repeated over a limited acidity range at an ionic strength of 0.5 M. The corresponding results are $k_{12} = (0.9 \pm 0.2) \times 10^{-2}$ s^{-1} and $k_{13} = (5.9 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C, from which it follows that k_{12} is indeed very close to k_7.

The acid-catalyzed path, i.e., $k_{13}[H^+]$, completely outweighs the water-catalyzed processes (k_{12}) under the high-ionic-strength conditions and probably involves the acid-promoted breakage of the Co–NH_3 bond. For a mechanism of the type

$$Co(NH_3)_5SO_3^+ + H^+ \xrightarrow[\text{slow}]{k_{13}} Co(NH_3)_4SO_3^+ + NH_4^+ \xrightarrow[\text{fast}]{H_2O} \textit{trans}\text{-}Co(NH_3)_4(SO_3)OH_2^+ \quad (15)$$

$k_{obsd} = k_{13}[H^+]$. This process differs to some extent from that reported for the formation of *trans*-$Co(NH_3)_4(SO_3)_2^-$ from $Co(NH_3)_5SO_3^+$, where NH_3 was released in the rate-determining step (k_7 in reaction 9). The release of NH_4^+ is expected to be accompanied by a significantly smaller positive $\Delta\bar{V}^{\ddagger}_{exptl}$ value, due to the difference in the partial molar volumes of NH_3 and NH_4^+.[51,52] The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) in Table VI are close to those reported for k_7 in Table V and point to the similarity in mechanisms. However, due to the lower $\Delta\bar{V}^{\ddagger}_{exptl}$ value, we cannot exclude the possibility of an I_d mechanism:

$$Co(NH_3)_5SO_3^+ + H_3O^+ \overset{K_{14}}{\rightleftharpoons} (Co(NH_3)_5SO_3^+,H_3O^+) \xrightarrow{k_{15}} \textit{trans}\text{-}Co(NH_3)_4(SO_3)OH_2^+ + NH_4^+ \quad (16)$$

In this case $k_{obsd} = k_{15}K_{14}[H^+]/(1 + K_{14}[H^+])$, which simplifies to $k_{obsd} = k_{15}K_{14}[H^+]$, since no significant curvature was observed in the plot of k_{obsd} vs. $[H^+]$ for the data in Table VI. A small negative value for $\Delta\bar{V}(K_{14})$ may contribute toward $\Delta\bar{V}^{\ddagger}_{exptl}$, since charge concentration occurs during the encounter complex formation reaction. The resulting positive value of $\Delta\bar{V}^{\ddagger}_{exptl}$ (Table VI) may indicate a positive contribution from the interchange process (k_{15}) and as such emphasize the dissociative nature of this reaction.

In conclusion, the results of this study clearly illustrate the strong dissociative nature of the reaction processes, especially when induced by the trans effect of the sulfito ligand.

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Registry No. $Co(NH_3)_5SO_3^+$, 53108-45-5; *trans*-$Co(NH_3)_4(SO_3)_2^-$, 62559-96-0; *trans*-$Co(NH_3)_4(SO_3)OH_2^+$, 48052-50-2.

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[52] Horne, R. A. "Water and Aqueous Solutions"; Wiley: New York, 1972; Chapter 13.

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Kinetics and Mechanism of the Formation of Violet Peroxychromate in Aqueous Solution

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The kinetics and mechanism of the formation of violet peroxychromate, $HCrO_6^-$, have been studied with use of a stopped-flow method. The rate law is $d[CrO_5(OH)^-]/dt = k[HCrO_4^-][H^+][H_2O_2]$ with a third-order Arrhenius rate constant of $k = 10^{7.8\pm0.5} \exp[(-5000 \pm 600 \text{ cal})/RT]$. A three-step mechanism is proposed which is similar to one previously suggested by Wilkins et al. for the formation of blue peroxychromate. Enthalpies and entropies of activation for the rate-determining step have been calculated and are found to be 6.6 ± 1.0 kcal and −14 ± 4 cal/K, respectively.

Introduction

When hydrogen peroxide is added to a strongly acidic aqueous solution of dichromate, the well-known blue diperoxychromium(VI) species $CrO(O_2)_2{\cdot}H_2O$ rapidly forms:[1-3]

$$HCrO_4^- + 2H_2O_2 + H^+ \rightarrow CrO_5{\cdot}H_2O + 2H_2O \quad (1)$$

The kinetics of formation of $CrO_5{\cdot}H_2O$ have been extensively studied by Moore, Kettle, and Wilkins,[4] Orhanovic and Wilkins,[5] and Funahashi, Uchida, and Tanaka.[6] The reaction is third-order overall, being first order in each of the species H^+, H_2O_2, and $HCrO_4^-$. The rate constant at 0.1 M ionic strength is reported to be

$$k = 10^{7.6\pm0.2} \exp[(-4500 \pm 200 \text{ cal})/RT] \text{ M}^{-2} \text{ s}^{-1}$$

If the same reactants are mixed under less acidic conditions, pH 4–7, violet diperoxychromium(VI), $CrO_5(OH)^-$, is formed according to[7]

$$HCrO_4^- + 2H_2O_2 \rightarrow HCrO_6^- + 2H_2O \quad (2)$$

Finally, in alkaline solution the reaction yields still another product, the red-brown tetraperoxychromate(V), CrO_8^{3-}.

We have undertaken a study of the kinetics and mechanism of formation of violet peroxychromate in aqueous solution. In particular, we are interested in comparing the mechanism of this reaction with the closely related ones yielding the blue and red-brown peroxychromates. Since the reaction (2) like (1) is over in a matter of seconds, we have used stopped-flow techniques to study its kinetics. The progress of the reaction can be followed spectrophotometrically at 540 nm, where $HCrO_6^-$ has a strong absorption band ($\epsilon_{540} = 510$ M^{-1} cm^{-1} [8]). The rate law was determined with the method of initial rates. In the application of this method the effect of systematic variations in initial reactant concentrations on the initial reaction rates is used to determine the concentration dependence of each species in the rate law. Both the rate law and the third-order rate constant k have been determined at 15.0, 25.0, and 35.0 °C.

Experimental Section

All reagents were of the highest purity commercially available and were used without further purification. Potassium dichromate and

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[1] Glasner, A.; Steinberg, M. *J. Chem. Soc.* **1957**, 2569.
[2] Evans, D. F. *J. Chem. Soc.* **1957**, 4013.
[3] Tuck, D. G.; Walters, R. M. *Inorg. Chem.* **1963**, *2*, 3404.
[4] Moore, P.; Kettle, S. F. A.; Wilkins, R. G. *Inorg. Chem.* **1966**, *5*, 466.
[5] Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.
[6] Funahashi, S.; Uchida, F.; Tanaka, M. *Inorg. Chem.* **1978**, *17*, 2784.
[7] Griffith, W. P. *J. Chem. Soc.* **1962**, 3948.
[8] Bartlett, B. L.; Quane, D. *Inorg. Chem.* **1973**, *12*, 1925.

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Table I. Measured Reaction Rate Orders with Respect to $[HCrO_4^-]$, $[H^+]$, and $[H_2O_2]$ for the Formation of Violet Peroxychromate

temp, °C[a]	$[HCrO_4^-]$	$[H^+]$	$[H_2O_2]$
15	1.07 ± 0.4	0.97 ± 0.3	0.98 ± 0.2
25	1.17 ± 0.4	0.88 ± 0.4	1.00 ± 0.4
35	0.89 ± 0.4	0.94 ± 0.3	0.92 ± 0.3

[a] ±0.2 °C.

nitric acid were obtained from Matheson Coleman and Bell, Inc., and J. T. Baker Co., respectively. Both hydrogen peroxide (30%) and potassium nitrate were from Fisher Scientific, Inc. The potassium nitrate was used to adjust the ionic strength of all solutions to 0.1 M. The uncertainty in all temperature measurements was less than 0.2 °C. The concentrations of the three reactants were systematically varied over the following ranges: $[H_2O_2]$, 0.2–0.6 M; $[H^+]$, (3–9) $\times 10^{-5}$ M (pH 4.03–4.51); $[HCrO_4^-]$, (5×10^{-4})–(1×10^{-3}) M. We did not vary the acidity over as wide a range as other authors have done with the blue peroxychromate system. This is because at higher pHs significant amounts of red-brown peroxychromate form and at lower pHs formation of the blue peroxychromate will occur. Kinetic runs with $[HCrO_4^-]$ below 0.5 mM were not done because of the relatively small absorbance changes that occur during the reaction and the difficulty of measuring them accurately. Furthermore, we chose not to do runs with $[HCrO_4^-]$ greater than approximatey 1 mM. At this concentration, approximately 10% of Cr(VI) exists as dichromate. The linearity of the pseudo-first-order plots in terms of $HCrO_4^-$ constructed by Wilkins et al.[4] for the blue peroxychromate reaction suggests that dichromate at the concentrations encountered here does not react appreciably to give $CrO_5{\cdot}H_2O$ or other products. It seems unlikely, therefore, that it is involved in a rapid parallel reaction under the conditions in which violet peroxychromate is formed. As the Cr(VI) formality increases, so does the dichromate concentration. At [Cr(VI)] = 2 mM, dichromate already accounts for greater than 15% of Cr(VI). In order to avoid the ambiguities associated with parallel reactions involving $Cr_2O_7^{2-}$, which would become more important at higher dichromate concentrations, we chose to keep the Cr(VI) formality below 1 mM.

Studies on blue peroxychromate have used the method of isolation in which both $[H_2O_2]$ and $[H^+]$ are much greater than $[HCrO_4^-]$. This is not possible when the formation of violet peroxychromate is studied since $[H^+]$ must be kept less than 10^{-4} M. For this reason, we used the method of initial rates.

Results

We determined the rate law for the formation of violet peroxychromate at 15.0, 25.0, and 35.0 °C. In each case, an expression of the form

$$-d[HCrO_4^-]/dt = k[HCrO_4^-]^x[H^+]^y[H_2O_2]^z \qquad (3)$$

fits the data well. The exponents found for each temperature are presented in Table I. Given the uncertainties in the measurement of each exponent, we think it reasonable to conclude that each is unity in the temperature range 15–35 °C. There are three equilibria involving Cr(VI) that potentially could affect the determination of x (eq 4–6). Under

$$\begin{gathered} Cr_2O_7^{2-} + H_2O \rightleftarrows 2HCrO_4^- \\ K_{25\,°C}(I = 0.1) = 0.018\ M^{-1} \quad (\text{ref } 9) \end{gathered} \qquad (4)$$

$$\begin{gathered} HCrO_4^- \rightleftarrows CrO_4^{2-} + H^+ \\ K_{25\,°C}(I \to 0) = 3.2 \times 10^{-7}\ M \quad (\text{ref } 10) \end{gathered} \qquad (5)$$

$$\begin{gathered} H_2CrO_4 \rightleftarrows HCrO_4^- + H^+ \\ K_{25\,°C}(I = 1) = 6.3\ M \quad (\text{ref } 11) \end{gathered} \qquad (6)$$

the conditions of this experiment, pH ~4 and $[K_2Cr_2O_7] \approx 5 \times 10^{-4}$ M, both CrO_4^{2-} and H_2CrO_4 represent less than 1% of the total Cr(VI) in solution. However, 5–10% of Cr(VI) is present as $Cr_2O_7^{2-}$ with the balance, approximately 90%, existing as $HCrO_4^-$. The quantity of $HCrO_4^-$ which appears in the rate law represents *actual* $HCrO_4^-$ concentration. This quantity was calculated from the reported equilibrium constants[9] for reaction 4 at an ionic strength of 0.1 M at 14.5, 25, and 34.5 °C (0.014, 0.018, and 0.021 M^{-1}, respectively).

Table II. Observed Rate Constants, k, for the Formation of Violet Peroxychromate

temp, °C[a]	$10^{-4}k$, $M^{-2}\ s^{-1}$ [b]	temp, °C[a]	$10^{-4}k$, $M^{-2}\ s^{-1}$ [b]
15	1.08 ± 0.04	35	1.89 ± 0.07
25	1.59 ± 0.13		

[a] ±0.2 °C. [b] The uncertainties in the rate constants do not include any potential systematic error in the extinction coefficient for $HCrO_6^-$.

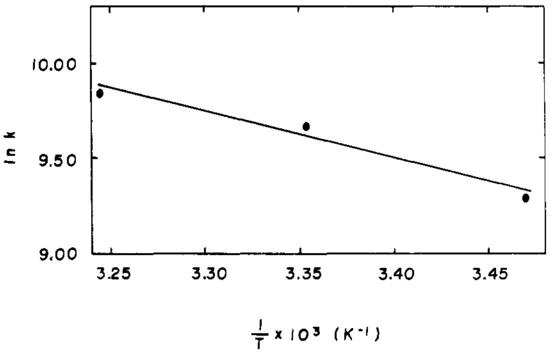

Figure 1. Plot of the third-order rate constant, k in eq 3, vs. $1/T$ for the formation of violet peroxychromate.

The observed rate constants at each temperature, k in eq 3, are presented in Table II. The rate constants are calculated directly from the measured initial rates and initial concentrations with exponents of exactly 1 for each species appearing in the rate expression. As mentioned previously, the extinction coefficient for $HCrO_6^-$ is from Bartlett and Quane,[8] $\epsilon_{540} = 510$ $M^{-1}\ cm^{-1}$. A plot of ln k vs. $1/T$, Figure 1, gives $k = 10^{7.8\pm0.5}$ $\exp[(5000 \pm 600\ \text{cal})/RT]$ as the rate constant for reaction 2.

Discussion

Wilkins et al.[4,5] have proposed the mechanism given in Scheme I for the formation of blue peroxychromate. The observed rate constant, k, would be equal to k_2K_B.

Scheme I

$$HCrO_4^- + H^+ \overset{K_B}{\rightleftarrows} H_2CrO_4 \quad \text{(fast equilibrium)}$$

$$H_2CrO_4 + H_2O_2 \xrightarrow{k_2} H_2CrO_5 + H_2O \quad \text{(slow)}$$

$$H_2CrO_5 + H_2O_2 \xrightarrow{k_3} CrO_5{\cdot}H_2O + H_2O \quad \text{(fast)}$$

Since the formation of the blue and violet peroxychromates proceed according to identical rate laws, it is likely that the corresponding mechanisms are similar. In fact, a simple modification of the last step, which reflects the less acidic conditions under which $HCrO_6^-$ is produced, yields the violet species without changing the rate expression:

$$H_2CrO_5 + H_2O_2 \xrightarrow{k'_3} CrO_5(OH)^- + H_2O + H^+ \quad \text{(fast)}$$

According to this mechanism, the observed k would still be equal to k_2K_B. This suggests that the rate constant expressions for formation of both the blue and the violet species would be the same. Comparison of the two expressions for k confirms our expectations. It would appear, therefore, that except for

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(9) Howlett, K. E.; Sarfield, S. *J. Chem. Soc. A* **1968**, 683.
(10) Linge, H. G.; Jones, A. L. *Aust. J. Chem.* **1968**, *21*, 2189.
(11) Haight, G. P.; Richardson, D. C.; Coburn, N. H. *Inorg. Chem.* **1964**, *3*, 1777.

Table III. Data Used in the Calculation of the Arrhenius Activation Energy, the Enthalpy of Activation, and the Entropy of Activation for the Second Step in the Formation of Violet Peroxychromate

temp, °C	$10^{-4}k$, $M^{-2}\ s^{-1}$	K_B,[a] M^{-1}	$10^{-4}k_2$, $M^{-1}\ s^{-1}$	$\ln (k_2/T)$
15	1.08	0.18	6.00	5.339
25	1.59	0.16	9.94	5.809
35	1.89	0.14	13.5	6.082

[a] Evaluated for an ionic strength of 1.0 (see ref 10). The values for K_B at 15 and 35 °C are calculated by using the integrated van't Hoff equation with $\Delta H^\circ = -2.1$ kcal.

the last step the formation of blue and violet peroxychromates proceed via a common mechanism.

It is possible to extract from our data an activation energy, enthalpy, and entropy for the rate-determining step of the violet reaction. Using the data presented in Table III, one obtains the Arrhenius rate expression for step 2

$$k_2 = 10^{10.2\pm0.8} \exp [(-7200 \pm 1000 \text{ cal})/RT]$$

A plot of $\ln (k_2/T)$ vs. $1/T$ gives an activation enthalpy and entropy of 6.6 ± 1.0 kcal and −14 ± 4 cal/K, respectively, for the slow step. A parallel analysis by ourselves of Wilkins' data[4] for the blue reaction gives $\Delta H^{\ddagger} = 6.0$ kcal and $\Delta S^{\ddagger} = -15$ cal/K, substantiating the view that the blue and violet reactions have common rate-determining steps.[12]

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Registry No. $HCrO_4^-$, 15596-54-0; H_2O_2, 7722-84-1; $HCrO_6^-$, 40330-52-7.

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(12) It should be noted that Orhanovic and Wilkins[5] have reported an enthalpy and entropy of activation for $CrO_5 \cdot H_2O$ formation of 3900 cal and −26 cal/K, respectively. These numbers are not obtained from k_2 but rather appear to be calculated with the third-order rate constant k. As such, their values for $\Delta H^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$ would not be comparable to our own.

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Homolytic Decomposition of Tertiary Organochromium(III) Complexes and Evidence for Their Decomposition via Reactions with Aliphatic Free Radicals. A Pulse Radiolysis Study[1]

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The rates of homolytic decomposition of $Cr{-}C(CH_3)_2OH^{2+}$, $Cr{-}C(CH_3)_2CO_2H^{2+}$, and $Cr{-}C(CH_3)_2CN^{2+}$ are 0.15 s^{-1}, 4 s^{-1}, and $10^4 < k < 10^6\ s^{-1}$, respectively. The reaction of some aliphatic free radicals, $\cdot R$ with $Cr^{III}{-}R$ complexes is very fast, $k_3 \geq 10^8\ M^{-1}\ s^{-1}$. The rate of reaction of $Cr^{2+}(aq)$ with H_2O_2 is $k_{16} = (3.7 \pm 0.7) \times 10^4\ M^{-1}\ s^{-1}$ in good accord with the literature value. These results are discussed in detail.

Introduction

Saturated aliphatic free radicals are known to react with $Cr^{2+}(aq)$ to form organochromium(III) complexes:[3,4]

$$Cr^{2+}(aq) + \cdot R \rightarrow Cr^{III}{-}R \qquad (1)$$

The rates of reaction 1 are high, (1×10^7)–$(1 \times 10^9)\ M^{-1}\ s^{-1}$, for all the free radicals studied.[4] Some of the aliphatic residues rearrange due to the influence of the tervalent chromium.[4,5] All the aliphatic organochromium(III) complexes studied[3d,4] were shown to decompose heterolytically in aqueous solutions via

$$Cr^{III}{-}R \xrightarrow{H_2O} Cr^{III}(aq) + RH \qquad (2)$$

Recently Espenson and co-workers have shown that in the presence of efficient scavengers for $Cr^{2+}(aq)$ and/or $\cdot R$ (α-hydroxyalkyl)- and (α-alkoxyalkyl)chromium(III) complexes decompose homolytically.[5] The results indicate that the rate of homolysis increases with the introduction of steric hindrance to the chromium–carbon bond.[5] In another study Espenson[6] reported the formation of $Cr{-}CH_2CN^{2+}$, $Cr{-}CH_2CH_2CN^{2+}$, and $Cr{-}CH_2CH(CH_3)CN^{2+}$, which are all relatively stable in aqueous solutions. However, the formation of $Cr{-}CH(CH_3)CN^{2+}$ and $Cr{-}C(CH_3)_2CN^{2+}$ was not observed though the corresponding free radicals are known to be formed. It was suggested that the latter observation is due to a high rate of homolysis of the latter two complexes.[6]

We decided to try to measure the rates of homolysis of $Cr{-}CH(CH_3)CN^{2+}$ and $Cr{-}C(CH_3)_2CN^{2+}$ using the pulse radiolytic technique, which enables the observation of short-lived intermediates.[7,8] For comparison we decided to measure also the rates of homolysis of $Cr{-}C(CH_3)_2CO_2^+$ and $Cr{-}C(CH_3)_2OH^{2+}$ (the latter was measured in order to check the technique). We were unable to measure the rate of homolysis of $Cr{-}CH(CH_3)CN^{2+}$ but report here the rates of homolysis of the other complexes, which increase along the series Cr–

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(2) (a) Argonne National Laboratory. (b) Nuclear Research Centre Negev. (c) Ben-Gurion University of the Negev.

(3) (a) Anet, F. A. L.; Leblanc, E. *J. Am. Chem. Soc.* **1957**, *79*, 2649. (b) Kochi, J. K.; Davis, D. D. *Ibid.* **1964**, *86*, 5264. (c) Coombes R. G.; Johnson, M. D.; Winterton, J. *J. Chem. Soc. A* **1965**, 7029. (d) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117. (e) Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 2488.

(4) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(5) Kirker, G. W.; Bakač, A.; Espenson, J. H., personal communication.

(6) Funke, L. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 897.

(7) Matheson, M.; Dorfman, L. M. "Pulse Radiolysis"; MIT Press: Cambridge, MA, 1969.

(8) Meyerstein, D. *Acc. Chem. Res.* **1978**, *11*, 43.

0020-1669/82/1321-4016$01.25/0