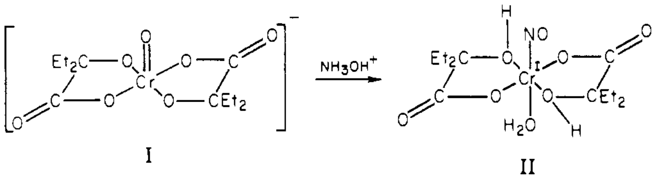
Electron Transfer. 58. A Four-Electron Reduction, Converting Chromium(V) to Chromium(I)

Sir:

A number of chelated chromium(V) derivatives of 2-hydroxyalkanoic acids were characterized in 1979.[1] Complexes of this type are powerful and versatile oxidants, aqueous solutions of which may be significantly stabilized by addition of the free carboxylato ligand.[2] We here describe the reduction, using hydroxylamine, of sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) to a species having properties corresponding to the chelated chromium(I) complex II. This transformation involves the transfer of four electrons to a metal center. Our evidence favors a mechanism in which these are transferred in a single transaction rather than in a pair of separable two-electron steps.



The (carboxylato)chromium(V) complex, I (10^{-2} M), reacted smoothly with NH_3OH^+ in an HOAc–OAc⁻ buffer in the presence of a 5- to 40-fold excess of the parent carboxylic acid, consuming 96% of an equimolar quantity of reductant but producing no detectable nitrogen-containing gas. Two yellow-brown chromium products, the ratio of which depended on the quantity of excess carboxylato ligand taken, were formed. The first of these, which was not absorbed on cation-exchange resin (and was therefore considered to bear no net positive charge), exhibited maxima at 560 (ϵ 29 M^{-1} cm^{-1}) and 441 nm (ϵ 85). The second complex, eluted rapidly from such a resin with 0.18 M $HClO_4$,[3] had maxima at 560 (ϵ 25) and 438 nm (ϵ 55). With the parent carboxyl ligand in 27-fold excess, only the first product was obtained. Strong absorbance near 440 nm is not at all characteristic of Cr(III) complexes of O-donor ligands[4] but has been reported for $Cr(H_2O)_5NO^{2+}$, which was prepared by Ardon and Herman[5] from NO and $Cr(ClO_4)_2$.

Spectral and magnetic studies by Griffith[6] have demonstrated that Ardon's complex and several closely related species are NO^+ derivatives of Cr(I) rather than NO^- derivatives of Cr(III). Measured magnetic susceptibilities[7] of our products are compared to those of the Cr(V) starting material, the product of the Cr(V)–N_2H_4 reaction,[2] Ardon's Cr(I) complex,[5,6] and $Cr(H_2O)_6^{3+}$ in Table I. The magnetic moment of the uncharged hydroxylamine reduction product is very nearly the same as that for the complex formulated as Cr^I-$(H_2O)_5NO^{2+}$, whereas the moment for the singly charged product is only slightly higher (possibly reflecting a Cr^{III} impurity). The data for the hydroxylamine products then indicate the presence of only one unpaired electron per chromium atom and point to the conclusion these are low-spin complexes of chromium(I). Moreover, we observe strong IR absorbances at 1780 and 1860 cm^{-1} (corresponding closely to the stretching frequencies reported[6] for coordinated $N{\equiv}O^+$) but none near 1120 cm^{-1} (which is considered to be characteristic of coordinated $N{=}O^-$).[8] Since our complexes have lower positive charges than that of Ardon, we conclude that carboxylato ligation persists in the reaction products (as has been reported[2] 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.

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).

The rate law for the reaction, which may be expressed as eq 1 (where $[Cr^V]_T$ represents total chromium(V) and $HLig^-$

$$\text{rate} = \frac{k_2[Cr^V]_T[NH_3OH^+]}{\left(\frac{k_{-1}}{k_1}[HLig^-] + 1\right)\left(1 + \frac{k_{-2}}{k_3}[H^+]\right)} \qquad (1)$$

the unbound carboxylato ligand), is consistent[9] 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 2–6. For reactions at 25

$$[(Lig^{2-})_2CrO(OH_2)]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Lig^{2-})CrO(OH) + HLig^- \qquad (2)$$

$$(Lig^{2-})CrO(OH) + NH_3OH^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{“P”}}{(Lig^{2-})CrO(OH)(NH_2OH)} + H^+ \qquad (3)$$

$$P \xrightarrow{k_3} (HLig^-)Cr^1(NO)(OH)(OH_2) \qquad (4)$$

$$\underset{\text{III}}{(HLig^-)Cr^1NO(OH)(OH_2)} \xrightarrow[\text{rapid}]{HLig^-,\ k_4} [(HLig^-)_2Cr^1NO(OH)]^- \qquad (5)$$

$$\text{III} \xrightarrow[\text{rapid}]{H_2O,\ k_5} (HLig^-)Cr^1NO(OH)(OH_2)_2 \qquad (6)$$

°C and $\mu = 0.60$ ($LiClO_4$), kinetic parameters giving the best fit to our data are $k_{-1}/k_1 = 17.4 \pm 0.8$ M^{-1}, $k_2 = 0.38 \pm 0.04$ M^{-1} s^{-1}, and $k_{-2}/k_3 = (2.8 \pm 0.3) \times 10^4$ M^{-1}. Observed distributions of the two Cr(I) products at known concentrations of added ligand lead to the ratio $k_4/k_5 = 59 \pm 8$ M^{-1}.

The reduction of carboxylato-bound chromium(V) with NH_3OH^+ thus resembles the corresponding reaction with $N_2H_5^+$ in that both require preliminary loss of one ligand per Cr(V) and both appear to proceed through a Cr^V–N precursor. Differences arise after the initial act of electron transfer. The two-electron oxidation of bound hydrazine[2] yields N_2H_2, which, either free or ligated, undergoes rapid external oxidation of N_2. In contrast, the Cr^{III}–N^I species arising (in principle) from a two-electron transaction in the hydroxylamine system quickly (perhaps instantaneously) undergoes a second internal two-electron transfer, yielding the Cr^I(NO) products we observe. The occurrence of this very unexpected net change of four electrons, 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

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[1] Krumpolc, M.; Boček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

[2] Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

[3] Separations were carried out on Bio-Rad 50W-A2 sulfonate resin, H^+ form, at 2 °C.

[4] 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.

[5] Ardon, M.; Herman, J. I. *J. Chem. Soc.* **1962**, 507.

[6] Griffith, W. P. *J. Chem. Soc.* **1963**, 3286.

[7] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

[8] Griffith, W. P.; Lewis, J.; Wilkinson, G. *J. Chem. Soc.* **1961**, 775.

[9] Equation 1 may be derived from the sequence (2)–(4) by application of the steady-state approximation to the precursor, P, and to the mono(carboxylato) intermediate $(Lig^{2-})CrO(OH)$. It is further assumed that equilibrium 2 is established very rapidly in comparison to subsequent steps and that the proton lost in the dissociation is derived from the hydrated[1] form of the original Cr(V) chelate. Individual values of k_{-2} and k_3 cannot be determined from steady-state experiments alone.

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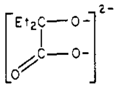
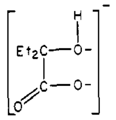
Table I. Magnetic Moments of Some Chromium Complexes[a]

complex	source	μ_{eff}, μ_B
$Cr(H_2O)_6^{3+}$		3.9
$[(Lig)_2Cr^{V}O]^-$ [b] (I)	$Na_2Cr_2O_7$ + $Et_2C(OH)COOH$[1]	1.9
$[(HLig)Cr^{III}(H_2O)_4]^{2+}$ [c]	$[(Lig)_2Cr^{V}O]^-$ + N_2H_4[2]	3.5
$(HLig)_2Cr^{I}NO(H_2O)$ (II)	$[(Lig)_2Cr^{V}O]^-$ + NH_2OH[d]	2.3
$(HLig)Cr^{I}NO(H_2O)_3^+$	$[(Lig)_2Cr^{V}O]^-$ + NH_2OH[e]	2.6
$[Cr^{I}(H_2O)_5NO]^{2+}$	$Cr(H_2O)_6^{2+}$ + NO[5]	2.2[f]

[a] Measured in solution at 293 K, by using the procedure of Evans.[7] [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 6.

by strong metal-to-ligand back-bonding.[10]

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

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Oxidation-Reduction Reactions of Complexes with Macrocyclic Ligands. Electronic Requirements of Inner-Sphere Electron-Transfer Pathways[1]

Sir:

Reactivity patterns in those transition metal complex reactions in which transfer of a bridging ligand accompanies electron transfer[2] are poorly understood.[3,4] This is in contrast to the relatively sophisticated level of understanding of reactivity patterns in simple outer-sphere electron-transfer reactions.[3,5-9] Again in contrast to outer-sphere reactions, for which free energy dependencies are reasonably well established and for which there is a great deal of information about free energy independent reactivities,[3,5-9] most of the available information about inner-sphere reactions is complicated by unknown (sometimes indeterminable) contributions of the free energy change accompanying electron transfer.

We have been examining the inner-sphere electron-transfer reactions of complexes containing macrocyclic ligands.[10] In such systems it is often possible to determine self-exchange rate constants and/or cross-reaction rate constants and equilibrium constants for inner-sphere reaction pathways. A number of features of the information acquired about free energy independent inner-sphere reactivities has led us to postulate that many aspects can be usefully described, taking account of the homolytic bond-breaking/bond-making process across the reaction coordinate, in terms of a three-center (M–S–M′) transition-state bonding interaction.[10b,c] We have now found that inner-sphere reaction rates are appropriately sensitive to the number of electrons present in the orbitals used in the formal transition-state bonding arrangement. In addition, orthogonality of the three-center-bonding orbital and the electron-transfer donor–acceptor orbital appears eliminate the kinetic advantage of the inner-sphere pathway.

We have been investigating the oxidation–reduction reactions of $Ni^{III,II}(N_4)$ and $Cu^{III,II}(N_4)$ couples (N_4 = a 14-membered, tetraaza macrocyclic ligand). These couples are strongly oxidizing, but good-quality cyclic voltammometric data may often be obtained in strongly acidic aqueous solutions (Table I), and in a few cases the oxidized complexes may be generated electrochemically, or chemically, and persist in very acidic solutions for periods up to a few hours (Table I and ref 11). In some of the systems and media studied, the oxidized complexes are known only as short-lived transients generated in flash photolysis experiments.

We have been examining several reactions of the Ni(III)–Ni(II) and Cu(III)–Cu(II) couples, but in this report we wish to emphasize the constrasts in $Co(OH_2)_6^{3+}$ and $Co(OH_2)_5Cl^{2+}$ oxidations of the $M^{II}(N_4)$ complexes:

$$Co(OH_2)_5Cl^{2+} + M^{II}(N_4) \xrightarrow{H_2O} Co(OH_2)_6^{2+} + M^{III}(N_4)Cl \quad (1)$$

The results, summarized in Table I, illustrate what may be general features of the inner-sphere reaction pathway. Some of the complementary information obtained with other reagent combinations is also presented in Table I. Both rate patterns and spectra of the oxidation products of $Ni^{II}(N_4)$ complexes indicate that Cl^--bridged inner-sphere reaction pathways do occur. Oxidations of $Cu^{II}(N_4)$ complexes give products at equilibrium with solvent species even on the flash photolysis time scale, and neither rate patterns nor product spectra distinguish between outer-sphere and inner-sphere pathways for reactions of these copper complexes.

The inner-sphere and outer-sphere rate constants, k^{IS} and k^{OS}, have been found to span very large ranges. As a measure of the deviations of observed rates, from those expected for outer-sphere reaction pathways, it is useful to consider the

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(1) Partial support of this research by the National Institutes of Health (Grant AM 14341) and the National Science Foundation (Grant CHE 80-05497) is gratefully acknowledged.

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