$$\underset{\text{III}}{Tl_2Sn(OEt)_6} + SnCl_2 \rightarrow \underset{\text{IV}}{Sn_2(OEt_6)} + 2TlCl \qquad (2)$$

combustion analysis, and exhibits physical properties similar to $[Sn(OEt)_4]_4$, as expected.

Further studies are in progres to aid the structural assignment in solution and characterization of the hydrolysis products of III and IV. Knowledge of the solution structure of such species is essential to determine the fundamental steps involved in the pyrolytic and hydrolytic conversion of tin alkoxides to tin oxides (via oxotin alkoxides), especially since tin species containing oxygen ligands exhibit a vast structural chemistry.[32]

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Supplementary Material Available: Table 1 (atomic coordinates and thermal parameters), Tables 2 and 3 (bond lengths and angles), and tables 4 and 5 (anisotropic displacement coefficients and H atom coordinates (5 pages); Table 6 (observed and calculated structure factors) (7 pages). Ordering information is given on any current masthead page.

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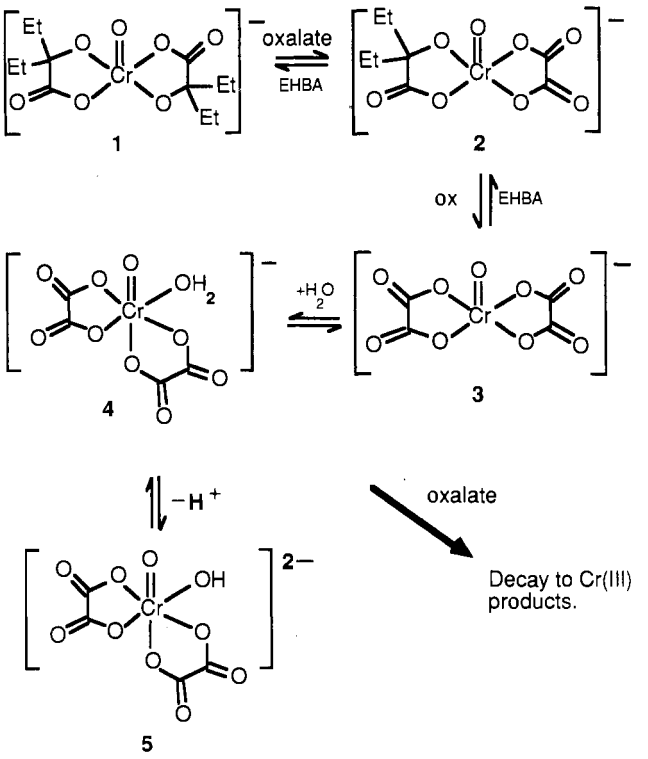
Ligand Exchange and Reduction Reactions of Oxochromate(V) Complexes: Characterization of the Common Chromium(V) Intermediates in the Reductions of Chromium(VI) and of *trans*-Bis(2-ethyl-2-hydroxybutanoato(2–))oxochromate(V) by Oxalic Acid

Chromium(V) intermediates play an important role in the mechanisms of Cr(VI) oxidations commonly used in organic chemistry[1-5] and are implicated as the active carcinogens in Cr(VI)-induced cancers.[6-8] However, Cr(V) chemistry is poorly characterized, and only a few Cr(V) complexes have been isolated (e.g. *trans*-bis(2-ethyl-2-hydroxybutanoato(2–))oxochromate(V), **1**).[1,2,9] Despite detailed studies on the mechanisms of Cr(VI) oxidations of organic substrates, we report here that even the mechanism which has been studied in most detail (the oxidation of oxalic acid)[2,4,5] is incorrect. This arose because the structures

Scheme I



of the Cr(V) intermediates were wrongly assigned as monooxalato complexes, on the basis of EPR and kinetic analyses.[5] The more detailed studies we report here have enabled the structures of these complexes to be reassigned as bis(oxalato(2–))oxochromate(V) (**3**) and *cis*-aquabis(oxalato(2–))oxochromate(V) (**4**). A crucial part of the determination of these structures is that these intermediates are also common to the reduction of **1** by oxalic acid. This also establishes, for the first time, the importance of a ligand exchange preequilibrium (Scheme I) as the first step in the oxidation of organic substrates by **1**. While this had previously been suggested on the basis of kinetic data,[2] such ligand exchange chemistry in these reactions has not been characterized previously. The combination of electrochemical and EPR spectroscopic techniques that are used in this study is likely to enable the characterizations of the intermediates in many other oxidation reactions of high-valent chromium and thus aid in the elucidation of the mechanisms of these complex redox reactions. In addition, these results indicate that common Cr(V) intermediates are responsible for the mutagenicity of either Cr compound toward *Salmonella typhimurium* TA100, and are important in delineating the mechanism(s) of the rapid in vitro cleavage of DNA by Cr(V).[6]

Our EPR spectroscopic studies on the oxidation of oxalic acid by CrO_3[10] confirm that two Cr(V) complexes (g = 1.9766 (2), A_{iso} = 18.1$_5$ ± 0.2 G; g = 1.9714 (2), A_{iso} = 21.9 (2) G) form and decay with the same rate constants. The g values reported here are more accurate than those in the literature,[5] and the isotropic hyperfine parameters have not been reported previously. Under the same conditions, the reaction of **1** with oxalic acid results in two signals identical with those reported above,[11] but a third Cr(V) signal assigned to (2-ethyl-2-hydroxybutanoato-(2–))(oxalato(2–))oxochromate(V) (**2**, g = 1.9783 (2), Figure 1) is observed at a g value similar to that of **1** (g = 1.9785 (2) in the absence of oxalic acid). At concentrations of oxalic acid ≥100 mM, the ratio of this third signal to the other two signals is dependent linearly on the concentration ratio oxalic acid:EHBA released,[12] showing that the equilibrium involves the exchange of only one EHBA ligand for an oxalate ligand.[13] All three

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(10) Experimental conditions: 50% aqueous acetic acid; 25 °C.
(11) The apparent difference in the ratio of the two peaks of **3** and **4** in the two reactions arises from the overlap of the signals due to **2** and **3**.
(12) EHBA = 2-ethyl-2-hydroxybutanoate(2–).

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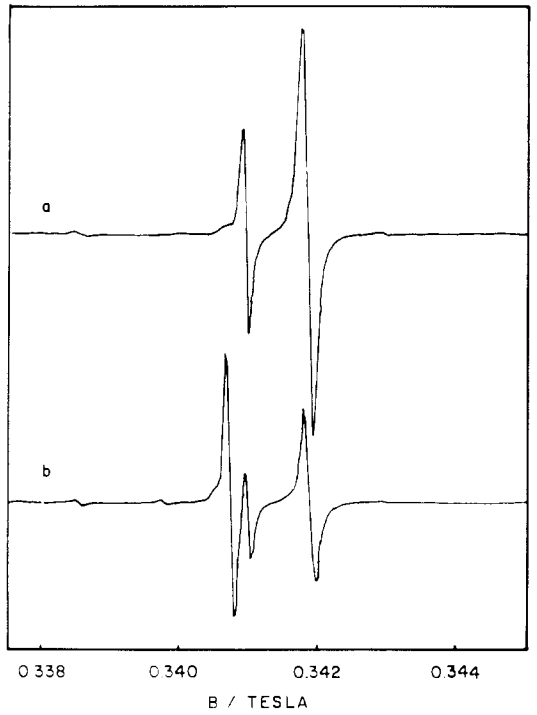

Figure 1. 9.4315-GHz EPR spectra of the Cr(V) intermediates produced in solutions containing 200 mM oxalic acid and 4 mM Cr in 50% aqueous acetic acid: (a) CrO_3; (b) **1**.

signals[14] decay at comparable rates; therefore, these Cr(V) intermediates are in rapid equilibrium compared to the time scale of their subsequent reduction to Cr(III).

Electrochemical studies (Figure 2) of the reaction of **1** with oxalic acid show two Cr(V)/Cr(IV) couples, (0.9 and 0.5 V vs Ag/AgCl/KCl(saturated)), while only one Cr(V)/(IV) couple is detected (0.9 V) in the corresponding CrO_3/oxalic acid reaction.[15] The ratio of the two responses in the **1**/oxalate system is a function of the concentration of oxalic acid, the concentration of EHBA, and the scan rate in cyclic voltammetry (CV). The irreversible reduction (CV) at 0.8 V is less dominant at low oxalic acid and/or high EHBA concentrations.[16] At higher scan rates, the reduction peak at 0.8 V decreases with respect to that at 0.35 V, until a limit is established whereby the relative heights of the two peaks do not change and the response at 0.35 V exhibits quasi-reversible behavior. From these results, the ligand exchange reaction is shown to be on the millisecond to second time scale, depending on the concentration of oxalic acid. Complex **1** has an irreversible reduction in 50% aqueous acetic acid at more negative potentials (0.15 V), hence establishing that the parent complex is not a major component of the equilibrium reaction mixture.

Roček correctly concluded that the two Cr(V) complexes generated in the CrO_3/oxalate reaction have the same number of oxalato ligands but was incorrect in assigning them as mono(oxalato) complexes of Cr(V) on the basis of kinetic data.[5] From the experimental conditions (20-fold excess oxalic acid) and our EPR results, it is clear that bis(oxalato(2-))oxochromate(V) complexes are responsible for the accumulation of Cr(V). This

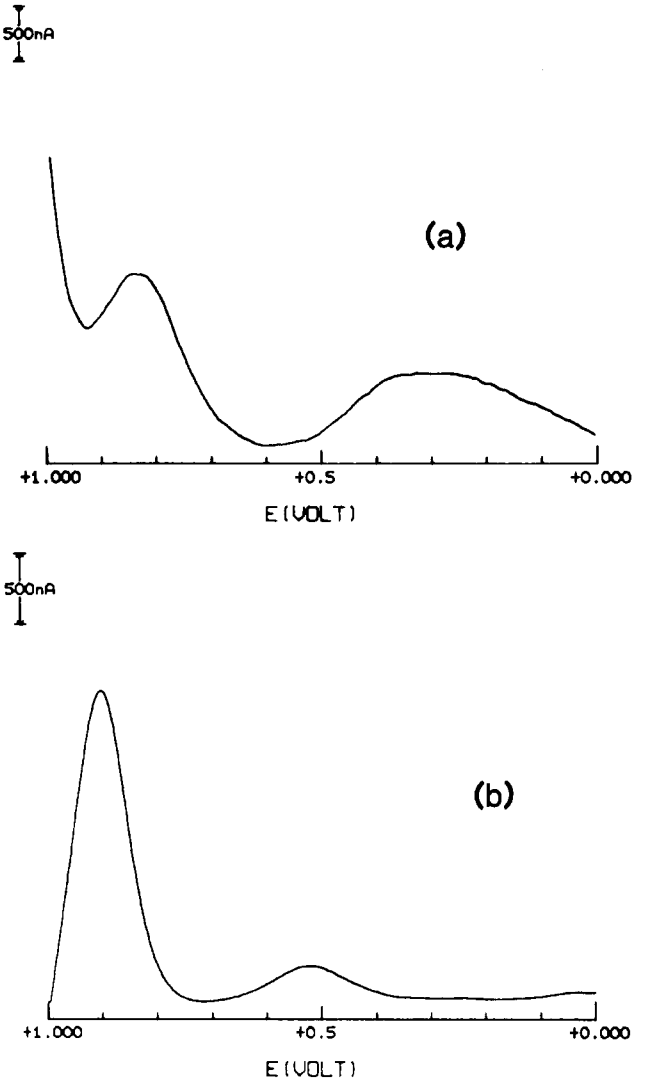

Figure 2. Differential-pulse voltammograms of the reduction of the Cr(V) intermediates produced in solutions containing 200 mM oxalic acid and 5 mM Cr in 50% aqueous acetic acid: (a) CrO_3; (b) **1**. The peak at +0.9 V corresponds to the irreversible Cr(V) reduction of the equilibrium mixture of **3** and **4**; the peak at 0.3 V in part a corresponds to the reduction of unreacted Cr(VI), and the peak at +0.5 V in part b corresponds to the Cr(V)/(IV) couple of **2**. Experimental conditions: pulse amplitude = 50 mV; scan rate = 4 mV s^{-1}; sample width = 20 ms; pulse width = 60 ms; pulse period = 1000 ms; scan direction = negative; reference electrode = Ag/AgCl/KCl(saturated).

is evident from the ligand exchange equilibrium, where removal of the last EHBA ligand from $[Cr(EHBA)(ox)O]^-$ is linearly dependent on the concentration of oxalic acid. This would not be the case if the EHBA complex was converted to a complex containing only one oxalate ligand. It also means that the details of the mechanism previously proposed[5] for the reduction of Cr(VI) by oxalic acid are incorrect. The addition of acetic anhydride (dehydrating agent) to the reaction mixture in glacial acetic acid results in the disappearance of one EPR signal,[5] confirming that it is an aqua complex, **4**. **3** and **4** are in such rapid equilibrium that they cannot be distinguished on the electrochemical (millisecond) time scale used here, but distinct signals are observed on the much faster (microsecond) EPR time scale. Further evidence in support of the structure of **4** is that its EPR signal splits into two (g = 1.9719 and g = 1.9714) at higher pH values. We ascribe this to the deprotonation of the aqua ligand to form hydroxobis(oxalato(2-))oxochromate(V) (**5**). Similar observations have been made for the acid/base equilibria involving the alkanolate ligands of **1**.[17] The cis geometry of **4** has been assigned on the

(13) At lower concentrations of oxalic acid, the nonlinear dependence of the peak ratios with the concentration ratios of the ligands suggest that the signal at $g = 1.9783$ comprises that of the parent compound **1** which is overlapping with that of complex **2**.

(14) When the same ligand exchange reaction is monitored in water, rather that 50% aqueous acetic acid, four EPR signals are observed, i.e., those for all of the species **2**–**5**.

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basis of the X-ray structure of the isoelectronic *cis*-aquabis(oxalato(2−))oxovanadate(IV).[18] These results also show that the six-coordinate geometry becomes more favorable as the bulky EHBA ligands are replaced by oxalate ligands.

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Articles

Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

Stepwise, Metal-Assisted Decarboxylation Promoted by Manganese: Reactivity Relationship between Manganese and Vanadium

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Manganese(III) complexes of the ligand ethylenebis[(*o*-hydroxyphenyl)glycine], $Mn(EHPG)^-$, are shown to oxidatively decarboxylate in methanol, DMF, and acetone solutions to generate derivatives of [ethylenebis(salicylideneaminato)]manganese(III), $Mn(SALEN)^+$. This process occurs via air oxidation of $Mn^{III}(EHPG)^-$ to form $Mn^{IV}(EHPG)$, which subsequently loses CO_2 and one proton, forming [*N*-(2-(*o*-salicylideneamino)ethyl)(*o*-hydroxyphenyl)glycinato]manganese(III), $Mn^{III}(EHGS)$. $Mn^{III}(EHGS)$ is also air sensitive and will further decarboxylate to $Mn^{III}(SALEN)^+$. When this reaction is completed in acetone, X-ray-quality crystals of $Mn^{III}(SALEN)$[2-(3-oxobutenyl)phenolate] are recovered. This very loosely associated solid-state dimer contains a rare example of monodentate phenolate coordination to Mn(III). The generation of $Mn^{III}(SALEN)^+$ has been followed by electrochemistry and paramagnetic NMR spectroscopy. $Mn^{III}(EHPG)^-$ shows an oxidative wave in methanol with $E_0 = +450$ mV and in DMF with $E_0 = +300$ mV (vs SCE). Bulk electrolysis at +600 mV in methanol quantitatively (by the passage of four electrons) generates $Mn^{III}(SALEN)^+$, which has an Mn(III)/Mn(II) reduction at −250 mV. The paramagnetic NMR spectrum of a mixture of *rac* and *meso* isomers of $Mn^{III}(EHPG)^-$ in CD_3OD shows resonances at +26.3, −18.6, and −34.6 ppm (*rac* isomer) and +27.8, +24.0, −2.4, −16.5, −22.5, −32.5, and −35.5 ppm (*meso* isomers). After 9 days, the spectrum of $Mn^{III}(SALEN)^+$ has developed completely with resonances at −4.1, −23.2, and −28.9 ppm. $Mn^{III}(EHGS)$ is not produced in sufficient quantities to be detected under these conditions. In contrast, DMF solutions of $Mn^{III}(EHPG)^-$ (shifts at +27.3, +24.8, −2.4, −18.0, −21.6, −32.0, and −35.5 ppm, *meso* isomer) slowly form $Mn^{III}(EHGS)$ with features at +45.6, +28.6, +13.1, −9.4, −19.5, and −27.7 ppm, and ultimately one recovers $Mn^{III}(SALEN)^+$ with peaks at +29.5, −2.4, −22.3, and −25.4 ppm. In contrast, the $Fe^{III}(EHPG)^-$, $Cu^{II}(EHPG)^{2-}$, and $Ga^{III}(EHPG)^-$ complexes are air stable. This metal-assisted, oxidative decarboxylation is analogous to that previously described for $V^VO(HEHPG)$, which was shown to generate V(III) species as intermediates. Therefore, this facile decarboxylation reaction appears to be promoted by using ions that can cycle through three oxidation states and suggests that a cycle for the manganese-facilitated process includes both Mn(IV) and Mn(II). X-ray parameters for $Mn^{III}(SALEN)$[2-(3-oxobutenyl)phenolate]: $MnC_{26}H_{23}N_2O_4$, mol wt 482.4, monoclinic ($P2_1/c$), $a = 12.200$ (4) Å, $b = 14.104$ (4) Å, $c = 13.584$ (3) Å, $\beta = 103.74$ (2)°, $V = 2270$ (1) Å^3, $Z = 4$, 3503 unique data collected with $0 < 2\theta < 45°$, 1708 data with $I > 3\sigma(I)$. The best model gave $R = 0.044$ and $R_w = 0.039$.

Introduction

The biological chemistry of manganese is garnering considerable attention due to the recent demonstration of this element as an important cofactor in the generation[1] and metabolism[2,3] of O_2^{n-} (where $n = 0$–2). A mononuclear metal center has been established[4] for manganese superoxide dismutase. The manganese catalases of *Thermus thermophilus*[2c,d] and *Lactobacillus plantarum*[2e] apparently have dinuclear active centers. One proposal for the metal nuclearity of the oxygen-evolving complex[5] includes a mononuclear component, although there is considerable controversy in this area.[1,6]

The structure and reactivity relationship between iron and manganese, and its importance to biological properties of these elements, has been established for some time. Iron complexes have

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