed under these conditions, the spectra of the unseparated reaction products indicate that $Cr(CN)_6^{3-}$ is not the major product of the oxidation under conditions where eq 9 and 10 obtain.

Discussion

At sufficiently low hydroxide and high cyanide ion concentrations the reaction between chromium(II) and hydrogen peroxide proceeds predominantly by reactions 3 and 4. Evidently both $Cr(CN)_6^{4-}$ and $Cr(CN)_5H_2O^{3-}$ react much more rapidly with H_2O_2 than with HO_2^-. An analogous situation obtains in the oxidation of cobalt(II), where it has been found that H_2O_2, but not HO_2^-, reacts with $Co(CN)_5^{3-}$.[19] The rate constants for these reactions are compared in Table II. The reaction of H_2O_2 with $Cr(CN)_6^{4-}$ almost certainly proceeds by an outer-sphere mechanism.[9] By contrast, an inner-sphere mechanism has been proposed[19] for the reaction of H_2O_2 with $Co(CN)_5^{3-}$. This reaction may be written in terms of the formation

Table II. Second-Order Rate Constants[a] for the Reduction of Hydrogen Peroxide at 25.0° and Ionic Strength 1.0 *M*

Reductant	*k*, $M^{-1}\ sec^{-1}$	*E*°, V	Ref
$Cr(CN)_6^{4-}$	3.3×10^2	−1.14	*b*
$Cr(CN)_5H_2O^{3-}$	3.6×10^3		*b*
$Co(CN)_5^{3-}$	7.4×10^2	≤−0.81	*c, d*
$Fe(H_2O)_6^{2+}$	5.8×10^1	+0.73	*e*
$Cr(H_2O)_6^{2+}$	2.1×10^3	−0.41	*f, g*

[a] The rate constants are defined by d ln (reductant)/d*t* = $-2k \cdot [H_2O_2]$. [b] This work. [c] Reference 19, ionic strength 0.5 *M*. [d] D. N. Hume and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 71, 867 (1949). [e] H. N. Po and N. Sutin, *Inorg. Chem.*, 7, 621 (1968). [f] This reaction proceeds by parallel one- and two-equivalent paths. The rate constant presented in the table was calculated from $0.693/0.14[H_2O_2]t_{1/2}$, where $t_{1/2}$ is the half-time for the formation of the chromium(III) dimer at 250 nm in 1.0 *M* perchloric acid. The dimer typically contains 14% of the total chromium(III) (ref 27). Evidently the one-equivalent path predominates under ordinary conditions (1.0 *M* perchloric acid and excess hydrogen peroxide). [g] G. Davies and N. Sutin, unpublished observations.

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(18) The computer program was based on the Los Alamos Scientific Laboratory Reports LA-2367 by R. H. Moore and R. K. Zeigler, 1959, and LA-2367 Addenda by P. McWilliams, 1962. This program was generously supplied by Dr. T. W. Newton. Each rate constant was weighted according to the reciprocal of its square since the percentage error in k_{obsd} was approximately constant.

(19) P. B. Chock, R. B. K. Dewar, J. Halpern, and L.-Y. Wong, *J. Amer. Chem. Soc.*, 91, 82 (1969).

of a precursor complex as follows.

$$Co(CN)_5^{3-} + H_2O_2 \rightleftharpoons [Co(CN)_5H_2O_2]^{3-} \qquad (11)$$

$$[Co(CN)_5H_2O_2]^{3-} \longrightarrow Co(CN)_5OH^{3-} + OH \qquad (12)$$

$$Co(CN)_5^{3-} + OH \xrightarrow{\text{rapid}} Co(CN)_5OH^{3-} \qquad (13)$$

$Co(CN)_5^{3-}$ is a low-spin, square-pyramidal d^7 complex with the donor electron in the d_{z^2} orbital,[20] whereas $Cr(CN)_6^{4-}$ is a low-spin, octahedral d^4 complex with the donor electron in a t_{2g} orbital. The lone electron in the d_{z^2} orbital of $Co(CN)_5^{3-}$ evidently repels an entering group, or, put somewhat differently, there is a considerable loss of stabilization energy when the low-spin d^7 complex goes from a square-pyramidal to an octahedral configuration. In any event, $Co(CN)_5^{3-}$ shows little tendency to add a sixth ligand.[21] However, despite the differences in the structures and properties of $Co(CN)_5^{3-}$ and $Cr(CN)_6^{4-}$, the rate constants for the reaction of H_2O_2 with $Co(CN)_5^{3-}$ (inner-sphere) and $Cr(CN)_6^{4-}$ (outer-sphere) are remarkably similar. This similarity may well be due to a fortuitous cancellation of effects. If such a cancellation is not responsible for the similarity of the rate constants, then the similar rates imply that a comparable amount of reorganization takes place around the two metal centers prior to the electron transfer, that the oxygen–oxygen bond in hydrogen peroxide is stretched by the same amount in the transition state for the two reactions (because of the instability of $H_2O_2^-$, the products of the reaction between $Cr(CN)_6^{4-}$ and H_2O_2 are taken to be $Cr(CN)_6^{3-}$, OH, and OH^-),[23] and that the effective driving forces for the two reactions are comparable, a requirement which is consistent with estimates of the free energy changes for the reactions.[24]

The relatively rapid rate of the reaction between H_2O and $Cr(CN)_5H_2O^{3-}$ suggests that this reaction, too, proceeds by an inner-sphere mechanism.

$$Cr(CN)_5H_2O^{3-} + H_2O_2 \rightleftharpoons [Cr(CN)_5H_2O_2]^{3-} + H_2O \qquad K_b$$

$$[Cr(CN)_5H_2O_2]^{3-} \xrightarrow{k_3} Cr(CN)_5OH^{3-} + OH$$

The kinetic data give $K_b \leqslant 20\ M^{-1}$ and $k_3 \geqslant 1.8 \times 10^2\ sec^{-1}$. As discussed above, the electron-transfer step in the inner-sphere reduction of hydrogen peroxide is about 5.3 kcal mol^{-1} more favorable than in the corresponding outer-sphere reduction. In addition, the inner-sphere reaction is favored by the thermodynamic stability of the $M(CN)_5OH^{3-}$ products. Similar considerations show that the stability of the products has a particularly large effect on the rate of oxidation of the aquo ions $Cr(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{2+}$.

The reactions of H_2O_2 with $Fe(H_2O)_6^{2+}$ and with $Cr(H_2O)_6^{2+}$ proceed predominantly by one-equivalent paths.[26,27] As is evident from the rate constants for these reactions presented in Table II, H_2O_2 reacts more rapidly with $Cr(H_2O)_6^{2+}$ than with $Fe(H_2O)_6^{2+}$. This reactivity difference is expected on the baisis of free energy considerations. However, at first sight it appears somewhat surprising that H_2O_2 reacts more rapidly with $Cr(H_2O)_6^{2+}$ than with $Cr(CN)_6^{4-}$, despite the much more negative reduction potential of the cyanide couple.[28] The enhanced reactivity of $Cr(H_2O)_6^{2+}$, and also $Fe(H_2O)_6^{2+}$, can be rationalized if, as seems reasonable, the aquo ions react by inner-sphere mechanisms, and the primary products of these reactions are the very stable $(H_2O)_5MOH^{2+}$ complexes rather than $M(H_2O)_6^{3+}$ ions.

$$M(H_2O)_6^{2+} + H_2O_2 \rightleftharpoons [M(H_2O)_5H_2O_2]^{2+} + H_2O$$

$$[M(H_2O)_5H_2O_2]^{2+} \longrightarrow M(H_2O)_5OH^{2+} + OH$$

Under these conditions the couples for the aquo ions are

$$MOH^{2+} + e = M^{2+} + OH^-$$

rather than

$$M^{3+} + e = M^{2+}$$

In terms of this interpretation the effective reduction potentials of the chromium(II)–chromium(III) and iron(II)–iron(III) couples are −0.99 and +0.08 V (calculated from values of $1.1 \times 10^{-4}\ M$ and $1.7 \times 10^{-3}\ M$ for the hydrolysis constants of $Cr(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$), respectively.[29-32] The potential of

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(20) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3356 (1967).

(21) It has been estimated[22] that the equilibrium constant for the reaction $Co(CN)_5^{3-} + CN^- \rightleftharpoons Co(CN)_6^{4-}$ lies in the range 10^{-1} to $10^{-4}\ M^{-1}$.

(22) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, **85**, 2517 (1963).

(23) In terms of this interpretation the symmetry of the donor orbital has but a small effect on the reaction rate.

(24) The effective driving force for the reaction is $\Delta G_r°$, the free energy change for the reaction when the two reactants are a distance r apart, rather than $\Delta G°$, the standard free energy change when the reactants are infinitely far apart.[25] In the systems being discussed it is necessary to correct $\Delta G°$ for any differences in the number of particles produced in the rate-determining step. In order to put all the systems on the same basis it is convenient to write the reaction between $Cr(CN)_6^{4-}$ and H_2O_2 in terms of the formation of a precursor complex.

$$Cr(CN)_6^{4-} + H_2O_2 \rightleftharpoons [Cr(CN)_6||H_2O_2]^{4-}$$

$$[Cr(CN)_6||H_2O_2]^{4-} \longrightarrow Cr(CN)_6^{3-} + OH + OH^-$$

Evidently three particles are produced from one particle in the electron-transfer step, and it is therefore necessary to increase the value of $\Delta G°$ for this step (that is, it is necessary to make the driving force for the actual electron-transfer step less favorable) by the translational energy of two particles, which amounts to 0.46 V or 10.6 kcal mol^{-1}. Similarly, it is necessary to increase the value of $\Delta G°$ for the electron-transfer step in the reaction of H_2O_2 with $Co(CN)_5^{3-}$ by 0.23 V or 5.3 kcal mol^{-1}. These considerations thus make the driving force for the outer-sphere reaction some 5.3 kcal mol^{-1} less favorable than for the analogous inner-sphere reaction, all other factors being equal. In a more detailed treatment allowance should be made for the rotational freedom of OH and OH^- in the activated complex for the reaction, but this correction is expected to be smaller than the translational energy correction. The above discussion assumes, of course, that $Cr(CN)_6^{3-}$, OH, and OH^-, rather than $Cr(CN)_6^{3-}$ and $H_2O_2^-$, are the primary products of the reaction of H_2O_2 with $Cr(CN)_6^{4-}$. Note that when all the reactions compared are already on the same basis (for example, two particles → two particles), then there is no advantage in writing the reaction in two steps, except, perhaps when the precursor complexes have very different stabilities.

(25) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

(26) T. J. Conocchioli, E. J. Hamilton, and N. Sutin, *J. Amer. Chem. Soc.*, 87, 926 (1965).

(27) M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1959).

(28) Although the reaction of H_2O_2 with $Cr(H_2O)_6^{2+}$ was run in acidic solution while the reaction of H_2O_2 with $Cr(CN)_6^{4-}$ was studied in basic solution, a direct comparison of the rates of these reactions can be made despite the fact that the formal potential of the hydrogen peroxide couple is a function of pH. The reason that such a comparison is valid is that the reaction rates are related to the free energy changes for the actual electron transfer steps and not to the free energy changes for the overall reactions.

(29) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

(30) R. M. Milburn and W. C. Vosburgh, *J. Amer. Chem. Soc.*, 77, 1352 (1955).

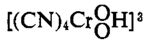
(31) The equilibrium constant for the reaction $Co(CN)_5H_2O^{2-} \rightleftharpoons Co(CN)_5OH^{3-} + H^+$ is $2 \times 10^{-10}\ M$ at 40°.[32] Note that as expected the hydrolysis constants of the soft ions $Co(CN)_5H_2O^{2-}$ and $Cr(CN)_5H_2O^{2-}$ are much smaller than the hydrolysis constants of the hard ions $Cr(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$. Consequently the oxidation of the soft ions benefits less than the oxidation of the hard ions from the formation of hydroxide complexes as products.

(32) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1, 573 (1962).

the $Cr(H_2O)_6^{2+}/Cr(H_2O)_5OH^{2+}$ couple is seen to lie close to that for the $Cr(CN)_6^{4-}/Cr(CN)_6^{3-}$ couple, and indeed the aquo system becomes the better reducing agent once allowance is made for the 0.23 V favoring the inner-sphere reduction of hydrogen peroxide.[33] To summarize, the pattern of the reactivity of H_2O_2 with $Cr(CN)_6^{4-}$, $Cr(CN)_5H_2O^{3-}$, and $Cr(H_2O)_6^{2+}$ follows the order expected from a consideration of the effective driving forces for the reactions.[34]

Although the reactions of $Cr(CN)_6^{4-}$ and of $Cr(CN)_5H_2O^{3-}$ with H_2O_2 have been written as one-equivalent changes, the kinetic data are equally consistent with a two-equivalent scheme involving the formation of chromium(IV). Mild support for the one-equivalent interpretation is provided by the stoichiometric data. If it is assumed that the hydroxyl radical does not discriminate between $Cr(CN)_6^{4-}$ and $Cr(CN)_5H_2O^{3-}$, and that the ratio k_0/k_1 does not change on going from $[CN^-] = 1\ M$ to $[CN^-] = 5\ M$, then the yield of $Cr(CN)_6^{3-}$ in $[CN^-] = 5\ M$ is calculated to be 90%, which is consistent with the 78% yield found by Haim and Wilmarth.[9] On the other hand, the chromium(IV) species produced in a two-equivalent change would be substitution-labile, and they could undergo ligand replacement reactions which might lead to a lower yield of $Cr(CN)_6^{3-}$. These considerations are admittedly speculative and detailed product analyses (which are very difficult to obtain in this system) are required before a distinction between a one-equivalent and a two-equivalent mechanism can be made with confidence. Fortunately, as mentioned above, there is independent evidence that at least in some systems H_2O_2 reacts preferentially as a one-equivalent oxidant.

Another interesting feature of this study is the evidence obtained for the formation of a relatively stable complex between chromium(II) and peroxide at low cyanide and high hydroxide ion concentrations. This is shown in eq 5 and 6. Comparison of the values of k_2 and k_3 reflects the stability of the complex with respect to intramolecular electron transfer. In view of its stability it seems reasonable to ascribe to the complex a structure in which the two chromium–oxygen distances are similar.



$$[(CN)_4Cr\genfrac{}{}{0pt}{}{O}{O}H]^{3-}$$

The proposed mode of attachment of the oxygen atoms has some similarities to the coordination of peroxide in other transition metal complexes.[35] The observation that chromate is formed when the oxidation is carried out at higher hydroxide and peroxide ion concentrations is consistent with the formation of chromium complexes containing less than four coordinated cyanide ions under these conditions.

Finally, the observation that $Cr(CN)_6^{3-}$ is formed in good yield in the reaction of oxygen with $Cr(CN)_6^{4-}$ while dimeric products are produced in the reaction of aqueous and ammoniacal solutions of chromium(II) with oxygen, has provoked much discussion concerning the importance of such factors as spin states, the "conductivity" of the ligands, and the symmetry of the donor orbitals in these systems.[9,36,37] The rate laws for the oxidation of the various chromium(II) complexes are undoubtedly very complicated, and it may therefore be unwise to attempt further speculation about the mechanisms of these reactions at this time. The results of the present study do nevertheless show that despite the formation of $Cr(CN)_6^{3-}$ at high cyanide concentrations, an inner-sphere mechanism provides the preferred pathway for the reaction of the chromium(II)–cyanide complexes with hydrogen peroxide. Moreover, the free energy considerations show that the driving force for the rate-determining step is not related in any simple manner to the overall free energy change for reactions in which bonds are broken and/or more than one equivalent is transferred.

Acknowledgment. It is a pleasure to acknowledge helpful discussions of the free energy considerations with Professor R. A. Marcus.

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[33] Additional rate variations can arise from differences in the stabilities of the precursor complexes.

[34] The observation that H_2O_2 reacts much more rapidly with Fe^{2+} than with $Fe(CN)_6^{4-}$ can similarly be understood if $FeOH^{2+}$ rather than Fe^{3+} is the primary iron(III) product of the former reaction.

[35] J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964).

[36] N. Sutin in "Oxidases and Related Redox Systems," T. E. King, H. S. Mason, and M. Morrison, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p 37.

[37] H. Taube, *J. Gen. Physiol.*, **49**, 29 (1966).