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Contribution from The Laboratory of Analytical Chemistry, Faculty of Science,
Nagoya University, Nagoya, 464 Japan

Reactions of Hydrogen Peroxide with Metal Complexes.[1] 3. Thermodynamic and Kinetic Studies on the Formation, Dissociation, and Decomposition of Peroxochromium(VI) Complexes in Acid Media

SHIGENOBU FUNAHASHI, FUMIO UCHIDA, and MOTOHARU TANAKA*

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The stoichiometry and kinetics of the formation and dissociation of the peroxochromium(VI) complex, so-called perchromic acid, and of the decomposition of the latter to yield Cr(III) have been studied spectrophotometrically by using a stopped-flow technique at an ionic strength of 3.0 M (H, $\mathrm{NaClO_4}$) over the range of hydrogen ion concentration 0.01–3.0 M at temperatures between 15 and 35 °C. The formation constant of chromic acid is $K^{\mathrm{H}} = [\mathrm{H_2CrO_4}][\mathrm{HCrO_4}^-]^{-1}[\mathrm{H}^+]^{-1} = 0.16 \pm 0.02\ \mathrm{M}^{-1}$ (25 °C) ($\Delta H = 0 \pm 1\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = -15 \pm 2\ \mathrm{J\ K^{-1}\ mol^{-1}}$). The measurement of evolved oxygen gas confirmed the following stoichiometry: $2\mathrm{HCrO_4}^- + 8\mathrm{H}^+ + 3\mathrm{H_2O_2} \rightleftharpoons 2\mathrm{Cr}^{3+} + 3\mathrm{O_2} + 8\mathrm{H_2O}$. The stoichiometry for the formation of the oxodiperoxochromium(VI) complex is consistent with the expression: $\mathrm{HCrO_4}^- + \mathrm{H}^+ + 2\mathrm{H_2O_2} \rightleftharpoons \mathrm{CrO(O_2)_2} + 3\mathrm{H_2O}$ with $K_{\mathrm{f}} = [\mathrm{CrO(O_2)_2}][\mathrm{HCrO_4}^-]^{-1}[\mathrm{H}^+]^{-1}[\mathrm{H_2O_2}]^{-2} = (2.0 \pm 0.2) \times 10^7\ \mathrm{M}^{-3}$ (25 °C) and the corresponding thermodynamic parameters $\Delta H = -58 \pm 10\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = -55 \pm 30\ \mathrm{J\ K^{-1}\ mol^{-1}}$. The protonation constant of the oxodiperoxochromium(VI) complex was determined to be $0.15 \pm 0.02\ \mathrm{M}^{-1}$ (25 °C) ($\Delta H = 27 \pm 10\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = 76 \pm 35\ \mathrm{J\ K^{-1}\ mol^{-1}}$). The formation rate of the peroxochromium(VI) complexes is expressed as $\mathrm{d}[\mathrm{CrO_5}']/\mathrm{d}t = k_1[\mathrm{H_2CrO_4}][\mathrm{H_2O_2}] - k_{-1}'[\mathrm{CrO(O_2)_2}][\mathrm{H_2O_2}]^{-1}$, where $[\mathrm{CrO_5}']$ indicates the sum of the concentrations of $\mathrm{CrO(O_2)_2}$ and $\mathrm{Cr(OH)(O_2)_2}^+$, k_1 (25 °C) $= (9.3 \pm 0.2) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ ($\Delta H_1^\ddagger = 17 \pm 1\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S_1^\ddagger = -93 \pm 5\ \mathrm{J\ K^{-1}\ mol^{-1}}$), and a rate constant for the reverse reaction, i.e., dissociation of the peroxochromium(VI) $k_{-1}'(25\ °\mathrm{C}) = (6.1 \pm 0.2) \times 10^{-4}\ \mathrm{M\ s^{-1}}$ ($\Delta H_{-1}^\ddagger = 80 \pm 5\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S_{-1}^\ddagger = -36 \pm 20\ \mathrm{J\ K^{-1}\ mol^{-1}}$). The rate law for decomposition of the peroxochromium(VI) complexes is $-\mathrm{d}[\mathrm{CrO_5}']/\mathrm{d}t = k_2[\mathrm{CrO(O_2)_2}][\mathrm{H}^+] + k_3[\mathrm{Cr(OH)(O_2)_2}^+][\mathrm{H}^+]$ with $k_2(25\ °\mathrm{C}) = 0.25 \pm 0.02\ \mathrm{M^{-1}\ s^{-1}}$ ($\Delta H_2^\ddagger = 81 \pm 5\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S_2^\ddagger = 17 \pm 15\ \mathrm{J\ K^{-1}\ mol^{-1}}$) and $k_3(25\ °\mathrm{C}) = 1.8 \pm 0.3\ \mathrm{M^{-1}\ s^{-1}}$ ($\Delta H_3^\ddagger = 73 \pm 15\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S_3^\ddagger = 6 \pm 50\ \mathrm{J\ K^{-1}\ mol^{-1}}$). Mechanisms for the formation and decomposition of the peroxochromium(VI) complexes are presented and discussed.

Introduction

Although there have been numerous studies on transition-metal peroxides,[2] the kinetic behavior of the peroxy species has been little investigated. Peroxides, besides having an intrinsic interest of their own, are of considerable and growing importance in relation to the catalytic oxidation involving hydrogen peroxide or dioxygen, the catalytic decomposition of hydrogen peroxide itself, and the storage and use of oxygen in biological systems.

The decomposition of hydrogen peroxide by chromium(VI) species occurs over a wide range of pH.[3-5] Especially, it has been well-known that when chromic acid solutions are treated with hydrogen peroxide, a deep blue color rapidly appears but does not persist long. In acid solution, complexity arises, not only because of the protonation of $\mathrm{CrO_4}^{2-}$ giving rise to $\mathrm{HCrO_4}^-$ and $\mathrm{H_2CrO_4}$ but also because of the condensation of chromium(VI) anions yielding dichromate and possibly larger condensed molecules. Furthermore, the reduction of chromium(VI) by hydrogen peroxide at various concentration levels can lead to greater complexity.

We have studied the reaction of hydrogen peroxide with chromium(VI) at the chromium concentration as low as possible and at the large excess hydrogen peroxide concentration in order to avoid complexity of the reaction. We have also elucidated the protonation equilibria of $\mathrm{HCrO_4}^-$, the stoichiometry of blue perchromic acid formation, and the overall reaction of hydrogen peroxide and hydrogen chromate anion.

Experimental Section

Reagents. Chromic acid solutions were prepared by dissolving primary standard grade potassium dichromate which was dried for 3 h at 110 °C. Sixty percent hydrogen peroxide containing no stabilizing agent (Mitsubishi Edogawa Kagaku Co., Tokyo, Japan) was distilled under reduced pressure. The stock solutions of about 10^{-2} M hydrogen peroxide were standardized with a standard potassium permanganate solution. A spontaneous decomposition of ca. 10^{-2} M hydrogen peroxide at room temperature was ca. 0.5% for 1 month. Reagent grade perchloric acid was used for perchloric acid solutions which were standardized by titration against weighed quantities of sodium carbonate. Sodium perchlorate was prepared by neutralizing reagent grade 60% perchloric acid with reagent grade sodium carbonate. Impurities of heavy-metal ions in the sodium perchlorate solution were removed together with active carbon as hydroxides at pH 8.5. Sodium perchlorate was then recrystallized twice from distilled water.

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Measurements. A highly sensitive spectrophotometer (SM 401, Union Giken, Osaka, Japan) was used for spectral measurements. The spectrophotometer enabled us to measure spectra at full scale of 0.01 optical density. Reactions were followed spectrophotometrically by means of a stopped-flow technique using a Union Giken RA-401 stopped-flow spectrophotometer with the drive syringes and the mixing chamber thermostated to within ±0.2 °C. Experiments were carried out using a 1.00-cm flow-through cell, the dead time being ca. 5 ms. Transmission curves for reactions were stored in a transient recorder (SM-450, Union Giken), the curves being monitored with a synchroscope (V-018 Memoriscope, Hitachi, Tokyo, Japan) and displayed on an X-Y recorder. Mostly the reactions were followed at 580 nm, the wavelength of the maximum absorption for the oxodiperoxochromium(VI) complex, where the absorbance from all species except for peroxochromium(VI) complexes is negligible. Some runs performed at some other wavelengths gave consistent results. The kinetic runs were carried out under pseudo-first-order conditions, hydrogen peroxide being in large excess over chromium(VI). First-order kinetic plots were linear to greater than 90% completion of reaction. Duplicate measurements gave results in agreement within ±2%. Ionic strength was maintained at 3.0 M with sodium perchlorate and perchloric acid. Hydrogen ion concentration (0.01–3.0 M) was so high that the change of hydrogen ion concentration during reactions was negligible in the absence of any buffer. At very high acidity solutions of chromium(VI) were reported to change slowly to chromium(III).[6] In our case, however, no change in absorbance was observed during 24 h.

The evolved oxygen was measured using a Beckman Fieldlab Oxygen Analyzer with a polarographic oxygen electrode (Beckman Instrument Co., Model 39550) which was sealed from the atmosphere. The oxygen electrode was calibrated before and after each oxygen determination by using air-saturated water at 25.0 ± 0.1 °C. Calibration before and after the oxygen determination was reproducible to within ±2% of full scale. The oxygen concentration in air-saturated water at 25 °C was determined to be 2.52 × 10^{-4} M by both the Winkler method[7] and the Asahina method.[8] The value is in good agreement with the literature value[9] (2.54 × 10^{-4} M).

ESR spectra were recorded with a Japan Electron Optics Laboratory Co., Ltd., spectrometer (Model JES-ME-1X) in X-band frequencies employing 100-kHz field modulation. Under conditions where the half-life time of decomposition of the oxodiperoxochromium(VI) complex was several minutes, we were able to follow ESR spectra of reacting solutions from 1 min after the start of reactions.

Results

Formation Constant of Chromic Acid. It is expected, from known values of the dimerization constant of $HCrO_4^-$, that when the total Cr(VI) concentration is 8 × 10^{-5} M, as in the case in most of this work, more than 98% Cr(VI) exists as monomeric chromium(VI).[10] Therefore the dimerization of monomeric Cr(VI) need not be taken into account in the present study. It is thus possible to study directly the equilibrium

$$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4 \qquad (1)$$

by following changes in absorption spectra. The formation constant of H_2CrO_4 was determined from the apparent molar absorption coefficient $\bar{\epsilon}$ of monomeric Cr(VI) at different hydrogen ion concentrations:

$$K^H = \frac{[H_2CrO_4]}{[HCrO_4^-][H^+]} = \frac{\epsilon_1 - \bar{\epsilon}}{(\bar{\epsilon} - \epsilon_2)[H^+]} \qquad (2)$$

$$\bar{\epsilon} = \frac{\epsilon_1[HCrO_4^-] + \epsilon_2[H_2CrO_4]}{[HCrO_4^-] + [H_2CrO_4]} = \frac{\epsilon_1 + \epsilon_2[H^+]K^H}{1 + [H^+]K^H} \qquad (3)$$

where ϵ_1 and ϵ_2 are the molar absorption coefficients of $HCrO_4^-$ and H_2CrO_4, respectively. Rearranging eq 2, we have

$$\frac{[H^+]}{\epsilon_1 - \bar{\epsilon}} = \frac{1}{\epsilon_1 - \epsilon_2}[H^+] + \frac{1}{(\epsilon_1 - \epsilon_2)K^H} \qquad (4)$$

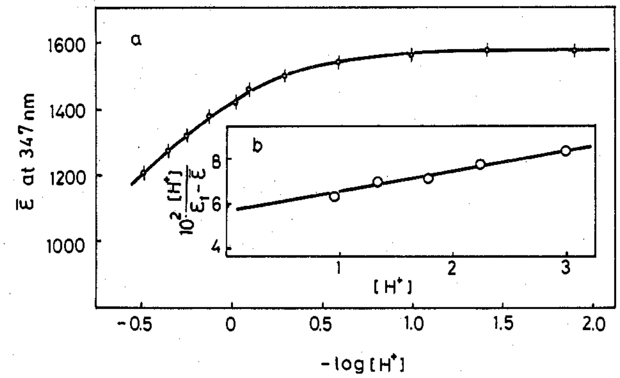

Figure 1. Determination of the formation constant of H_2CrO_4 at I = 3.0 M and 25 °C: (a) dependence of apparent molar absorption coefficient $\bar{\epsilon}$ on −log [H^+]; (b) plot according to eq 4 for the protonation of $HCrO_4^-$. Vertical lines indicate the range of error. The solid curve is calculated with the constants obtained.

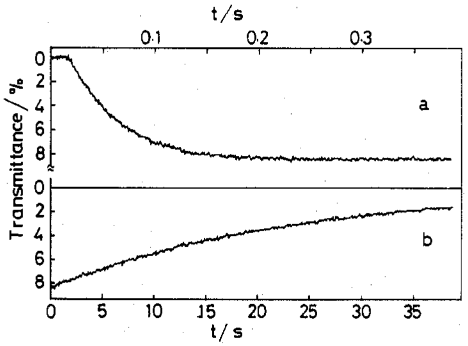

Figure 2. Stopped-flow trace showing (a) formation and (b) decomposition of blue perchromic acid (C_{Cr} = 8.00 × 10^{-5} M, $C_{H_2O_2}$ = 7.82 × 10^{-3} M, [H^+] = 2.21 × 10^{-1} M, I = 3.0 M, 25 °C, 580 nm).

The plot of $\bar{\epsilon}$ vs. −log [H^+] according to eq 3 is shown in Figure 1a. Figure 1b shows the plot according to eq 4. We obtained ϵ_1 = 1570, ϵ_2 = 460, and K^H = 0.16 ± 0.02 M^{-1} at I = 3.0 M and 25 °C, which agrees with the value obtained by Haight et al.[6] (0.19 M^{-1}). Data at 20, 30, and 35 °C do not differ from the value at 25 °C within experimental errors indicated with vertical lines in Figure 1a. Thermodynamic parameters were thus estimated as $\Delta H = 0 \pm 1$ kJ mol^{-1} and $\Delta S = -15 \pm 2$ J K^{-1} mol^{-1}.

Formation Equilibria of the Oxodiperoxochromium(VI) Complex. In the reaction of hydrogen chromate anion with hydrogen peroxide in acidic solution, the formation of the intermediate species, so-called blue perchromic acid, was sufficiently fast as compared to the subsequent decay: the absorbance maximum observed in traces obtained at 580 nm may reasonably be assumed to correspond to a state of equilibrium between reactants and intermediates (see Figure 2). When [H_2O_2] increased at constant C_{Cr} and [H^+], $\bar{\epsilon}$ did not increase beyond a limiting value which was directly proportional to C_{Cr}. All the Cr(VI) may thus be regarded as being present as an intermediate at equilibrium. The molar absorption coefficient of the intermediate was 530 ± 40 M^{-1} cm^{-1}. Under conditions where uncomplexed Cr(VI) was present at equilibrium, the measured values of $\bar{\epsilon}$ were found to be dependent on both [H^+] and $C_{H_2O_2}$. Thus we assume the reaction

$$HCrO_4^- + H^+ + 2H_2O_2 \rightleftharpoons CrO(O_2)_2 + 3H_2O \qquad (5)$$

$$K_f = \frac{[CrO(O_2)_2]}{[HCrO_4^-][H^+][H_2O_2]^2} \qquad (6)$$

where $CrO(O_2)_2$ is the oxodiperoxochromium(VI) complex.[11,12] Then we have the relationship

$$\log \frac{[CrO(O_2)_2]}{C_{Cr} - [CrO(O_2)_2]} = \log \frac{\bar{\epsilon}}{\epsilon_\infty - \bar{\epsilon}} \qquad (7)$$

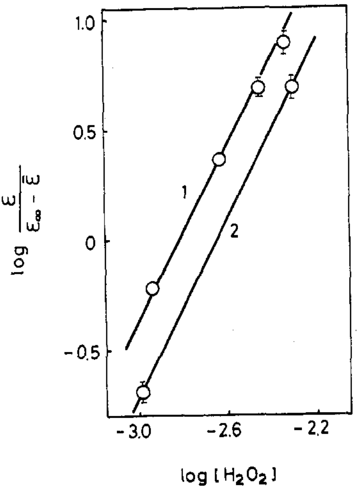

Figure 3. Dependence of hydrogen peroxide on formation of the oxodiperoxochromium(VI) complex (C_{Cr} = 8.00 × 10^{-5} M, I = 3.0 M, 25 °C, 580 nm): 1, $[H^+]$ = 1.99 × 10^{-2} M; 2, $[H^+]$ = 1.00 × 10^{-2} M.

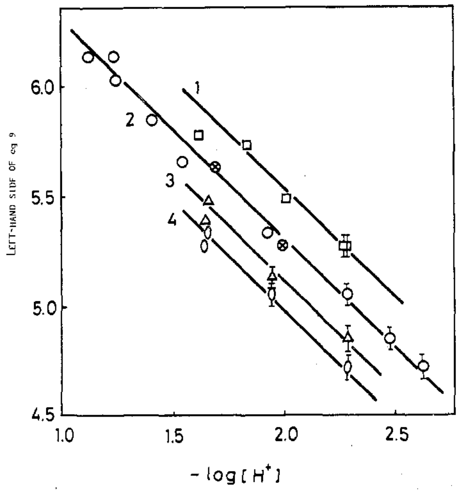

Figure 4. Dependence of hydrogen ion on formation of the oxodiperoxochromium(VI) complex (C_{Cr} = 8.00 × 10^{-5} M, $C_{H_2O_2}$ = 1.08 × 10^{-3} M, I = 3.0 M, 580 nm): 1, 20 °C; 2, 25 °C; 3, 30 °C; 4, 35 °C; ⊗, values estimated from the data in Figure 3.

where $\bar{\epsilon}$ and ϵ_∞ are the apparent molar absorption coefficient for chromium and the molar absorption coefficient of $CrO(O_2)_2$, respectively. Combining eq 6 and 7, we have

$$\log \frac{\bar{\epsilon}}{\epsilon_\infty - \bar{\epsilon}} = 2 \log [H_2O_2] + \log ([H^+]K_f) - \log (1 + [H^+]K^H) \quad (8)$$

where $[H_2O_2]$ is given by $[C_{H_2O_2} - 2(\bar{\epsilon}/\epsilon_\infty)C_{Cr}]$. Equation 8 can be rearranged to give eq 9. Plots of $\log [\bar{\epsilon}/(\epsilon_\infty - \bar{\epsilon})]$

$$\log \frac{\bar{\epsilon}}{\epsilon_\infty - \bar{\epsilon}} - 2 \log \left(C_{H_2O_2} - 2\frac{\bar{\epsilon}}{\epsilon_\infty}C_{Cr} \right) + \log (1 + [H^+]K^H) = -(-\log [H^+]) + \log K_f \quad (9)$$

against $\log [H_2O_2]$ according to eq 8 are linear with a slope of −2 (Figure 3). We have two peroxo groups per chromium atom. Plots of the values of the left-hand side of eq 9 vs. −log $[H^+]$ are linear with a slope of −1 (Figure 4). Therefore the formation constant of the oxodiperoxochromium(VI) complex should be given by eq 6. This provides supporting evidence for Evans' finding[17] that the formation of perchromic acid involves two molecules of H_2O_2 for each chromate ion. Values of K_f and their thermodynamic parameters are tabulated in Table I.

Table I. Equilibrium Constants K_f and K_f^H and Corresponding Thermodynamic Parameters^a

temp/°C	$\log K_f$	$\log K_f^H$
20	7.53 ± 0.05	−0.91 ± 0.05
25	7.30 ± 0.05	−0.82 ± 0.05
30	7.11 ± 0.05	−0.74 ± 0.05
35	6.98 ± 0.05	−0.67 ± 0.05
ΔH/kJ mol^{-1}	−58 ± 10	27 ± 10
ΔS/J K^{-1} mol^{-1}	−55 ± 30	76 ± 35

^{a} I = 3.0 M.

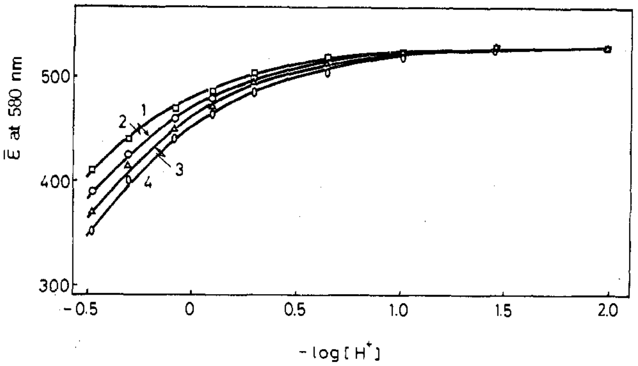

Figure 5. Change of absorbance due to the protonation of the oxodiperoxochromium(VI) complex (C_{Cr} = 8.00 × 10^{-5} M, $C_{H_2O_2}$ = 7.61 × 10^{-3} M, I = 3.0 M): 1, 20 °C; 2, 25 °C; 3, 30 °C; 4, 35 °C. The solid curves were calculated with the constants listed in Table II.

Protonation Constant of the Oxodiperoxochromium(VI) Complex. Absorbances at 580 nm due to peroxochromium(VI) complexes decrease considerably with increasing hydrogen ion concentration (Figure 5). This may be attributable to the protonation of the oxo group in the oxodiperoxochromium(VI) complex, i.e.

$$CrO(O_2)_2 + H^+ \rightleftharpoons Cr(OH)(O_2)_2^+ \quad (10)$$

Thus the apparent molar absorption coefficient can be expressed as

$$\bar{\epsilon} = \frac{\epsilon_\infty + \epsilon_\infty' K_f^H[H^+]}{1 + K_f^H[H^+]} \quad (11)$$

where ϵ_∞ and ϵ_∞' are the molar absorption coefficients of $CrO(O_2)_2$ and $Cr(OH)(O_2)_2^+$, respectively, and $K_f^H = [Cr(OH)(O_2)_2^+][CrO(O_2)_2]^{-1}[H^+]^{-1}$. The protonation constant was determined and is included in Table I.

Overall Reaction of Hydrogen Chromate Ion with Hydrogen Peroxide. In the reaction of hydrogen chromate anion with hydrogen peroxide, we observed the evolution of 1.50 ± 0.05 mol of dioxygen/g-atom of Cr. This points to the stoichiometry

$$2HCrO_4^- + 8H^+ + 3H_2O_2 \rightleftharpoons 2Cr^{3+} + 3O_2 + 8H_2O \quad (12)$$

Thus the decomposition of the oxodiperoxochromium(VI) complex is formulated as

$$2CrO(O_2)_2 + 6H^+ \rightleftharpoons 2Cr^{3+} + 3O_2 + H_2O_2 + 2H_2O \quad (13)$$

Kinetics of Formation of Peroxochromium(VI) Complexes. Under conditions where the reverse reaction can be neglected in the kinetic study in the presence of a large excess of H_2O_2, the rate equation for the formation of peroxochromium(VI) complexes[18] is written as

$$d[CrO_5']/dt = k_f(C_{Cr} - [CrO_5']) \quad (14)$$

where $[CrO_5']$ refers to the sum of the concentrations of $CrO(O_2)_2$ and $Cr(OH)(O_2)_2^+$, k_f is a conditional first-order rate constant, and $C_{Cr} = [H_2CrO_4] + [HCrO_4^-] + [CrO(O_2)_2] + [Cr(OH)(O_2)_2^+]$. The plot of $\ln (C_{Cr} - [CrO_5'])/C_{Cr}$ against

Table II. Conditional First-Order Rate Constant k_f[a]

$10^3 \times C_{H_2O_2}$/M	[H$^+$]/M	k_f/s^{-1} (25 °C)	$10^3 \times C_{H_2O_2}$/M	[H$^+$]/M	k_f/s^{-1} (25 °C)
2.61	0.502	15.2	12.2	3.26×10^{-2}	5.50
3.91	0.509	23.8	7.82	3.00	200
5.21	0.500	29.0	7.82	2.00	146
7.82	0.500	47.0	7.82	1.26	94.0
10.4	0.503	57.5	7.82	0.798	60.0
2.44	3.26×10^{-2}	1.24	7.82	0.501	47.0
3.65	3.26×10^{-2}	1.62	7.82	0.221	22.5
4.87	3.26×10^{-2}	2.06	7.82	9.27×10^{-2}	10.0
7.31	3.26×10^{-2}	3.22	7.82	3.39×10^{-2}	3.6
9.74	3.26×10^{-2}	4.25	7.82	1.04×10^{-2}	1.3

[H$^+$]/M	k_f/s^{-1} [b] (20 °C)	[H$^+$]/M	k_f/s^{-1} [b] (30 °C)	k_f/s^{-1} [b] (35 °C)
3.00	159	3.01	143	315
2.00	104	2.01	164	175
1.26	72.0	1.27	114	143
0.798	57.0	0.803	83.0	104
0.501	40.0	0.504	51.0	64.0
0.221	19.6	0.226	25.5	27.3
9.27×10^{-2}	8.2	9.80×10^{-2}	11.9	14.6
3.39×10^{-2}	2.9	3.34×10^{-2}	4.2	5.2
1.04×10^{-2}	1.1	9.11×10^{-3}	1.5	2.3

[a] $C_{Cr} = 8.00 \times 10^{-5}$ M, $I = 3.0$ M. [b] $C_{H_2O_2} = 7.82 \times 10^{-3}$ M.

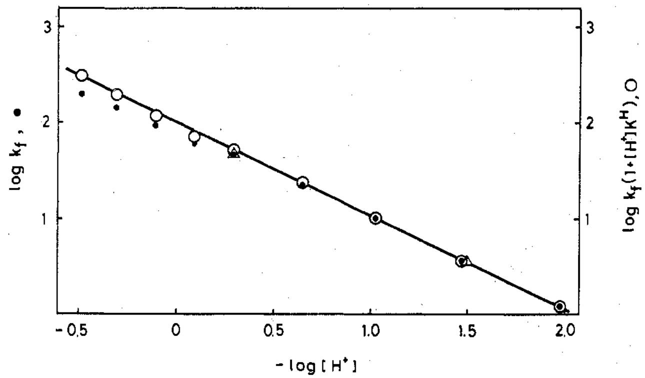

Figure 6. Dependence of the formation rate on the hydrogen ion concentration: ●, plot of log k_f vs. −log [H$^+$]; O, plot of log [$k_f(1 + [H^+]K^H)$] vs. −log [H$^+$]; △, log k_f estimated from the data obtained at several different concentrations of hydrogen peroxide at a fixed acidity.

reaction time is linear, so that the rate is of the first order with respect to chromium(VI). The reaction is also exactly first order in [H_2O_2] at a fixed acidity, and k_f depends on the concentration of hydrogen ion (see Table II and Figure 6).

The rate of the peroxo-complex formation is expressed as

$$\frac{d[CrO_5']}{dt} = k_1[H_2CrO_4][H_2O_2] + k_2'[HCrO_4^-][H_2O_2] = \frac{k_1[H^+]K^H + k_2'}{1 + [H^+]K^H}[H_2O_2][Cr(VI)] \qquad (15)$$

and then the conditional first-order rate constant is given by

$$k_f = \frac{k_1[H^+]K^H + k_2'}{1 + [H^+]K^H}[H_2O_2] \qquad (16)$$

Plots of log k_f vs. −log [H$^+$] in Figure 6 deviate from the straight line with a slope of −1 with increasing hydrogen ion concentration. However, plots of log [$k_f(1 + [H^+]K^H)$] vs. −log [H$^+$] lie along the straight line. This fact indicates that we have no k_2' path and that the peroxo-complex formation proceeds only through the reaction of H_2CrO_4 with H_2O_2. Judging from equilibrium data[19] for H_2O_2, the values of the proton dissociation constants for $H_3O_2^+$ and H_2O_2 are of such magnitude as to preclude inclusion of $H_3O_2^+$ and HO_2^- in the present reaction system: $[H^+][H_2O_2]/[H_3O_2^+] \simeq 10^3$, $[H^+][HO_2^-]/[H_2O_2] = 10^{-11.27}$. Thus the proton dependence in the peroxo-complex formation is ascribed to diffusion-controlled protonation to hydrogen chromate anion prior to the rate-determining step. Orhanović and Wilkins have proposed the same rate equation.[20] The rate constant k_1 at various temperatures and the corresponding parameters are summarized in Table III.

Table III. Rate Constants k_1 and k_{-1}' and Corresponding Activation Parameters[a]

temp/°C	k_1/M^{-1} s^{-1}	k_{-1}'/M s^{-1}
20	$(8.0 \pm 0.2) \times 10^4$	$(3.5 \pm 0.2) \times 10^{-4}$
25	$(9.3 \pm 0.2) \times 10^4$	$(6.1 \pm 0.2) \times 10^{-4}$
30	$(10.1 \pm 0.2) \times 10^4$	$(1.1 \pm 0.1) \times 10^{-3}$
35	$(12.0 \pm 0.2) \times 10^4$	$(1.8 \pm 0.1) \times 10^{-3}$
$\Delta H^{\ddagger}$/kJ mol^{-1}	17 ± 1	80 ± 5
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	-93 ± 5	-36 ± 20

[a] I = 3.0 M.

Table IV. Rate Constants k_f and k_r[a]

$10^3 C_{H_2O_2}$/M	k_0/s^{-1}	k_f/s^{-1}	k_r/s^{-1}
1.22	1.07	0.53	0.54
2.44	1.24	0.99	0.25
3.65	1.62	1.45	0.17
4.87	2.06	1.94	0.12
7.31	3.22	3.13	0.09
9.74	4.25	4.18	0.07
12.2	5.50	5.44	0.06

[a] $C_{Cr} = 8.00 \times 10^{-5}$ M, [H$^+$] = 3.26×10^{-2} M, $I = 3.0$ M, 25 °C.

Kinetics of Dissociation of H_2O_2 **from the Oxodiperoxochromium(VI) Complex.** The formation of the oxodiperoxochromium(VI) complex is expressed as[11]

$$H_2CrO_4 + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CrO_2(O_2) + 2H_2O \qquad (17)$$

$$CrO_2(O_2) + H_2O_2 \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} CrO(O_2)_2 + H_2O \qquad (18)$$

where k_1 is the rate constant for the formation and k_{-1} is the rate constant for the dissociation of H_2O_2. We define the equilibrium constant for eq 18 as eq 19. Unfortunately this

$$K_f' = [CrO(O_2)_2]/[CrO_2(O_2)][H_2O_2] \qquad (19)$$

constant could not be determined. From the relationship

$$k_{-1}' = k_{-1}/K_f' = k_1K^H/K_f \qquad (20)$$

we can estimate values of k_{-1}' from available values of k_1, K^H, and K_f. The values at various temperatures are presented in Table III.

We followed the reaction shown by eq 17 and 18, under conditions where the reverse reaction cannot be neglected in the kinetic study. Conditional first-order rate constant k_0 is obtained from the slope of a plot of log [$(A_\infty - A_t)/(A_\infty - A_0)$] against reaction time: $k_0 = k_f + k_r$. Values of k_f and k_r are calculated from the equilibrium constant K_f and k_0. As apparent from the values in Table IV, k_f is proportional to the concentration of H_2O_2 and k_r is inversely proportional to the concentration of H_2O_2. The results are identical with those obtained above: $k_f = k_1K^H[H^+][H_2O_2]/(1 + [H^+]K^H)$ with $k_1 = (9.5 \pm 0.5) \times 10^4$ M^{-1} s^{-1}, and $k_r = k_{-1}'/[H_2O_2]$ with $k_{-1}' = (6.1 \pm 0.2) \times 10^{-4}$ M s^{-1}. Moreover, from ten data over the range of 3×10^{-2}–2×10^{-1} M hydrogen ion concentrations, k_1 and k_{-1}' were found to be $(8.7 \pm 1.0) \times 10^4$ and $(5.8 \pm 0.8) \times 10^{-4}$, respectively. Both k_1 and k_{-1}' are independent of hydrogen ion concentrations.

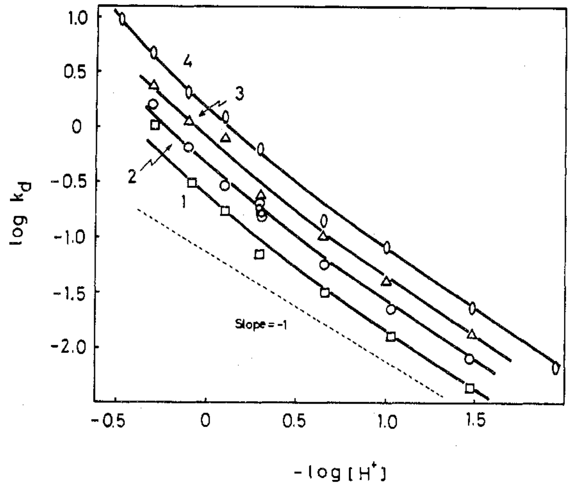

Figure 7. Plots of log k_d vs. -log [H^+]: 1, 20 °C; 2, 25 °C; 3, 30 °C; 4, 35 °C. The solid curves were calculated with the rate constants listed in Table V.

Table V. Rate Constants k_2 and k_3 and Activation Parameters[a]

temp/°C	$k_2/M^{-1}\ s^{-1}$	$k_3/M^{-1}\ s^{-1}$
20	0.13 ± 0.02	1.1 ± 0.3
25	0.25 ± 0.02	1.8 ± 0.3
30	0.40 ± 0.02	3.0 ± 0.3
35	0.72 ± 0.10	5.0 ± 0.3
$\Delta H^{\ddagger}$/kJ mol^{-1}	81 ± 5	73 ± 15
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	17 ± 15	6 ± 50

[a] $I = 3.0$ M.

Kinetics of Decomposition of Peroxochromium(VI) Complexes. The stoichiometry for the decomposition is

$$2CrO(O_2)_2 + 6H^+ \rightleftharpoons 2Cr^{3+} + 3O_2 + H_2O_2 + 2H_2O \quad (21)$$

The conditional first-order rate constant k_d for the decomposition of the peroxo complex was obtained under various pseudo-first-order conditions. k_d is independent of [H_2O_2] over the range of H_2O_2 concentration 2.61 × 10^{-3}–1.04 × 10^{-2} M, but it depends on [H^+]. A plot of log k_d against -log [H^+] shown in Figure 7 indicates that the limiting slope tends to be -1 at lower acidity. This dependence can be accounted for by the rate equation

$$-\frac{d[CrO_5']}{dt} = k_2[CrO(O_2)_2][H^+] + k_3[Cr(OH)(O_2)_2^+][H^+] = \frac{k_2 + k_3K^H[H^+]}{1 + K^H[H^+]}[H^+][CrO_5'] \quad (22)$$

and then k_d is given by $k_d = (k_2[H^+] + k_3K^H[H^+]^2)/(1 + K^H[H^+])$. The solid lines in Figure 7 are theoretical curves calculated from the obtained rate constants. The results of the kinetic analysis are tabulated in Table V. According to Orhanović and Wilkins[20] the decomposition of perchromic acid is first order in $CrO(O_2)_2$ and second order in hydrogen ion. The result does not agree with ours.

We measured oxygen gas as a function of reaction time for reaction with a half-life time longer than a few minutes. The rate of oxygen evolution at [H^+] = 9.93 × 10^{-3} M was exactly first order with respect to the oxodiperoxochromium(VI) complex, and it corresponded to the rate of disappearance of the oxodiperoxochromium(VI) complex at 580 nm.

Discussion

Oxidation–reduction reactions involving the chromium(III)–chromium(VI) couple have been extensively investigated.[21] In several instances, the initial step in the reduction of the hydrogen chromate anion involves the formation of a chromium(VI)–substrate complex.[22] Since some data are now available on the kinetics of chromium(VI)–substrate complexes, we compare those with that for the formation of the oxodiperoxochromium(VI) complex. All of the rate laws under consideration are represented in the form of eq 23, where X

Table VI. Kinetic Data for Formation of Chromium(VI)–Substrate Complexes: rate law = $k_f^H[HCrO_4^-][H^+][X]$

substrate X	$k_f^H/M^{-2}\ s^{-1}$ (25 °C)	pH range	ref
$H_2PO_4^-$	(1.2 ± 0.7) × 10^5	3.5–6.6	*a*
$H_2PO_3^-$	5 × 10^5	4–5	*b*
$HCrO_4^-$	(6.2 ± 0.4) × 10^5 [h]	2–4	*c*
$HS_2O_3^-$	3.7 × 10^5	1.5–2.7	*d*
NCS^-	(5.4 ± 0.4) × 10^5	1–2.2	*e*
$(NH_3)_5CoOH^{2+}$	4 × 10^5	2.3–4	*f, g*
H_2O_2	(1.5 ± 0.3) × 10^4 [i]	−0.5–2	this work

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$$\text{rate} = k_f^H[HCrO_4^-][H^+][X] \quad (23)$$

denotes a substrate. The available values of k_f^H are presented in Table VI.

All rate constants so far determined for such reactions have values in the range 1 × 10^5–7 × 10^5 $M^{-2}\ s^{-1}$. To explain the rate constants independent of the nature of the ligand involved, Lin and Beattie[23] postulated the diffusion-controlled protonation of coordinated hydroxide as the rate-determining step. Haim[22] proposed, based on the previous postulation,[20] a more likely mechanism involving protonation of the hydroxo group of $HCrO_4^-$ as the first step with the subsequent rate-determining loss of water:

(a) diffusion-controlled protonation

$$CrO_3(OH)^- + H^+ \rightleftharpoons CrO_3(H_2O) \quad (24)$$

(b) rate-determining substitution of "the coordinated water" by the incoming ligand

$$CrO_3(H_2O) + X \rightarrow CrO_3X + H_2O \quad (25)$$

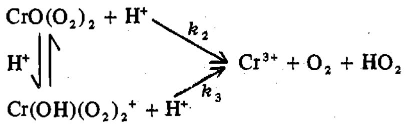
Except for the Cr–H_2O_2 system reactions in Table VI have been carried out at the hydrogen ion concentration lower than 0.1 M where the chromic acid contribution is not distinguishable. Judging from our present results, the proton dependence given by eq 23 should be attributable to the protonation of hydrogen chromate ion to give chromic acid. Independence of k_f^H of the nature of incoming ligands invokes the loss of a water molecule from the chromic acid after the weak addition of a substrate X to the chromium center as the most important feature of the activation process. Thus the processes may be expressed as

$$CrO_3(H_2O) + H_2O_2 \rightleftharpoons CrO_3(H_2O), H_2O_2 \underset{\text{rds}}{\overset{\text{rds}}{\rightleftharpoons}} CrO_2(O_2) + 2H_2O \quad (26)$$

$$CrO_2(O_2) + H_2O_2 \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} CrO(O_2)_2 + H_2O \quad (27)$$

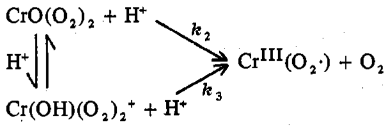
The final process of incorporation of the second H_2O_2 is fast. For the dissociation of H_2O_2 from the oxodiperoxochromium(VI) complex, we have the predissociation equilibrium as shown in eq 27 prior to the rate-determining cleavage of the bound peroxo.

Mechanism I



$$CrO_5' + HO_2 \rightarrow Cr^{3+} + H_2O_2 + 2O_2$$

Mechanism II



$$CrO_5' + Cr^{III}(O_2\cdot) \rightarrow 2Cr^{3+} + H_2O_2 + 2O_2$$

It should be pointed out that the activation enthalpy for k_1 is smaller and the value of the activation entropy is negatively larger as compared to those of complexation of most metal ions in the Eigen mechanism. $\Delta H^{\ddagger}$ for the formation of the oxodiperoxochromium(VI) complex is very similar in magnitude to the value for the dichromate formation (Table VI). This suggests, though it does not prove, that the rate-determining step is of the same type.

Most of the work on the decomposition of the peroxy species has been performed at high concentrations of reagents.[24-26] In the present study experiments have been carried out under simpler conditions where the concentration of chromium(VI) is lower than 10^{-4} M. On the basis of the established rate law we postulate Mechanisms I and II for the decomposition of peroxochromium(VI) complexes. As already stated, the decomposition of peroxochromium(VI) complexes is of the first-order in hydrogen ion, probably due to the protonation of a coordinated peroxo group. The protonation may facilitate two-electron transfer from the other coordinated peroxo to the central chromium atom, giving rise to one oxygen molecule. In the same sense, the two-electron transfer in the protonated peroxochromium complex $Cr(OH)(O_2)_2^+$ may be easier than in $CrO(O_2)_2$. In fact, k_3 is about 10 times greater than k_2. Subsequent one-electron transfer from the other peroxo to chromium gives trivalent chromium and a hydroperoxyl radical (HO_2)[27] (Mechanism I) or trivalent chromium with a peroxyl radical ($Cr^{III}(O_2\cdot)$) (Mechanism II). Produced HO_2 or $Cr^{III}(O_2\cdot)$ reacts rapidly with peroxochromium(VI) complexes (CrO_5') finally yielding one hydrogen peroxide and two oxygen molecules. According to the previous finding[28] the HO_2 disproportionation is not fast compared to the disappearance of CrO_5', because the concentration of HO_2 may be very low (less than 10^{-6} M).[29] The present mechanism is the, so-called, three-electron oxidation–reduction mechanism proposed by Roček et al. and confirmed in many reaction systems involving chromium(VI).[30]

Knowing ESR spectra of chromium(III) and -(V)[31,32] and HO_2,[33] we measured ESR spectra of our systems in order to gain additional information on the mechanism. Under our experimental conditions no ESR spectra corresponding to Cr(V) and HO_2 were observed. After the complete conversion of Cr(VI) to Cr(III) the sample solution showed a single very broad line spread over about 1000 G. This ESR spectrum is almost the same as that of a mixture of chromium(III) and hydrogen peroxide solutions under the same conditions and was very similar to the spectrum reported.[31] However we cannot rule out the mechanisms through HO_2 and/or Cr(V) since their concentrations in the reaction system should be undetectably low because of their high reactivity.

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Registry No. $HCrO_4^-$, 15596-54-0; H_2O_2, 7722-84-1; $CrO(O_2)_2$, 35262-77-2.

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(11) The terminology used in the paper: peroxo, covalently bound dioxygen resembling O_2^{2-}; peroxo complex, complex containing metal-bound peroxo ligand(s); oxo, covalently bound monatomic oxygen resembling O^{2-} (the dioxo, O_2, is not to be confused with peroxo, (O_2)).
(12) Perchromic acid may be extracted into ether where it is more stable and, on addition of pyridine to the ether solution, the compound $CrO(O_2)_2(py)$ is obtained. This product is monomeric in benzene and essentially diamagnetic.[13] From these facts we may formulate perchromic acid as aqua, ether, or pyridine adducts of the molecule $CrO(O_2)_2$ containing Cr(VI).[14] The X-ray analysis of the oxodiperoxopyridinechromium(VI)[15] and oxodiperoxo-2,2′-bipyridylchromium(VI)[16] complexes provides additional evidence for the oxodiperoxoaquachromium(VI). Thus the coordination around the central chromium atom can be described in terms of a somewhat distorted pentagonal pyramid. Henceforth we use the formulation $CrO(O_2)_2$ which contains one or two water molecules in the coordination sphere.
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