

tungsten concentration  $10^{-2}$ – $5 \times 10^{-4}$  *m* are  $\text{WO}_4^{2-}$ ,  $\text{HWO}_4^-$ , and  $\text{H}_2\text{WO}_4$  and the polynuclear species (6,7), (6,10), and (12,18). The 12-tungsten species is not stable above 200 °C while the 6-tungsten species persist to 290 °C in the more concentrated solutions. The equilibrium quotients relating these species have been determined as a function of temperature and ionic strength, as summarized in Table IV.

(2) Reduction of tungsten(VI) to lower valence states was observed but was determined to be stoichiometrically insignificant at the experimental conditions and  $\text{H}_2$  pressures of 0.7–3.5 MPa.

(3) Ion pairing of  $\text{Na}^+$  with  $\text{HWO}_4^-$  and  $\text{WO}_4^{2-}$  is apparently less extensive than with either  $\text{OH}^-$  or  $\text{Cl}^-$  on an iso-coulombic basis.

(4) Hydrous sodium polytungstates precipitated during some of the runs at high total tungsten concentrations. These solids exhibit retrograde solubilities. One solid, identified by X-ray diffraction analysis, was  $\text{Na}_2\text{O} \cdot (\text{WO}_3)^{1/2} \cdot (\text{H}_2\text{O})_{8-40}$ , tungsten phase C of Freedman and Leber.<sup>20</sup>

(5) From Figure 3 and Table IV, it is apparent that in near-neutral, mildly to strongly saline, 150–300 °C solutions

at total tungsten concentrations of  $10^{-4}$ – $10^{-5}$  *m*, the most important tungsten species will be tungstate ( $\text{WO}_4^{2-}$ ) and bitungstate ( $\text{HWO}_4^-$ ). Tungstic acid will be important only at low pH values. Consequently the most significant equilibrium to be considered in tungsten ore-depositing solutions is  $\text{H}^+ + \text{WO}_4^{2-} \rightleftharpoons \text{HWO}_4^-$ . Equations 11 and 12 provide the means of calculating this equilibrium in the range 25–300 °C,  $I = 0$ –5.12 *m*.

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**Supplementary Material Available:** Tables IX (smoothed thermodynamic parameters for the formation of species (1,1), bitungstate, according to eq 1) and X (hydrolysis schemes tested on the data of Tables II and III by using eq 8–10) (11 pages). Ordering information is given on any current masthead page.

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## Kinetics of the Reaction of the Bis( $\mu$ -oxalato)bis( $\mu$ -acetato)diaquodiruthenium(II,III) Anion with $\text{Ti}(\text{H}_2\text{O})_6^{3+}$

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Reduction of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  by  $\text{Ti}^{3+}$  (at 25 °C, in 1.0 M  $\text{LiCF}_3\text{SO}_3$ ) involves formation of an intermediate containing two ruthenium atoms and one titanium atom ( $K_f = \text{ca. } 3 \times 10^2 \text{ M}^{-1}$ ). Intramolecular electron transfer within the conjugate base of that intermediate has a rate constant of  $3 \times 10^5 \text{ s}^{-1}$ . The relatively slow rate of intramolecular ET is ascribed to energy mismatch between electron-donor and -acceptor orbitals.

In previous papers,<sup>1</sup> we have established that electron-transfer (hereafter, ET) reactions having Ru(III) complexes as oxidants and Ti(III) species as reductants involve a variety of mechanisms. In the absence of suitable bridging groups, outer-sphere ET occurs if an electron-delocalizing ligand is present on either redox partner. If a ligand with an open coordination position, and a  $\pi$ -electron system that facilitates overlap between electron-donor and electron-acceptor orbitals, is present on the oxidant, then an inner-sphere mechanism prevails and the rate-limiting step is formation of the binuclear activated complex. There is evidence for rate-limiting ET if 3-formylpentane-2,4-dione is the bridging ligand. Carboxylate ligands are efficient bridges and give rise to substitution-limited reactions. Wieghardt, Sykes, and their co-workers<sup>2</sup> have used binuclear  $\mu$ -carboxylato Co(III) complexes to study the ET through intervening groups, in reactions in which the reductant attacks at a lead-in group remote from the site of coordination of the bridging group to the oxidant metal atom. For  $\mu$ -carboxylato complexes, attack of the reductant at the unco-

ordinated oxygen atom of the coordinated carboxyl group is forestalled by the second metal atom.

Recently,  $\mu$ -carboxylato complexes containing two ruthenium atoms have been the subject of intense study. Particular attention has been given to metal–metal bonding in such complexes.<sup>3</sup> Diruthenium complexes studied heretofore have not contained noninsulating ligands that also included remote lead-in groups. We set out to synthesize complexes that would make it possible to study Ru(III)–Ti(III) ET reactions that are mediated by carboxylate ligands in which adjacent attack on oxygen was blocked by coordination. Our previous work has shown that oxalate was an effective mediator of Ru(III)–Ti(III) ET both when monocoordinated and when bi-coordinated. This paper provides evidence that ET from Ti(III) through the remote carboxyl group of a  $\mu$ -oxalato ligand bridging two ruthenium atoms is slower than the corresponding reaction of monomeric oxidants.

### Experimental Section

Initial attempts to substitute oxalate for acetate in  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$  yielded a variety of products; some of these were monomeric and others were dimers with one oxalate per dimer unit.<sup>1b</sup>

**Bis( $\mu$ -oxalato)bis( $\mu$ -acetato)diaquodiruthenium(II,III) Acid Dihydrate.**  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$  (0.2 g) was added to a solution made by dissolving 0.15 g of oxalic acid in 200 mL of water. The solution was allowed to stand at room temperature until no further change

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in absorption spectrum occurred (4 days) then reduced to 10 mL on a rotary evaporator. The dark product passed directly through a Sephadex G-10 column (though the starting complex was retained) but was retained on Sephadex G-15. The product moved as a single band when eluted with acidified 0.2% LiCl. The eluate was reconcentrated and treated with acetone, to yield a brown powder that was washed with ether and air-dried.

Ruthenium was determined colorimetrically at the Ru(VI)–Ru(VII) isosbestic point. Water was determined by drying at 110 °C for 1 h. This procedure did not cause decomposition. Oxalate was determined by treating a solution of the product with  $\text{CaCl}_2$  in small excess. The precipitate obtained after digestion (0.5 h) was collected, washed, and titrated by  $\text{MnO}_4^-$ . Alternatively, total reducing capacity was determined by dissolving solid samples in dilute acid and treating with  $\text{Ce}^{4+}$  in excess, and the  $\text{RuO}_4$  thus produced was swept out by a stream of dinitrogen. After reaction was complete, remaining  $\text{Ce}^{4+}$  was back-titrated with oxalic acid. When  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$  was subjected to this procedure, the amount of oxidant consumed corresponded to an average oxidation state for ruthenium of 2.5+. When samples of the oxalate-containing powder product were so treated, the amount of oxidant consumed was consistent with the same average oxidation state for ruthenium, after correction for the titre corresponding to the amount of oxalate that had been shown to be present by calcium oxalate analysis.

Anal. Found/calcd for  $\text{HRu}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ :<sup>4</sup> Ru, 33.2/33.4; C, 13.9/15.9; H, 3.1/3.1;  $\text{C}_2\text{O}_4^{2-}$ , 28.3/29.1;  $\text{H}_2\text{O}$  11.8/12.6. Solution spectrum of the powder product (bands, nm (1000 $\epsilon$ )): 375 (3.6), 475 (1.1), 1125 (0.08) (only small dependence on acidity (1 < pH < 4)). This indicates that  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  is a weaker Brønsted base than is  $\text{Ru}_2(\text{CH}_3\text{COO})_4^+$ , for which an acid–base equilibrium is measurable by spectrophotometric titration. The IR spectrum (KBr pellets) of  $\text{HRu}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$  shows bands at 3500 (br), 2910 (w), 1700–1670 (s), 1395 (s), 805 (sp, m), and 700 (sp, m)  $\text{cm}^{-1}$ . Evans' method gave  $\mu_{\text{eff}}$  per two ruthenium atoms as 4.22  $\mu_B$ . Quasi-reversible cyclical voltammograms, corresponding to a one-electron reduction of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  and reoxidation of the product of that reduction, were obtained at carbon-paste electrodes and gave –0.19 V vs. NHE for the reduction potential of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  in 0.9 M  $\text{LiCF}_3\text{SO}_3$ –0.1 M  $\text{HCF}_3\text{SO}_3$ . No other redox reaction was observed in the voltammogram. The ESR spectrum of  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$  in methanol at –78 °C was relatively uncomplicated,<sup>5</sup> but the ESR spectrum of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  was richer,<sup>2c</sup> showing seven lines shifted upfield of the lines of  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$ .

Procedures, apparatus, and reagents used for kinetic studies were generally as previously described.<sup>1</sup> Kinetic experiments were performed with solutions made by dissolving  $\text{HRu}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$  dihydrate in dilute acid.

## Results

When Ti(III) was added to solutions containing  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ , absorbance between 375 and 550 nm first increased and then decreased. The extinction coefficient of the intermediate had a maximum at 400 nm. Spectrophotometric titration showed that 1 mol of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  was consumed for each mole of Ti(III) added. Kinetic data were fitted in terms of a double exponential, yielding two rate constants. That for the faster change was designated  $k_f$ , that for the slower change was designated  $k_s$ . A linear-least-squares program was used to estimate a trial value of  $k_s$  from kinetic data taken on the decreasing slope; with use of this value, a second linear-least-squares treatment was applied to data taken prior to the maximum absorbance, to estimate a trial value for  $k_f$ . All the data were then displayed on a CRT and compared with simulation, by using the parameters derived by the double-least-squares program. Parameters were adjusted, taking account of instrumental factors, until the simulation agreed with the data within experimental scatter. Reproducibility of  $k_f$  was  $\pm 10\%$ . Kinetic data are in Table I.

Table I. Rates of Reaction of  $\text{Ti}^{3+}$  and  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  (25.0 °C,  $\mu = 1.0$  M ( $\text{LiCF}_3\text{SO}_3$ ))

[Ti]/mM	[H <sup>+</sup> ]/mM	$k_f/s^{-1}$	$k_f(\text{calcd})/s^{-1}$	$k_s/s^{-1}$
1.0	24	9.2	9.3	1.35
2.0	24	8.4	9.6	1.39
3.0	24	12.5	9.8	1.28
6.0	24	13.5	9.9	1.39
9.0	24	10.3	9.9	0.98
12.0	24	10.4	9.9	1.35
12.5	24	12.6	9.9	1.41
14.0	24	13.9	10.0	1.39
12.3	28	12.4	9.0	1.40
12.0	32	10.4	8.1	1.33
1.2	35	3.2	6.4	0.81
1.2	35	2.9	6.3	0.75
1.6	35	3.2	6.7	0.74
2.4	35	5.1	7.2	0.73
4.0	35	4.4	7.3	0.78
6.6	35	5.9	7.5	0.54
6.6	35	6.1	7.5	0.75
6.6	35	6.4	7.5	0.69
10.1	35	11.0	7.6	0.82
18.0	35	6.1	7.6	1.01
7.0	47	4.7	6.0	0.12
7.0	47	7.9	6.0	0.87
12.3	48	6.1	5.9	0.81

The value of  $k_f$  depended on [Ti(III)] at low [Ti(III)] but was independent of [Ti(III)] at high [Ti(III)]. The high-[Ti(III)] limiting rate increased as [H<sup>+</sup>] decreased. The value of  $k_s$  was independent of [Ti(III)] but increased somewhat as [H<sup>+</sup>] decreased.

## Discussion

The three main bands in the electronic spectrum of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  correspond to bands in the spectrum of  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$ . This qualitative similarity indicates a common overall structure. The behavior of the product on Sephadex is consistent with the presence of two ruthenium atoms in each anion. The magnetic moment observed for  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  is similar to that of  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$ , indicating the same number of unpaired electrons (three) in each dimer. By analogy with  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$ , the band at 475 nm for  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  is assigned as a  $\pi-\pi^*$  transition and the band at 1125 nm as a  $\delta-\delta^*$  transition. Bathochromic shift suggests<sup>6</sup> that the Ru–Ru interaction is weakened in  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  relative to that in  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$ . The LUMO of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  then lies at lower energies than that of  $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$ .

Wieghardt<sup>7</sup> reports that  $\mu$ -oxalato groups that are coordinated to two metal ions through a single carboxylate show C–O stretching frequencies at 1660 and ca. 1690  $\text{cm}^{-1}$ . The IR spectrum of  $\text{HRu}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$  indicates that oxalate is present in this form, rather than in the corresponding protonated form (for which bands at ca. 1750 and 1625  $\text{cm}^{-1}$  would be expected) or as a five-membered ring with one metal atom coordinated to oxygens from both carboxyl groups (for which a C–O stretch at 1625–1640  $\text{cm}^{-1}$  would be expected). The effect of the presence of oxalate on the ESR spectrum indicates that the electronic bonding system of oxalate is involved in the metal–metal bonding manifold.

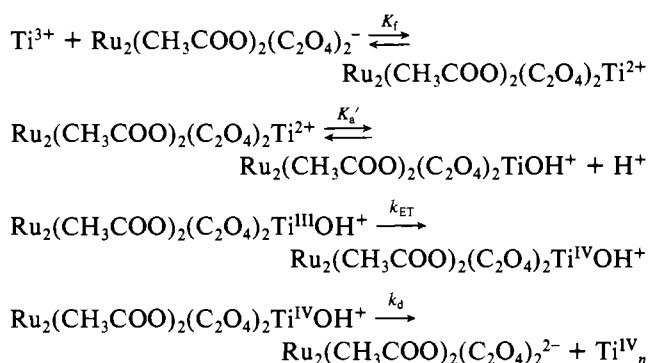
Rates of outer-sphere Ru(III)–Ti(III) redox reactions are sensitive to the thermodynamic driving force.<sup>1</sup> On the basis of the reduction potential measured for  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  and the rates of authentic outer-sphere reactions, it can be predicted that the rate constant of the

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outer-sphere reaction of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  and  $\text{TiOH}^{2+}$  would be about  $0.3 \text{ M}^{-1} \text{ s}^{-1}$  and that for  $\text{Ti}^{3+}$  would be expected to be  $0.02 \text{ M}^{-1} \text{ s}^{-1}$ . Both of these mechanisms predict slow overall rates, and a linear dependence of redox rate on  $[\text{Ti(III)}]$ . Neither of these features are observed.

Nonlinear dependence of rate on  $[\text{Ti(III)}]$  for the reduction of  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  indicates formation of a trinuclear complex in which one oxalate group binds a titanium atom to the diruthenium oxidant. The reaction rate decreases as acidity increases, even in the range of  $[\text{Ti(III)}]$  in which the rate is independent of  $[\text{Ti(III)}]$ . This base catalysis cannot be understood on the basis of deprotonation of  $\text{Ti}^{3+}$  but requires an acid-base equilibrium involving the intermediate.<sup>2d</sup> The following mechanism for the reaction between  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  and  $\text{Ti(H}_2\text{O)}_6^{3+}$  is consistent with the observed data and also is consistent with results of prior studies of related systems:



The charge of the present oxidant should make the rate constant formation of the intermediate larger than the rate constant ( $k = 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) measured for formation of the corresponding intermediate in the reduction of monomeric

ruthenium(III) oxalato complexes. (Ti(III) substitution reactions have associative character.) If the first two steps are rapidly established equilibria, this mechanism would yield

$$k = \frac{k_{\text{ET}}K_fK_a'[\text{Ti(III)}]}{[\text{H}^+] + K_a'[\text{Ti(III)}][\text{H}^+] + K_fK_a'[\text{Ti(III)}]} \quad (1)$$

Values of  $k_s$  (calcd) in Table I are computed by using eq 1 and the values  $K_f = 300 \text{ M}^{-1}$ ,  $K_a' = 0.013 \text{ M}^{-1}$ , and  $k_{\text{ET}} = 30 \text{ s}^{-1}$ . The data require  $K_f > 200 \text{ M}^{-1}$ . The estimate of  $K_a$  used is conservative, in view of the fact that in the Ti(III) reduction<sup>1b</sup> of  $\text{Co(NH}_3)_5\text{F}^{2+}$ , a reaction that involves deprotonation of Ti(III) contained in a similar intermediate, the value of  $K_a$  is  $0.07 \text{ M}^{-1}$ . The limiting rate of  $3 \times 10^5 \text{ s}^{-1}$  reached at high  $[\text{Ti(III)}]$  is a measure of  $k_{\text{ET}}$ , the rate of intramolecular ET within the conjugate base of the initial trinuclear intermediate. If the intermediate were as weak an acid as  $\text{Ti}^{3+}$ , then  $k_{\text{et}} < 10^3 \text{ s}^{-1}$ , still 2 orders of magnitude smaller than the corresponding value for monomeric oxidants.

Although oxalate is an efficient bridging group for ET from Ti(III) when part of a monomeric Ru(III) complex, the ET reaction involving Ti(III) and the  $\mu$ -oxalato dimer is relatively slow. This can be understood since spectra indicate that the LUMO of the oxalato dimer (the electron-acceptor orbital of the redox reaction) lies at higher energy than does the corresponding orbital of the monomeric oxidants. Increase of energy gap between donor and acceptor orbitals would decrease the effective overlap between these orbitals. Thermodynamic driving force is small for the reactions of interest here. Electronic factors such as orbital energy match then become of major importance. It may be possible to use systems like these to control ET in solution-phase and also, perhaps, solid-phase reactions.

**Registry No.**  $\text{HRu}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$ , 88968-52-9;  $\text{Ru}_2(\text{CH}_3\text{COO})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ , 86570-54-9;  $\text{Ti(H}_2\text{O)}_6^{3+}$ , 17524-20-8.

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## Kinetics of the Manganese(III)-Sulfur(IV) Reaction in Aqueous Perchloric Acid Solutions

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The reaction of Mn(III) with S(IV) has been studied in perchloric acid solutions. The stoichiometry of the reaction is one  $\text{Mn}^{3+}$  consumed per  $\text{SO}_2$  consumed, and the production of dithionate was confirmed. The reaction shows a strong inverse dependence on acid concentration. At 5.92 M acid concentration and over the temperature range 15.4–34.9 °C, the rate constant is  $k = (1.1 \pm 0.5) \times 10^7 \exp(-1970 \pm 100/T) \text{ M}^{-1} \text{ s}^{-1}$ .

### Introduction

Oxidation of S(IV) by oxygen (autoxidation) in aqueous solution is known to be catalyzed by manganese ions,<sup>1,2</sup> and a considerable amount of work has been devoted to understanding the kinetics and mechanism of the overall reaction.<sup>3-9</sup> The interest in the autoxidation reaction has increased because of concern about the rate of conversion of S(IV) to S(VI) in flue gas scrubbers, in atmospheric water droplets, and in biological systems. In spite of this interest, the mechanism of S(IV) oxidation by dissolved oxygen is not established. Al-

though early work suggested that it involved the induced oxidation of a complex of Mn(II) and  $\text{SO}_2$  with the subsequent reaction of Mn(III) with another S(IV) species,<sup>2</sup> recent work using EPR failed to detect any change in the concentration

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