

Mechanism of Formation of Thiosulfatochromium(VI) Ion and Direct Evidence for Nucleophilic Catalysis of the Hydrolysis of Dichromate Ion

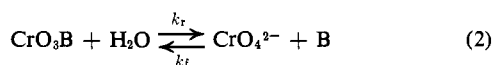
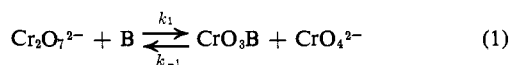
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Abstract: The kinetics of the formation of thiosulfatochromate ion from hydrogen thiosulfate and hydrogen chromate ions has been examined in aqueous solution at 25.0° and ionic strength of 0.11 *M* (NaClO₄). For the reaction $\text{HS}_2\text{O}_3^- + \text{HCrO}_4^- \rightarrow \text{O}_3\text{CrSSO}_3^{2-} + \text{H}_2\text{O}$, $k_t = (2.0 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$, $k_r = (2.1 \pm 0.2) \text{ sec}^{-1}$, and $K_{eq} = (1.1 \pm 0.2) \times 10^4 \text{ M}^{-1}$. The equilibrium constant and extinction coefficients suggest that the complex is sulfur bonded. The reaction conforms to the general mechanism proposed previously for substitution on HCrO_4^- involving rate-determining proton transfer, even though the equilibrium constant is at least 100 times larger than for other complexes of HCrO_4^- . Using the newly determined rate constant for the hydrolysis of thiosulfatochromate ion, the thiosulfate catalyzed hydrolysis of dichromate ion was reexamined at pH 6.5–7.0. Spectroscopic and kinetic evidence was obtained for the formation of thiosulfatochromate ion in this reaction, providing the first direct evidence for the nucleophilic catalysis of dichromate hydrolysis.

Rate-determining proton transfer has been observed in the formation of complexes between HCrO_4^- and species such as H_2PO_4^- ,² H_2PO_3^- ,³ and SCN^- ,⁴ as well as in the formation of dichromate ion by condensation of HCrO_4^- with itself.⁵ According to the principle of microscopic reversibility, this requires that proton transfer also occur in the activated complex for the hydrolysis of dichromate ion, a requirement which has been confirmed by the recent observation of general acid catalysis of this reaction.⁵

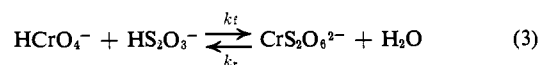
One mechanism proposed³ to account for general acid–base catalysis of dichromate hydrolysis involves formation of a five-coordinate intermediate by attack of water on one of the chromium atoms, with the catalyst simply mediating proton transfer. The possibility of nucleophilic catalysis has also been advanced⁶ to account for the observation that some species which are poor bases but good nucleophiles are very good catalysts for dichromate hydrolysis. This mechanism postulates formation of a CrO_3B intermediate by attack of catalyst B on one of the chromium atoms, followed by hydrolysis of the intermediate.



No direct evidence for such intermediates has previously been obtained, presumably because they hydrolyze rapidly.

Several authors have recently reported the formation of a complex between thiosulfate and hydrogen chro-

mate as the first step in the chromium(VI) oxidation of thiosulfate.^{7,8}



The values obtained for the formation constant of the thiosulfatochromium(VI) complex are 100 times larger than the largest formation constant known for other complexes of chromium(VI). This implies either that the formation rate constant k_t is exceptionally large and thus at variance with the general mechanism for substitution on HCrO_4^- advanced previously,⁴ or that the hydrolysis rate constant k_r is exceptionally small, presenting the possibility of the detection of thiosulfatochromate(VI) ion as an intermediate in the catalyzed hydrolysis of dichromate anion.

The present study was undertaken with two purposes: first, to determine whether the general mechanism involving proton transfer in the rate-determining step of substitution reactions on chromium(VI) is applicable to substitution by a more polarizable species such as thiosulfate ion, and second, to determine the kinetic parameters for the formation and hydrolysis of thiosulfatochromate ion. From these it could be ascertained whether this species would be detectable as an intermediate in order to obtain definitive evidence for or against the nucleophilic catalysis mechanism in the hydrolysis of dichromate ion.

Experimental Section

Chemicals. Reagent grade sodium dichromate, sodium perchlorate, sodium thiosulfate, sodium hydroxide, disodium monohydrogen phosphate, and perchloric acid were used without further purification. All solutions were prepared using deionized water. Occasionally, concentrated solutions (1 *M*) of sodium thiosulfate were slightly opalescent and were filtered before use to give a clear solution.

Spectra. Apparent isosbestic wavelengths for the three species $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , and HCrO_4^- were determined by obtaining the spectra of solutions containing $2.0 \times 10^{-3} \text{ M Cr(VI)}$ in 0.01 *M* pH 5 potassium biphthalate–sodium hydroxide and pH 6 and 7 mono-

(1) Fellow of the Alfred P. Sloan Foundation, 1971–1973.
 (2) S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *J. Amer. Chem. Soc.*, **90**, 6018 (1968), and references therein.
 (3) S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *Acta Chem. Scand.*, **23**, 3277 (1969).
 (4) C.-T. Lin and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 3011 (1972).
 (5) R. Baharad, B. Perlmutter-Hayman, and M. A. Wolff, *J. Phys. Chem.*, **73**, 4391 (1969).
 (6) B. Perlmutter-Hayman and M. A. Wolff, *ibid.*, **71**, 1416 (1967), and references therein.

(7) I. Baldea and G. Niac, *Inorg. Chem.*, **7**, 1232 (1968).
 (8) M. I. Edmonds, K. E. Howlett, and B. L. Wedzicha, *J. Chem. Soc. A*, 2866 (1970).

sodium dihydrogen phosphate-sodium hydroxide buffers in 1.0-mm cells on a Beckman Acta V spectrophotometer. Two isosbestic wavelengths so determined were 338 and 443 nm.

Apparatus and Measurements. The stopped-flow apparatus has been described previously.² The reactant solutions, driving syringes, and mixing and observation chambers were maintained at $25.0 \pm 0.1^\circ$ by thermostated water from a circulating constant-temperature bath. The optical path length was determined by measuring the absorbances at 372 nm of five basic Cr(VI) solutions, varying in concentration from 1.00×10^{-4} to 5.00×10^{-4} M, both on the flow apparatus and in a 1-cm Pyrex cell on a Beckman Acta V spectrophotometer. The ratios of the absorbances gave an optical pathlength in the stopped-flow spectrometer of 2.52 ± 0.02 mm. Using the balancing potential circuit, zero- and infinite-time transmittances of the complex formation reaction could be obtained and the corresponding absorbances used to determine the equilibrium constant for the complex by a technique previously described.⁹

The kinetics of complex formation were studied at 420 and at 350 nm, absorbance maxima for the complex and HCrO_4^- , respectively. Concentration ranges used were $[\text{Cr(VI)}] = 9.96 \times 10^{-5}$ – 3.97×10^{-4} M, $[\text{Na}_2\text{S}_2\text{O}_3] = 1.99 \times 10^{-4}$ – 2.00×10^{-3} M, and $[\text{H}^+] = 2.03 \times 10^{-3}$ – 3.03×10^{-2} M. The concentration of the stock $\text{Na}_2\text{S}_2\text{O}_3$ solution was determined immediately before each set of runs by standardization with KIO_3 , using starch indicator. The ionic strength was maintained at 0.11 M by addition of appropriate amounts of 1.0 M NaClO_4 . Under these conditions, complex formation was virtually complete within 0.5 sec or less, whereas half-times for the subsequent redox reaction between Cr(VI) and $\text{S}_2\text{O}_3^{2-}$ are on the order of 30 sec.⁷ Even at the highest concentrations used, a steady infinite-time transmittance could be obtained, indicating no interference from the redox reaction. The absorbance changes observed at both 420 and 350 nm were generally less than 0.04 absorbance unit, so the recorded traces could be treated as absorbance-time curves without significant error. Five or six traces were recorded and analyzed for each set of concentrations and the average values of k_{obsd} and zero- and infinite-time absorbances determined.

The kinetics of dichromate hydrolysis in the presence of a large excess of thiosulfate were studied on a Sutin-type stopped-flow spectrophotometer² modified by replacing one of the 20-ml driving syringes with a 2.5-ml Hamilton gas-tight syringe. The diameters of the syringe plungers were 4.2 and 19.6 mm, giving a calculated mixing ratio of 21.6:1. Preliminary experiments mixing 0.5 M HClO_4 containing bromphenol blue indicator in a 1:22 ratio with 0.01 M NaOH or 0.01 M NaOH in 0.5 M NaClO_4 gave perfectly flat absorbance vs. time curves, demonstrating the absence of any Schlieren-type mixing effects caused by differing solution viscosities. However, the infinite-time absorbance was considerably lower than expected. Apparently slight overdriving after stopping allowed more of the colorless solution from the large syringe into the observation chamber, lowering the infinite-time absorbance. This was verified by placing the colored solution in the larger of the driving syringes, whereupon a slightly larger than expected infinite-time absorbance was observed. This problem was avoided by triggering the storage oscilloscope in the flow mode and stopping the driving syringes by turning off the magnetic clutch as soon as possible after triggering. This method did not produce such sharp stopping as with the stopping syringe, since the magnetic clutch did not stop instantaneously. Hence the very early part of the reaction (up to about 50 msec after stopping) was not observable and complete kinetic curves could not be obtained.

All pH measurements were made with a Radiometer PHM26C pH meter using a glass electrode with a saturated calomel electrode as the reference electrode.

Computer analyses of the coupled rate equations for the nucleophilic catalysis mechanism were performed on an EAI 580 analog computer and the resulting kinetic and absorbance curves recorded on an X-Y plotter.

Formation of Thiosulfatochromate(VI). Results

Kinetics. The formation of $\text{CrS}_2\text{O}_6^{2-}$ was studied by mixing solutions of $\text{S}_2\text{O}_3^{2-}$ with solutions of chromium-(VI) of sufficiently low concentration that more than 95% of the uncomplexed Cr(VI) existed as HCrO_4^- . The absorption spectrum⁷ of $\text{CrS}_2\text{O}_6^{2-}$ indicates that

(9) G. P. Haight, Jr., D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, **3**, 1777 (1964).

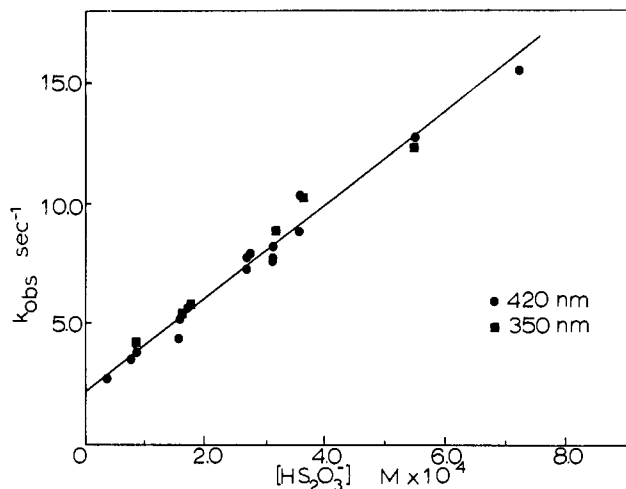


Figure 1. The dependence of k_{obsd} on $[\text{HS}_2\text{O}_3^-]$ at 420 (●) and 350 nm (■).

the extinction coefficient of $\text{CrS}_2\text{O}_6^{2-}$ is larger than that of HCrO_4^- at 420 nm, and smaller than that of HCrO_4^- at 350 nm. First-order rate constants, k_{obsd} , could be obtained from linear plots of $\log(A_t - A_\infty)$ vs. time. At both wavelengths, good linearity was found for over three half-lives with a 5- to 20-fold concentration excess of $\text{S}_2\text{O}_3^{2-}$. Table I gives some representative

Table I. Kinetics of Formation of $\text{CrS}_2\text{O}_6^{2-}$ at $25.0 \pm 0.1^\circ$, $\mu = 0.11 \pm 0.01$ M, 420 nm

$[\text{Cr(VI)}]_0$, $M \times 10^4$	$[\text{Na}_2\text{S}_2\text{O}_3]_0$, $M \times 10^3$	$[\text{HClO}_4]_0$, $M \times 10^2$	k_{obsd} , sec^{-1}
1.00	2.00	3.04	15.6 ± 2.0
1.00	2.00	2.03	12.9 ± 0.7
0.997	0.995	3.00	8.95 ± 0.40
1.98	1.99	1.00	7.75 ± 0.40
1.98	0.995	2.00	7.29 ± 0.12
1.00	1.00	1.01	5.23 ± 0.19
2.00	0.998	0.506	3.79 ± 0.11
2.00	2.00	0.203	3.61 ± 0.10
2.00	0.998	0.203	2.81 ± 0.10

kinetic data.

A plot of k_{obsd} against $[\text{HS}_2\text{O}_3^-]$ gives a straight line as shown in Figure 1. The second acid dissociation constant¹⁰ of thiosulfuric acid is

$$K_a = [\text{H}^+][\text{S}_2\text{O}_3^{2-}]/[\text{HS}_2\text{O}_3^-] = 5.4 \times 10^{-2} \text{ M}$$

The variation in hydrogen ion concentration during the reaction due to this equilibrium is less than 2%, so that the concentration of HS_2O_3^- is approximately constant in the presence of excess thiosulfate.

Assuming that reaction 3 is observed, it can be shown that

$$k_{\text{obsd}} = k_f[\text{HS}_2\text{O}_3^-] + k_r \quad (4)$$

Analysis of 18 data points at 420 nm and 6 points at 350 nm with an inverse square weighted least-squares program gave the values $k_f = (2.0 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_r = 2.1 \pm 0.2 \text{ sec}^{-1}$. The observed rate law can also be written, of course, as $k_{\text{obsd}} = k_f^{\text{H}^+}[\text{H}^+][\text{S}_2\text{O}_3^{2-}] + k_r$ with $k_f^{\text{H}^+} = 3.7 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}$.

(10) F. M. Page, *J. Chem. Soc.*, 1719 (1953).

A few experiments performed with a fivefold excess of chromium(VI) also gave linear plots of $\log(A_t - A_\infty)$ against time. Using the value of k_r determined above together with the known concentration of chromium(VI), a value of $k_f = (2.3 \pm 0.2) \times 10^4 M^{-1} \text{sec}^{-1}$ was calculated.

Although hydrogen ion catalysis has been observed²⁻⁴ in other substitution reactions on HCrO_4^- , the plot of k_{obsd} against $[\text{HS}_2\text{O}_3^-]$ shows no sign of deviation from linearity at the highest hydrogen ion concentration used. Increasing interference from the subsequent redox reaction at higher hydrogen ion concentrations precludes extending the range much further to search for catalytic effects. Hydrogen ion catalysis is not excluded by these studies, but an upper limit of approximately $1 \times 10^5 M^{-2} \text{sec}^{-1}$ is set for $k_f^{\text{H}^+}$ for a term in the rate law of the form $k_f^{\text{H}^+}[\text{H}^+][\text{HS}_2\text{O}_3^-] \cdot [\text{HCrO}_4^-]$.

The Formation Constant and Extinction Coefficients of $\text{CrS}_2\text{O}_6^{2-}$. From the kinetic results, the equilibrium constant for complex formation can be calculated to be $(9.5 \pm 1.0) \times 10^3 M^{-1}$. This compares reasonably well with a value of $(1.24 \pm 0.14) \times 10^4 M^{-1}$ reported by Baldea and Niac.⁷ A value of $2.4 \times 10^5 M^{-2}$ has been reported, although the units were not clearly stated.⁸ Multiplication by the acidity constant of HS_2O_3^- gives a value of $1.3 \times 10^4 M^{-1}$, at 20° and ionic strength 0.17 *M*, again in fair agreement with the present results.¹¹

A spectrophotometric method⁹ based on the absorbance at the completion of the complex formation reaction was used to determine K_{eq} and ϵ for $\text{CrS}_2\text{O}_6^{2-}$ independently of the kinetics results. The extinction coefficients of HCrO_4^- used in the calculations were the literature values of $228 M^{-1} \text{cm}^{-1}$ at 420 nm⁷ and $1563 M^{-1} \text{cm}^{-1}$ at 350 nm.¹² These are in good agreement with the values of $248 \pm 12 M^{-1} \text{cm}^{-1}$ and $1545 \pm 77 M^{-1} \text{cm}^{-1}$ calculated from the observed zero-time absorbances, considering the 5-msec delay between mixing and observation of the reactant solutions. The results of these calculations are presented in Table II,

Table II. K_{eq} and ϵ for $\text{CrS}_2\text{O}_6^{2-}$ at 0.11 *M* Ionic Strength

Method	$K_{\text{eq}} \times 10^{-4}$ M^{-1}	ϵ , $M^{-1} \text{cm}^{-1}$	Ref
	λ 420 nm		
Kinetic	0.93 ± 0.10^b	1143 ± 120^b	This work
Spectrophotometric ^a	1.08 ± 0.22^b	1128 ± 92^b	This work
Successive approximation	1.24 ± 0.14^c	1040 ± 40^c	7
	λ 350 nm		
Kinetic	0.93 ± 0.10^b	804 ± 93^b	This work
Spectrophotometric ^a	1.3^d	688^d	8
Continuous flow		750^c	7

^aReference 9. ^b 25°. ^c 20°. ^d Ionic strength 0.17 *M*, 20°.

together with the results from the kinetics studies and the values available in the literature. There is good agreement among both the equilibrium constants and the extinction coefficients determined by various methods. From these results we conclude that K_{eq}

(11) This point was confirmed in a personal communication from K. E. Howlett.

(12) W. G. Davies and J. E. Prue, *Trans. Faraday Soc.*, **51**, 1045 (1955).

is approximately $(1.1 \pm 0.2) \times 10^4 M^{-1}$ in the range 0.1–0.2 *M* ionic strength and 20–25°.

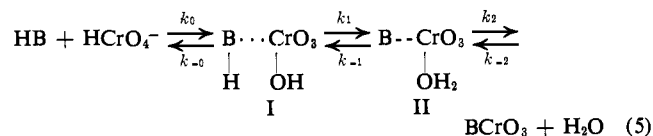
Discussion

The thiosulfatochromate ion is unique among the known heteropolyanions of Cr(VI) in two ways: its large formation constant and the red shift of the spectral band that usually occurs at about 350 nm in chromium(VI) complexes. This band, ascribed to a charge-transfer transition, occurs at very nearly 350 nm in HCrO_4^- , CrPO_7^{3-} , and CrSO_7^{2-} , but is shifted to 390 nm in $\text{CrS}_2\text{O}_6^{2-}$.

Interpretations of the significance of this spectral shift differ. Howlett, *et al.*,⁸ apparently do not consider the shift significant, stating that the similarity of the HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and $\text{CrS}_2\text{O}_6^{2-}$ spectra suggests a Cr–O bond, formulating the intermediate as $\text{O}_3\text{CrO}_3\text{S}_2^{2-}$. Baldea and Nica point out that the absorbance maximum occurs almost exactly at 350 nm for HCrO_4^- , CrPO_7^{3-} , and CrSO_7^{2-} , all of which have Cr–O bonds; *i.e.*, the nature of the R group in a Cr–O–R chromophore apparently does not significantly affect the position of the charge-transfer band. They also point out that the maximum for CrO_3Cl^- , in which there is presumably a Cr–Cl bond, is shifted to about 360 nm and ascribe this effect to the replacement of an oxygen atom by a somewhat less electronegative chlorine atom. Also, the maximum for CrO_4^{2-} occurs at 372 nm, consistent with a greater electron-donating ability for a Cr–O oxygen than for a Cr–O–R oxygen. They observe that the even larger shift observed for $\text{CrS}_2\text{O}_6^{2-}$ is quite consistent with the assumption that there is a Cr–S bond rather than a Cr–O bond in this species and formulate it as $\text{O}_3\text{CrSSO}_3^{2-}$.

The exceptionally large formation constant for $\text{CrS}_2\text{O}_6^{2-}$ may also be taken as indirect evidence for a Cr–S bond. Table III summarizes the equilibrium constants for some Cr(VI) heteropolyanions. The fact that the constant for $\text{CrS}_2\text{O}_6^{2-}$ is two to three orders of magnitude larger than any of the others listed implies a major difference in bond strengths between such species as CrSO_7^{2-} and $\text{CrS}_2\text{O}_6^{2-}$. It seems most reasonable to ascribe this to the difference between Cr–O and Cr–S bonding, respectively.

The kinetic parameters for $\text{CrS}_2\text{O}_6^{2-}$ determined herein provide an important test of a recently proposed general mechanism of formation for complexes of this general type.⁴ This mechanism involves formation of a weak five-coordinate intermediate followed by rate-determining proton transfer and subsequent loss of a water molecule from chromium(VI), as shown in eq 5. According to this mechanism, the first five-



coordinate intermediate (I) has only a weak B–Cr bond and is in rapid equilibrium with the reactants. The equilibrium constant K_0 is determined primarily by electrostatic effects and does not depend strongly on the chemical nature of B. Proton transfer (k_1) is rate determining. With these assumptions, $k_f = K_0 k_1$ and $k_r = k_{-1}/k_2 = k_f/K_{\text{eq}}$. Formation of the strong B–Cr bond occurs subsequent to the proton transfer.

Table III. Equilibrium Constants for Cr(VI) Heteropolyanions

Reaction	μ, M^{-1}	K_{eq}	Ref
$HCrO_4^- + HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$	1.0	98	a
$HCrO_4^- + HSO_4^- \rightleftharpoons CrSO_7^{2-} + H_2O$	3.0	4.1	a
$HCrO_4^- + H_3PO_4 \rightleftharpoons H_2CrPO_7^- + H_2O$	0.25	9.4	a
$HCrO_4^- + H_2PO_4^- \rightleftharpoons HCrPO_7^{2-} + H_2O$	0.25	2.9	a
$HCrO_4^- + H_2PO_4^- \rightleftharpoons HCrPO_7^{2-} + H_2O$	3.0	6 ± 2	2
$HCrO_4^- + HSO_3^- \rightleftharpoons CrS_1O_6^{2-} + H_2O$	0.5	36 ± 1	b
$HCrO_4^- + HS_2O_3^- \rightleftharpoons CrS_2O_6^{2-} + H_2O$	0.11	$(1.2 \pm 0.5) \times 10^4$	This work
$HCrO_4^- + H^+ + Cl^- \rightleftharpoons CrO_3Cl^- + H_2O$	1.0	17 ^c	This work
$HCrO_4^- + H^+ + CNS^- \rightleftharpoons CrO_3SCN^- + H_2O$	0.3	220 ± 25^c	4

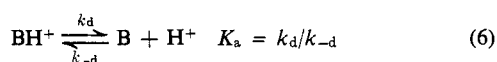
^a Reference 9 and references therein. ^b G. P. Haight, Jr., F. Perchonock, F. Emmenegger, and G. Gordon, *J. Amer. Chem. Soc.*, **87**, 3835 (1965). ^c Units, M^{-2} .

Table IV. Kinetic Parameters for Formation of Cr(VI) Complexes

$HX^{(n+1)} + HCrO_4^- \rightleftharpoons XCrO_3^{n-} + H_2O$						
$HX^{(n+1)-}$	K_a^a	K_{eq}	$k_t, M^{-1} \text{ sec}^{-1}$	$k_t, \text{ sec}^{-1}$	$k_t^{H^+}, M^{-2} \text{ sec}^{-1}$	Ref
$HCrO_4^-$	3×10^{-6}	98	2	2.7×10^{-2}	6.6×10^6	c
$H_2PO_4^-$	6×10^{-8}	6	Neg ^b		1.2×10^6	2
$H_2PO_3^-$	3×10^{-7}	8			5×10^5	3
$HS_2O_3^-$	5.4×10^{-2}	1×10^4	2×10^4	2		This work
HSCN	>1	220			5.4×10^6	4

^a $K_a = [H^+][X^{n-}]/[HX^{(n+1)-}]$. ^b Negligible compared to H^+ catalyzed reaction. ^c J. H. Swinellart and G. W. Castellan, *Inorg. Chem.*, **3**, 278 (1964).

If the interaction between HB and $HCrO_4^-$ in intermediate I is sufficiently weak so as not to affect the acidity of the BH species, then the rate of proton transfer can be estimated from the equilibrium acid dissociation constant of BH. This is possible, since the rate of recombination of the proton and a conjugate base B is generally diffusion controlled with a second-order rate constant



of about $10^{10} M^{-1} \text{ sec}^{-1}$. Consequently, $k_1 \sim k_{-d}K_a = 10^{10}K_a$.

The present results are consistent with this mechanism. For $HS_2O_3^-$, $K_a = 5 \times 10^{-2} M$, giving an estimate for k_1 of $5 \times 10^8 \text{ sec}^{-1}$. From the observed value of $k_t = 2 \times 10^4 M^{-1} \text{ sec}^{-1}$, a value of K_0 is calculated to be $4 \times 10^{-5} M^{-1}$, consistent with the assumption of a very weak association.

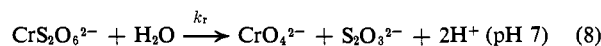
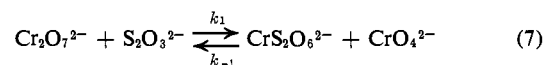
Rate constants for the formation of complexes with $HCrO_4^-$ are collected in Table IV. The rate constants for the hydrogen ion catalyzed formation reactions are nearly constant, independent of the nature and acidity of the entering species HB. This requires that the reverse hydrolysis rates catalyzed by hydrogen ion depend inversely on the overall equilibrium constant for formation of the complex and implies that the B-Cr bond is very weak in the activated complex. Comparison of the two available uncatalyzed formation rate constants for substitution by $HS_2O_3^-$ and $HCrO_4^-$ on $HCrO_4^-$ suggests that these rates are directly proportional to the acidity of the entering species HB as proposed by the above mechanism. The uncatalyzed rate of substitution by $HS_2O_3^-$ is four orders of magnitude greater than that for $HCrO_4^-$, and $HS_2O_3^-$ is a stronger acid than $HCrO_4^-$ by four orders of magnitude. This again suggests very weak bonding between HB and $HCrO_4^-$ in the transition state, since the acidity of HB is apparently not substantially affected in the

activated complex. The formation constants are not directly related to the acidity of HB and consequently the rates of the uncatalyzed hydrolysis reactions depend on the particular nature of the complex of chromium(VI).

Thiosulfate Catalysis of Dichromate Hydrolysis. Results

With the determination of the formation and hydrolysis rate constants for $CrS_2O_6^{2-}$, the thiosulfate catalysis of the hydrolysis of dichromate ion can now be examined to determine whether the reaction occurs by nucleophilic attack on dichromate ion or by general acid-base catalysis.

The reactions of interest at pH 7 are



At pH 7 the predominant monomeric chromium(VI) species is CrO_4^{2-} rather than $HCrO_4^-$. Furthermore, at pH 7, formation of $CrS_2O_6^{2-}$ from $HCrO_4^-$ can be neglected and hydrogen ion and hydroxide ion catalysis of the dichromate hydrolysis are negligible.⁶ If the buffer concentration is kept low and the thiosulfate concentration high, the major pathway for hydrolysis must be through the $CrS_2O_6^{2-}$ intermediate if the nucleophilic catalysis mechanism is correct.

Kinetics Observations. There appears to be an isosbestic point in the spectra of the three species $Cr_2O_7^{2-}$, $HCrO_4^-$, and CrO_4^{2-} at approximately 443 nm, although these observations could only be made by varying the pH since the dichromate ion is not stable at pH 7. The absorbance of $CrS_2O_6^{2-}$ is greater than that of $Cr_2O_7^{2-}$ or CrO_4^{2-} at this wavelength. Thus a maximum in absorbance should be observed during the hydrolysis of dichromate in the presence of high thiosulfate concentrations owing to the formation and hydrolysis

of $\text{CrS}_2\text{O}_6^{2-}$ if it is formed in sufficient concentration. In contrast, if thiosulfate acts as a general acid-base catalyst without formation of a thiosulfatochromate intermediate, no change in absorbance is expected at this wavelength.

Kinetics experiments were performed on the modified Sutin stopped-flow apparatus, mixing solutions of $2 \times 10^{-2} M$ or $4 \times 10^{-2} M$ Cr(VI) in $1.0 M$ NaClO_4 at pH 4-5 (unbuffered) in a 1:22 ratio with $0.02 M$ pH 7 phosphate buffer containing $1.0 M$ NaClO_4 and with solutions of 0.02 , 0.05 , and $0.5 M$ $\text{Na}_2\text{S}_2\text{O}_3$ in the $0.02 M$ pH 7 buffer. The 0.02 and $0.05 M$ $\text{Na}_2\text{S}_2\text{O}_3$ solutions also contained $1.0 M$ NaClO_4 . In the absence of thiosulfate, no change in absorbance was observed at 440 nm . This value is the observed isobestic wavelength for dichromate ion and monomeric chromium(VI) species at approximately pH 7, which had been estimated as 443 nm by spectroscopic measurements at different acidities. The isobestic point is independent of chromium(VI) concentration, and its observation indicated that there were no appreciable effects due to the large mixing ratio. With $2 \times 10^{-2} M$ Cr(VI) and $0.02 M$ $\text{Na}_2\text{S}_2\text{O}_3$ a flat absorbance *vs.* time curve was also obtained. However, with the same Cr(VI) concentration and $0.5 M$ $\text{S}_2\text{O}_3^{2-}$, a relatively rapid rise in absorbance was observed, partially obscured by poor stopping of the flow, followed by a nearly first-order decay with a half-time of about 515 msec . *The maximum in absorbance at 440 nm is interpreted as direct evidence for the formation of $\text{CrS}_2\text{O}_6^{2-}$ by nucleophilic substitution on $\text{Cr}_2\text{O}_7^{2-}$.*

Further evidence for the formation of a thiosulfatochromate intermediate is obtained from the effect of different initial concentrations of CrO_4^{2-} . According to the mechanism described by eq 7 and 8, an increase in the chromate concentration should inhibit the overall hydrolysis of dichromate. The initial chromate concentration after mixing $2 \times 10^{-2} M$ Cr(VI) and $0.5 M$ $\text{S}_2\text{O}_3^{2-}$ is about $2.4 \times 10^{-4} M$ (at the measured pH of 6.5 after mixing), and the half time for the decay of the absorbance is about 515 msec . The initial chromate concentration after mixing $4 \times 10^{-2} M$ Cr(VI) and $0.5 M$ $\text{S}_2\text{O}_3^{2-}$ is about $3.0 \times 10^{-4} M$ (at the measured pH of 6.7), and the half-time for the decay in this case is found to be about 625 msec . A further check on the effect of chromate was made by mixing $2 \times 10^{-2} M$ Cr(VI) with a $0.5 M$ $\text{S}_2\text{O}_3^{2-}$ solution which was also $1 \times 10^{-3} M$ in Cr(VI) . The initial chromate concentration after mixing (at the measured pH of 6.6) was about $7.6 \times 10^{-4} M$, and the half-time for the decay was found to be about 1000 msec . This decrease in the observed rate is consistent with the predicted chromate inhibition if nucleophilic catalysis occurs.

The hydrolysis reaction was also studied at 313 nm , where dichromate is the major absorbing species. A decrease in absorbance with time is observed, but the rate of the decrease increases by only a factor of about 5 with a tenfold increase in thiosulfate concentration, again consistent with formation of $\text{CrS}_2\text{O}_6^{2-}$.

Discussion

The observation of an absorbance maximum corresponding to formation and hydrolysis of the thiosulfatochromate intermediate and the qualitative evi-

dence of chromate inhibition constitute strong evidence supporting the nucleophilic catalysis mechanism of dichromate hydrolysis by thiosulfate in neutral solution. A complete kinetic analysis of the reaction requires determination of k_1 , since k_r has been determined independently and the ratio k_1/k_{-1} can be calculated from the equilibrium constant for the formation of $\text{CrS}_2\text{O}_6^{2-}$, the equilibrium constant for the dichromate-hydrogen chromate reaction, and the acid dissociation constant of hydrogen chromate ion.

A value of the second-order rate constant, $k_N = 2.9 M^{-1} \text{ sec}^{-1}$, has been reported by Perlmutter-Hayman and Wolff⁶ for the thiosulfate catalyzed hydrolysis of dichromate, but the reverse reaction (7) and possible interference due to hydrolysis of the intermediate were not considered. Using this value of $2.9 M^{-1} \text{ sec}^{-1}$ as a lower limit for k_1 , a lower limit of $5.2 \times 10^3 M^{-1} \text{ sec}^{-1}$ can be calculated for k_{-1} . With these rate constants and the independently determined value of 2.0 sec^{-1} for k_r , an analog computer was used to calculate the concentrations of the various species under the conditions of the original experiments,⁶ taking $0.01 M$ as a representative thiosulfate concentration. At the time of maximum concentration of thiosulfatochromate, the rate of the reverse reaction (7) is only 10% of the forward reaction. The rate of the forward reaction is only one-half of the rate of the hydrolysis of the thiosulfatochromate intermediate, however, and thus the forward reaction is not the rate-determining step. Consequently, k_1 must be larger than the observed k_N .

Analog computer analysis of the reaction under the conditions employed in the present study also predicted that the observed rate of decay ($k_{\text{obsd}} = 1.4 \text{ sec}^{-1}$) of the thiosulfatochromate intermediate responsible for the maximum in absorbance should be less than the known rate of hydrolysis ($k_r = 2.0 \text{ sec}^{-1}$). Finally, the predicted magnitude of the absorbance maximum agreed moderately well with the observed increase. A complete kinetic analysis was not possible due to the experimental difficulties associated with the stopped-flow apparatus using a large mixing ratio. Experimental values of k_1 and k_{-1} are consequently unavailable.

Summary

Substitution on hydrogen chromate ion by thiosulfate to form thiosulfatochromate(VI) ion in acidic solution occurs with a rate constant which is consistent with a mechanism requiring rate-determining proton transfer. The formation constant and absorption spectrum suggest a sulfur bonded product.

Observation of this complex as an intermediate in the thiosulfate catalyzed hydrolysis of dichromate ion in neutral solution provides the first direct evidence for the nucleophilic catalysis mechanism of dichromate hydrolysis. Thus, in solutions of low acidity in which a mechanism requiring proton transfer is no longer favorable, nucleophilic catalysis provides an alternate pathway for the hydrolysis of dichromate ion.

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