duced in eq. 5 to yield

$$D_\infty - D_t = M\{[ROH_2NCS^{+2}]_t - [ROH_2NCS^{+2}]_\infty\} + N[R(NCS)Cl^{+2}]_t \quad (6)$$

where M and N are defined as

$$M = l\left(\frac{E_{FeNCS}K[Fe^{+3}]_0}{1 + K[Fe^{+3}]_0} + E_{CO} - E_{ROH_2NCS}\right)$$

$$N = l\left(\frac{E_{FeNCS}K[Fe^{+3}]_0}{1 + K[Fe^{+3}]_0} + E_{CO} - E_{RNCSCl}\right)$$

Introducing eq. 3 and 4 in eq. 6 and simplifying

$$D_\infty - D_t = [R(NCS)Cl^+]_0\left(N - \frac{Mk_a}{k_p + k_a}\right)e^{-(k_p + k_a)t}$$

Therefore a plot of log $(D_\infty - D_t)$ vs. t will have a slope equal to $-(k_p + k_a)/2.3$. For the case of *trans*-Co(en)$_2$(NCS)Cl$^+$, k_a is negligible compared to k_p, and the slope is $-k_p/2.3$.

Appendix B

Treatment of the Data for cis-Co(en)$_2$Cl$_2^+$. The definitions used in Appendix A are followed. In addition, ROH$_2$Cl^{+2} is used to denote the *cis* isomer, and E is the extinction coefficient of both *cis*-Co(en)$_2$Cl$_2^+$ and *cis*-Co(en)$_2$OH$_2$Cl^{+2} at the isosbestic point (505 mμ).

The differential equations for the kinetic sheme are integrated by standard methods, and the solutions are added to give

$$[RCl_2^+]_t + [ROH_2Cl^{+2}]_t = Qe^{-(k_d^a + k_d^{Fe}[Fe^{+2}])t} - Se^{-(k_c^t + k_c^{Fe}[Fe^{+2}])t} \quad (7)$$

where Q and S are defined as

$$Q = \frac{[RCl_2^+]_0\{k_c^t + (k_c^{Fe} - k_d^{Fe})[Fe^{+2}]\}}{k_c^t - (k_c^{Fe} - k_d^{Fe})[Fe^{+2}] - k_d^a}$$

$$S = \frac{[RCl_2^+]_0k_d^a}{k_c^t - (k_c^{Fe} - k_d^{Fe})[Fe^{+2}] - k_d^a}$$

Equation 8 is derived from the contributions of all species to light absorption and from stoichiometric considerations.

$$D_t - D_\infty = l(E - E_{Co})([RCl_2^+]_t + [RClOH_2^{+2}]_t) \quad (8)$$

Substitution of eq. 7 in eq. 8 yields

$$D_t - D_\infty = Ue^{-(k_d^a + k_d^{Fe})[Fe^{+2}]t} - Ve^{-(k_c^t + k_c^{Fe}[Fe^{+2}])t} \quad (9)$$

where $U = l(E - E_{Co})Q$ and $V = l(E - E_{Co})S$.

At relatively long times the first exponential in eq. 9 becomes negligible and eq. 10 is obtained. From eq. 10, the linear portion of the log $(D_t - D_\infty)$ vs.

$$[D_t - D_\infty] \text{ (for } t \text{ large)} = -Ve^{-(k_c^t + k_c^{Fe}[Fe^{+2}])t} \quad (10)$$

t plot gives a slope equal to $-(k_c^t + k_c^{Fe}[Fe^{+2}])/2.3$.

D_c is defined as the value of D obtained by extrapolating the linear portion of the log $(D_t - D_\infty)$ vs. t plot to zero time. Therefore

$$[D_c - D_\infty] \text{ (for } t \text{ small)} = Ve^{-(k_c^t + k_c^{Fe}[Fe^{+2}])t} \quad (11)$$

Subtracting eq. 11 from eq. 9, we obtain

$$D_t - D_c = Ue^{-(k_d^a + k_d^{Fe}[Fe^{+2}])t} \quad (12)$$

From eq. 12, a plot of log $(D_t - D_c)$ vs. t gives a slope equal to $-(k_d^a + k_d^{Fe}[Fe^{+2}])/2.3$.

The Mechanism of the Oxidation of Sulfur(IV) by Chromium(VI) in Acid Solution[1]

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The reactions between chromium(VI) and sulfur(IV) have been studied in aqueous acid solution. The stoichiometry varies from a Cr(VI)/S(IV) mole ratio of 1:2 to 2:3 as the starting concentrations are changed in the range $0.12 \leq [Cr(VI)]/[S(IV)] \leq 1.4$. The kinetics of the reaction path which gives 1:2 stoichiometry in 0.5 M sodium acetate buffer in the range $4.18 \leq pH \leq 5.05$ follow the rate law

$$-d[Cr(VI)]/dt = k_{obsd}[Cr(VI)][S(IV)]^2[H^+]/\{1 + K_1[S(IV)]\}$$

K_1 is interpreted to be the equilibrium constant for the formation of $CrSO_6^{2-}$ from HSO_3^- and $HCrO_4^-$ and has a value of 36 M^{-1}. The rate constant k_{obsd} is 1.37×10^8 M^{-3} sec.$^{-1}$ at 25.0°. The activation energy is 4.5 kcal./mole and the activation entropy is -13 e.u. A mechanism is proposed and compared with the Westheimer mechanism for organic oxidations with Cr(VI)

and with Mason's mechanism for the Cr(VI)-As(III) reaction.

Introduction

It has been known for a long time that the oxidation of sulfur(IV) by oxidizing agents such as chromium(VI) and manganese(VII) yielded dithionate as well as sulfate as the reaction products.[2,3] It appeared as though this were a reaction in which several different techniques could be used to obtain information with respect to chromium(VI) oxidation–reduction reaction mechanisms. These techniques included rapid mixing and standard kinetics by means of spectrophotometry, oxygen-18 tracer analysis, and careful analysis of the stoichiometry of the reaction. All three of these measurements could be useful individually in ascertain-

(1) Presented in part before the Inorganic Chemistry Division, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

(2) J. Kleinberg, W. Argersinger, and E. Griswold, "Inorganic Chemistry," D. C. Heath and Co., Boston, Mass., 1960, p. 448.

(3) H. Basset, *J. Chem. Soc.*, **83**, 692 (1903).

ing the mechanism of the proposed reaction. In addition, recent studies on the condensation of $HCrO_4^-$ with weak oxy acids[4] have suggested that the conditions of the reaction between chromium(VI) and excess sulfur(IV) in acid media were such that an intermediate of the type $CrSO_6^{2-}$ might be anticipated.

Experimental

Reagents. Analytical grade chemicals were used throughout the study without further purification. Solutions were prepared in water which was purified by distillation and ion exchange.[5] The solutions of chromium(VI) were standardized iodometrically and by determining the optical density at 350 mμ, where the species $HCrO_4^-$ has an extinction coefficient of 1580 M^{-1} cm.$^{-1}$. Sodium sulfite solutions were stored under an atmosphere of nitrogen and were standardized by using an excess of standard I_3^- solution followed by back titration with standard sodium thiosulfate. The sulfur(IV) solutions were usually prepared by dissolving an exact amount of sodium sulfite in water which was made oxygen-free by the passage of commercial nitrogen through the solution. Solutions were never stored longer than 8 hr. The freshly prepared solutions of sodium sulfite showed approximately 1% less sulfur(IV) than was expected from the amount of sodium sulfite dissolved.

The loss of sulfur(IV) as sulfur dioxide and by air oxidation was a constant hazard and attempts were made to minimize these losses; it was possible to minimize the air oxidation of sulfur(IV) such that no more than 1% air oxidation occurred in any kinetic experiment. Solutions of $HCrO_4^-$ were prepared by dissolving sodium chromate in equivalent amounts of perchloric acid.

The buffer solutions were prepared from acetic acid and sodium acetate. Although at the onset it appeared that the corresponding phosphate and citrate buffers could be useful, this possibility was discarded due to possible complex ion formation with $HCrO_4^-$.[4] Complexation effects due to the reaction between $HCrO_4^-$ and $HC_2H_3O_2$ appeared to be minimized in this reaction.

The exact amount of buffer and acid needed to protonate the solutions of sulfur(IV) was prepared prior to mixing and this solution was mixed with the chromium(VI) solution in a time short compared to the half-life of the reaction.

Stoichiometry. Sulfur(IV) and chromium(VI) were mixed in various ratios over a range of concentrations. The excess of either reagent was determined iodometrically. In the case of excess sulfur(IV), iodine was added immediately to minimize air oxidation. Attempts to determine the chromium(III) produced spectrophotometrically lead to inconsistent results due to small color changes in the solution which are visible for periods lasting well beyond those necessary to complete the oxidation–reduction process. It is likely that a complex such as $[SO_4Cr^{III}]^+$ forms initially and dissociates only slowly. Basset[3] has observed in agreement with our observations that immediately following the reaction between sulfur(IV) and chromium(VI),

(4) G. P. Haight, Jr., D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, 3, 1777 (1964).
(5) G. Gordon and A. Andrewes, *ibid.*, 3, 1733 (1964).

the sulfate produced did not immediately precipitate upon the addition of barium chloride.

Kinetics. Individual kinetic experiments were carried out by one of two different techniques, dependent on the lifetime of the reaction. For reactions which lasted several minutes or longer, standard mixing techniques were utilized. These experiments were performed in glass-stoppered absorption cuvettes contained in a Beckman Model DU spectrophotometer. The compartment was thermostated at 25 $\pm$ 0.5°. In these experiments, the reaction was initiated by the addition of excess sodium sulfite to approximately 5 $\times$ 10^{-4} M chromium(VI) contained in acetic acid buffer solution at 0.5 M ionic strength. It was possible to obtain spectrophotometric readings within 20 to 30 sec. of mixing. By means of this technique, it was very difficult to obtain consistent results with the sulfur(IV) concentrations below 0.001 M owing to air oxidation and volatilization of sulfur dioxide during the actual mixing. Variation in the pH of these solutions was obtained by adding perchloric acid or sodium hydroxide to the stock solution. The pH for each individual experiment was determined by means of a Beckman Model G pH meter at the conclusion of the run.

The second technique used for obtaining kinetic data was by means of a rapid mixing syringe,[6] which was used to deliver, in 30 msec., 0.607 ml. of sulfur(IV) into a 2-cm. spectrophotometric cell which contained 5.70 ml. of chromium(VI). For these rapid mixing experiments, the spectrophotometer cell was contained in a thermostated compartment of a Cary 14 spectrophotometer. The kinetic results were obtained by photographing the output of the preamplifier directly by means of an oscilloscope and attached Polaroid camera as has been described elsewhere.[6]

In both series of kinetic experiments, the disappearance of the species $HCrO_4^-$ was followed at 350 and 430 mμ. At 350 mμ the low concentration of chromium(III) formed [2–5 $\times$ 10^{-4} M] showed no detectable absorbance. However, at 430 mμ, chromium(III) has an extinction coefficient of 13.7 M^{-1} cm.$^{-1}$ and the concentration of the $HCrO_4^-$ was obtained by correction of the observed optical density readings. At 580 mμ, the $HCrO_4^-$ and $Cr_2O_7^{2-}$ are nearly as transparent as water, and the reaction can be followed by measuring the change in optical density due to the chromium(III) species produced.

Tracer Experiments. The rates of oxygen exchange between HSO_3^- and water or $HCrO_4^-$ and water are reported to be rapid.[7,8] If these reactions are slower, however, than the corresponding oxidation–reduction process described in this paper, oxygen-18 tracer studies may be useful to obtain additional information with respect to the mechanism of reaction in the presence of excess sulfur(IV) as shown in eq. 1. Chromium(III) is generally considered to be a nonlabile species with respect to oxygen exchange with solvent.[9-11]

$$2HCrO_4^- + 4HSO_3^- + 6H^+ = 2Cr^{+3} + 2SO_4^{2-} + S_2O_6^{2-} + 6H_2O$$
(1)
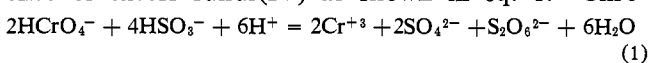
(6) R. C. Thompson and G. Gordon, *J. Sci. Instr.*, 41, 480 (1964).
(7) J. Halperin and H. Taube, *J. Am. Chem. Soc.*, 74, 375 (1952).
(8) R. Hollyer, Ph.D. Dissertation, University of Western Ontario, 1963.
(9) J. P. Hunt and H. Taube, *J. Chem. Phys.*, 19, 602 (1951).
(10) R. Plane and H. Taube, *J. Phys. Chem.*, 56, 33 (1952).
(11) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, 76, 5960 (1954).

Unfortunately, the chromium(III) species which is the product of the reaction cannot be used for isotopic analysis of its hydration shell owing to a subsequent reaction between the hexaaquochromic ion and the excess sulfur(IV). For example, if a solution of sulfur(IV) is added to aqueous chromium(III), a green complex forms immediately and the resulting chromium species cannot be precipitated by the addition of sodium phosphate, sodium ferricyanide, sodium ferrocyanide, or sodium tetraphenylborate. This complex also is not adsorbed on a Dowex-50 cation-exchange column. In the course of the studies of the kinetics of the reaction in the presence of excess sulfur(IV) at 580 mμ, a slight increase in the optical density was observed after the initial oxidation–reduction reaction was over, which also suggests that chromium(III) was undergoing further reaction. Additional observations on this complex itself will be reported elsewhere.[12]

Therefore, in the resulting solutions, only the product sulfate was analyzed by precipitation as barium sulfate, and its isotopic oxygen composition was determined by modification of the Anbar technique.[13] For this modification, approximately 80 mg. of dried barium sulfate was mixed with an equal amount of dry potassium ferrocyanide. The mixture was degassed for approximately 30 min. at 400°. The temperature was raised to 650° for approximately 3 hr. and the condensable gases were collected in a liquid nitrogen cooled trap. The noncondensable gases were discarded and the condensable portion was redistilled from a $-78°$ bath into special U-tubes which contained zinc amalgam at liquid nitrogen temperature. The remaining steps of the purification were similar to those reported by Anbar and Guttmann[13] and were followed by mass spectrometric analysis of the resulting carbon dioxide.

The actual conditions obtained for the tracer experiments were similar to those used for the stoichiometric and kinetic experiments described above. The final volume after mixing was approximately 5 ml., and the starting concentrations of chromium(VI) and sulfur(IV) were approximately 10^{-2} and 10^{-1} M, respectively. Mixing was carried out under an atmosphere of nitrogen in an attempt to preclude the possibility of air oxidation. After mixing, the reaction flask was quickly stoppered and connected to a vacuum line, and after removal of most of the water, concentrated perchloric acid was allowed to enter the reaction vessel. The sample was further vacuum dried until all of the excess sulfur dioxide had been removed and barium sulfate could be precipitated without further precautions. Several blank experiments were carried out by using oxygen- and sulfate-free sodium sulfite. The mixing for these blank experiments was carried out in a closed and strictly oxygen-free atmosphere. Two different types of experiments were carried out and these are described below. Water of normal isotopic composition is defined as onefold enriched.

(1) Sulfur(IV) of normal isotopic composition and maintained at pH 4.65 was oxidized with oxygen-18 enriched sodium chromate contained in 10^{-3} M sodium hydroxide. A typical experiment involved the rapid addition of the basic sodium chromate solution

(12) G. Gordon, to be published.
(13) M. Anbar and S. Guttmann, *Intern. J. Appl. Radiation Isotopes*, 5, 233 (1959).

to appropriate amounts of sodium sulfite, sodium acetate buffer, and water contained in a cell by means of the rapid mixing apparatus.[6] These experiments were carried out at room temperature and melting ice temperature with 4.8-fold enriched sodium chromate. The enrichment of the product sulfate was 1.0-fold, which indicates that if oxygen transfer from the chromium(VI) to the sulfur(IV) occurs, isotopic equilibrium with the solvent obtains more rapidly than the corresponding oxidation–reduction process, in that the rate of exchange between sulfate ion and water was shown to be very slow. Additional experiments were carried out in which the sodium sulfite solution was injected into the oxygen-18 enriched basic sodium chromate solution with no measurable change in the final enrichment of the sulfate product. Verification of these experiments was furnished in a tracer experiment in which an acetate buffer which contained barium chloride was injected into an alkaline sodium chromate solution such that barium chromate would precipitate almost immediately upon mixing. The enrichment of the precipitate was found to be 2.2-fold compared with the initial sodium chromate solution which was 4.8-fold, which indicates that the exchange between CrO_4^{2-} and water is fairly rapid compared to the rate of precipitation of $BaCrO_4$.

(2) Chromium(VI) in solvent of normal isotopic composition was used to oxidize sulfur(IV) contained in oxygen-18 enriched water. A typical experiment consisted of the preparation of a sodium sulfite solution in the appropriate sodium acetate buffer in oxygen-18 enriched water of approximately 4.2-fold enrichment. A solution of chromium(VI) and 10^{-3} M sodium hydroxide was rapidly injected into the sodium sulfite solution at 0°. The oxygen-18 content of the resulting sulfate was approximately 3.8-fold enriched. The apparent difference in enrichment of the product sulfate from the value of 4.2 is due to the oxygen-18 dilution of the solvent by water of normal composition which was added with the chromium(VI). Once again, if transfer of oxygen-18 from the chromium(VI) species in an inner-sphere type reaction did occur, the enrichment of the product sulfate should be considerably lower than 3.8. The results of these experiments indicate that isotopic equilibrium between the chromium(VI) and sulfur(IV) species, or the intermediate $[CrSO_6^{2-}]$ (*vide infra*), and solvent obtains more rapidly than the substitution inert species, sulfate, is formed.

Results

Stoichiometry. The results of a series of experiments in which the normality of a 0.394 M sulfur(IV) solution was determined by the addition of excess I_3^-, MnO_4^-, and $HCrO_4^-$ were 0.394, 0.383, and 0.357 M, respectively. Since the oxidation potential of the I^-–I_3^- couple is too low to permit the production of dithionate, iodine oxidizes sulfur(IV) completely to form sulfur(VI). The deviations observed for the reactions with permanganate and dichromate are caused by the production of small concentrations of dithionate. The results of a series of experiments in which the mole ratio of chromium(III) produced to sulfur(IV) consumed are shown in Tables I and II as a function of the initial concentrations of chromium(VI) and sulfur(IV). It should be noted that both the

Table I. Stoichiometry of the Reaction of Sulfur(IV) with Excess Chromium(VI) in Acetate Buffer at pH 4.7 at 25°

$[Cr(VI)]_0,^a$ M	$[S(IV)]_0,^a$ M	$[Cr(VI)]_0/$ $[S(IV)]_0$	Limiting ratio $[Cr(III)]_{produced}/$ $[S(IV)]_{consumed}^b$
0.0171	0.0135	1.27	0.642
0.0160	0.0188	0.85	0.646
0.0092	0.0068	1.35	0.628
0.0089	0.0099	0.90	0.636
0.0156	0.0197	0.79	0.640^c
0.0154	0.0183	0.84	0.637
0.0150	0.0202	0.74	0.639
0.0154	0.0185	0.83	0.649^d
0.0154	0.0175	0.88	0.614^e
0.0154	0.0184	0.84	0.642^f

^{a} Initial concentration. ^{b} The ratio was determined as $\{[Cr(VI)]_0 - [Cr(VI)]_\infty\}/[S(IV)]_0$. ^{c} Stood 30 min. before analysis. ^{d} With 1 M HCl. ^{e} With 1 M H$_2$SO$_4$. ^{f} With 1 M HAc.

Table II. Stoichiometry of the Reaction of Excess Sulfur(IV) with Chromium(VI) in Acetate Buffer at pH 4.7 at 25°

$[Cr(VI)]_0,^a$ M	$[S(IV)]_0,^a$ M	$[Cr(VI)]_0/$ $[S(IV)]_0$	Limiting ratio $[Cr(III)]_{produced}/$ $[S(IV)]_{consumed}$
0.00500	0.0202	0.25	0.559
0.00333	0.0269	0.12	0.518
0.0040	0.0243	0.16	0.512
0.0075	0.0502	0.15	0.551
0.0080	0.0402	0.20	0.586
0.0141	0.0591	0.24	0.604
0.0150	0.0502	0.30	0.615

^{a} Initial concentration.

Table III. Results of Kinetics Experiments in the Chromium(VI)–Sulfur(IV) Reaction in Acetate Buffer at pH 4.65 and at 25°

$[Cr(VI)]_0,^a$ $M \times 10^4$	$[S(IV)]_0,^a$ $M \times 10^3$	$k_1 \times$ $10^{-8}, M^{-3}$ sec.$^{-1}$
2.08	2.33^b	1.19
2.08	2.27^c	1.32
2.08	2.20^d	1.24
2.08	1.97^e	1.31
2.08	1.97^f	1.23
5.00	2.52^g	1.12^i
5.00	2.52^h	1.19^i
0.800	3.40	1.11
2.26	2.41	1.19
2.26	9.13	1.07
4.53	8.8	1.08
18.2	9.4	1.07^i
90.5	28.6	0.74^i
45.2	42.8	0.57^k
2.26	47.3	0.52
4.52	47.0	0.52
18.0	45.7	0.52
90.0^l	90.0	0.42
18.1^m	16.9	0.92
2.26^m	4.2	1.26
2.26^m	9.2	0.98

^{a} Calculations based on the assumption d[S(IV)]/dt = 2d[Cr(VI)]/dt; the reported values of k_1 were calculated by using the average sulfur(IV) concentration obtained during the course of the reaction. The ionic strength was 0.5 M with sodium acetate–acetic acid buffer. ^{b} pH 4.67. ^{c} pH 4.60. ^{d} pH 4.18. ^{e} pH 4.39. ^{f} pH 4.20. ^{g} pH 5.05. ^{h} pH 4.97. ^{i} Determined from initial slope. ^{j} Determined from the integrated form $-\{1/[\beta + 2(HCrO_4^-)]\} + \{[2.3/\beta] \log [\beta + 2(HCrO_4^-)]/[HCrO_4^-]\}$, where $\beta = [HSO_3^-]_0 - 2[HCrO_4^-]_0$. ^{k} The same value of $k_1 \pm 2\%$ was obtained by means of either the integrated rate expression or by means of the initial slope. ^{l} The high concentrations of sulfur(IV) and chromium(VI) result in a considerable change in stoichiometry as shown in Table II. This datum point was not used to determine the average value of k_1 or k_2. ^{m} Ionic strength was 1.0 M with sodium nitrate and buffer.

initial concentration and the initial chromium(VI)–sulfur(IV) ratio have been varied. From the results in Table I, it is difficult to see any apparent trend, which seems to suggest that even with a small excess of chromium(VI) at least two competing paths at comparable rates are available. The results in Table II indicate that in the presence of excess S(IV) the stoichiometry is rather sensitive to the initial Cr(VI) concentration, but less sensitive to the S(IV) concentration. Apparently, the 2:1 [S(IV)]/[Cr(VI)] stoichiometry is favored primarily by low [Cr(VI)]$_0$ and secondarily by high [S(IV)]$_0$.

Kinetics. Owing to the change in stoichiometry of the reaction from that shown in eq. 1 in the presence of stoichiometric or excess chromium(VI), the principal reactions which were studied were those in the presence of excess sulfur(IV). For all of the experiments under these conditions, graphs of the log of the optical density as a function of time were linear, which is used as evidence that the reaction is indeed first order with respect to chromium(VI). The slopes of these graphs were proportional to the square of the concentration of sulfur(IV) and to the first power of the hydrogen ion concentration, which suggests the rate law

$$-d[Cr(VI)]/dt = k_1[Cr(VI)][S(IV)]^2[H^+] \quad (2)$$

Even in the reactions with high chromium(VI) concentrations (0.01 M) where appreciable concentrations of dichromate ion are present, the rate continues to be proportional to the concentration of the principal species of chromium(VI) present in solution, HCrO$_4^-$. These results are summarized in Table III.

For some of the experiments, where appreciable changes in the sulfur(IV) concentration occurred, it was necessary to use the integrated form of eq. 2 as it is rewritten as eq. 3. The value of β was that derived

$$-d[Cr(VI)]/dt = k_1[Cr(VI)]\{\beta + 2[Cr(VI)]^2[H^+]\} \quad (3)$$

from the stoichiometry at low chromium(VI) concentrations. These data also give good linear graphs for more than 90% of each experiment and values of the rate constant, k_1, consistent with the other values shown in Table III. This serves as the test for the hypothesis that the limiting stoichiometry at low chromium(VI) concentration is indeed 2 moles of sulfur(IV) per mole of chromium(VI) consumed. Additional experiments showed that the reaction products had no observable effects on the measured rates of the reaction. Careful examination of the data presented in Table II suggests that at higher concentrations of sulfur(IV) and chromium(VI) the proposed rate law is not adequate to describe the reaction. Since the order of the reaction with respect to sulfur(IV) concentration appears to be decreasing, several other forms of the rate law which reflect this change were tried.

A plot of $1/k_1$ *vs.* [S(IV)] is linear with a slope of $(2.64 \pm 0.12) \times 10^{-7}$ M^{-2} sec. and an intercept of $(7.3 \pm 0.2) \times 10^{-9}$ M^{-3} sec. which gives the modified rate law

$$-d[Cr(VI)]/dt = k_2K_1[Cr(VI)][S(IV)]^2[H^+]/\{1 + K_1[S(IV)]\} \quad (4)$$

The resulting value[14] of k_2/K_1 was $(1.37 \pm 0.06) \times 10^8 \ M^{-3}$ sec.$^{-1}$ and that for K_1 was $36 \pm 1 \ M^{-1}$.

The first-order dependence of the hydrogen ion concentration shown in eq. 2 and 4 was established by varying the hydrogen ion concentration in the range pH 4.18 to 5.05 by using a sodium acetate buffer. Since the predominant sulfur(IV) species present under these conditions is HSO_3^-, the range of the reaction could possibly be extended from pH 3.4 to 5.5 by means of appropriate buffers. A sodium citrate–citric acid buffer appeared to be useful for this purpose in that it has a high buffer capacity over the whole range. Unfortunately, the rates of the reaction in the presence of a citrate buffer are considerably different from those observed in the acetate buffer. This would be in agreement with the results of Haight, Richardson, and Coburn[4] in which they have shown spectrophotometrically that chromium(VI) forms complexes with many other oxy anions, excepting acetate.

In order to do additional experiments with excess chromium(VI), it would be necessary to keep the chromium(VI) concentration in at least 10-fold excess of the sulfur(IV) concentration. Under these conditions, major deviations from the stoichiometry shown in eq. 1 occur and, in addition, the complex formation between chromium(III) and bichromate reported by King and Neptune[15] becomes important. The complex $CrCrO_4^+$ or $CrCrO_4H^{2+}$ has an optical density greater than that observed for chromium(III) alone. Unfortunately, the extinction coefficients for this complex are not known nor are the formation constants or the kinetics of the formation reaction. In addition, the chromium(III) produced will undergo a variety of secondary reactions which would interfere with its photometric determination.

Some additional experiments were carried out to extend the work of King and Neptune[15] in an attempt to determine the extinction coefficient and formation quotient for the chromium(III)–chromium(VI) dimer. Unfortunately, as they have pointed out, the extinction coefficient and the formation quotient of the complex are somewhat small and high concentrations of chromium(VI) cannot be achieved owing to the dimerization of chromium(VI) to form the dichromate ion. Typical Job's method curves[16] were plotted in an attempt to verify that a 1:1 complex was formed. A slight shift toward lower chromium(III) concentrations was observed, probably due to the dimerization of chromium(VI). If the slope of the Job curve is used to calculate the equilibrium constant and extinction coefficient[17] for the chromium(III)–chromium(VI) species which is more strongly absorbing than either of these species separately, an extinction coefficient of $10 \pm 3 \ M^{-1}$ cm.$^{-1}$ at 690 mμ and $9 \pm 3 \ M^{-1}$ cm.$^{-1}$ at 700 mμ and a formation quotient of approximately 3 are obtained. The large error associated with this formation quotient is much greater than that which would be needed to successfully study the kinetics of formation of this complex. Additional observations were made,

(14) A least-squares treatment of the data was made by means of a program supplied by the Computer Science Laboratory of the University of Maryland. The reported standard deviations are computed directly by the least-squares program with unit weights for each datum point.

(15) E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

(16) P. Job, *Ann. Chim.* (Rome), **10**, 9, 113 (1938).

(17) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 841 (1949).

Table IV. Results of the Sulfur(IV)–Chromium(VI) Reaction at Various Temperatures

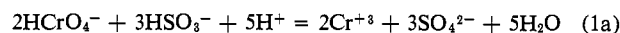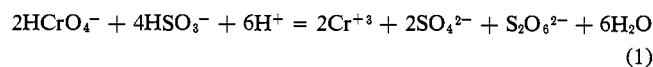| Temp. °C	$k_2 \times 10^{-6}$, M^{-2} sec.$^{-1}$
13.0	2.81
18.0	3.45
22.5	3.55
29.5	4.37
35.0	5.09

however, that solutions with chromium(III) and bichromate concentrations of $\lesssim 1.5 \times 10^{-3} \ M$ show no detectable enhancement of the absorption spectrum in the range 340–360 mμ where the chromium(VI)–sulfur(IV) reaction was studied under conditions of excess sulfur(IV).

In order to determine the activation energy and entropy for the sulfur(IV)–chromium(VI) reaction, it was studied in the temperature range of 13 to 35° at five additional temperatures. These reactions were studied by using 1 M sodium acetate buffer at a pH of 4.65 and a total ionic strength of 0.5. For these reactions, the initial chromium(VI) concentration was $2.28 \times 10^{-4} \ M$ and the sulfur(IV) concentration was in the range of $(2.3–3.4) \times 10^{-3} \ M$. These results are shown in Table IV. Each individual datum point is the average of at least three experiments which agreed to better than $\pm 3\%$. The calculated activation enthalpy (ΔH^*) is 4.5 kcal./mole and the activation entropy (ΔS^*) is -13 e.u.

One observation particularly apparent at *low* temperatures was that the reaction was initially slower than would have been expected on the basis of eq. 4. This effect was attributed to the rate of formation of a steady-state concentration of a reaction intermediate (*vide infra*). However, the initial slow portion of the reaction was relatively small and it did not appreciably affect the calculation of the activation energy or rate constants for the reaction.

Discussion

The stoichiometry of the reaction between chromium(VI) and sulfur(IV) can be explained in terms of competition between two over-all reactions.
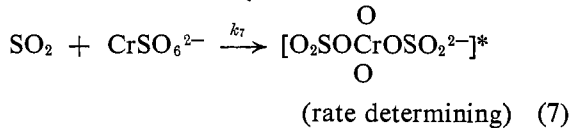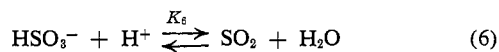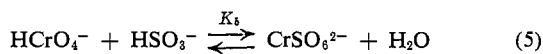
$$2HCrO_4^- + 4HSO_3^- + 6H^+ = 2Cr^{+3} + 2SO_4^{2-} + S_2O_6^{2-} + 6H_2O \quad (1)$$

$$2HCrO_4^- + 3HSO_3^- + 5H^+ = 2Cr^{+3} + 3SO_4^{2-} + 5H_2O \quad (1a)$$

The rate law obtained applies only to reaction 1. A satisfactory mechanism must explain the rate law, the tendency toward reaction 1a at high [Cr(VI)], and the observation that SO_4^{2-} is bound to Cr(III) at the conclusion of the reaction. The kinetics were studied under conditions of acidity where the reactants are principally HSO_3^- and $HCrO_4^-$. $HCrO_4^-$ is known to undergo condensation[4] with itself and such species as HSO_4^- and $H_2PO_4^-$ to form $Cr_2O_7^{2-}$, $CrSO_7^{2-}$, and $HCrPO_7^{2-}$. Chromate esters $(ROCrO_3^-)$ are involved in oxidations of alcohols.[18] It seems reasonable therefore to suggest a pre-equilibrium which involves the condensation of HSO_3^- with $HCrO_4^-$ to give $O_2SOCrO_3^{2-}$ to account for the denominator term in the rate law.

With this in mind, the stoichiometric and kinetic results may be compared with the well-known West-
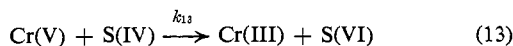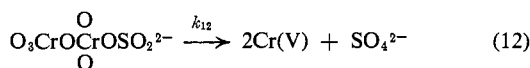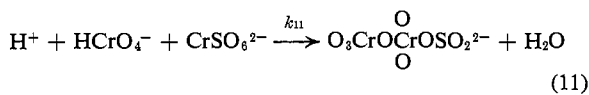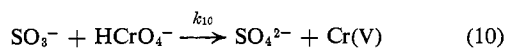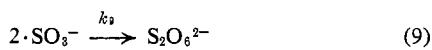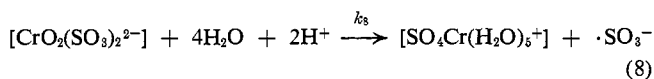
(18) F. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

heimer chromate ester mechanism, which involves chromium(IV) intermediates. $HCrO_4^-$ has been found to form esters with alcohols which decompose to give Cr(IV). The Cr(IV) may disproportionate, react with Cr(VI), or oxidize weak one-electron reducing agents (e.g., Mn^{2+}) in solution. Bisulfite ion has the unusual combined ability to form a chromate ester; reduce Cr(VI) to Cr(IV); and, by forming dithionate radicals ($\cdot SO_3^-$), act as a one-electron reducing agent for Cr(IV).

The following mechanism is consistent with all of the kinetic and stoichiometric observations. How the solvent water and hydrogen ion participate is only conjecture.

$$HCrO_4^- + HSO_3^- \underset{K_5}{\rightleftarrows} CrSO_6^{2-} + H_2O \qquad (5)$$

$$HSO_3^- + H^+ \underset{K_6}{\rightleftarrows} SO_2 + H_2O \qquad (6)$$

$$SO_2 + CrSO_6^{2-} \xrightarrow{k_7} [O_2SOCrOSO_2^{2-}]^* \qquad O$$
$$\text{(rate determining)} \qquad (7)$$

where the asterisk signifies an activated complex.

$$[CrO_2(SO_3)_2^{2-}] + 4H_2O + 2H^+ \xrightarrow{k_8} [SO_4Cr(H_2O)_5^+] + \cdot SO_3^- \qquad (8)$$

$$2\cdot SO_3^- \xrightarrow{k_9} S_2O_6^{2-} \qquad (9)$$

$$SO_3^- + HCrO_4^- \xrightarrow{k_{10}} SO_4^{2-} + Cr(V) \qquad (10)$$

$$H^+ + HCrO_4^- + CrSO_6^{2-} \xrightarrow{k_{11}} O_3CrOCrOSO_2^{2-} + H_2O \qquad O$$
$$(11)$$

$$O_3CrOCrOSO_2^{2-} \xrightarrow{k_{12}} 2Cr(V) + SO_4^{2-} \qquad O$$
$$(12)$$

$$Cr(V) + S(IV) \xrightarrow{k_{13}} Cr(III) + S(VI) \qquad (13)$$

The first five steps account for the kinetics and stoichiometry under conditions where reaction 1 is dominant.

If reaction 7 is the rate-determining step, the rate law is

$$\text{rate} = \frac{k_7 K_6 K_5 [HCrO_4^-][HSO_3^-]^2[H^+]}{1 + K_5[HSO_3^-]}$$

and from eq. 5, it is possible to estimate

$$K_5 = \frac{[CrO_6^{2-}]}{[HSO_3^-][HCrO_4^-]} = 36$$

Since values for formation constants[4,19] for such species as $Cr_2O_7^{2-}$, $CrSO_7^{2-}$, $H_2CrAsO_6^-$, and the like range from 4 to 100, this appears to be a reasonable value. If K_6 is estimated to be ≈ 100, this leads to a value of 3.8×10^4 M^{-1} sec.$^{-1}$ for k_7 (the product $k_7 K_6$ is k_8 in eq. 8). Reaction 6 is postulated as a reasonable way for one hydrogen ion to participate in the formation of the activated complex shown in eq. 7. This activated complex can decompose (assisted by water and protons) in one step to give Cr(III) bound to SO_4^{2-} and $\cdot SO_3^-$ from which $S_2O_6^{2-}$ may be derived. This accounts for the limiting stoichiometry in which half of the sulfur is oxidized to $S_2O_6^{2-}$ and the other half to SO_4^{2-}. Steps 9, 11, 12, and 13 are needed to explain the tend-

(19) J. G. Mason and A. D. Kowalak, *Inorg. Chem.*, 3, 1248 (1964).

ency for complete conversion of S(IV) to S(VI) at high Cr(VI). Here an analogous activated complex which involves the condensation of $CrSO_6^{2-}$ with CrO_3 rather than SO_2 is postulated. We suspect Cr(V) is probably directly bound to SO_2 through oxygen during reduction to Cr(III) since SO_4^{2-} is bound to Cr(III) at the end of the reaction.

In comparison with Westheimer's[18] mechanism for Cr(VI) oxidation of alcohols and Mason's[19] mechanism for Cr(VI) oxidation of H_3AsO_3, we find significant differences. The rate of the reaction reported here is many orders of magnitude greater than either the oxidation of alcohol or arsenite. Although we postulate "ester formation" in this case, significant formation of Cr(IV) as an active intermediate must be ruled out. One can postulate that the sequence

$$Cr(VI) + S(IV) \longrightarrow Cr(IV) + S(VI) \qquad (14)$$

$$Cr(IV) + S(IV) \longrightarrow Cr(III) + S(V) \qquad (15)$$
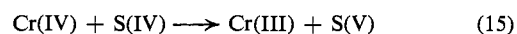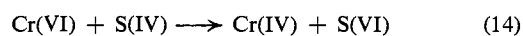
will account for the stoichiometry of reaction 1. To account for the kinetics, however, reaction 14 would have to be reversible with significant amounts of back reaction. We believe that the sulfate ion is too inert with respect to reduction for the back reaction to occur. Further it seems likely that reaction 14 would occur *via* formation of $CrSO_6^{2-}$ by analogy with Mason's mechanism[19] for oxidation of arsenite. The reaction of the [Cr-(VI)-As(III)] complex to give Cr(IV) (eq. 16) has a

$$O_2AsOCrO_3^{-3} + H_2O \longrightarrow [Cr^{IV}AsO_4] \qquad (16)$$
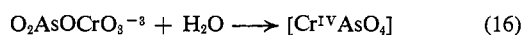
rate constant of about 10^{-4} compared to k_7 of 10^4, which suggests that the formation of Cr(IV) is too slow to play a significant part in sulfite oxidation. A step such as reaction 11 could account for the $[Cr(VI)]^2$ term at high [Cr(VI)] in the rate law for arsenite oxidation.[19] Either reaction 9 or reaction 11 could account for the change in stoichiometry at high $HCrO_4^-$ concentration. We are inclined to favor reaction 9 since its competition with reaction 10 could be very sensitive to the initial Cr(VI) concentration and less sensitive to the initial S(IV) concentration. Reaction 11 should compete with reaction 7 and the competition should be more or less equally sensitive to either [S-(IV)]$_0$ or [Cr(VI)]$_0$. Since reaction 11 would block the one-step three-electron reaction of Cr(VI), it could very well inhibit the reaction and no inhibition is observed.

The apparent inhibition by S(IV) of the reduction of Cr(VI) is explained in terms of the extent of formation of $CrSO_6^{2-}$, whereas Mn^{2+}, for example, inhibits reduction of Cr(VI) by alcohols by trapping Cr(IV) and preventing the reaction

$$Cr(IV) + Cr(VI) \longrightarrow 2Cr(V) \qquad (17)$$
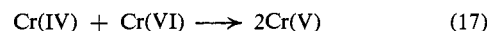
Bisulfite ion through its ability to form anhydride condensates with $HCrO_4^-$ and its property of being both a 1- and 2-equiv. reducing agent provides a unique path for reduction of Cr(VI) directly to Cr(III), by-passing the highly energetic intermediates Cr(IV) and Cr(V). The difference in the rate of reaction of Cr(VI) with S(IV) and As(III) makes study of the oxidation of H_3PO_3 by Cr(VI) an interesting future problem.