

and subsequently hydrolyzed to the sulfone in high yield.

Experimental Section

Materials. The compounds used in this work were obtained from commercial sources [CsF (Aldrich), $\text{CF}_2=\text{CFCl}$, $\text{CF}_2=\text{CHCl}$, $\text{CFCl}=\text{CFCl}$, $\text{c-C}_4\text{F}_6$, $\text{CF}_3\text{SO}_2\text{Cl}$ (PCR)] and used without further purification.

General Procedure. Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum manifold equipped with a Heise Bourdon tube gauge and a Televac vacuum gauge, which were connected directly to the manifold. Gaseous materials were measured with the assumption of the ideal gas law. Nonvolatile materials were weighed. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer using a 10-cm cell equipped with KBr windows for volatile compounds and using a liquid film on KBr plates for nonvolatile liquids. ^{19}F NMR spectra were obtained on a Varian EM-360L spectrometer and a JEOL FX-90Q spectrometer operating at 54.6 and 84.3 MHz, respectively. ^1H NMR spectra were recorded on either a Varian EM-360 or EM-360L spectrometer operating at 60.0 MHz or a JEOL FX-90Q spectrometer at 89.56 MHz. All bands are reported relative to CCl_3F or Me_4Si . The usual solvent was CDCl_3 . Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany, or at the University of Idaho.

Reaction of C_2F_4 with $\text{CF}_3\text{SO}_2\text{F}$. To a 75-mL stainless-steel vessel equipped with a stainless-steel Hoke valve and ball bearings were added 136 mmol of predried CsF, 209 mmol of diglyme (dried over sodium), and 49 mmol of $\text{CF}_3\text{SO}_2\text{F}$. A 9.9-mmol sample of C_2F_4 was added, and the reaction mixture was heated to 100 °C (1 h) with shaking (10 min). Additional amounts of C_2F_4 were added (with shaking, 1 h): 11.8 mmol (90 °C, 1 h) and 20.5 mmol (80–90 °C, 57 h). The products of the reaction were separated by fractional condensation; $\text{CF}_3\text{SO}_2\text{CF}_2\text{CF}_3$ was obtained in 53% yield. The infrared spectrum has the following bands (cm^{-1}): 1425 (s), 1329 (m), 1240 (vs, sh at 1213), 1117 (ms), 980 (m), 880 (w), 834 (w), 761 (w), 622 (s, sh at 650), 558 (m), 524 (m). The ^{19}F NMR spectrum consists of three peaks: CF_3S (ϕ -71.2), CF_2 (ϕ -112.9), and CF_3C (ϕ -78.8) in the ratio of 3:2:3; $J_{\text{CF}_3\text{S}-\text{CF}_2} = 8.4$ Hz, $J_{\text{CF}_3\text{C}-\text{CF}_2} = 1.3$ Hz, and $J_{\text{CF}_3\text{S}-\text{CF}_3\text{C}} = 2.3$ Hz. A molecular ion was not observed but other appropriate fragment ions were found: 183 ($\text{M} - \text{CF}_3$)⁺, 133 ($\text{M} - \text{CF}_2\text{CF}_3$)⁺,

119 ($\text{M} - \text{CF}_3\text{SO}_2$)⁺, 100 ($\text{M} - \text{CF}_3\text{SO}_2\text{F}$)⁺, and 69 (CF_3)⁺.

Anal. Calcd: S, 12.72; F, 60.3. Found: S, 12.87; F, 61.1.

Reaction of $\text{CF}_3\text{SO}_2\text{F}$ with $\text{CF}_2=\text{CFCl}$, $\text{CF}_2=\text{CHCl}$, $\text{CFCl}=\text{CFCl}$, and $\text{c-C}_4\text{F}_6$. With use of essentially the same method reported for C_2F_4 , these fluoroolefins reacting with $\text{CF}_3\text{SO}_2\text{F}$ failed to produce any sulfone derivative except in trace quantities.

Reaction of Excess C_2F_4 with SO_2F_2 . To the 75-mL stainless-steel vessel used with $\text{CF}_3\text{SO}_2\text{F}$ were added 57 mmol of CsF, 237 mmol of diglyme, and 15.1 mmol of SO_2F_2 . Excess C_2F_4 was then added (49.8 mmol), and the mixture was warmed to 32 °C (12 h) and at room temperature (67 h) with vigorous shaking. The products of the reaction were separated by fractional condensation. The following products were found in the -78 °C trap: $(\text{CF}_3\text{CF}_2)_2\text{SO}_2$, 2.8 mmol; $(\text{CF}_3\text{CF}_2)_2\text{SO}$, 1.0 mmol. The trap at -146 °C contained a reactive compound, which when warmed to room temperature in glass decomposed. The -40 °C trap contained diglyme and the dimer of TFE.

Reaction of C_2F_4 with SO_2F_2 . To a 150-mL stainless-steel reaction vessel equipped with a stainless-steel Whitey valve and stainless-steel ball bearings were added 82 mmol of CsF, 248 mmol of diglyme, 16.5 mmol of SO_2F_2 , and 18.9 mmol of C_2F_4 . The reaction was shaken vigorously (108 h) at room temperature. The products of the reaction were separated by fractional condensation. The following products were found: $(\text{CF}_3\text{CF}_2)_2\text{SO}$, 0.4 mmol; $(\text{CF}_3\text{CF}_2)_2\text{SO}_2$, 0.1 mmol; $\text{CF}_3\text{CF}_2\text{SO}_2\text{F}$, 1.1 mmol. Other products identified were SO_2F_2 , and the dimer of C_2F_4 . The fraction of -196 °C also contained an unidentified substance that could not be characterized due to its instability.

Reaction of $\text{CF}_3\text{S(O)F}_2\text{CF}_2\text{CF}_3$ with Water. To a 100-mL Pyrex glass vessel equipped with a Kontes Teflon stopcock and Teflon-coated stirring bar were added 44 mmol of CsF, 6 mmol of H_2O , and 0.75 mmol of $\text{CF}_3\text{S(O)F}_2\text{CF}_2\text{CF}_3$. After the mixture was stirred at room temperature for 3 days, 0.46 mmol of $\text{CF}_3\text{SO}_2\text{CF}_2\text{CF}_3$ was recovered; yield 61%. The infrared of the product agreed with that found previously by reacting C_2F_4 with $\text{CF}_3\text{SO}_2\text{F}$.

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Registry No. C_2F_4 , 116-14-3; $\text{CF}_3\text{SO}_2\text{F}$, 335-05-7; $\text{CF}_3\text{SO}_2\text{CF}_2\text{CF}_3$, 84416-69-3; SO_2F_2 , 13709-54-1; $(\text{CF}_3\text{CF}_2)_2\text{SO}_2$, 14930-22-4; $(\text{CF}_3\text{CF}_2)_2\text{SO}$, 33622-19-4; $\text{CF}_3\text{CF}_2\text{SO}_2\text{F}$, 354-87-0; $\text{CF}_3\text{S(O)F}_2\text{CF}_2\text{CF}_3$, 33564-24-8.

(18) Sauer, D. T.; Shreeve, J. M. *Z. Anorg. Allg. Chem.* 1971, 385, 113.

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 60. Reduction of Carboxylato-Bound Chromium(V) with Hydroxylamine¹

N. RAJASEKAR, R. SUBRAMANIAM, and E. S. GOULD*

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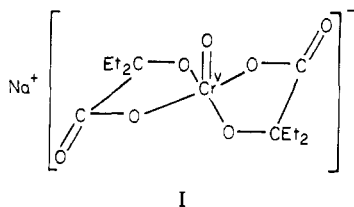
The chelated bis(carboxylato)chromium(V) complex I reacts smoothly with NH_2OH^+ at pH 3.6–4.7 in the presence of an excess of the parent carboxylic acid. The spectral, magnetic, and ion-exchange properties of the chromium products support the formulation of these as structures II and III, NO^+ derivatives of low-spin chromium(I) rather than NO^- complexes of chromium(III). The reaction is retarded by increasing acidity or by addition of unbound carboxylato ligand. The empirical rate law (eq 1) is consistent with a mechanism initiated by rapid and reversible loss of one carboxylato group from the Cr(V) oxidant (with $K_{\text{diss}} = 5.8 \times 10^{-2}$ M), followed by formation of a Cr(V)– NH_2OH precursor complex (with attendant deprotonation) ($k = 0.38 \text{ M}^{-1} \text{ s}^{-1}$) and then by an act of internal electron transfer involving a net 4e change. It further appears that the two Cr(I)–NO products, one an uncharged dichelate and the other a 1+ monochelate, result from a competition between the parent carboxylate anion and solvent water for a coordinatively unsaturated Cr(I) intermediate. No evidence for intervention of a chromium(III) intermediate was obtained.

The first air-stable water-soluble carboxylato derivatives of chromium(V) were described in 1979.² Shortly afterward,

experiments dealing with the reduction, using hydrazine, of one of these complexes, sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I) were reported;³ this study indicated that the reaction proceeded smoothly through a pair

(1) Joint sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant No. 8022881) is gratefully acknowledged.

(2) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* 1979, 101, 3206.
(3) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* 1981, 20, 3176.



of 2e transactions, the first of which was rate determining, and that the active chromium(V) species was formed reversibly by loss of a carboxyl ligand from ligand from oxidant I.

In the present paper we describe the reaction of carboxylato-bound chromium(V) with hydroxylamine, a reductant that is structurally similar to hydrazine but that is found to differ markedly from the latter in aspects of its redox behavior. Undoubtedly the most novel feature of this study is the conversion of chromium(V) to chromium(I), a net transfer of 4e in what appears to be a single transaction.

Experimental Section

Hydroxylammonium chloride and hydroxylammonium sulfate (Alfa products) were used as received. Lithium perchlorate was prepared as described.⁴ Solutions of hydroxylammonium perchlorate were prepared by treatment of hydroxylammonium sulfate with an equivalent quantity of Ba(ClO₄)₂ and filtering off the precipitated BaSO₄. Hydroxylamine concentrations were estimated by the method of Bray and co-workers,⁵ in which NH₃OH⁺ is oxidized by excess Fe(III) at 100 °C and the Fe(II) formed titrated in the cold with KMnO₄. Sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I) was prepared as a monohydrate as described by Krumpolc,² was kept at 0 °C, and was purified by precipitation from acetone-hexane shortly before use. Cation-exchange resin (Bio-Rad 50W-X2; 200–400 mesh), used in separation of reaction products, was pretreated as described.⁶

Rate Measurements. Rates were estimated from measurements of decreases in absorbance at 510 nm, a Cr(V) absorption maximum,² with a Beckman 5260 recording spectrophotometer.³ Ionic strength was regulated with thrice-recrystallized LiClO₄. Kinetic runs were carried out in the pH range 3.7–5.0 HOAc–OAc[−] buffers since Cr(V) solutions having pH values outside this range slowly decompose. Rates were not affected by addition of OAc[−], provided that constant pH was maintained by addition of HOAc. Oxidations were first order each in Cr(V) and NH₃OH⁺ but were generally run under pseudo-first-order conditions with at least a 10-fold excess of NH₃OH⁺. Conversions were followed for at least 5 half-lives. Rate constants from successive half-lives within a single run agreed to within 6%, and average values did not differ significantly from those obtained from the slopes of logarithmic plots of absorbance differences against reaction times. Specific rates from replicate runs checked to better than 8%. Temperatures were kept at 25.0 ± 0.2 °C during all kinetic experiments.

Stoichiometric Studies. The stoichiometry of the Cr^V–NH₃OH⁺ reaction, with oxidant in excess, was determined by adding a measured deficiency of the hydroxylammonium salt to the Cr^V solution, waiting 1 h for virtual completion of the reaction, and then measuring the decrease in absorbance at 510 nm. Extinction coefficients of the Cr(V) complex and the chromium reduction product were taken as 162 and 15 M^{−1} cm^{−1}, respectively. The necessary correction for the slow decomposition of the Cr(V) derivative in the absence of hydroxylamine was minimized by carrying out the reaction in an acetate buffer to which 2-ethyl-2-hydroxybutyric acid had been added. With the reductant in excess, stoichiometry was determined by adding a measured deficiency of the Cr(V) complex to the NH₃OH⁺ solution, allowing 60 min for completion of the reaction, and then estimating the unreacted NH₃OH⁺ as described.⁵ Representative results are summarized in Table I.

Examination of the Chromium Reaction Products. A number of Cr^V–NH₃OH⁺ reaction mixtures, 0.07 M in NH₃OH⁺ClO₄[−] and 0.006 M in Cr(V), each having a known concentration of added 2-ethyl-2-hydroxybutyrate, were allowed to react for 60 min, after which the

Table I. Stoichiometry of the Cr^V–NH₃OH⁺ Reaction^a

10 ³ × [NH ₃ OH ⁺], M	10 ³ × [Cr ^V], M	10 ³ × Δ[NH ₃ OH ⁺], M	10 ³ × Δ[Cr ^V], M	Δ[Cr ^V]/Δ[NH ₃ OH ⁺]	medium ^b
0.89 ^c	1.72		0.80	0.90	A
1.01 ^d	2.07		0.97	0.96	B
1.86 ^e	3.39		1.82	0.98	A
0.89 ^e	3.11		1.03	1.16	A
0.66 ^e	3.11		0.62	0.94	A
2.00 ^c	1.54	1.70		0.90	B
55.0 ^e	9.84	10.7		0.92	C
82.6 ^e	9.84	10.3		0.96	C

^a Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I). ^b Reaction media: A, 0.12 M HOAc + 0.20 M NaOAc + 0.0054 M ligand; B, 0.40 M HOAc + 0.20 M NaOAc + 0.0120 M ligand; C, 0.40 M HOAc + 0.08 M NaOAc + 0.011 M ligand (ligand 2-ethyl-2-hydroxybutyric acid). ^c NH₃OH⁺ClO₄[−]. ^d NH₃OH⁺Cl[−]. ^e (NH₃OH⁺)₂SO₄^{2−}.

mixtures were subjected to cation-exchange chromatography at 2 °C (Bio-Rad 50W-X2 sulfonate resin, H⁺ form; 200–400 mesh) as described.^{7–9} Separations generally required about 6 h. Two chromium-containing species, both yellow-brown, were obtained. The first, eluted with water alone, exhibited absorption maxima near 560 (ε 29 M^{−1} cm^{−1}) and 441 nm (ε 85). A second complex, eluted with 0.18 M HClO₄, had maxima at 560 (ε 25) and 438 nm (ε 55). The product distribution, as measured by the relative number of moles of chromium present in the two fractions, was a sensitive function of the concentration of carboxylato ligand present before reduction. When the ratio [ligand]/[Cr^V] was 4.2, the faster moving fraction constituted 54 mol % of the recovered product; when this ratio was increased to 27, the faster fraction was found to be 93% of the product. However, addition of excess ligand after completion of the primary reaction did not alter the ratio of products. Recovery of total chromium was 75–80% but was not further decreased by a second passage. Concentrated solutions of both products in D₂O exhibited strong absorption at 1780 and 1860 cm^{−1}.

Neither yellow-brown species appeared to be changed on treatment with 0.1 M HClO₄ at 70 °C for over 30 min. Both were slowly converted to Cr(H₂O)₅Cl²⁺ on treatment with dilute HCl and to Cr(H₂O)₆³⁺ with H₂O₂–HClO₄.

For purposes of comparison, the complex ion Cr(H₂O)₅NO²⁺ was prepared, as described by Ardon and Herman,¹⁰ by treatment of aqueous Cr(ClO₄)₂ with nitric oxide¹¹ in the absence of air. The spectrum of this complex, which was eluted very slowly from sulfonate resin with 0.3 M HClO₄, featured maxima at 322 (ε 96), 448 (ε 126), and 560 nm (ε 29) in agreement with the spectrum reported.¹⁰

Measurements of Paramagnetic Susceptibility. Susceptibilities of the reaction products were estimated by the procedure of Evans,¹² in which the shift in the NMR absorption frequency of the methyl hydrogens of added *t*-BuOH in the presence of paramagnetic species was measured. This method was standardized by measurements on Cr(ClO₄)₃ solutions; the effective magnetic moments of Cr(III) derivatives lie in the range 3.75–3.85 μ_B.¹³

Results and Discussion

Stoichiometric studies (summarized in Table I) tell us that each mole of Cr(V) consumes very nearly 1 mol of hydroxylamine and thus imply that the net changes in oxidation states of the two reactants are equal in magnitude but in opposite directions. Analogy to the known³ reduction of Cr(V) by hydrazine (with which hydroxylamine is isoelectronic) would perhaps suggest that Cr(V) is reduced here to Cr(III) and that

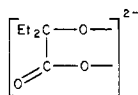
- (4) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.
 (5) Bray, W. C.; Simpson, M. E.; MacKenzie, A. A. *J. Am. Chem. Soc.* **1919**, *41*, 1363.
 (6) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

- (7) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.
 (8) For estimation of extinction coefficients for eluted Cr(III) species, aliquots of each fraction were oxidized with basic H₂O₂, and the total chromium content was determined as CrO₄^{2−}.⁹
 (9) Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A* **1952**, *48*, 414.
 (10) Ardon, M.; Herman, J. I. *J. Chem. Soc.* **1962**, 507. These authors report absorption maxima at 323 (ε 92 M^{−1} cm^{−1}), 449 (ε 120), and 559 nm (ε 28) for this complex.
 (11) Blanchard, A. A. *Inorg. Synth.* **1946**, *2*, 126.
 (12) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
 (13) Figgis, B. B.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37. (See Table XVIII in this review.)

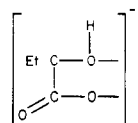
Table II. Magnetic Moments of Some Chromium Complexes^a

complex	source	μ_{eff} , μ_{B}
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$		3.9
$[(\text{Lig})_2\text{Cr}^{\text{V}}\text{O}]^{-b}$ (I)	$\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Et}_2\text{C}(\text{OH})\text{COOH}^2$	1.9
$[(\text{HLig})\text{Cr}^{\text{III}}(\text{H}_2\text{O})_4]^{2+c}$	$[(\text{Lig})_2\text{Cr}^{\text{V}}\text{O}]^{-} + \text{N}_2\text{H}_4^3$	3.5
$(\text{HLig})_2\text{Cr}^{\text{I}}\text{NO}(\text{H}_2\text{O})$ (II)	$[(\text{Lig})_2\text{Cr}^{\text{V}}\text{O}]^{-} + \text{NH}_2\text{OH}^d$	2.3
$(\text{HLig})\text{Cr}^{\text{I}}\text{NO}(\text{H}_2\text{O})_3^+$ (III)	$[(\text{Lig})_2\text{Cr}^{\text{V}}\text{O}]^{-} + \text{NH}_2\text{OH}^e$	2.6
$[\text{Cr}^{\text{I}}(\text{H}_2\text{O})_5\text{NO}]^{2+f}$	$\text{Cr}(\text{H}_2\text{O})_6^{2+} + \text{NO}^{10}$	2.2 ^f

^a Measured in solution at 293 K, by using the procedure of Evans.¹² ^b Lig =



^c HLig =



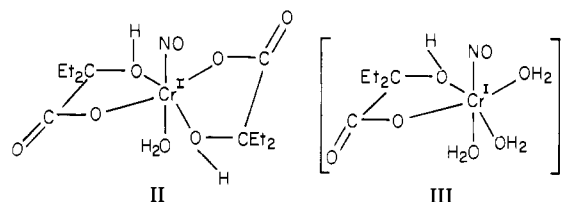
^d Principal product when reaction is carried out with a 27-fold excess of ligand. ^e Principal product when reaction is carried out with a 4-fold excess of ligand. Products separated by cation-exchange chromatography (see text). ^f Reference 16a.

hydroxylamine also undergoes a 2e change, i.e., that is oxidized to the nitroxyl (NOH) or hyponitrite ($\text{N}_2\text{O}_2^{2-}$) level. However, the properties of the products are not at all in accord with such an inference.

Under conditions where disproportionation of the Cr(V) complex is minimal (pH 3.5–5.0; with the parent carboxylate ligand in large excess), reduction with NH_3OH^+ yields no detectable nitrogen-containing gas, for during the reaction the nitrogenous product becomes affixed to the reduced chromium center. Two reaction products, both yellow-brown (in contrast to the blue complex resulting from the reduction³ with N_2H_5^+), are obtained; their ratio depends on the quantity of excess carboxylate ligand taken. The first of these is not absorbed on cation-exchange resin and is therefore taken to bear no net positive charge; the second exhibits elution behavior corresponding to that of a 1+ complex. Strong absorption near 440 nm, observed for both fractions, is not characteristic of Cr(III) complexes having oxygen-donor ligands^{14,15} but has been reported for $\text{Cr}(\text{H}_2\text{O})_5\text{NO}^{2+}$, which has been prepared by Ardon and Herman¹⁰ from NO and $\text{Cr}(\text{ClO}_4)_2$.

Spectral and magnetic studies by Griffith^{16a} have demonstrated that Ardon's complex and several closely related species are $\text{N}=\text{O}^+$ derivatives of Cr(I), rather than $\text{N}=\text{O}^-$ derivatives of Cr(III). Measured magnetic susceptibilities¹² of our products are compared to those of the Cr(V) reactant, the product of the Cr(V)– N_2H_4 reaction,³ Ardon's Cr(I) complex,^{10,16a} and $\text{Cr}(\text{nH}_2\text{O})_6^{3+}$ in Table II. The magnetic moment of the uncharged hydroxylamine reduction product is seen to be very nearly the same as that for the complex formulated as $\text{Cr}^{\text{I}}(\text{H}_2\text{O})_5\text{NO}^{2+}$, whereas the moment for the singly charged product is only slightly greater (possibly reflecting a Cr^{III} impurity). The data for the hydroxylamine products then indicate the presence of only one unpaired

electron per chromium and point to the conclusion that these are low-spin complexes of chromium(I) in which the metal center has the configuration $(t_{2g})^5$. This inference is confirmed by our observation of strong IR absorbances at 1780 and 1860 cm^{-1} (corresponding closely to the stretching frequencies reported^{16a} for coordinated $\text{N}=\text{O}^+$) but none near 1120 cm^{-1} (which is considered to be characteristic of coordinated $\text{N}=\text{O}^-$).^{16b} Since our complexes have lower positive charges than Ardon's, we conclude that carboxylato ligation persists in the reaction products (as has been reported³ for the reaction of the same oxidant with N_2H_5^+), that our uncharged product features two bound carboxyl groups (II), and that the product exhibiting 1+ elution behavior has one such group (III).^{17,18}



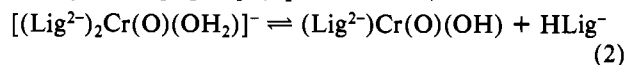
Examination of kinetic profiles at a variety of wavelengths gave no evidence for intercession of a chromium(III) intermediate formed or destroyed on a time scale comparable to that for production of Cr(I).

Representative kinetic data are listed in Table III. The reaction is seen to be retarded by increasing acidity or by addition of unbound carboxylate ligand. (The latter is designated as HLig⁻ to differentiate it from the dinegative form, Lig²⁻, bound to Cr(V) in the chelated starting material.) Neither variation, however, is steep enough to correspond to a simple inverse-first-order dependence. Within the range of concentrations indicated in Table III, rates conform to eq 1.

$$\text{rate} = \frac{a[\text{NH}_3\text{OH}^+][\text{Cr}^{\text{V}}]}{(1 + b[\text{HLig}^-])(1 + c[\text{H}^+])} \quad (1)$$

An iterative nonlinear least-squares refinement,¹⁹ minimizing the function $(k_{\text{obsd}} - k_{\text{calcd}})^2$ (where the k 's represent pseudo-first-order rate constants with NH_3OH^+ in excess), yielded the parameters $a = 0.376 \pm 0.035 \text{ M}^{-1} \text{ s}^{-1}$, $b = 17.4 \pm 0.8 \text{ M}^{-1}$, and $c = (2.88 \pm 0.34) \times 10^4 \text{ M}^{-1}$. Table III also compares observed rates with those calculated by using rate law 1.

The $b[\text{HLig}^-]$ term in the denominator of (1) indicates partition of the Cr(V) reactant between ligation levels that differ by a HLig⁻ group (equilibrium 2²⁰):



with the monoligated species the reactive form and the diligated anion inactive.

In like manner, the $c[\text{H}^+]$ term in (1) suggests partition of one of the reactants between two protonation levels, of which only the deprotonated form is perceptibly reactive, with the

- (14) Chromium(III) complexes having carboxylate ligands (chelated or unchelated), coordinated water, or combinations of these exhibit a maximum in the range 406–418 nm,¹⁵ in addition to a (somewhat broader) peak at 555–575 nm. Incorporation of an N-donor ligand shifts these maxima to higher energies.
- (15) See, for example: (a) Hamm, R. E.; Johnson, R. L.; Perkins, R. H.; Davis, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 4469. (b) Gould, E. S.; Taube, H. *Ibid.* **1964**, *86*, 1318. (c) Butler, R. D.; Taube, H. *Ibid.* **1965**, *87*, 5597. (d) Schlafer, H. L. *Z. Phys. Chem. (Frankfurt am Main)* **1957**, *11*, 65.
- (16) (a) Griffith, W. P. *J. Chem. Soc.* **1963**, 3286. (b) Griffith, W. P.; Lewis, J.; Wilkinson, G. *Ibid.* **1961**, 775.

- (17) In both proposed structures, II and III, the nitrosyl group is situated trans to ligated water. In view of the known¹⁸ trans-labilizing effectiveness of coordinated NO in octahedral systems, it is suggested that complexes in which this group lies trans to carboxyl would undergo rapid aquation in the media used. Labilization of the trans-H₂O groups in the structures shown would lead merely to replacement of coordinated water by solvent water.
- (18) See, for example: Myers, R. J.; Spencer, J. B. *J. Am. Chem. Soc.* **1964**, *86*, 522.
- (19) The trial value of parameter b for this refinement was obtained by plotting $1/K_{\text{obsd}}$ vs. $[\text{HLig}^-]$ at constant $[\text{H}^+]$. Similarly, the trial value of c was obtained by plotting $1/k_{\text{obsd}}$ vs. $[\text{H}^+]$ with $[\text{HLig}^-]$ held constant. The trial value of a was derived from a plot of $1/k_{\text{obsd}}$ vs. $[\text{NH}_3\text{OH}^+]$ at low values of $[\text{HLig}^-]$ and $[\text{H}^+]$. Individual data points were unweighted for the refinement, which converged after two cycles.
- (20) It is suggested that the proton lost in the dissociation is derived from the hydrated form of the original Cr(V) chelate. A number of carboxyl derivatives of this type, including that considered here, are reported to be strongly hydrated.²

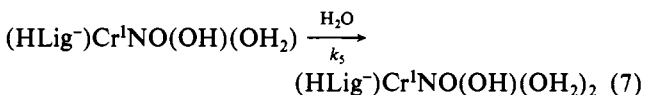
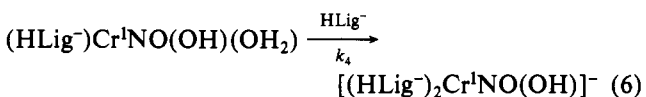
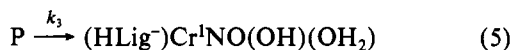
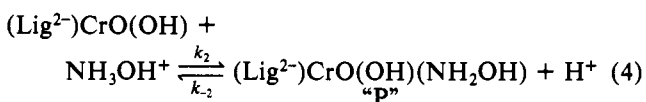
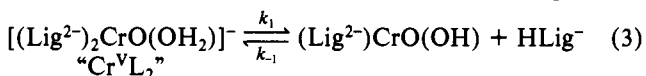
Table III. Representative Kinetic Data for the Reaction of Sodium Bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) with NH_3OH^+ ^a

$[\text{NH}_3\text{OH}^+]$, M	$10^4[\text{Cr}^{\text{V}}]$, ^b M	$10^2[\text{LigH}_2]$, ^c M	$10^2[\text{HLig}^-]$, ^d M	$10^5[\text{H}^+]$, ^d M	10^3k_{obsd} , ^e s ⁻¹	10^3k_{calcd} , ^f s ⁻¹
0.112	8.27	1.19	1.08	4.92	14.0	14.6
0.084	8.27	1.19	1.08	4.92	10.5	10.0
0.084	5.86	1.19	1.08	4.92	11.6	10.0
0.084	3.90	1.19	1.08	4.92	11.6	10.0
0.056	8.27	1.19	1.08	4.92	7.2	7.3
0.084	9.21	2.38	2.16	4.92	10.0	9.5
0.084	9.21	4.80	4.38	4.92	7.4	7.4
0.084	9.21	4.85	4.41	4.92	7.3	7.4
0.084	9.21	9.21	8.35	4.92	5.8	5.3
0.074	15.2	1.65	1.08	27.0	3.5	2.7
0.074	15.2	1.42	1.17	9.8	5.8	6.0
0.074	15.2	1.32	1.17	3.9	10.4	10.8
0.074	15.2	1.22	1.17	1.97	16.7	14.7

^a Reactions were carried out at 25 °C in 0.60 M LiClO_4 . ^b Sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I). ^c 2-Ethyl-2-hydroxybutyric acid (total added). ^d Concentrations of H^+ and 2-ethyl-2-hydroxybutyrate (HLig^-) were calculated by taking the $\text{p}K_{\text{A}}$ of the parent acid as 3.32 (ref 3) and that of the buffer acid, acetic acid, as 4.61 (ref 21, p 364). ^e Pseudo-first-order rate constants = $-\text{d} \ln [\text{Cr}^{\text{V}}] / \text{d}t$. ^f Calculated from the rate law (1) in the text with a taken as $0.38 \text{ M}^{-1} \text{ s}^{-1}$, b as 17.4 M^{-1} , and c as $2.9 \times 10^4 \text{ M}^{-1}$ (see text).

reciprocal $1/c$ ($=3.5 \times 10^{-5} \text{ M}$) corresponding to the acidity constant governing this equilibrium. This inference, however, is inadmissible in the present case, for neither hydroxylamine ($\text{p}K_{\text{A}} = 6.1$)²¹ nor the $\text{Cr}(\text{V})$ complex²² exhibits a K_{A} value in the appropriate range.

Our results are consistent with a mechanism featuring intervention of a Cr^{V} -hydroxylamine precursor complex (P), formed reversibly with expulsion of H^+ . The suggested sequence is shown as eq 3-7. It is assumed that steps 6 and



7, in which HLig^- and H_2O compete for the coordinatively unsaturated chromium(I) intermediate, are much more rapid than the internal electron transfer (step 5). Application of the steady-state approximation to the precursor, P, and to the monocarboxylate intermediate, $(\text{Lig}^2)^-\text{CrO}(\text{OH})$, leads to the rate expression

$$\text{rate} = \frac{[\text{Cr}^{\text{V}}\text{L}_2][\text{NH}_3\text{OH}^+]}{k_2k_3[\text{NH}_3\text{OH}^+] + k_{-1}[\text{HLig}^-]} \frac{k_1k_2k_3}{k_{-2}[\text{H}^+] + k_3} \quad (8)$$

If the k_{-1} term in the denominator of (8) is taken to be much larger than the k_2k_3 term, (8) may be simplified to

$$\text{rate} = \frac{[\text{Cr}^{\text{V}}\text{L}_2][\text{NH}_3\text{OH}^+]}{k_{-1}[\text{HLig}^-]} \left[\frac{k_1k_2}{1 + \frac{k_{-2}}{k_3}[\text{H}^+]} \right] \quad (9)$$

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(22) The spectrum of the $\text{Cr}(\text{V})$ complex has been found³ to be invariant between pH 3 and 5. Attempted determinations of the $\text{p}K_{\text{A}}$ for this derivative in the absence of excess ligand are complicated by decomposition, at pH values above 5, to $\text{Cr}(\text{III})$, CrO_4^{2-} , and the parent carboxylic acid.

Table IV. Distribution of Chromium Reduction Products from Reaction of Carboxylato-Bound Chromium(V) with Hydroxylamine^a

$10^3 \times (\text{Cr}^{\text{V}})$, ^b M	$[\text{LigH}^-]$, ^c M	mol of II ^d $\times 10^6$	mol of III ^d $\times 10^6$	k_4/k_5 , ^e M ⁻¹
5.75	0.0234	4.55	3.79	51
7.44	0.20	15.2	1.12	66

^a Reactions were carried out at 25 °C in HOAc-OAc^- buffers; separations were accomplished by using ion-exchange chromatography (see Experimental Section). ^b Sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I). ^c 2-Ethyl-2-hydroxybutyrate. ^d Proposed structures for chromium(I) products II and III are given in the Results and Discussion. ^e Ratio of specific rates at which LigH^- and H_2O compete for the proposed chromium(I) intermediate (reactions 6 and 7 in text), estimated as $(\text{mol of II})(\text{mol of III})^{-1} [\text{LigH}^-]^{-1}$.

The latter may, in turn, be rewritten in terms of the total concentration of chromium(V), $[\text{Cr}^{\text{V}}]_{\text{T}}$:

$$\text{rate} = \frac{k_2[\text{Cr}^{\text{V}}]_{\text{T}}[\text{NH}_3\text{OH}^+]}{\left(\frac{k_{-1}}{k_1}[\text{HLig}^-] + 1 \right) \left(1 + \frac{k_{-2}}{k_3}[\text{H}^+] \right)} \quad (10)$$

Expression 10 is seen to be algebraically equivalent to the observed rate law, (1), with $1/b = k_1/k_{-1}$ (the dissociation constant pertaining to loss of HLig^-), $c = k_{-2}/k_3$ (a measure of the competition between reactions involving the precursor), and a and k_2 (the limiting specific rate at very low values of $[\text{H}^+]$ and $[\text{HLig}^-]$). Individual values of k_{-2} and k_3 cannot be determined from steady-state experiments alone.

The proposed mechanism implies that virtually every act of electron transfer involves the monoligated intermediate formed in step 3. Since our ion-exchange studies indicate that a fraction of the final product is the diligated complex, II, we infer that the latter is formed by reaction of the free ligand in solution with the $\text{Cr}(\text{I})$ product subsequent to the redox process. If the di- and monoligated chromium(I) products, II and III, arise from a common intermediate (through reactions 6 and 7)²³ and if interconversion between these products, once formed, is negligible, the ratio $[\text{II}]/[\text{III}]$ may be taken to equal $k_4[\text{HLig}^-]/k_5$. The ratio of specific rates, k_4/k_5 , but not the individual values, may then be estimated from the product distribution from a reaction with $[\text{HLig}^-]$ in known excess. Although we have not pursued this point, the ratio calculated for a reaction mixture in which $[\text{HLig}^-]$

(23) Note that the indicated product from reactions 6 and 7 differ from the proposed structures II and III only in their degree of protonation.

is 0.023 M is seen (Table IV) to be in fair agreement with that for $[HLig^-] = 0.20$ M. Note that in the second of these mixtures over 93% of the recovered chromium product is the diligated species.

In sum, the reduction of carboxylato-bound chromium(V) with hydroxylamine resembles the corresponding reduction with hydrazine³ in that both reactions require preliminary loss of one ligand per Cr(V) and both appear to proceed through a Cr^V-N precursor formed with attendant loss of a proton. Significant differences between the two systems arise after the initial act of electron transfer. The 2e oxidation of bound hydrazine yields N₂H₂, which, in either the free or ligated state (we cannot at present say which), undergoes further rapid external oxidation to N₂. In contrast, the Cr^{III}-N^I species,

arising (in principle) from a 2e transaction in the hydroxylamine system, quickly (perhaps instantaneously) undergoes a second internal 2e transfer, yielding the Cr^I(NO) products we observe. The occurrence of this very unexpected net change of 4e, in what approaches a single transfer, may reasonably be attributed, in major part, to the unusually marked mutual stabilization of the NO⁺ group and the chromium(I) center by strong metal-to-ligand back-bonding.²⁴

Registry No. I, 84622-43-5; II, 84622-44-6; III, 84583-15-3; NH₂OH, 7803-49-8.

(24) See, for example: Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* 1966, 7, 277.

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Venezia, Venice, Italy, and C. K. Ingold Laboratories, University College, London, England

Reactivity of Sulfoxides toward the Tetrachloroplatinate(II) Anion

GIULIANO ANNIBALE,¹ LUCIO CATTALINI,*¹ LUCIANO CANOVESE,¹ GIANNI MICHELON,¹ GIAMPAOLO MARANGONI,¹ and MARTIN L. TOBE²

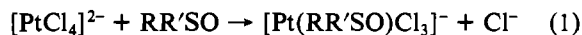
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The kinetics of the reactions between $[PtCl_4]^{2-}$ and a series of sulfoxides, $(CH_3)_2SO$, $(CH_3)(C_2H_5)SO$, $(C_2H_5)_2SO$, $(c-C_4H_8)SO$, $(2-ClC_2H_4)(CH_3)SO$, $(C_6H_5)(CH_3)SO$, $(p-CH_3C_6H_4)(CH_3)SO$, $(p-ClC_6H_4)(CH_3)SO$, $(p-CH_3OC_6H_4)(CH_3)SO$, $(n-C_3H_7)(CH_3)SO$, and $(n-C_3H_7)_2SO$, have been studied in 95:5 vol % methanol/water at 25 °C and $\mu = 1.0$ (LiCl). In all cases the reaction is the simple replacement of one chloride by a sulfoxide. The second-order rate constants are insensitive to the change in inductive effect on changing the substituents but decrease with increasing bulk. An interpretation is proposed in terms of the intimate mechanism of the substitution, and a comparison is made with the behavior of thioethers and amines.

In recent years much has been published to indicate a number of peculiarities in the behavior of sulfoxides in platinum-group chemistry.³ These ligands are known to bind Pd(II) and Pt(II) through sulfur unless there are steric reasons to prevent this, in which case oxygen bonding is observed.⁴ Dimethyl sulfoxide exerts a moderate trans effect^{5,6} but is a relatively poor nucleophile,⁷ a combination which is also observed for ethene⁸ but which is otherwise uncommon. In spite of the moderate trans effect, the product of the reaction between $[PtCl_4]^{2-}$ and $(CH_3)_2SO$ is *cis*- $[Pt(Me_2SO)_2Cl_2]$,⁴ although there is evidence for the presence of the trans isomer as a labile intermediate. Two *cis* sulfoxides exert a considerable labilizing effect on one another^{9,10} while the displacement of a single sulfoxide is generally very slow.^{11,12} In spite of the inertness of a single coordinated sulfoxide, dimethyl sulfoxide has been used as a solvent for the study of substitution reactions in d⁸ systems without any apparent interference from irreversible solvolysis.¹³

In palladium(II) systems the entry of sulfoxides into $PdCl_4^{2-}$ is rapid and reversible and the equilibrium constants have been determined.¹⁴ The second successive equilibrium constant for dimethyl sulfoxide in this system is some 2 orders of magnitude less than the first, and it is another example of the parallel in the behavior of sulfoxides and olefins.

The study of sulfoxides as nucleophiles has been confined until now to the reaction between $[PtCl_n(H_2O)_{4-n}]^{(2-n)-}$ and $(CH_3)_2SO$,⁷ and as a part of our investigation of the role of electronic and steric effects on the nucleophilicity of ligands with common donor atom features, we have extended our studies from amines, heterocyclic nitrogen bases, and thioethers to sulfoxides. In this paper we report the kinetics of the reactions



where RR'SO is one of a series of 11 sulfoxides.

Experimental Section

Materials. An aqueous solution of Na₂PtCl₄ was obtained by treating the required amount of K₂PtCl₄ in water with excess NaClO₄ and filtering off the precipitated KClO₄. A known volume (5 cm³) of this solution was diluted to 100 cm³ with methanol containing the required amount of LiCl to keep the ionic strength at $\mu = 1.0$. This

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