terminal N–CH_3 distance is 1.474 Å, which compares well with the average of equatorial and axial N–CH_3 distances in $[Me_2NBH_2]_3$, 1.49 Å. The average N–B–N angle in isomer I, 108.9°, is consistent with the anticipated tetrahedral environment for the boron atoms, and the angle is similar to the average N–B–N angles in $[H_2NBH_2]_3$ (107.2°) and $[H_2NBCl_2]_3$ (109°). The average N–B–N angle in $[Me_2NBH_2]_3$, 114°, on the other hand, is considerably more open. The average B–N–B angle, 116.5°, is more open than the N–B–N angle, and it resembles the average angles in $[H_2NBH_2]_3$ (115.9°), $[H_2NBCl_2]_3$ (120.1°), and $[Me_2NBH_2]_3$ (113°). The B–N–C angles are essentially constant in the eee isomer at 110.4°, and this angle is related to the B–N–C angle in $[Me_2NBH_2]_3$. Least-squares-planes calculations provide dihedral angles between the basal four-atom planes and the three-atom planes (three symmetry-related sets), and the B–N–B planes, 47.6°, are slightly more tilted than the N–B–N planes, 44.3°, from the B_2N_2 planes.

The structure of the eea isomer, of course, closely resembles that of the eee isomer with the axial methyl group positioned on N(3). As expected this slightly distorts the parameters involving N(3). The average B–N bond distance is 1.578 Å with the average B–N bond distance involving N(3) being 1.591 Å and the average derived from bonds to N(1) and N(2) being 1.571 Å. On the other hand, the N–CH_3 distances are nearly constant, $(N–C)_{av}$ = 1.481 Å. The average N–B–N angle, 108.5°, compares favorably with that found in isomer I while the average B–N–B angle, 114.7°, is closed down compared to the angle in isomer I. Interestingly, the B–N–C angles for N(3) are significantly more open, $(B–N(3)–C)_{av}$ = 113.4°, than the average of the remaining B–N–C angles, 110.1°. In addition, the dihedral angle between the B(2)N(3)B(4) plane and the N(1)B(2)B(4)N(5) basal plane, 50.1°, is greater than the dihedral angle between the N(1)B(6)N(5) plane and the basal plane, 47.7°.

Although no serious attempt has been made in this study to elucidate the mechanism for the formation of 1,3,5-trimethylcycloborazane from $H_3B\cdot THF$ and $MeNH_2$, it is worth pointing out that two sets of experiments were performed which possibly impact on the mechanism proposed by Beachley[15] involving ionic four-coordinate boron species. Heating $CH_3NH_2\cdot BH_3$ in monoglyme and following the reaction by ^{11}B NMR spectroscopy did not result in the observation of tricoordinate or tetracoordinate ionic boron species (δ –25 to –30 and –10 to +8) in the ^{11}B NMR spectrum. Instead, the resonance for the amine borane (δ –18.0) slowly decreased and the resonance for **1** (δ –5.4) grew in without appearance of intermediate species. Similarly, the reaction of $MeNH_2\cdot HCl + LiBH_4$ in a 1:1 ratio in monoglyme was followed by ^{11}B NMR. After 4 h at 25 °C the ^{11}B NMR spectrum showed only peaks for $LiBH_4$ (δ –40.5) and $MeNH_2\cdot BH_3$ in a 1:4 ratio. Refluxing the mixture for 2 h showed **1**, $LiBH_4$, and $MeNH_2BH_3$ in a 4:19:1 ratio, and after 18 h only **1** and $MeNH_2\cdot BH_3$ were observed in an 18:1 ratio. Clearly, ionic species may only be present in these systems if their lifetimes are short. More detailed experiments would be required to provide further information regarding the interesting condensation process acting in the formation of **1**.

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Registry No. **1** (isomer I), 60619-50-3; **1** (isomer II), 60619-49-0; $CH_3NH_2\cdot BH_3$, 1722-33-4; $H_3B\cdot THF$, 14044-65-6; CH_3NH_2, 74-89-5.

Supplementary Material Available: Listings of anisotropic thermal factors and hydrogen atom parameters (4 pages); listings of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Electron Transfer. 78. Reduction of Carboxylato-Bound Chromium(V) with Bisulfite. A "Clock Reaction" Involving Chromium(IV)[1]

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The chelated chromium(V) complex bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) reacts with HSO_3^- in aqueous solutions buffered by the ligand acid, 2-ethyl-2-hydroxybutyric acid. The stoichiometry, in the presence of excess HSO_3^-, lies close to 1:1, but the reaction passes through an intermediate, the properties of which correspond to those of a Cr(IV) complex. The latter functions as a catalyst for the primary conversion. The slow buildup of this intermediate, followed by its sudden consumption (after Cr^V is depleted), results in a "clocklike" character for this reaction if monitored at or near 600 nm. The proposed mechanism for this reaction (eq 2–5 in the text) involves 1e oxidations of HSO_3^- to the radical anion $SO_3^{\bullet-}$ by both Cr(V) and Cr(IV) and competition for $SO_3^{\bullet-}$ between Cr(IV) and Cr(V). Differential equations based on the proposed mechanism, in conjunction with suitably selected values for the component rate constants and for molar absorbances for the chromium species, reproduce the observed kinetic profiles. The reaction of HSO_3^- with Cr(V) is much slower than that with the more strongly reducing Cr(IV); the rate ratio is consistent with an outer-sphere mechanism for both HSO_3^- reactions. In contrast, the radical anion $SO_3^{\bullet-}$ reacts with Cr(V) 20–35 times more rapidly than with Cr(IV). This inversion of relative rates, which is the basis for the autocatalyis, suggests the operation of an inner-sphere path for the Cr(V)–radical reaction.

Carboxylato chelates of chromium(V), the facile preparations of which were described in 1979,[3] react with an array of inorganic reductants, and these reactions exhibit considerable mechanistic diversity. Early studies[4] presupposed that "even-electron" reductants would reduce Cr(V) smoothly to Cr(III), whereas 1e reductants would react through the intermediate state, Cr(IV), which, depending upon its reactivity, might or might not be detectable. It is now clear that this is an oversimplification. Reduction by hydroxylamine[5] yields, instead of a Cr(III) species,

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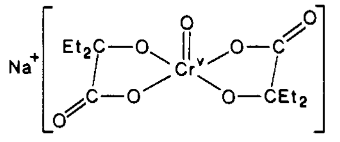
Table I. Stoichiometry of the Cr(V)–HSO_3^- Reaction[a]

$10^3[Cr^V]$ taken, M	$10^3[HSO_3^-]$ taken, M	$10^3[HSO_3^-]$ remaining,[b] M	$10^3[HSO_3^-]$ consumed, M	$\Delta[HSO_3^-]/\Delta[Cr^V]$
5.21	12.8	7.51	5.3	1.02
6.28	57.0	51.0	6.0	0.96
4.59	37.3	33.0	4.3	0.94

[a] Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). Reactions were carried out in buffered solutions that were 0.05 M each in 2-hydroxy-2-ethylbutyric acid and its sodium salt (pH 3.4). [b] Determined by adding excess $Cr_2O_7^{2-}$ and titrating the unreacted Cr^{VI} with KI–$Na_2S_2O_3$.[12]

one or more NO^+ complexes of Cr(I), whereas reaction with uranium(IV)[6] (which is generally considered a 2e reductant) appears to proceed through the intermediates Cr(IV) and U(V).

Despite these complications, and encouraged by Kochi's report of facile oxygen transfer from Cr^VO complexes to olefins and phosphines,[7a] we anticipated that reduction of Cr(V) chelate I with sulfur(IV) (which often, but not always,[7b] is a 2e reductant) would proceed in a straightforward manner, possibly by oxygen transfer, to yield Cr(III) and SO_4^{2-}. In actuality, this reaction proved to be remarkably complicated, featuring not only the intervention of Cr(IV) and the radical anion $SO_3^{\bullet-}$ but also autocatalysis by Cr(IV), resulting in most unusual kinetic behavior.



I

Experimental Section

Materials. Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (complex I) was prepared as its monohydrate as described[3] and was purified by recrystallization from acetone–chloroform.[8] Sodium perchlorate (used as the supporting electrolyte in kinetic experiments) and sodium sulfite[9,10] (Alfa Products) were used without further purification. The "ligand acid", 2-hydroxy-2-ethylbutyric acid (Aldrich) was crystallized from benzene–hexane before use. Cation-exchange resin (Bio-Rad 50W-X2; 200-400 mesh) was pretreated before use as described.[11]

Stoichiometric Studies. The reaction between Cr(V) chelate I and bisulfite was carried out in a buffered solution, which was 0.05 M each in 2-hydroxy-2-ethylbutyric acid and its sodium salt (pH 3.4), with HSO_3^- taken in excess. At the conclusion of the reaction, $[H^+]$ was increased to 1 M by careful addition of sulfuric acid, unreacted S(IV) was destroyed by addition of excess $Cr_2O_7^{2-}$, and the excess Cr(VI) was immediately estimated iodometrically.[12] Titration data, summarized in Table I, indicate that the net redox reaction proceeds with 1:1 stoichiometry provided that the reductant is in excess. When equivalent quantities of oxidant and reductant are taken or when the oxidant is in excess, the reaction is much slower and appears to be incomplete. Typically, in the case of a reaction mixture that is 0.003 M each in Cr(V) and HSO_3^-, approximately 40% of the added Cr(V) remains after 10 h.

Examination of the Chromium(III) Reaction Products. A number of reaction mixtures, each 0.003 M in Cr(V), 0.05 M in the ligand acid, and 0.05 M in its sodium salt, were treated with measured quantities of excess HSO_3^-. The Cr(III) spectra of the resulting solutions, after completion of the redox reaction, depended perceptibly on the ratio of HSO_3^- to Cr(V) taken. When this ratio was 2:1, absorption maxima were at 585 ($\epsilon = 52$ M^{-1} cm^{-1}) and 420 nm ($\epsilon = 63$), but as this ratio was increased progressively to 20:1, these maxima shifted gradually to 575 and 450 nm with no significant change in molar absorbances. In each case, acidification of the reaction product to pH 1 with $HClO_4$ generated a spectrum with maxima at 587 ($\epsilon = 49$) and 416 nm ($\epsilon = 60$), corresponding to the Cr(III) product formed from reduction of Cr(V) chelate I with Ti(III),[13] Eu(II),[8] or VO^{2+}.[8,14]

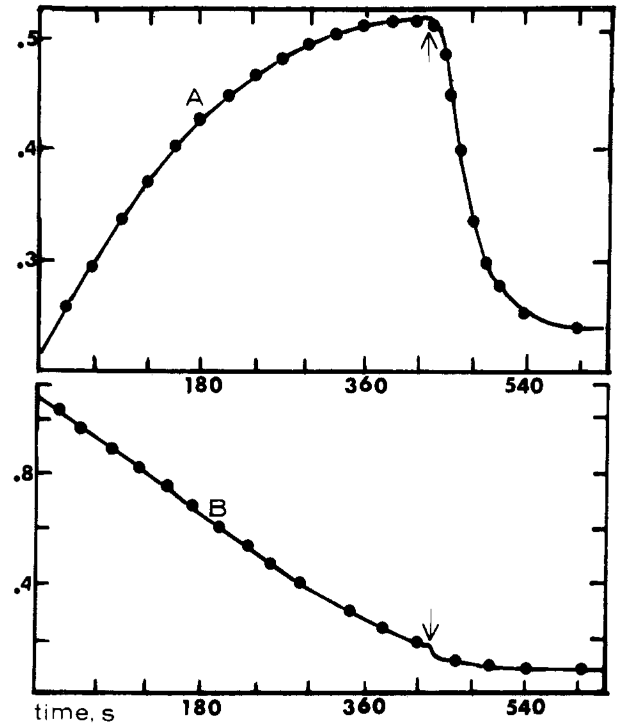


Figure 1. Kinetic profiles at 600 (curve A) and 385 nm (curve B) for reaction of Cr(V) chelate I (1.10×10^{-3} M) with sulfite (9.68×10^{-3} M) at 21 °C. The supporting medium was 0.05 M each in 2-ethyl-2-hydroxybutyric acid and its sodium salt (pH 3.4); $\mu = 0.5$ M ($NaClO_4$). Optical path lengths were 5.00 cm for curve A and 1.00 cm for curve B. Note the sharp "breakpoint" in curve A at 426 s. The principal absorbing species is Cr(IV) in curve A and Cr(V) in curve B. The solid lines are experimental curves, whereas the small circles represent absorbance changes calculated from sequence (6)–(9) in the text, taking k_1 and k_3 as 0.023 and 3.1 M^{-1} s^{-1} and the ratio k_2/k_4 as 30. Extinction coefficients used (M^{-1} cm^{-1}): (600 nm) Cr(III), 43; Cr(IV), 560; Cr(V), 41; (385 nm) Cr(III), 64; Cr(IV), 255; Cr(V), 970.

The product from reaction of 0.008 M Cr(V) with 0.10 M HSO_3^- (λ_{max} 576 and 442 nm) was adsorbed on anion-exchange resin (Dowex 1-X8, Cl^- form). A portion (comprising 60% of the total chromium) was eluted with 1.0 M NaCl and exhibited maxima at 580 ($\epsilon = 52$) and 432 nm ($\epsilon = 64$). The remainder of the Cr(III) adhered tightly and could not be eluted with 1.0 M Na_2SO_4.

Kinetic Measurements. Reactions were monitored by following absorbance changes at 385, 400, 510, 600, and 720 nm, on a Cary 14 or Beckman Model 5260 recording spectrophotometer. Ultimately, measurements at 385 and 600 nm proved to be most informative. Total ionic strength was maintained near 0.5 M by addition of $NaClO_4$, and pH values were regulated by addition of measured quantities of 2-ethyl-2-hydroxybutyric acid ($pK_A = 3.32$)[4] and its sodium salt. Temperatures were kept at 21.0 ± 0.2 °C throughout all kinetic runs. Since reactions with Cr(V) in excess were both incomplete and inconveniently slow, all kinetic runs were carried out with HSO_3^- in at least 10-fold excess.

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(7) (a) Siddall, T. L.; Miyaura, N.; Huffmann, J. C.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1983**, *1185*. (b) See, for example: Yost, D. M.; Russell, H., Jr. *Systematic Inorganic Chemistry of the Fifth-and-Sixth-Group Nonmetallic Elements*; Prentice-Hall: Englewood Cliffs, NJ, 1944; p 358.

(8) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.

(9) S(IV) exists primarily as HSO_3^- within the pH range examined here. Conversion to SO_2(aq) ($pK_1 = 1.62$, $pK_2 = 6.79$; $\mu = 0.50$ M)[10] or to SO_3^{2-} does not appear to play a part in the systems considered.

(10) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1976; Vol. 4, p 78.

(11) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

(12) See, for example: Swift, E. H. *A System of Chemical Analysis*; Prentice-Hall: Englewood Cliffs, NJ, 1940; p 82. Delay in back-titration is avoided here to minimize the (slow) reaction between $Cr_2O_7^{2-}$ and the ligand acid.[3]

(13) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.

(14) What appears to be the same transformation occurs when the Cr(V)–HSO_3^- product is passed through a sulfonate cation-exchange resin in its H^+ form, but only a portion (55% of the chromium taken) is eluted with water. As in earlier work,[8,13] a pale green band, corresponding to a partially aquated product, remains and may be eluted with 0.5 M $HClO_4$. Separations were carried out by using a column 5 cm long with a capacity of 2.0 mequiv. For estimation of extinction coefficients of Cr(III) species, fractions were oxidized with basic H_2O_2, and total Cr was determined as chromate. See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A* **1952**, *48*, 414.

In no instances were simple exponential kinetic curves obtained. At 510 nm (an absorption maximum for Cr(V) chelate I) the slope of the curve increased during the first several minutes and then remained relatively constant through the major part of the reaction. In addition, a small but sudden drop in absorption occurred near the end. The latter feature could be made much more prominent by monitoring the reaction at 600 nm (Figure 1, curve A), where Cr(V) and the Cr(III) product have nearly equal molar absorptivities, and was less marked at 720 and 385 nm (curve B), where Cr(V) absorbs much more strongly than Cr(IV). The "breakpoint" appear sooner as [HSO_3^-] was increased but disappeared if excess Ce(III) was added to the reaction mixture. The nature of the curves before the breakpoints suggested autocatalysis, but the primary reaction was not catalyzed by a portion of the spent reaction mixture from an earlier run.

Fits of the kinetic profiles to a sequence featuring autocatalysis by Cr(IV) (see Discussion) was achieved by using the computer program INTEGRAL to generate curves that could be compared to those observed.[15,16]

Examination of the reaction during its very early stages using stopped-flow spectrophotometry revealed no irregularities indicative of very rapid kinetic events during the first 0.01–2.0 s of reaction. No reaction was evident when the poorly reducing anion SeO_3^{2-} was substituted for HSO_3^- in the mixture, confirming our view (see the following section) that the observed intermediate was generated by redox rather than coordination of chromium(V) by a chalcogen(IV) species.

Results and Discussion

Stoichiometry experiments with HSO_3^- in excess (Table I) show that the reaction involves very nearly equimolar quantities of Cr(V) and HSO_3^- and rules out the formation of dithionate, $S_2O_6^{2-}$, in more than minor amounts. The principal conversion may thus be represented schematically as (1). However, the failure of the

$$\mathrm{Cr(V)} + \mathrm{S(IV)} \rightarrow \mathrm{Cr(III)} + \mathrm{S(VI)} \qquad (1)$$

reaction to go to completion when equivalent quantities of the reactants are taken, or when Cr(V) is in excess, indicates that a portion of the added HSO_3^- is converted to an unreactive form, almost certainly a sulfito complex of Cr(III). This inference is in accord with the recognized[17] ability of sulfite to enter the coordination sphere of Cr(III) rapidly at pH values similar to those employed here and also with our examination of the Cr(III) products from reactions with sulfite in excess.

The relatively high extinction coefficents (50–60 M^{-1} cm^{-1}) of these products indicate that they are bis-chelated complexes of Cr(III).[8] They are not, however, the bis chelate $[(Lig)_2(H_2O)_2Cr(III)]^+$, which is formed from the reduction of Cr(V) complex I with VO^{2+},[8] Eu^{2+},[8] or Ti(III),[11] but they undergo rapid conversion to this diaquochromium(III) chelate on acidification. Moreover, the anion-exchange elution behavior of our products indicates the presence of two components, both of them negatively charged. That component easily eluted with 1 M Cl^- may be assigned a −1 charge and a formula $[(Lig)_2(H_2O)Cr^{III}(OSO_2)]^-$, whereas that remaining on the column after treatment with 1 M SO_4^{2-} has a charge more negative than −2 and is probably $[(Lig)_2Cr^{III}(OSO_2)_2]^{3-}$. The proportion of the bis(sulfito) complex increases as the concentration of HSO_3^- taken increases, as reflected in the progressive spectral shifts perceived for the spent reaction mixtures. Even with 0.10 M HSO_3^-, however, limiting spectra are not observed for the Cr(III) product. The rapid conversion of these sulfito complexes to the diaquo bis chelate on acidification almost certainly results from H^+-induced breakage of S^{IV}–O rather than Cr^{III}–O bonds, as substitution reactions at Cr(III) centers in aqueous solution are generally slow.[18]

We are reluctant to ascribe mechanistic significance to the formation of these sulfito species, since incorporation of sulfite could have occurred after formation of the Cr(III) product, rather than at intermediate stage(s) in the reaction sequence.

Kinetic profiles at 2 of the 5 wavelengths used to monitor the Cr(IV)–HSO_3^- reaction appear in Figure 1. In curve B (taken at 385 nm), the principal absorbing species is the Cr(V) chelate I. The rate of consumption of Cr(V) is seen to increase slightly during the first 150 s, after which it remains nearly constant until 300 s, finally decreasing during the final stages of reaction. The major portion of curve B points to the operation of an autocatalytic process in which the usual drop in reaction rate due to depletion of a reactant is compensated by the growth of a catalytic species. However, neither of the major products (SO_4^{2-} or the (sulfito)chromium(III) complex formed), exhibits catalytic activity in this reaction. In addition, a barely perceptible "nick" in curve B occurs 430 s after mixing.

That this "nick" is not an artifact can be shown by monitoring the reaction at 600 nm (curve A). Here, Cr(V) and the Cr(III) product have very nearly equal molar absorptivities, but the resulting kinetic curve indicates the growth of a strongly absorbing intermediate during the first 426 s (at which point virtually all Cr(V) is consumed) and then a sudden drop in the concentration of this intermediate. The sharpness and high reproducibility (with respect to time) of this drop allows us to classify this as a "clock reaction", i.e. a chemical system in which a sudden marked change occurs after a precise waiting period.[19] The shape of the profile at 600 nm suggests that the intermediate absorbing at this wavelength is being quickly depleted by a reaction that is inhibited by Cr(V) when the latter is present. This inhibition cannot be due to a reaction of Cr(V) with HSO_3^-, as S(IV) is in excess throughout the reaction. It appears instead that Cr(V) is acting as scavenger for another (non-chromium) intermediate species, present in very small concentration.

We propose the principal catalytic species to be a Cr(IV) complex, as it is present throughout the reaction but is destroyed near the end of each run via reduction by sulfite. The gradual growth and sudden disappearance of this complex is depicted in curve A; both the autocatalysis and the unusual spectral features disappear when Ce(III) is added to the reaction mixture, reflecting the reported[20] action of that lanthanide center in catalyzing the disproportionation of Cr(IV).

The reaction series given in (2)–(5), but no other sequence that we can devise, is in accord with our qualitative and quantitative observations. Each step is a single-electron transaction, and the

$$\mathrm{Cr^V} + \mathrm{S^4} \xrightarrow{k_1} \mathrm{Cr^{IV}} + \mathrm{S^5} \quad (\mathrm{S^4} = \mathrm{HSO_3^-}) \qquad (2)$$

$$\mathrm{Cr^V} + \mathrm{S^5} \xrightarrow{k_2} \mathrm{Cr^{IV}} + \mathrm{S^6} \quad (\mathrm{S^6} = \mathrm{SO_4^{2-}}) \qquad (3)$$

$$\mathrm{Cr^{IV}} + \mathrm{S^4} \xrightarrow{k_3} \mathrm{Cr^{III}} + \mathrm{S^5} \qquad (4)$$

$$\mathrm{Cr^{IV}} + \mathrm{S^5} \xrightarrow{k_4} \mathrm{Cr^{III}} + \mathrm{S^6} \qquad (5)$$

sequence involves the intervention not only of Cr(IV), but also of the $SO_3^{\bullet-}$ radical anion[21] (abbreviated S^5). At the beginning

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(15) Kinetic fits, which utilized a fourth-order Runge–Kutta integration technique,[16] were accomplished by a Fortran-77 or by a Fortran-IV program, INTEGRAL, and were executed on a Burroughs B6800 or on a Prime 750 computer system. The Fortran-IV version of the program, for which we thank Professor Gilbert Gordon (Miami University, Oxford, OH), was modified to incorporate the appropriate differential equations and stoichiometry. Copies of the modified program may be obtained from R.N.B.

(16) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. *Tech. Chem.* **1974**, *6*, 764.

(17) See, for example: Moritzen, P. A.; El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1985**, *24*, 313.

(18) For a summary of "pseudosubstitution reactions" of this type, see, for example: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; p 229.

(19) There is a substantial, although scattered, literature dealing with clock reactions. See, for example: (a) Eggert, J. *J. Chem. Soc.* **1917**, 197. (b) Sorum, C. H.; Charlton, F. S.; Neptune, J. A.; Edwards, J. O. *J. Am. Chem. Soc.* **1952**, *74*, 219. (c) Barrett, R. L. *J. Chem. Educ.* **1955**, *32*, 78. (d) Elliott, E. M.; Levin, M. *Ibid.* **1967**, *44*, A341. (e) Lyndrum, M. L. *Ibid.* **1972**, *49*, 30. (f) Baker, A. D.; Casadevall, A. *Ibid.* **1980**, *57*, 515. (g) Burnett, M. G. *Ibid.* **1982**, *59*, 160. (h) Citri, O.; Epstein, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 357.

(20) Doyle, M.; Swedo, R. J.; Roček, J. *J. Am. Chem. Soc.* **1973**, *95*, 8352.

(21) Evidence supporting the intervention of $SO_3^{\bullet-}$ has been reported for a variety of systems. See, for example: (a) Bassett, H.; Parker, W. G. *J. Chem. Soc.* **1951**, *1540*. (b) Higginson, W. C. E.; Marshall, J. W. *Ibid.* **1957**, 447. (c) Chantry, G. W.; Horsfield, A.; Morton, J. R. *Mol. Phys.* **1962**, *5*, 233. (d) Norton, C. J.; Seppi, N. F.; Reuter, M. J. *J. Org. Chem.* **1968**, *33*, 4158. (e) Behar, D.; Fessenden, R. W. *J. Phys. Chem.* **1971**, *75*, 2752.

Table II. Kinetic Parameters for the Reduction of Carboxyl-Bound Chromium(V) with Sulfur(IV)[a]

10^4[Cr(V)], M	10^3[HSO_3^-], M	[Lig^-],[b] M	[HLig],[c] M	pH	breakpt, s	k_1,[d] $M^{-1}\ s^{-1}$	k_3,[d] $M^{-1}\ s^{-1}$	k_2/k_4[d]	$\epsilon_{Cr(IV)}$,[d,e] $M^{-1}\ cm^{-1}$
11.0	9.68	0.050	0.050	3.4	426	0.023	3.1	30	560
5.52	11.0	0.025	0.025	3.4	288	0.027	3.4	35	500
5.00	4.35	0.010	0.010	3.4	660	0.033	4.1	20	280
5.80	5.72	0.025	0.025	3.4	675	0.022	3.6	36	490
3.43	10.3	0.075	0.075	3.4	720	0.013	1.5	35	590
10.2	10.3	0.100	0.100	3.4	816	0.013	1.2	35	620
7.25	8.25	0.050	0.016	3.8	186	0.025	4.6	35	600
9.63	9.2	0.050	0.150	2.8	522	0.023	2.1	30	320

[a] Reactions were carried out at 21 °C in 0.5 M $NaClO_4$. Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I); S(IV) was added as sodium sulfite. [b] 2-Ethyl-2-hydroxybutyrate. [c] 2-Ethyl-2-hydroxybutyric acid. [d] Parameters obtained from best fit of integrated forms of (6) and (10) to experimental kinetic curves (see text). [e] 600 nm.

of the reaction, only (2) and (3) take place, but as Cr^{IV} accumulates, (4) assumes importance, yielding an increased concentration of S^5 radical anion. The shapes of the curves indicate that the latter reacts more rapidly with Cr^V than with Cr^{IV}, but reaction with Cr^V regenerates Cr^{IV} via (3) (hence the autocatalysis). When Cr^V is exhausted, only (4) and (5) occur, resulting in the nearly pseudo-first-order consumption of Cr^{IV}.

The sequence given in (2)–(5) generates differential rate equations

$$-\frac{d[Cr^V]}{dt} = k_1[Cr^V][S^4] + k_2[Cr^V][S^5] \quad (6)$$

$$-\frac{d[S^4]}{dt} = k_1[Cr^V][S^4] + k_3[Cr^{IV}][S^4] \quad (7)$$

$$+\frac{d[Cr^{IV}]}{dt} = k_1[Cr^V][S^4] + k_2[Cr^V][S^5] - k_3[Cr^{IV}][S^4] - k_4[Cr^{IV}][S^5] \quad (8)$$

$$+\frac{d[S^5]}{dt} = k_1[Cr^V][S^4] + k_3[Cr^{IV}][S^4] - k_2[Cr^V][S^5] - k_4[Cr^{IV}][S^5] \quad (9)$$

Applying the steady-state approximation to the radical anion S^5 and then substituting the resulting expression for [S^5] into (6) yields (10), where $a = k_2/k_4$. Use of the Runge–Kutta integration

$$-\frac{d[Cr^V]}{dt} = k_1[Cr^V][S^4] + \frac{a[Cr^V][S^4](k_1[Cr^V] + k_3[Cr^{IV}])}{a[Cr^V] + [Cr^{IV}]} \quad (10)$$

technique[16] for this system involved selection of (7) and (10)[22a] and the choice of a 15-s time interval between kinetic points. Changes in [Cr^{IV}] and [Cr^{III}] were related stoichiometrically to changes in [Cr^V] and [S^4], and values of k_1, k_3, and the ratio k_2/k_4 (=a) were allowed to vary.[22b] Integration then yielded the concentrations of each of the chromium oxidation states and that of bisulfite at 15-s intervals. Incorporation of molar absorbances of Cr^{III}, Cr^{IV}, and Cr^V yielded calculated values for the optical density of the reaction mixture at each point.[23,24]

Values of the parameters k_1, k_3, k_2/k_4, and $\epsilon_{Cr(IV)}$ giving the closest agreement between calculated and observed absorbances are included in Table II. Calculated absorbances (solid circles) generated from one set of these parameters are compared with the appropriate experimental values (the continuous curves) in Figure 1. As curve A emphasizes, the "clocklike" nature of the reaction reflects the gradual growth and sudden decay of Cr(IV). Interestingly, the maximum concentration of Cr(IV), achieved at the "breakpoint", is, in this case, only 11% of [Cr(V)] taken.

Although the rate constants and the $\epsilon_{Cr(IV)}$ values resulting from our kinetic treatment are too few and of insufficient precision to justify an overall refinement embracing all eight runs, we note that both the Cr^V–S^4 reaction (k_1) and the Cr^{IV}–S^4 reaction (k_3) are retarded by excess ligand anion (Lig^-), but both dependencies are less steep than that corresponding to an inverse proportionality. Instead, these inhibitions exhibit kinetic saturation at [Lig^-] near 0.1 M. The implication here is that both oxidation states are involved in rapid ligation equilibria, with the fully ligated species less reactive than the partially ligated in each case, a situation calling to mind that observed for the Cr^V–U^{IV} reaction.[6] In addition, k_3, but not k_1, appears to be affected by a protonation equilibrium, probably involving Cr^{IV},[9] and this equilibrium is reflected also in the perceived variation of $\epsilon_{Cr(IV)}$ with pH.[25]

The principal Cr(III) products are bis chelates having structures related to the Cr(V) reactant, except for sulfite substitution at the axial position(s) (which very probably occurs at the Cr(IV) or Cr(III) stage.) The persistance of this structural unit during both steps of the sequence ($Cr^V \rightarrow Cr^{IV} \rightarrow Cr^{III}$) is, however, not diagnostic of mechanism, for it has been observed also in the outer-sphere reduction of Cr(V) chelate I with Ti(III)[13] and the inner-sphere reductions of the same oxidant with Fe(II)[24] and VO^{2+}.[8] The feature common to those several reactions is that reduction of the chelated Cr(IV) intermediate, irrespective of mechanism, is more rapid than ligand substitution about the Cr(IV) center, which results in aquation. The ligand sheath about Cr(IV) does not appear to survive, however, in reactions with the less strongly reducing species Mn(II) and Ce(III).[26,27]

As expected, the reaction of HSO_3^- with Cr(V) is much slower than that with the much more strongly reducing Cr(IV),[28-31] the ratio of specific rates (k_1/k_3) ranging from 0.006 to 0.011, depending upon the reaction medium. This ratio falls below the estimated upper limit (0.05) for the corresponding ratio pertaining to the outer-sphere reductions of Cr(V) and Cr(IV) by $Ti(OH)^{2+}$,[13] and hence is consistent with an outer-sphere mechanism for both HSO_3^- reactions, although it does not demand this.[32] The corresponding ratio for reactions of Cr(V) and Cr(IV) with radical

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(22) (a) In practice, this procedure is effective if any two of the three differential equations, (6), (7), and (8), (with the appropriate substitution for [S^5]) are used. (b) None of the sulfur species absorbs appreciably at the wavelengths considered. The preliminary estimate of k_1 was made from the initial slope at 385 nm, whereas that of k_3 was obtained from the rapid decrease in absorbance beyond the inflection point at 600 nm. The calculated shapes of the kinetic curves proved to be much less sensitive to the values of k_1 and k_3 than to the ratio k_2/k_4.

(23) Values of $\epsilon_{Cr(III)}$ and $\epsilon_{Cr(V)}$ were taken from the final and initial absorbances of the reaction mixture, whereas $\epsilon_{Cr(IV)}$ was estimated from earlier work[24] dealing with the Cr(V)–Fe(II) system. The latter parameter was allowed to vary during the refinement procedure, but the former two were fixed.

(24) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.

(25) A protonation equilibrium ($pK_A = 3.4$; 23 °C, $\mu = 0.4$ M) involving Cr(IV) in 2-hydroxy-2-ethylbutyrate systems has been reported by Fanchiang.[8]

(26) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

(27) (a) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33. (b) Ogard, A. E.; Taube, H. *Ibid.* **1958**, *62*, 357.

(28) Formal potentials for $Cr^{VI} \rightarrow Cr^V$ and for $Cr^V \rightarrow Cr^{IV}$ have been estimated[29] as 0.60 and 1.39 V, respectively, values which have been critically considered by Linck.[30] These potentials, in conjunction with the value 1.20 V for $Cr^{VI} \rightarrow Cr^{III}$,[31] lead to a formal potential of 1.61 V for $Cr^{IV} \rightarrow Cr^{III}$. Note that these values apply to 1 M H^+; each is expected to be pH-dependent, but the dependencies need not be of the same type. There can be no doubt, however, that Cr^{IV} is an exceedingly strong oxidant in the system at hand.

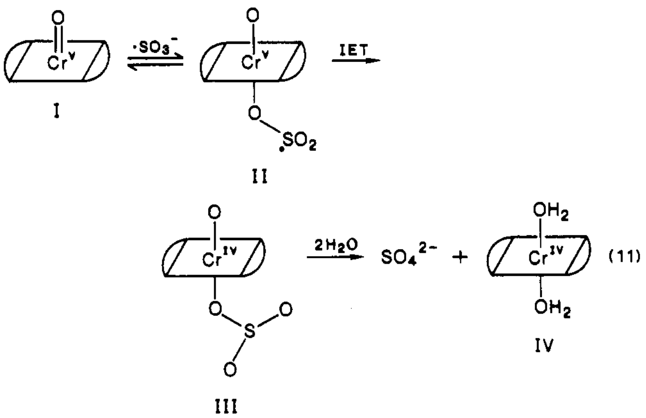
(29) Csanyi, L. J. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1972, Vol. 7, p 510.

(30) Linck, R. G. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1974**, *9*, 191.

(31) Beattie, J. K.; Haight, G. P., Jr. *Prog. Inorg. Chem.* **1972**, *17*, 97.

(32) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

anion $SO_3^{\bullet -}$ (k_2/k_4 = 20–35) points to an inner-sphere path for the Cr^V–S^5 reaction, (3). The latter is represented schematically as (11), in which formation of the precursor complex, II, from



the $SO_3^{\bullet -}$ radical anion and the Cr(V) chelate I precedes internal electron transfer (IET) to form the Cr(IV)–S(VI) intermediate, III, which features an electron-deficient sulfur atom. Complex III then undergoes rapid hydration (at sulfur) and aquation (at Cr^{IV}) to yield the $Cr^{IV}(H_2O)_2$ complex, IV.[33] We cannot say why such a mechanism (or one related to it) is favored for the Cr^V–S^5 reaction but not for the remaining steps in the proposed series, (2), (4), and (5). We note, however, that Cr^V–S^5 may be the only one of the four steps that involves interaction between a radical and oxo-bound chromium center.[34]

Finally, it may be asked whether additional systems will exhibit the type of kinetic behavior observed here. If we retain the same oxidant, three constraints are imposed on the reductant. First, it must be able to entertain both 1e and 2e changes, with the 1e product stable enough to undergo partition between subsequent reaction paths; reagents in this class include nitrite, dithionite, chlorite, vanadium(III), substituted hydroquinones, and aromatic amines. Second, the lower oxidation state must react more rapidly with Cr(IV) than with Cr(V) (in accord with the relative formal potentials of the two oxidants);[28] this is probably the case for each of the indicated reductants. Most important, there must be a reversal of relative oxidation rates (pertaining to Cr^{IV} and Cr^V) in going from the reductant to the 1e intermediate; i.e., this intermediate must react more rapidly with Cr^V than with Cr^{IV}. Experience with earlier systems[6,8,13] suggests that metal-center reductants are unlikely to fulfill the latter requirement. However the behavior of oxygenated reductants and more complicated organic molecules remains to be examined.

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Registry No. I, 84622-43-5; HSO_3^-, 15181-46-1; Cr^{4+}, 15723-28-1.

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[33] It is assumed that loss of the monodentate sulfate ligand from the Cr(IV) center is much more rapid than loss of the chelating carboxylato group. Our experiments yield no evidence for formation of significant quantities of a (sulfato)chromium(III) product.

[34] The ligand configuration about Cr(IV) in solution is, at present, uncertain. Although a 5-coordinate oxo ion (analogous to that in Cr^V and V^{IV}) is not unreasonable, an octahedral configuration (analogous that in Cr^{III}) has also been suggested. See, for example: Espenson, J. H. *Acc. Chem. Res.* **1970**, *3*, 347.

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Electron Transfer. 79. Reductions of Organic Disulfides by Vitamin B_{12s} (Cob(I)alamin)[1]

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Vitamin B_{12s} (cob(I)alamin) reacts rapidly and completely with organic disulfides in aqueous media, yielding the corresponding thiols and cob(II)alamin, whereas reactions of the cobalt(II) complex with disulfides are slow and incomplete. Reactions are first order in both B_{12s} and disulfide and are generally accelerated three- to sevenfold by monoprotonation of a basic site on the oxidant. Rate enhancements resulting from diprotonation (when it occurs) are slight. Reduction of the monoanion of dithiodiacetic acid (I) is unexpectedly rapid, suggesting destabilization of the S–S bond by internal hydrogen bonding. Two different reaction sequences for the series, one involving a thiyl (RS•) intermediate and the other proceeding through a Co(III) transient, are consistent with the data at hand.

Earlier reports[2] by Espenson and co-workers described reductions of peroxides with cobalt(II) macrocycles, including vitamin B_{12r} (cob(II)alamin). These reactions were generally rapid, and analysis of the results suggested some diversity of mechanistic detail. It therefore appeared reasonable to examine analogous reductions of organic disulfides (RSSR). The principal reduction products, in aqueous media, were expected to be the corresponding thiols, with the overall transformations thus being closely related to those of importance in a variety of biosystems.[3] In our hands, however, reductions of disulfides with B_{12r} proved to be slow and incomplete, even at very low pHs, possibly reflecting the small difference in formal potentials of the reacting species.[4–6]

We therefore turned to reactions of disulfides with the much stronger reductant, vitamin B_{12s} (cob(I)alamin). As anticipated,[7,8]

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[1] Sponsorship of this work by the National Science Foundation (Grant No. 8313253) is gratefully acknowledged.

[2] (a) Espenson, J. H.; Martin, A. H. *J. Am. Chem. Soc.* **1977**, *99*, 5953. (b) Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38.

[3] See, for example: Ziegler, D. M. *Annu. Rev. Biochem.* **1985**, *54*, 305.

[4] Formal potentials (vs. NHE at pH 1) for B_{12r} and B_{12s} have been reported as +0.30 and –0.48 V, respectively;[5] both of these values are strongly pH dependent. Formal potentials for thiol–disulfide systems that are devoid of strongly electron-attracting or electron-repelling groups lie between +0.02 and +0.30 V at pH 0, and between –0.20 and –0.40 V at pH 7.[6]

[5] Lexa, D.; Saveant, J.-M. *Acc. Chem. Res.* **1983**, *16*, 235.

[6] See, for example: Clark, W. M. *Oxidation-Reduction Potentials of Organic Systems*; Williams and Wilkins: Baltimore, MD, 1960; p 486.

[7] The difference in formal potentials of B_{12r} and B_{12s} corresponds, by the Marcus model for outer-sphere reactions,[8] to a $10^{6.5}$-fold difference in specific rates. Substantial changes in this ratio are expected if one or both of these reductants utilizes an inner-sphere path.