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The Reaction between Chromate and Thiosulfate. II. The Kinetics of Tetrathionate Formation

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Stoichiometry and kinetics of the reaction between chromate and thiosulfate were studied under conditions of tetrathionate formation, *i.e.*, using large excesses of thiosulfate. The reaction kinetics was investigated spectrophotometrically at ionic strength 0.1 M and several hydrogen ion concentrations. The kinetic law

$$-\mathrm{d}(\mathrm{CrS_2O_6}^{2-})/\mathrm{d}t = (K/3)\{k_2 + k_3(\mathrm{H}^+)\}(\mathrm{HS_2O_3}^-)^2\mathrm{CrS_2O_6}^{2-})/\{1 + K(\mathrm{HS_2O_3}^-)\}$$

was derived with $k_2 = (1.42 \pm 0.21) \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_3 = (1.55 \pm 0.22) \times 10^4\ M^{-2}\ \mathrm{sec}^{-1}$ at 20°. The formation constant of the intermediate $CrS_2O_6^{2-}$ was found previously to be $K = 1.24 \times 10^4\ M^{-1}$. A reaction mechanism involving the transition states $CrO_2(OH)(S_2O_3)_2^{3-}$ and $CrO(OH)_2(S_2O_3)_2^{2-}$ was proposed in agreement with the experimental kinetics law. The influence of the temperature on the rate constants, between 15 and 35°, allowed us to calculate $\Delta H^{\ddagger} = 8.2 \pm 0.7$ kcal and $\Delta S^{\ddagger} = -20.8 \pm 2.5$ eu associated with k_2 and $\Delta H^{\ddagger} = 6.2 \pm 2.4$ kcal and $\Delta S^{\ddagger} = -17.7 \pm 8.0$ eu associated with k_3.

1. Introduction

The thiosulfate oxidation by chromate has been studied by Bell,[1] Stiasny and Das,[2] and Meunier.[3] At low concentrations the stoichiometry is in agreement with the bulk equation

$$2\mathrm{CrO_4}^{2-} + 6\mathrm{S_2O_3}^{2-} + 16\mathrm{H}^+ = 2\mathrm{Cr}^{3+} + 3\mathrm{S_4O_6}^{2-} + 8\mathrm{H_2O} \quad (1)$$

At higher concentrations sulfate and sulfur are also formed, according to

$$8\mathrm{CrO_4}^{2-} + 3\mathrm{S_2O_3}^{2-} + 34\mathrm{H}^+ = 8\mathrm{Cr}^{3+} + 6\mathrm{SO_4}^{2-} + 17\mathrm{H_2O} \quad (2)$$

Sulfur is supposed to be a product of the hydrogen ion decomposition of thiosulfate.

Isvetanovič and Relosavlijevič[4] have worked out a potentiometric method to titrate directly chromate by thiosulfate in the presence of Cu^{2+} ions, when tetrathionate is the only oxidation product of thiosulfate. Rao and Sarma[5] have tried to replace Cu^{2+} ions by other catalysts in acetate buffer at pH 4.5.

The mechanism and kinetics of the uncatalyzed reaction as well as of the catalyzed reaction have not yet been studied. The purpose of the present paper is the kinetic study of the reaction between chromate and thiosulfate in acid solutions.

As in other redox reactions involving chromate,[6-8] the well-known capacity of $HCrO_4^-$ ion to condense[9-11] leads to the formation of a transient heterodiacid by a fast equilibrium process

$$\mathrm{HCrO_4}^- + \mathrm{HS_2O_3}^- \rightleftharpoons \mathrm{H_2O} + \mathrm{CrS_2O_6}^{2-} \qquad (K) \qquad (3)$$

The results of a study of the thiosulfatochromate ion have been reported in a previous note.[12] An unusually high formation constant $K = 1.24 \times 10^4\ M^{-1}$ at 20° and ionic strength 0.11 M as well as spectral evidence for a Cr–S link have been found.

2. Experimental Section

Materials.—Analytical reagent grade chemicals were used without further purification. Stock solutions in twice distilled water were made and they were used to prepare the solutions of the requested concentration by dilution, freshly before each experiment. The $Na_2S_2O_3$ solutions were standardized with $K_2Cr_2O_7$ and KI. The ionic strength was kept constant by addition of an excess of $NaClO_4$ from a 1 M stock solution which was prepared by neutralization of 2 M $HClO_4$ by NaOH, the neutralization point at pH 7.00 ± 0.12 being controlled potentiometrically.

Kinetic Runs.—Reaction kinetics was followed spectrophotometrically, in a 1-cm cell of a Model VSU-1 Zeiss spectrophotometer with attachment for photorecording.[12,13] A signal, proportional to the transmitted light intensity, was recorded *vs.* time on photographic film. Time was marked on the same film by means of a metronome. The records were magnified to a proper size in order to allow an easy reading of the experimental data.

Temperature was kept constant by circulation of water from a Wobser U-8 thermostat through the water jacket of the cell holder. All solutions were kept in a temperature bath, connected to the same thermostat as the cell holder. At the end of each kinetic run the temperature was measured in the cell, using a thermometer divided in tenths of degrees Celsius.

Air oxygen was removed by bubbling purified CH_4 through the solutions in the cell as well as in the flasks. The bubbles had also the function to stir the solution in the photometer cell during the reaction.

The reaction was started by introducing 1 ml (±0.5%) of a solution containing $KHCrO_4$ and $HClO_4$ with a syringe into 4 ml of a mixture of $Na_2S_2O_3$ and $NaClO_4$ solutions. The mixing time was less than 0.4 sec.

The change of the transmitted light intensity was followed at 420 mμ with a spectral slit width of 1 mμ.

Stoichiometry.—A 10- or 25-ml sample of a $10^{-3}\ M$ $HCrO_4^-$ solution containing various amounts of $HClO_4$ was mixed with 50 or 100 ml of a $10^{-2}\ M$ $S_2O_3^{2-}$ solution. Exactly the same volume of an I_2 solution of the same concentration was then added after the reaction of the first two was completed. The excess iodine was finally titrated back with thiosulfate. The needed amount of thiosulfate was exactly the same as that consumed in the reac-

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[3] L. Meunier, *Chim. Ind.* (Paris), **1**, 275 (1918).

[4] R. J. Isvetanovič and S. Relosavlijevič, *Glasnik Khem. Drushtva, Biograd*, **11**, No 1/2, 63 (1940–1946).

[5] V. P. R. Rao and B. V. S. Sarma, *Anal. Chem.*, **37**, 1373 (1965).

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[11] M. Cohen and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4387 (1952).

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[13] I. Cadariu, G. Niac, and L. Oniciu, *Studia Univ. Babes-Bolyai, Ser Chem.*, **7** (1), 27 (1962).

tion with Cr(VI). Each experience was repeated also without addition of Cr(VI) in order to take into account the H^+-catalyzed decomposition of the thiosulfate. The corrections did not exceed 2% of the thiosulfate consumed in the redox reaction.

3. Results and Discussion

Preliminary tests showed an induction period, except in the case of a large thiosulfate excess. Other factors which shorten the induction period are H^+ ion concentration and temperature. The existence of the induction period, which has been observed also in other oxidations of the thiosulfate[14] as well as in reactions of Cr(VI),[8] suggests a rather complicated mechanism. Besides, we have to consider a set of protolytic and hydrolytic equilibria

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \qquad (K_h)$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \qquad (K_d)$$

$$H_2S_2O_3 \rightleftharpoons H^+ + HS_2O_3^- \qquad (K_1)$$

$$HS_2O_3^- \rightleftharpoons H^+ + S_2O_3^- \qquad (K_2)$$

and the formation of thiosulfatochromate (eq 3) as well.

According to the equilibrium constants[15-17] and the concentrations used in this work, the predominant Cr(VI) species in the absence of thiosulfate is $HCrO_4^-$, since the dimer is less than 1% of the monomer. Thiosulfate is in form of $S_2O_3^{2-}$ and $HS_2O_3^-$.

At high thiosulfate concentrations equilibrium 3 is as good as completely shifted to the right; therefore in the mixture the only absorbent species is $CrS_2O_6^{2-}$, with a very high molar absorptivity, ϵ_{420} 1040 M^{-1} cm^{-1},[2] compared to $\epsilon_{0,420}$ 228 M^{-1} cm^{-1} for $HCrO_4^-$. A high excess of thiosulfate is advantageous for other reasons too: the induction period disappears, and the thiosulfate oxidation to sulfate is minimized.

3.1. Stoichiometry.—As the data registered in Table I show, in a thiosulfate excess of about 50:1 in acidic media 96% of the chromate is used to oxidize the thiosulfate to tetrathionate, 4% being used probably to oxidize the thiosulfate to sulfate. Small amounts of sulfate were certainly formed during the reaction, as tests with Ba^{2+} showed. The stoichiometry experiments were made strictly under the same conditions as the kinetic runs, in order to make sure that parallel oxidation of thiosulfate to sulfate has a negligible contribution to the over-all kinetics. A stoichiometric study involving a wider range of concentrations and acidities is to be made simultaneously with the corresponding kinetic investigations.

3.2. Kinetics.—The absorbent species at 420 mμ are $HCrO_4^-$ and $CrS_2O_6^{2-}$. Thus the absorbance of a 1-cm path length cell is

$$A = \epsilon_0(HCrO_4^-) + \epsilon(CrS_2O_6^{2-}) \qquad (4)$$

As mentioned above, at higher concentrations and at large excesses of thiosulfate all of the present Cr(VI) is in the form of $CrS_2O_6^{2-}$. In this extreme case it will be a proportionality relationship between the reaction rates written as $-\mathrm{d}A/\mathrm{d}t$ and as $-\mathrm{d}(CrS_2O_6^{2-})/\mathrm{d}t$.

TABLE I

THE STOICHIOMETRY OF THE REDUCTION OF CHROMIUM(VI) IN THIOSULFATE EXCESS

10^4(Cr(VI)), M	$10^2(S_2O_3^{2-})_t$, M	$10^2(HClO_4)$, M	Time, min	$CrO_4^{2-}:S_2O_3^{2-}$
2.857	1.43	1.43	1.0	1:2.80
			2.0	1:2.76
2.857	1.43	0.715	2.0	1:2.88
3.3	1.66	1.66	1.5	1:2.80
			1.5	1:2.90
			1.5	1:2.87
			1.5	1:2.93
4.0	1.6	2.0	1.0	1:2.94
			1.0	1:2.90
2.0	1.0	0.48	1.5	1:2.83[a]
4.0	1.0	1.587	1.0	1:2.97[a]
			0.5	1:2.87[a]

[a] Titrations were made after the kinetic curves were recorded.

The rate law

$$r = -\frac{\mathrm{d}A}{\mathrm{d}t} = k_{\mathrm{exptl}}A^n \qquad (5)$$

may be written in logarithmic form

$$\log r = \log k_{\mathrm{exptl}} + n \log A \qquad (6)$$

The experimental records were corrected in order to eliminate the error due to the inertia of the electrometer wire, which has a time constant of 0.25 sec. Then tangents were drawn at different points and $-\mathrm{d}A/\mathrm{d}t$ was calculated. The plots of log $(-\mathrm{d}A/\mathrm{d}t)$ *vs.* log A were straight lines. The slope of these lines gave the reaction order with respect to the thiosulfatochromate ion and the cut of the ordinate led to the values of k_{exptl}. The data are given in Table II along with the initial rates $r_{t=0}$.

TABLE II

REACTION ORDER WITH RESPECT TO $CrS_2O_6^{2-}$ AND EXPERIMENTAL RATE CONSTANTS k_{exptl} AT 20°, μ = 0.11 M, AND (Cr(VI)) = 4×10^{-4} M

$10^3(S_2O_3^{2-})_t$, M	$10^3(H^+)$, M	$-\mathrm{d}A/\mathrm{d}t$	k_{exptl}, sec^{-1} From eq 6	k_{exptl}, sec^{-1} From eq 7	Order
1.2	7.26	0.041	0.105	0.102	1.01
0.9	8.0	0.026	0.077	0.078	1.03
0.6	9.18	0.022	0.058	0.053	1.15
0.3	9.4	0.0115	0.034	0.024	1.40

As Table II shows, the reaction order is 1 at high thiosulfate concentrations. Plots of log A *vs.* time are also straight lines up to more than 90% conversion, obeying the first-order equation

$$\log A = \log A_0 - 2.3kt \qquad (7)$$

The specific rate, calculated from the slope of these plots, is in agreement with the values given by eq 6. Since Cr(VI) is entirely in the form of $CrS_2O_6^{2-}$, the reaction order is also 1 with respect to $HCrO_4^-$, according to preequilibrium 3. The change of the initial Cr(VI) concentration in the range of 10^{-4}–6×10^{-4} M does not change the rate constant k_{exptl}. At lower $S_2O_3^{2-}$ concentrations there is an important amount of $HCrO_4^-$

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[14] G. Niac, Dissertation, University of Cluj, 1961.

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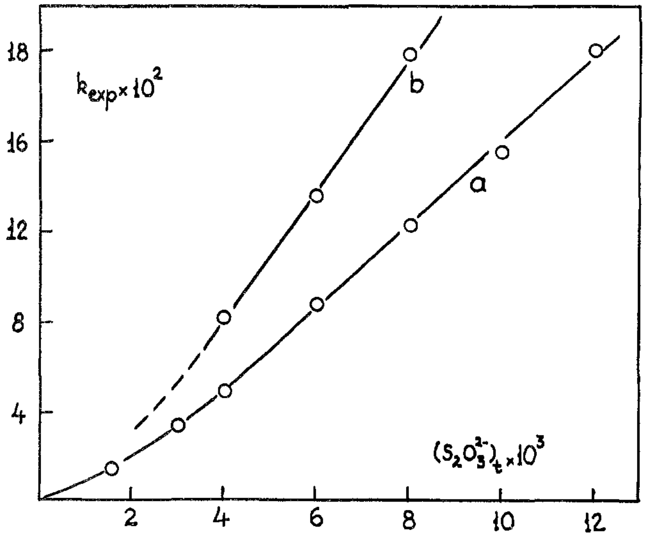


Figure 1.—Plots of k_{exptl} *vs.* total thiosulfate concentration at $\mu = 0.1\ M$, (Cr(VI)) = $4 \times 10^{-4}\ M$, and 25°: (a) (H^+) = $1.0 \times 10^{-2}\ M$; (b) (H^+) = $1.5 \times 10^{-2}\ M$.

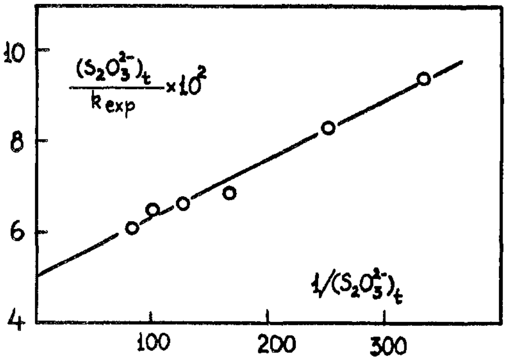


Figure 2.—Linearization of curve a in Figure 1.

in solution and a trend toward higher orders is evident in the last column of Table II.

At constant hydrogen ion concentrations the first-order rate constant k_{exptl} depends on the thiosulfate concentration as shown in Figure 1. This dependence tends to be linear at higher concentrations of thiosulfate. The initial nonlinear portion of the curves has the meaning of a higher reaction order due to preequilibrium 3.[14] The analytical expression of the curves in Figure 1 is the equation of a hyperbola

$$k_{exptl} = \frac{l(S_2O_3^{2-})_t^2}{1 + m(S_2O_3^{2-})_t} \qquad (8)$$

l and m being constants. The subscript t indicates total analytical concentration. At low thiosulfate concentrations $m(S_2O_3^{2-})_t \ll 1$, and eq 8 takes the form of a parabola according to the reaction order 2 with respect to the thiosulfate. At higher concentrations $m(S_2O_3^{2-})_t \gg 1$ and k_{exptl} varies with the first power of $(S_2O_3^{2-})_t$, the reaction being first order with respect to the thiosulfate. A plot of $(S_2O_3^{2-})_t/k_{exptl}$ *vs.* $1/(S_2O_3^{2-})_t$ gives a straight line as shown in Figure 2. The values $l = 7.35 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ and $m = 3.9 \times 10^2\ M^{-1}$ have been calculated from the slope and the cut of the line in Figure 2 which corresponds to curve a in Figure 1.

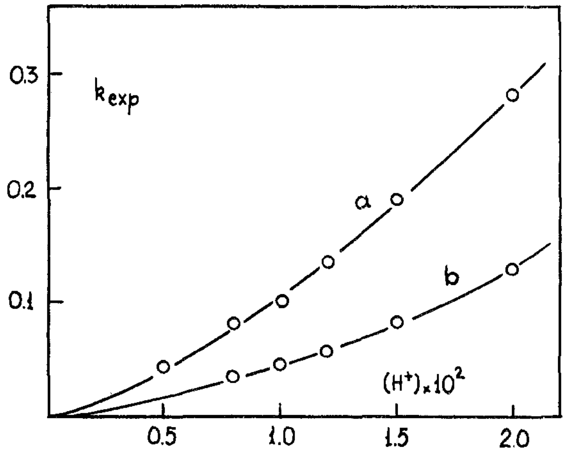


Figure 3.—The influence of hydrogen ion concentration on k_{exptl} at 25°, $\mu = 0.1\ M$, and (Cr(VI)) = $4 \times 10^{-4}\ M$: (a) $(S_2O_3^{2-})_t = 4 \times 10^{-3}\ M$; (b) $(S_2O_3^{2-})_t = 6 \times 10^{-3}\ M$.

The rate law at (H^+) = $10^{-2}\ M$ is

$$-\frac{d(CrS_2O_6^{2-})}{dt} = \frac{7.35 \times 10^3(S_2O_3^{2-})_t^2}{1 + [3.9 \times 10^2(S_2O_3^{2-})]}(CrS_2O_6^{2-}) \qquad (9)$$

The physical significance of l and m becomes clear by examining the influence of the hydrogen ion concentration on k_{exptl} if initial (Cr(VI)) and ($S_2O_3^{2-}$) are kept constant. Figure 3 shows the change of k_{exptl} with the hydrogen ion concentration in the range of 5×10^{-3}–$2 \times 10^{-2}\ M$, the concentration of $HCrO_4^-$ being constant ($4 \times 10^{-4}\ M$). Two $S_2O_3^{2-}$ concentrations were used: 4×10^{-3} and $6 \times 10^{-3}\ M$. The curves had a parabolic form. The reaction order with respect to the hydrogen ion was 1.2 for curve b and 1.5 for curve a. The order 1.5 was found also at other temperatures between 15 and 35°.

The fractional order suggests two parallel ways for the reaction, the one being first order and the other second order with respect to H^+. The curves could be described by the formula

$$k_{exptl} = a(H^+) + b(H^+)^2 \qquad (10)$$

Since acidic dissociation equilibria are established very rapidly, we assumed that $HS_2O_3^{2-}$ is one of the kinetically active species rather than $S_2O_3^{2-}$. The concentration of $HS_2O_3^-$ could be calculated from

$$(HS_2O_3^-) = \frac{(H^+)}{K_2 + (H^+)}(S_2O_3^{2-})_t \qquad (11)$$

and introducing this into the rate equation one obtains

$$-\frac{d(CrS_2O_6^{2-})}{dt} = \frac{l'\{k_2' + k_3'(H^+)\}\left\{\frac{(H^+)}{K_2 + (H^+)}\right\}^2(S_2O_3^{2-})_t^2}{1 + \left[m'\frac{(H^+)}{K_2 + (H^+)}(S_2O_3^{2-})_t\right]}(CrS_2O_6^{2-}) \qquad (12)$$

At the thiosulfate concentration $6 \times 10^{-3}\ M$, unity can be neglected in the denominator, and k_{exptl} will be given by

$$k_{exptl} = \{k_2'' + K_3''(H^+)\}\frac{(H^+)}{K_2 + (H^+)}(S_2O_3^{2-})_t \qquad (13)$$

Plotting $k_{exptl}\{K_2 + (H^+)\}/(H^+)$ as a function of (H^+) a straight line as shown in Figure 4 was obtained.

The values of k_2'' and k_3'', as computed from the slope and the cut of the line, were $60 \pm 12\ M^{-1}\ \text{sec}^{-1}$ and $(6.15 \pm 0.97) \times 10^3\ M^{-2}\ \text{sec}^{-1}$, respectively, at 25°.

3.3. Mechanism.—Under the circumstances of the study, the only Cr(VI) species present in the solutions is the intermediate thiosulfatochromate. The first order of the reaction with respect to the thiosulfatochromate as well as to thiosulfate shows the presence of both in the activated complex. This means the activated complex will contain one Cr(VI) and two thiosulfate ions. This suggests a two-electron exchange in one first step. Cr(VI) is reduced to Cr(IV), while tetrathionate is formed by simultaneous oxidation of both thiosulfate ions.

An evidence in favor of the direct formation of tetrathionate is given by the fact that no or very little formation of polymer was observed when the reaction was performed in the presence of methyl acrylate monomer, although a large amount of polyacrylate was formed during the oxidation of thiosulfate by iron(III) or copper(II).[14] The absence of Cr(V) as the result of the first step of the reduction of Cr(VI) is supported by the lack of success in the attempt to induce the reaction between Cr(VI) and I^- by thiosulfate. On the other hand a 1-equiv reducing agent like Fe(II) produces Cr(V) when it reduces Cr(VI), and therefore it induces promptly the I^-–Cr(VI) reaction.[18]

It seems reasonable to assume the formation of Cr(IV) in a first step which reacts further very fast in a one-electron exchange reaction with another thiosulfate ion resulting in one $S_2O_3^-$ free radical and Cr(III). It seems worth mentioning that the resulting Cr(III) could be immediately precipitated with Na_2HPO_4 if a perchloric solution was used. If acetic acid acted as a source of protons, no precipitation occurred. This was evidence for the fact that neither the tetrathionate nor the excess thiosulfate was in the first coordination sphere of the freshly formed Cr(III).

The above-mentioned facts led to the assumption of the mechanism

$$HCrO_4^- + HS_2O_3^- \rightleftharpoons H_2O + CrS_2O_6^{2-} \quad \text{(rapid)}\ (K) \qquad (14a)$$

$$CrS_2O_6^{2-} + HS_2O_3^- \xrightarrow{k_2} Cr(IV) + S_4O_6^{2-} \quad \text{(slow)} \qquad (14b)$$

$$CrS_2O_6^{2-} + HS_2O_3^- + H^+ \xrightarrow{k_3} Cr(IV) + S_4O_6^{2-} \quad \text{(slow)} \qquad (14c)$$

$$Cr(IV) + S_2O_3^{2-} \longrightarrow Cr(III) + S_2O_3^- \quad \text{(rapid)} \qquad (14d)$$

$$2S_2O_3^- \longrightarrow S_4O_6^{2-} \quad \text{(rapid)} \qquad (14e)$$

Reactions 14b and 14c are parallel. Reaction 14c may be formulated assuming an attack by the undissociated $H_2S_2O_3$

$$CrS_2O_6^{2-} + H_2S_2O_3 \longrightarrow Cr(IV) + S_4O_6^{2-} \qquad (15)$$

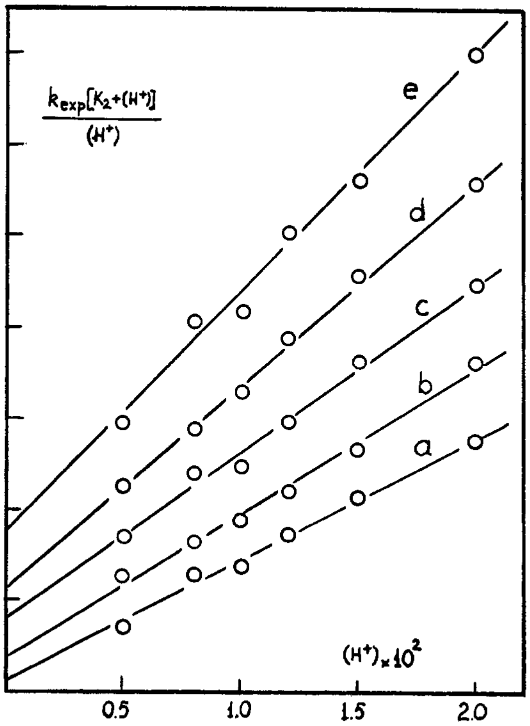
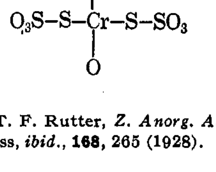


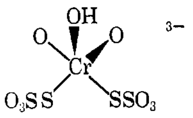
Figure 4.—Linearization of the curves k_{exptl} *vs.* (H^+) (Figure 3) at $(S_2O_3^{2-})_t = 6 \times 10^{-3}\ M$ and $(Cr(VI)) = 4 \times 10^{-4}\ M$: (a) 15.4°; (b) 20.1°; (c) 25.0°; (d) 29.6°; (e) 34.4°.

An activated complex like



$$O_3S-S-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{Cr}}-S-SO_3 \quad {}^{2-}$$

could be accepted but it is more likely to admit an electron transfer during the substitution process. The activated complex for the substitution reaction of the second thiosulfate could offer at the same time the lowest energy barrier both to the substitution and to the electron transfer, since the orbitals of the central chromium atom are disturbed. The process starts as a substitution and continues with a two-electron transfer and the elimination of tetrathionate. We may call this "substitution-induced electron transfer." The two proposed activated complexes for reactions 2 and 3 in (14) differ by one H^+, *i.e.*



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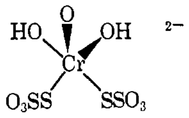
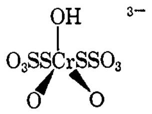


An attack on the side of the complex *trans* to the leaving group, for which the activated complex is supposed to be



leads probably to a thiosulfate exchange.

The attack by the sulfur ligand rather than by an oxygen ligand is consistent with the large value of the stability constant of $CrS_2O_6^{2-}$ in comparison with $CrSO_7^{2-}$,[10] where the linkage between two central atoms is made by an oxygen atom.

During the substitution process the two thiosulfate ligands get close together and the S–S bond could be

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[18] R. Luther and T. F. Rutter, *Z. Anorg. Allgem. Chem.*, **54**, 1 (1907); G. Wagner and W. Preiss, *ibid.*, **168**, 265 (1928).

TABLE III

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED CONSTANTS AT 20°, $\mu = 0.1\ M$, AND $(Cr(VI)) = 4 \times 10^{-4}\ M$

10^3 $(S_2O_3^{2-})_t$, M	$10^2(H^+)$, M	10^3 $(HS_2O_3^-)$, M	k_{exptl}, sec^{-1}	k_{calcd}, sec^{-1} From eq 16	k_{calcd}, sec^{-1} From eq 13
1.6	1.00	0.229	0.0104	0.0167	0.0226
3.0	0.94	0.402	0.034	0.025	0.038
6.0	0.50	0.457	0.032	0.0284	0.0334
6.0	0.80	0.700	0.058	0.0556	0.062
6.0	1.00	0.858	0.0825	0.0767	0.0839
6.0	1.20	0.990	0.106	0.100	0.108
6.0	1.50	1.189	0.145	0.139	0.148
6.0	2.00	1.487	0.229	0.212	0.224
9.0	0.80	1.05	0.078	0.086	0.093
12.0	0.726	1.28	0.102	0.1016	0.108

easily formed. The electron exchange deeply affects the structure of the chromium orbitals, and the symmetry changes from tetrahedral to octahedral.

Since the next step is very fast, there is little experimental support to make more assumptions on the mechanism.

The rate law derived from mechanism 14 and the stoichiometry $S_2O_3^{2-}:CrO_4^{2-} = 3:1$

$$-\frac{d(CrS_2O_6^{2-})}{dt} = \frac{K}{3}\frac{(HS_2O_3^-)^2}{1 + K(HS_2O_3^-)}\{k_2 + k_3(H^+)\}(CrS_2O_6^{2-}) \quad (16)$$

is in agreement with empirical law 12 with $k_2 = 3k_2'$ and $k_3 = 3k_3'$, or, neglecting 1 in comparison to $K(HS_2O_3^-)$, with eq 13.

There is a good agreement between the experimental and calculated values of k, as shown in Table III. The equilibrium constant K calculated from kinetic data has the same order of magnitude as calculated previously from equilibrium measurements.[12]

TABLE IV

THE EFFECT OF TEMPERATURE ON THE RATE CONSTANTS AT $\mu = 0.1\ M$

Temp, °C	$10^{-2}k_2$, M^{-1} sec^{-1}	$10^{-4}k_3$, M^{-2} sec^{-1}
15.4 ± 0.3	1.12 ± 0.18	1.34 ± 0.19
20.0 ± 0.2	1.42 ± 0.21	1.55 ± 0.22
25.0 ± 0.2	1.79 ± 0.36	1.85 ± 0.29
29.6 ± 0.2	2.13 ± 0.45	2.24 ± 0.05
34.4 ± 0.3	2.76 ± 0.54	2.63 ± 0.43

3.4. The Influence of the Temperature.—The velocity constants k_2 and k_3 were calculated from kinetic experiments carried out at five different temperatures between 15 and 35°, at acidities between 5×10^{-3} and $2 \times 10^{-2}\ M$, an ionic strength of 0.1 M, a Cr(VI) concentration of $4 \times 10^{-4}\ M$, and a thiosulfate concentration of $6 \times 10^{-3}\ M$. The straight lines in Figure 4 served to obtain k_2'' and k_3'' and by multiplying with 3 the values k_2 and k_3 as recorded in Table IV. Standard deviations were calculated by using for each point of the graph five to eight experimental data.

By means of the least-squares method, the activation enthalpies and entropies were obtained. For reaction 14b: $\Delta H^{\ddagger} = 8.2 \pm 0.7$ kcal and $\Delta S^{\ddagger} = -20.8 \pm 2.5$ eu. For the trimolecular reaction 14c: $\Delta H^{\ddagger} = 6.4 \pm 2.4$ kcal and $\Delta S^{\ddagger} = -17.7 \pm 8.0$ eu. Haight, *et al.*,[8] found for the reaction between SO_3^{2-} and Cr(VI) an activation entropy of −13 eu and an activation enthalpy of 4.5 kcal.

The proposed mechanism explains the formation of tetrathionate as the reaction product. At higher Cr(VI) concentrations and acidities sulfate is also formed and the mechanism could be quite different. This reaction path will be the subject of future investigations.

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N-Iodopyridinium Dichloroiodate(I)

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Mixing pyridine with an Andrews solution of dichloroiodate(I) in 5 M hydrochloric acid gives stable yellow crystalline material of formula $C_5H_5NI_2Cl_2$. Ultraviolet and infrared data supported by electrolytic, conductometric, and cryoscopic measurements suggest that this material is a double-charge-transfer complex of $C_5H_5NI^+$ and ICl_2^- ions. The rate and mechanism of aqueous hydrolysis to iodine and other unidentified material is discussed.

Introduction

Many molecular charge-transfer complexes can be prepared as crystalline solids by reaction of interhalogens with organic bases, particularly pyridine (py),[1−6] alkylpyridines,[2,7,8] halopyridines,[4] and dipyridyls.[9,10] Failkov and Musyka[11] concluded that the

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