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Reaction of Tris(oxalato)ruthenium(III) Anion with Titanium(III) and (Oxalato)titanium(III) Complexes

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We previously showed[1] that oxalate ion is highly efficient as a bridging ligand for ruthenium(III)–titanium(III) electron transfer (hereafter, ET). For most of the cases studied, ET between Ti(III) and monomeric Ru(III) oxidants is so rapid that the rate-limiting step in the overall redox process is formation of the binuclear complex.[2,3] In the case of ET through bridging oxalate to dimeric Ru(II, III) oxidants,[4] the situation is more complex. In addition, oxalate ion exerts a significant effect[5] as a nonbridging ligand on inner-sphere ET between Co(III) and Ti(III). We now report results of experiments designed to explore the effect of nonbridging oxalate (on both oxidant and reductant) on ET (through bridging oxalate) between Ru(III) and Ti(III).

Experimental Section

$K_3Ru(C_2O_4)_3 \cdot 8.5H_2O$ was prepared by the method of Witschy and Beattie.[6] Anal.[7] Found (calcd): C, 11.80 (11.49); Ru, 15.91 (15.91). Total reducing capacity of the solid to Ce(IV)[8] was consistent with an oxalate/Ru ratio of 3.0 ± 0.3. Wavelengths of maximum absorption (nm)/extinction coefficients (M^{-1} cm^{-1}) are 288/6 × 10^3 and 490/225, in reasonable accord with the literature.[9] Infrared absorption peaks at 1695, 1665, 1650, and 3450 (broad) cm^{-1} were in good agreement with those of a prior report.[10] Ti(III) solutions were prepared as before.[1] Acidic aqueous solutions of $Ru(C_2O_4)_3^{3-}$ decompose on standing.[11] Oxidant solutions were freshly prepared in neutral aqueous LiCl. Acid was added with Ti(III). Kinetic experiments were carried out at 25 °C in LiCl media of 1 M ionic strength. (Ti(III) reduces perchlorate ion.) Reactions were followed at 400 nm in the absence of added oxalate and 452 nm in the presence of added oxalate. Ti(III) was in large excess. Pseudo-first-order plots were linear for more than 3 half-lives, and rate constants (k_{obsd}) were reproducible to 5%. Values of k_{obsd} and the second-order rate constant (k_2 (M^{-1} s^{-1}) = $k_{\mathrm{obsd}}/[\mathrm{Ti}]_T$, where $[\mathrm{Ti}]_T$ is the total Ti(III) concentration:) are listed in Tables I and II. Those tables also contain values of k_{calcd}, computed on the basis described below.

For experiments in the absence of free oxalate ion, a plot of k_2 vs. $[H^+]^{-1}$ showed curvature, but a plot of k_2^{-1} vs. $[H^+]$ gave a straight line with slope 7.4 × 10^{-2} s and intercept 1.9 × 10^{-3} M s. This corresponds to $k_2 = kK/([H^+] + K)$, with $k = 5.3 \times 10^2$ M^{-1} s^{-1} and $K = 0.026$ M. The rate of reaction increased with increasing concentration of added oxalate.

Discussion

The reduction potential of $Ru(C_2O_4)_3^{3-}$ is[13] −0.56 V vs. NHE in dilute aqueous oxalic acid. Assuming a similar value for the media we employ, the second-order rate constant for the reduction of $Ru(C_2O_4)_3^{3-}$ by $TiOH^{2+}$ should be 10^{-3} M^{-1} s^{-1} for an outer-sphere mechanism.[1] The rate constant obtained for this reaction in the absence of free oxalate is 6 orders of magnitude higher, strongly indicating inner-sphere (bridged) ET. The value of K obtained here (0.02 M) is 1 order of magnitude larger than the acid-dissociation constant of Ti^{3+}. The acid dependence of k_2 indicates the formation of a binuclear complex which undergoes deprotonation prior to an electron-transfer step.

A mechanism that is consistent with our results for the reduction of $(C_2O_4)_2RuC_2O_4^{3-}$ by Ti(III) is

$$(C_2O_4)_2RuC_2O_4^{3-} + Ti^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(C_2O_4)_2RuC_2O_4Ti]$$

$$[(C_2O_4)_2RuC_2O_4Ti] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(C_2O_4)_2RuC_2O_4TiOH]^- + H^+$$

$$[(C_2O_4)_2Ru^{III}C_2O_4Ti^{III}OH]^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [(C_2O_4)_2Ru^{II}C_2O_4Ti^{IV}OH]^-$$

$$[(C_2O_4)_2Ru^{II}C_2O_4Ti^{IV}OH] \xrightarrow{k_4} \text{products} \quad \text{(fast)}$$

Applying the steady-state approximation to the concentrations of both of the intermediates, $(C_2O_4)_2RuC_2O_4Ti^{4+}$ and $(C_2O_4)_2RuC_2O_4TiOH^{3+}$, leads to the rate law[12]

$$k_{\mathrm{obsd}} = k_1k_2k_3[Ti^{3+}]/\{k_3(k_{-1} + k_2) + (k_2 + k_3)k_1[Ti^{3+}] + \{k_{-1} + k_1[Ti^{3+}]\}k_{-2}[H^+]\}$$

When k_{-1} is large (the intermediate is unstable), this simplifies to

$$k_f = \frac{K_1k_2k_3[Ti^{3+}]}{k_3 + k_{-2}[H^+]} \qquad (4.11)$$

where $K_1 = k_1/k_{-1}$. This form is consistent with the linear dependence on $[Ti^{3+}]$ and nonlinear dependence on $[H^+]^{-1}$ observed.

The observed value of K (which involves both formation and deprotonation of the intermediate) is similar to corresponding values obtained for redox systems that involve unstable precursor complexes.[12] The value of k observed for reduction of $Ru(C_2O_4)_3^{3-}$ is comparable to that obtained[16] for the reduction of $Co(C_2O_4)_3^{3-}$, but 2 orders of magnitude less than the corresponding value[1] for the reaction involving $Ru(NH_3)_4C_2O_4^+$. The rate of the latter reaction may be taken as a measure of the rate of substitution on Ti(III) by a monopositive species. Faster rates are observed for negatively charged species.[14] Lower rate constants for the tris(oxalato) oxidant indicates some degree of rate control by ET and/or deprotonation. Further indication of ET control is the similarity, noted above, of rates of reduction of Co(III) and Ru(III) reactions in this case, in contrast to the large rate difference normally found.[17]

When free oxalate ion is added, two additional reductants are present, $TiC_2O_4^+$ and $Ti(C_2O_4)_2^-$ (rate constants k' and k''). With use of the same values[5,14,15] as before[11] for K_1 and K_2 (the first and second acidity constants of oxalic acid) and K_3 and K_4 (the formation constants of the mono(oxalato)– and bis(oxalato)–Ti(III) complexes[11]), $[TiC_2O_4^+]$, $[Ti(C_2O_4)_2^{2-}]$, $[H^+]_f$, and $[C_2O_4^{2-}]_f$ were calculated iteratively from total acid concentration $[H^+]_T$, total oxalate concentration $[C_2O_4]_T$, and total Ti(III) concentration $[\mathrm{Ti}]_T$. (The free-acid concentration $[H^+]_f$ was held at 151 ± 1 mM.) It was previously shown[5] that

$$\{[k_{\mathrm{obsd}}\{1 + K[H^+]^{-1} + K_3[C_2O_4^{2-}]_f + K_3K_4[C_2O_4^{2-}]_f^2\} - kK[H^+]^{-1}]\}/K_3[C_2O_4^{2-}]_f = k' + k''k_4[C_2O_4^{2-}]_f$$

A plot of the LHS vs. $[C_2O_4^{2-}]_f$ gave a straight line with slope 1 × 10^8 M^{-2} s^{-1} and no intercept. Thus, $k' < 1$ M^{-1} s^{-1} and k'' = 3.2 × 10^3 M^{-1} s^{-1}. Reactivity of $Ti(C_2O_4)_2^-$ toward $Ru(C_2O_4)_3^{3-}$

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(18) Reviewers have pointed out that oxalate would be expected to stabilize upper oxidation states (Ru(III) and Ti(IV)) and to be more effective in this regard than either H_2O or hydroxide ion.

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Table I. Rate Constants for Ti(III) Reduction of $Ru(C_2O_4)_3^{3-}$[a]

$[H^+]$, mM	$[Ti]_T$, mM	k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}[b]	k_{calcd}, M^{-1} s^{-1}
20	2.36	0.69	292	297
20	3.54	1.04	294	297
25	3.54	0.99	279	268
25	4.72	1.2	267	268
25	5.9	1.67	283	268
40	2.36	0.51	216	207
40	3.54	0.73	206	207
40	4.72	0.99	210	207
40	5.9	1.16	197	207
50	2.36	0.40	170	180
50	5.9	1.02	173	180
75	2.95	0.40	136	135
75	4.72	0.64	136	135
100	2.596	0.29	112	109
100	2.83	0.33	117	109
125	2.95	0.25	85	91
125	4.43	0.36	81	91
125	5.90	0.52	88	91
150	4.43	0.31	70	78
150	5.90	0.44	75	78

[a] Conditions: in 1 M LiCl at $T = 25$ °C; $[Ru(III)]_T = 2.0 \times 10^{-4}$ M. [b] k_2 (M^{-1} s^{-1}) = $k_{obsd}/[Ti]_T$.

Table II. Rate Constants for Ti(III) Reduction of $Ru(C_2O_4)_3^{3-}$ in the Presence of Added Oxalate[a]

$[C_2O_4^-]_T$, mM	$[H^+]_T$, mM	k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}[b]	k_{calcd}, M^{-1} s^{-1}
7.5	159	0.82	320	426
10	164	1.20, 1.28	485	571
12.5	168	1.75	684	707
15	171	2.09, 1.97	793	832
17.5	175	2.25, 2.45	918	942
20	180	2.68, 2.73	1055	1039
22.5	185	2.77	1082	1125
25	188	3.43, 3.46	1344	1211
30	197	3.74	1461	1356

[a] Conditions: in 1 M LiCl at $T = 25$ °C; $[Ru(III)]_T = 2.0 \times 10^{-4}$ M. [b] k_2 (M^{-1} s^{-1}) = $k_{obsd}/[Ti]_T$.

is 2 orders of magnitude larger than the corresponding reactivities of $TiC_2O_4^+$ or of uncomplexed Ti(III) (at $[H^+]_f = 0.150$ M).

On Coulombic grounds, reaction of $Ru(C_2O_4)_3^{3-}$ with Ti^{3+} or $TiOH^{2+}$ would be expected to be faster than reaction of $TiC_2O_4^+$ or $Ti(C_2O_4)_2^-$. However, reaction of $Ru(C_2O_4)_3^{3-}$ with $Ti(C_2O_4)_2^-$ is 10 times faster than that with Ti(III). This effect was also noted[5] in reduction of $Co(NH_3)_5C_2O_4^+$. In both the present case and the case previously studied, nonbridging oxalate on the reductant side *increases* the rate of Ru(III)-Ti(III) ET through bridging oxalate ion. The result of the present study is that nonbridging oxalate on the oxidant side *reduces* the rate of Ru(III)-Ti(III) ET through bridging oxalate ion. That is, the effect on the redox rate of nonbridging oxalate located on ruthenium is just the opposite of the effect of nonbridging oxalate located on titanium. It does not appear that either the substitution reaction that leads to formation of the binuclear complex or the acid-base change that precedes ET within that intermediate accounts for this effect. Coordination of anionic oxalate should stabilize upper oxidation states, relative to lower ones. This is consistent with the effect of nonbridging oxalate on the reductant side, but contrary to the effect on the oxidant side. The most likely interpretation seems to be that interaction with the filled π orbitals on nonbridging oxalate raises the energy of the metal t_{2g} orbitals of the metal ions. This increases the rate when the nonbridging oxalate ions are on the reductant but decreases it when they are on the oxidant.

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Registry No. $Ru(C_2O_4)_3^{3-}$, 25072-75-7; $C_2O_4^{2-}$, 338-70-5; Ti^{3+}, 22541-75-9.

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Oxidation of (Tetraphenylporphyrin)chromium(III) Chloride by Styrene Ozonide

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Oxygen atom transfer to (*meso*-tetraphenylporphinato)metal(III) salts has received considerable attention in the modeling of peroxidase and cytochrome P-450 reactions. Searches continue for new oxygen-transfer agents that provide insights into the mechanisms of formation and reactions of higher valent metallooxoporphyrin species. Oxygen-transfer agents that can act as substrates after having delivered the oxygen atom to a metalloporphyrin are of particular interest. For example, the *p*-cyano-*N*,*N*-dimethylaniline formed upon oxygen transfer from *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide serves as a substrate for the higher valent metallooxoporphyrin.[1] The use of this type of oxygen-transfer reagent in the study of the dynamics of oxygen transfer and subsequent substrate oxidation has definite advantages. Percarboxylic acids serve well as oxygen-transfer agents, yielding metallooxoporphyrins two-electrons oxidized above the (porphinato)metal(III) state.[2] Ozonides are known to transfer oxygen to carboxylic acids to yield percarboxylic acids and two oxidizable aldehyde fragments.[3] It occurred to us that ozonides should be explored as possible double agents for oxygen transfer to (porphinato)metal(III) salts. We report herein the results of a study of the reaction of styrene ozonide with (*meso*-tetraphenylporphinato)chromium(III) chloride ($(TPP)Cr^{III}Cl$).

Experimental Section

The LD/FTMS system employs a Tachisto 215G pulsed TEA carbon dioxide laser coupled with a Nicolet FTMS-1000 Fourier transform mass spectrometer operated at a 3 T, with a 5.08 cm^3 analyzer cell constructed of 80 Transmissive etched stainless steel.[2] For the LD mass spectra reported here, the laser delivered approximately 0.3-0.4 J per 40-ns pulse at 10.6 μm. The laser beam was focused by a 10.16-cm focal length zinc selenide lens to a diameter of approximately 1 mm on the stainless-steel probe tip. Power density at the probe tip is estimated to be in the range of 10^8-10^9 W/cm^2. Negative ions were trapped in the cell by application of a -1.0-V trapping potential.

The sample (~0.5 mg) was dissolved in methanol and applied dropwise to a stainless-steel probe tip. The solvent was allowed to evaporate in air and then placed in the FTMS and pumped down until a gauge pressure of 1.0×10^{-8} Torr was obtained. In a typical experiment sequence, ions were formed by triggering the laser pulse with the FTMS filament off. Following a 3-s pump down delay, after the negative ions formed were trapped, an FTMS spectrum was obtained. Each spectrum resulted from a single laser pulse, and no spectral coaddition was employed.

The UV-vis spectra were measured on a Cary 118C spectrophotometer. Sytrene ozonide was prepared according to Criegee et al.[10]

Synthesis of Isoporphyrin I. A 200-mg sample of (tetraphenylporphinato)chromium(III) chloride (0.286 mmol) and 100 mg of styrene ozonide (0.657 mmol) were stirred in 10 mL of CH_2Cl_2 for 1 h at room temperature. The course of the reaction was monitored by UV-vis spectroscopy. The solvent was rotary-evaporated and the residue washed with 3 × 4 mL n-pentaine. The residue was dissolved in 2 mL of CH_2Cl_2 and chromatographed on silica gel (100 g, 70-230 mesh), eluting with CH_2Cl_2 containing 3 M MeOH. The main band (R_f 0.85) was collected. Recrystallization from CH_2Cl_2/hexane afforded 72 mg (30%, based on I: X = Cl, Y = $PhCO_2^-$) of a dark microcrystalline material. UV-vis: 423 ($\epsilon = 3.6 \times 10^4$), 447 ($\epsilon = 3.6 \times 10^4$), 800 ($\epsilon = 8.8 \times 10^3$), 880 nm ($\epsilon = 1.6 \times 10^4$).

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