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Titanium(III)-Ruthenium(III) Electron Transfer through 3,6-Dihydroxy-1,4-benzoquinonate Ligands: an Ultra-short *Insulated* Wire

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Substituents in positions 2 and 5 of a 3,6-dihydroxy-1,4-quinonate ligand (BQ^{2-}) bring about gross changes in the kinetics and mechanism by which ruthenium(III) complexes containing that ligand (with triethylenetetramine, trien, as spectator ligand) are reduced by aqueous titanium(III). Ti^{III}-reduction of $Ru(trien)(BQ)^+$ requires *two* mols of Ti^{III} per mol of Ru^{III}; the product is a Ru^{III} hydroquinonate complex. An intermediate is involved in this reaction. Both formation and decay of the intermediate follow the kinetic pattern characteristic of outer-sphere electron-transfer (ET). In contrast, reduction of the chloro-substituted analogue, $Ru(trien)(Cl_2BQ)^+$, by Ti^{III} has 1/1 stoichiometry, no detectable intermediate, and displays the rate behavior characteristic of *inner*-sphere reactions. A third pattern obtains for reduction of the methoxy-substituted analogue, $Ru(trien)((OMe)_2BQ)^+$ by Ti^{III}. This reaction has 1/1 stoichiometry, does not involve an intermediate, and follows outer-sphere kinetics. The difference in stoichiometry caused by change of substituents is understood to arise from stabilization of quinonoid radicals by both chloro- and methoxy-substituents. The inner-sphere mechanism in the case of $Ru(trien)(Cl_2BQ)^+$ is ascribed to higher basicity and complexing ability of oxygen in this species. When Ti^{III} reduces $Ru(trien)(BQ)^+$ that is encapsulated by α-cyclodextrin, 2/1 stoichiometry, with an intermediate, is observed, and the kinetic pattern changes from that characteristic of outer-sphere ET to that of inner-sphere electron transfer. Cyclodextrin changes the reaction mechanism by blocking attack of Ti^{III} on the face of the quinonate ring. The α-cyclodextrin-encapsulated quinonate ligand functions as an *insulated conductor* of charge between titanium and ruthenium centers.

Introduction

In $Ru^{III}-Ti^{III}$ electron-transfer (ET) reactions in aqueous media, relatively small changes in composition of the Ru^{III} oxidant can bring about a shift from one gross reaction mechanism to another. Some $Ru^{III}-Ti^{III}$ ET reactions follow simple outer-sphere mechanisms in which only $TiOH^{2+}$ - not Ti^{3+}- is effective as reductant, and display a linear free energy relationship (LFER) that extends over 9 orders of magnitude in rate constant[1]. (For Ti^{III}, $K_a = 4 \times 10^{-3}$ M.[2]) If ligands such as pentanedionate ion or iso-nicotinamide are present on Ru^{III}, then *both* Ti^{3+} and $TiOH^{2+}$ function as outer-sphere reductants, and both rate constants fall on the LFER. In the absence of electron-delocalizing ligands, reactions of Ti^{3+} with Ru^{III} complexes are slow, because of low overlap of donor and acceptor orbitals[3]. When ambidentate ligands with low-lying unfilled molecular π-orbitals (such as thiocyanate ion or acetate ion) are present, only Ti^{3+} (and not $TiOH^{2+}$) functions as reductant, and rates are faster than the LFER predicts−this mechanism[4] is inner-sphere ET with rate-limiting substitution on Ti^{III}. Some systems involve inner-sphere ET with charge-transfer is partially rate-limiting.[5] In the case of Ti^{III} reduction of $Ru(trien)(Cl_2BQ)^+$ (Cl_2BQ^{2-} is the dianion of 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone, Cl_2BQH_2), intramolecular ET is slower[6] than substitution on Ti^{III}. We now report further data on this system and on $Ru^{III}-Ti^{III}$ ET reactions involving bridging ligands derived from 3,6-dihydroxy-1,4-benzoquinone and its methoxy derivative.

Experimental Section

UV/visible spectra were recorded using a Hewlett-Packard 8451A diode array spectrometer. Infrared spectra (KBr disks) were recorded on a Midac FTIR. All compounds were EPR silent.[7] Cyclical voltammetry was performed in 0.1 M HCl/0.9 M LiCl at 24.0 ± 0.2 °C using a Bioanalytical Systems BAS100A electrochemical analyzer, with saturated calomel reference and glassy carbon working electrodes. CM-Sephadex 25 was used for ion-exchange experiments. E&R Microanalytical Laboratory, Inc. (Corona, NY), or Desert Analytics Laboratory (Tucson, AZ) performed carbon, hydrogen, and nitrogen analyses. Ruthenium analysis used a Buck model 200A atomic absorption spectrophotometer at 349.15 nm. (Yields are based on ruthenium.) Ti^{III} solutions were prepared and standardized under argon as described.[1−6] 2,5-Dihydroxy-1,4-benzoquinone (BQH_2), 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (Cl_2BQH_2), triethylenetetramine (trien), and α-cyclodextrin (α-CD) were reagent grade, used as received, and *cis*-$[Ru(trien)Cl_2]Cl$[8] was prepared according to published procedures. 2,5-Dimethoxy-3,6-dihydroxy-1,4-benzoquinone ($(OMe)_2BQH_2$) was synthesized by a variation of a method of Eistert and Bock.[9]

$[Ru(trien)(BQ)]Cl \cdot 6H_2O$. A 0.3 mmol sample of $[Ru(trien)Cl_2]Cl$ was dissolved in 10 mL of water to which several drops of 5 M HCl had been added. The yellow solution was reduced over Zn/Hg for 2 h

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(1) Barone, P.; Earley, J. E. *Inorg. Chem.* **1988**, *27*, 1378.

(2) Orhanovic, M.; Earley, J. E. *Inorg. Chem.* **1975**, *14*, 1478−1481.

(3) Earley, J. E.; Bose, R. N.; Berrie, B. H. *Inorg. Chem.* **1983**, *22*, 1836−1839.

(4) Lee, R. A.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 1739.

(5) (a) Berrie, B. H.; Earley, J. E. *Inorg. Chem.* **1984**, *23*, 774. (b) Bose, R. N.; Wagner, P. A.; Earley, J. E. *Inorg. Chem.* **1984**, *23*, 1132.

(6) For this system, the same rate law with $K = 60$ M^{-1} and $k = 110$ s^{-1} was previously reported: Lu, K.; Earley, J. E. *Inorg. Chem.* **1993**, *32*, 189.

(7) Electron paramagnetic spectroscopy (EPR) was performed on [Ru(trien)BQ]Cl, $[Ru(trien)(Cl_2BQ)]Cl$, and $[Ru(trien)((OMe)_2BQ)]Cl$. Polycrystalline powders were EPR silent at room temperature and at liquid nitrogen temperatures.

(8) Broomhead, J. A.; Kane-Maguire, L. A. P. *J. Chem. Soc. (A)* **1967**, 546.

(9) Eistert, B.; Bock, G. *Chem. Ber.* **1959**, *92*, 1239.

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while bubbled with argon. The color changed to the wine-red of $[Ru(trien)(H_2O)_2]^{2+}$. A 0.3 mmol sample of BQH_2 was dissolved in 10 mL of ethanol: 0.6 mmol of lithium methoxide was added. Argon was bubbled through the resulting red solution for 1 h. The ruthenium- and ligand-containing solutions were mixed and stirred under argon for 4 h. During this period, the color of the solution changed from purple to green. On air oxidation, a green precipitate appeared. This was filtered under argon and recrystallized twice from 0.1 M HCl (yield < 25%). Anal. (calcd): Ru, 18.6 (19.1); C, 27.20 (27.18); N, 10.14 (10.56). A 5 mg sample of the solid was redissolved in a minimum amount of distilled water and loaded onto a cation-exchange resin column: 1.23 mmol of titratable H^+ was released per mmol of Ru^{III} loaded. Elution with distilled water, and then with 0.05 M HCl/0.45 M LiCl, removed only one band, having the same UV/visible spectrum as the original solution.

$[Ru(trien)((OMe)_2BQ)](PF_6)$. A similar procedure was used, with 0.3 mmol of $(OMe)_2BQH_2$ substituted as ligand and PF_6^- as precipitant. The solid product was recrystallized twice from dilute acid (yield ~ 25%). Anal. (calcd): Ru, 18.7 (17.3). A 5.0 mg sample of the solid was redissolved in a minimum amount of water and loaded onto a cation exchange column: 1.06 mmol of titratable H^+ was released per mmol of Ru^{III} loaded. Elution with water, and then with 0.05 M HCl/0.45 M LiCl, removed only one band, having the same spectrum as the original solution.

$[Ru(trien)(Cl_2BQ)]Cl\cdot 2H_2O$. The same procedure was used, with 0.3 mmol of Cl_2BQH_2 substituted as ligand, and Cl^- as precipitant. The solid product was recrystallized twice from dilute acid. (yield ~ 20%) Anal. (calcd): Ru, 20.1 (19.2). A 5.0 mg sample of the solid was redissolved in a minimum amount of water and loaded onto an ion-exchange column: 1.01 mmol of titratable H^+ was released per mmol of Ru^{III} loaded. Elution with water and then with 0.05 M HCl/0.45 M LiCl removed only one band, having the same UV/visible spectrum as the original solution.

Stoichiometry of redox reactions was determined by spectrophotometric titration of mixtures of equivalent concentrations of the reagents. (Data are in the Supporting Information.) Kinetics experiments were carried out under pseudo-first-order conditions, with $[Ru^{III}]$ generally 0.10 mM and Ti^{III} in at least 10-fold excess. Rates were measured by monitoring an absorbance peak (LMCT) of the oxidant (520 nm for $[Ru(trien)((OMe)_2BQ)]^+$, 700 nm for $[Ru(trien)(Cl_2BQ)]^+$ and $[Ru(trien)(BQ)]^+$), in acidic solutions of ionic strength 1.00 +0.01 M (LiCl) using a computer-linked Durrum model 110 stopped-flow spectrometer. Temperature was usually 17.0 ± 0.2 °C: parameters quoted in the text pertain to that temperature. Absorbance-time curves were adequately fitted by single exponentials (in the cases of $Ru(trien)(Cl_2BQ)^+$ and $Ru(trien)((OMe)_2BQ)^+$) or double exponentials (in the case of $Ru(trien)(BQ)^+$, both with and without added α-CD). Reported values of rate constants are averages of two or more independent determinations. Precision is generally better than 5% for single exponentials and ~10% for biphasic reactions. Variation of the rate constant with $[Ti^{III}]$ is shown in Figure 1. Variation of the rate constant with $[H^+]^{-1}$ is shown in Figure 2. (Data are also given in tables in the Supporting Information.)

Results

Cyclic Voltammetry (CV). BQH_2, Cl_2BQH_2, and $(OMe)_2BQH_2$ all show irreversible redox behavior at the glassy carbon electrode, with widely separated CV peaks ($E_{p\,red}$, 0.0 V vs sce; $E_{p\,ox}$, 0.3 V vs sce). (The reduction product of the quinone is the corresponding hydroquinone.[10]) $Ru(trien)(BQ)^+$, $Ru(trien)(Cl_2BQ)^+$, and $Ru(trien)((OMe)_2BQ)^+$ yield CV peaks (somewhat less widely separated) at nearly the same potentials as the free quinones. (Data are in the Supporting Information.) The half-wave potential for all three quinones, and for the corresponding Ru^{III}(trien) complexes, is + 0.40 ± 0.03 V vs nhe. Similarity of CV behavior of Ru^{III}-trien-BQ complexes and free BQ ligands suggests that the ligand is the redox-active segment of the complex at the glassy carbon electrode.

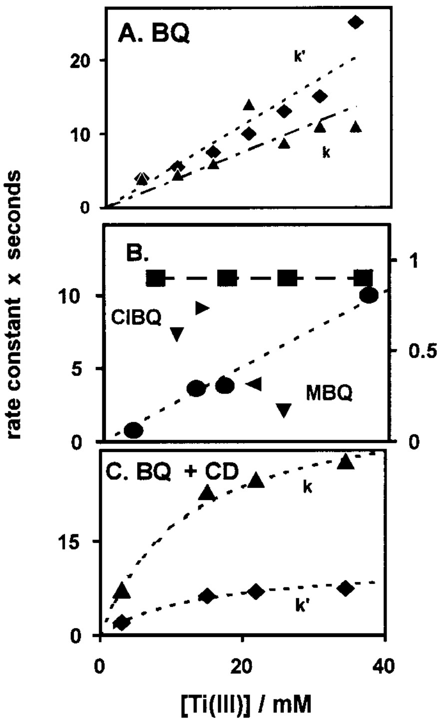

Figure 1. Dependence of rate constants for reductions of Ru^{III} complexes on $[Ti^{III}]$. (A) $Ru(trien)BQ^+$. Triangles, absorbance decrease; diamonds, absorbance increase. (B) $Ru(trien)Cl_2BQ^+$ (squares); $Ru(trien)(OMe)_2BQ^+$ (circles). (C) $Ru(trien)BQ^+$−α-cyclodextrin inclusion complex. Triangles, absorbance decrease; diamonds, absorbance increase.

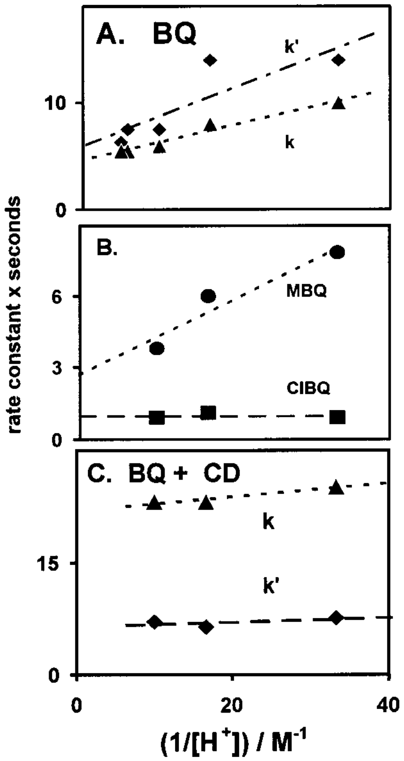

Figure 2. Dependence of rate constants for Ti^{III} reductions of Ru^{III} complexes on $[H^+]^{-1}$. (A) $Ru(trien)BQ^+$. Triangles, absorbance decrease; diamonds, absorbance increase. (B) $Ru(trien)Cl_2BQ^+$ (squares); $Ru(trien)(OMe)_2BQ^+$ (circles). (C) $Ru(trien)BQ^+$−α-cyclodextrin inclusion complex. Triangles, absorbance decrease; diamonds, absorbance increase.

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(10) Foster, R.; Foreman, M. I. Quinone Complexes. In *The Chemistry of the Quinonoid Compounds, Part I*; Panel, S., Ed.; John Wiley and Sons: New York, 1974; p 275.

Redox Reactions. When $\mathrm{Ti^{III}}$ reduces $\mathrm{BQH_2}$, 1.6 ± 0.4 mol of $\mathrm{Ti^{III}}$ are consumed per mole of oxidant. This reaction is much slower (time-scale of tens of minutes) than any other reaction reported here (tens of milliseconds).

Ru(trien)BQ$^+$. When $\mathrm{Ru(trien)BQ^+}$ is treated with $\mathrm{Ti^{III}}$, *two* (2.2 ± 0.4) moles of $\mathrm{Ti^{III}}$ are oxidized per mole of $\mathrm{Ru^{III}}$ complex. This process is biphasic: a small absorbance increase (rate constant k') is followed by a larger absorbance decrease (rate constant k). Rate constants for both processes increase as $[\mathrm{Ti^{III}}]$ increases (Figure 1A) and decrease as $[\mathrm{H^+}]$ increases (Figure 2A), according to the rate law

$$k = a[\mathrm{Ti^{III}}] + b[\mathrm{Ti^{III}}]/[\mathrm{H^+}] \qquad (1)$$

where, for the absorbance increase, $a' = 190 \pm 50\ \mathrm{s^{-1}\ M^{-1}}$ and $b' = 30 \pm 5\ \mathrm{s^{-1}}$ and, for the decrease, $a = 200 \pm 50\ \mathrm{s^{-1}\ M^{-1}}$ and $b = 15 \pm 5\ \mathrm{s^{-1}}$. The two phases of the reduction of $\mathrm{Ru(trien)BQ^+}$ by $\mathrm{Ti^{III}}$ have low dependence on temperature.[11]

Ru(trien)((OMe)$_2$BQ)$^+$. *One* (0.9 ± 0.2) mole of reductant is consumed per mole of oxidant in reduction of $\mathrm{Ru(trien)((OMe)_2)BQ)^+}$ by $\mathrm{Ti^{III}}$. Rate constants are linearly dependent on both $[\mathrm{Ti^{III}}]$ (Figure 1B.) and $[\mathrm{H^+}]^{-1}$ (Figure 2B.) The data correspond to the rate law

$$k = c[\mathrm{Ti^{III}}] + d[\mathrm{Ti^{III}}]/[\mathrm{H^+}] \qquad (2)$$

where $c = 170 \pm 20\ \mathrm{s^{-1}\ M^{-1}}$ and $d = 9 \pm 2\ \mathrm{s^{-1}}$.

Ru(trien)(Cl$_2$BQ)$^+$. *One* (1.0 ± 0.1) mole of $\mathrm{Ti^{III}}$ is oxidized per mole of $\mathrm{Ru(trien)(Cl_2BQ)^+}$. The value of k ($0.9 \pm 0.2\ \mathrm{s^{-1}}$) is independent of both acidity (Figure 2B) and $[\mathrm{Ti^{III}}]$ (Figure 1B).

Ru(trien)BQ$^+$ and α-Cyclodextrin (α-CD). When $\mathrm{Ru(trien)BQ^+}$ is mixed with equimolar amounts of α-CD, the UV spectrum and CV change so as to indicate formation[12] of an "inclusion complex"[13] with $K_{\mathrm{form}} = \sim 10^4\ \mathrm{M^{-1}}$. When this inclusion complex reacts with $\mathrm{Ti^{III}}$, *two* (1.8 ± 0.4) moles of $\mathrm{Ti^{III}}$ are oxidized per mole of $\mathrm{Ru^{III}}$. This reaction is characterized by biphasic absorbance-time traces. (A small absorbance increase precedes a large absorbance decrease). As $[\mathrm{Ti^{III}}]$ increases, both absorbance-increase and absorbance-decrease become faster, but both show mass-law-limitation in $[\mathrm{Ti^{III}}]$ (Figure 1C). Rate constants for both phases are independent of $[\mathrm{H^+}]$ (Figure 2C):

$$k = e[\mathrm{Ti^{III}}]/(1 + f[\mathrm{Ti^{III}}]) \qquad (3)$$

where, for the increase, $e' = (3100 \pm 200)\ \mathrm{s^{-1}\ M^{-1}}$ and $f' = (81 \pm 10)\ \mathrm{M^{-1}}$ and, for the decrease, $e = (810 \pm 50)\ \mathrm{s^{-1}\ M^{-1}}$; and $f = (70 \pm 5)\ \mathrm{M^{-1}}$.[14]

Discussion

IR, NMR, and UV/visible spectra all indicate that the complexes studied here are best considered to contain quinonate (rather than hydroquinonate) ligands.

Ru(trien)BQ$^+$. The 2/1 stoichiometry observed in reduction of $\mathrm{Ru(trien)BQ^+}$ by $\mathrm{Ti^{III}}$ suggests that the final product of this reaction is a $\mathrm{Ru^{III}}$-hydroquinonate complex, rather than a $\mathrm{Ru^{II}}$-quinonate complex. Biphasic kinetics—in the presence of cyclodextrin and also in its absence—shows that an intermediate is involved. Linear dependence of both k' and k on $[\mathrm{Ti^{III}}]$ and on $[\mathrm{H^+}]^{-1}$ indicates that reaction with $\mathrm{TiOH^{2+}}$ is important in both formation and destruction of that intermediate. Acid-independent components of both k' and k indicate that reaction with $\mathrm{Ti^{3+}}$ also occurs in both processes. The rate ratio between $\mathrm{Ti^{3+}}$ and $\mathrm{TiOH^{2+}}$ is consistent with the ratio previously observed for outer-sphere reductions of $\mathrm{Ru^{III}}$ complexes with electron-delocalizing ligands.[15] The process producing the more highly absorbing intermediate may be taken to correspond to outer-sphere reduction of $\mathrm{Ru^{III}}$ to $\mathrm{Ru^{II}}$. The subsequent process is considered to be outer-sphere ET from $\mathrm{Ti^{III}}$ to the quinonate ligand along with reoxidation of $\mathrm{Ru^{II}}$ to $\mathrm{Ru^{III}}$ and final production of a coordinated hydroquinonate ion − yielding the observed overall (two-equivalent) stoichiometry.[16]

Ru(trien)((OMe)$_2$BQ)$^+$. The 1/1 stoichiometry indicates a $\mathrm{Ru^{II}}$ product. The observed rate-law shows that *both* $\mathrm{Ti^{3+}}$ and $\mathrm{TiOH^{2+}}$ are involved in or prior to the rate-determining step—the reactivity pattern found when $\mathrm{Ti^{III}}$ acts as an outer-sphere reductant for $\mathrm{Ru^{III}}$ oxidants that contain electron-delocalizing ligands[3].[17]

Ru(trien)(Cl$_2$BQ)$^+$. Lack of dependence of the rate constant for reduction of $\mathrm{Ru(trien)(Cl_2BQ)^+}$ by $\mathrm{Ti^{III}}$ on either $[\mathrm{Ti^{III}}]$ or on $[\mathrm{H^+}]$ requires that the rate-limiting process be unimolecular, involving a $\mathrm{Ru^{III}{-}Ti^{III}}$ species, the concentration of which does not depend on either $[\mathrm{Ti^{III}}]$ or $[\mathrm{H^+}]$. This reaction features rate-limiting intramolecular ET where[18] $k = 0.9 \pm 0.2\ \mathrm{s^{-1}}$. For the rate to be independent of $[\mathrm{Ti^{III}}]$, as observed,[5] the equilibrium constant for formation of the inner-sphere complex must be $>150\ \mathrm{M^{-1}}$.

Ru(trien)BQ$^+$−α-Cyclodextrin Inclusion Complex. Reduction of this complex by $\mathrm{Ti^{III}}$ has 2/1 stoichiometry and follows biphasic kinetics, indicating involvement of an intermediate and eventual formation of a hydroquinonate product. Rate constants for both reactions are independent of $[\mathrm{H^+}]$. *Only* $\mathrm{Ti^{3+}}$—not

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(11) $[\mathrm{Ti^{III}}] = 5.0$ mM and $[\mathrm{H^+}] = 100$ mM: $\Delta H^{*\prime} = 35 \pm 15\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $\Delta S^{*\prime} = -110 \pm 10\ \mathrm{kJ\ mol^{-1}}$ and $\Delta H^* = 18 \pm 10\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $\Delta S^* = -170 \pm 20\ \mathrm{kJ\ mol^{-1}}$. See Figure 3 in the Supporting Information.

(12) Wavelengths of maximum absorbance, nm (log ϵ): 286 (4.6), 380 (sh), 438 (3.5), 700 (3.2). (Absorbance vs ligand concentration data are given in the Supporting Information.) Irreversible cyclic voltammograms gave the reduction peak potential of the inclusion complex as +250 mV vs NHE. The potential shifts to +350 mV on subsequent sweeps.

(13) D'Souza, V. T., Lipkowitz, K. B., Eds. *Chem. Rev.* **1998**, *98*, 1741−2076.

(14) These parameters were obtained using plots of $[\mathrm{Ti^{III}}]/k$ versus k.

(15) Redox reactions of $\mathrm{Ru(trien)BQ^+}$ at the graphite electrode are irreversible. The thermodynamic reduction potential must be significantly more anodic than the peak potential. Measured rate constants are at least 1 order of magnitude *larger* than expected on the basis of the LFER for simple $\mathrm{Ru^{III}{-}Ti^{III}}$ ET reactions. Activation parameters for the two phases of reduction of $\mathrm{Ru(trien)(BQ)^+}$ by $\mathrm{Ti^{III}}$ ($\Delta H^{*\prime} = 35\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $\Delta S^{*\prime} = -110\ \mathrm{kJ\ mol^{-1}}$ and $\Delta H^* = 18\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $\Delta S^* = -170\ \mathrm{kJ\ mol^{-1}}$) differ from activation parameters previously observed for reduction of $\mathrm{Ru^{III}}$ complexes by $\mathrm{Ti^{III}}$ in a way that suggests that a stable precursor complex is involved.

(16) It is not possible to determine the reaction sequence for consecutive chemical reactions, (whether [fast, then slow] *or* [slow, then fast]) based *solely* on kinetic time-series data. Two different values for the extinction coefficient of the intermediate can be calculated: $1180\ \mathrm{cm^{-1}\ M^{-1}}$ if the reaction corresponding to k' occurs first; and $1500\ \mathrm{cm^{-1}\ M^{-1}}$ when k is the rate constant for the initial reaction. The MLCT bands for $\mathrm{Ru^{II}}$ quinone complexes have extinction coefficients in the 700 nm region approximately 150% larger than the extinction coefficients for the corresponding LMCT bands in $\mathrm{Ru^{III}}$ quinone complexes. The extinction coefficient measured at 700 nm for the LMCT band of $\mathrm{Ru(trien)BQ^+}$ is $820\ \mathrm{cm^{-1}\ M^{-1}}$. The extinction coefficient for the intermediate is 140% larger than that for $\mathrm{Ru(trien)BQ^+}$ when k' is taken as the rate constant for the first reaction; the extinction coefficient for the intermediate is 180% larger when k is the rate constant for the first reaction. This indicates that k' and not k is the rate constant for the first reaction.

(17) As in the $\mathrm{Ru(trien)BQ^+}$ case, irreversibility of electrode reaction makes comparison with the LFER problematical, but both rates are faster than would be expected for simple outer-sphere ET.

(18) Rate constants for *outer-sphere* reduction by $\mathrm{Ti^{3+}}$ and $\mathrm{TiOH^{2+}}$ are then $<23\ \mathrm{s^{-1}\ M^{-1}}$ and $<600\ \mathrm{s^{-1}\ M^{-1}}$, respectively.

$TiOH^{2+}$—is effective as reductant in each case. This reactivitypattern has previously been observed in *inner-sphere* Ru^{III}−Ti^{III} reactions.[19] The mass-law-limited [Ti^{III}] dependence of both k' and k indicate that a mechanism involving formation of a Ru^{III}−BQ−Ti^{III} complex is involved in the generation of the intermediate, and also that a second complex (a Ru^{III}−semiquinonate−Ti^{III} species) is important in the ET process that destroys the intermediate.

Previous work indicated that Ru^{III}−Ti^{III} ET reactions could shift between mechanisms on slight provocation. The reactions studied here show that even the stoichiometry of such reactions is changeable. Ru(trien)(Cl_2BQ)$^+$ and Ru(trien)(($OMe)_2$BQ)$^+$ are reduced by Ti^{III} in *one*-electron processes, but reduction of Ru(trien)BQ$^+$ (with and without α-CD) requires *two* moles of Ti^{III}.

Ti^{III} reduction of Ru(trien)(($OMe)_2$BQ)$^+$, and of Ru(trien)-BQ$^+$ in the absence of α-CD, follow rate laws characteristic of outer-sphere electron-transfer reactions in which electron-delocalizing ligands facilitate mixing of electron-donor and electron-acceptor orbitals. A rather stable π-complex—with Ti^{III} located above the plane of the quinonate ring[20]—is the probable precursor of ET. The two one-electron redox processes involve monotonic *decrease* of intensity of a LMCT peak in the visible spectrum even though Ru^{II} complexes are more strongly absorbing than Ru^{III} species in this region. This suggests production of a Ru^{III} species with an added electron mainly located on the quinone-derived ligand, rather than on ruthenium. Both halogen- and alkoxy-substituents stabilize radicals.[21] (Electron-donating and also electron-withdrawing substituents provide orbitals suitable for delocalizing unpaired electrons.) Stabilization of a quinonoid radical favors one-electron reduction in both Ru(trien)(Cl_2BQ)$^+$ and Ru(trien)(($OMe)_2$)BQ)$^+$ cases.

The two one-electron reactions differ greatly from each other in kinetics and mechanisms: outer-sphere ET is observed for Ru(trien)(($OMe)_2$BQ)$^+$ while inner-sphere ET obtains for Ru(trien)(Cl_2BQ)$^+$. Electron-donating substituents lower electron affinity of *p*-benzoquinones.[22] In Ru(trien)(($OMe)_2$BQ)$^+$, a decrease in electron affinity (increase in basicity) of the quinone ring favors formation of a precursor complex[23] for outer-sphere ET, through approach of Ti^{III} perpendicular to the plane of the quinonate ring. In the case of Ru(trien)(Cl_2BQ)$^+$, a decrease in ring basicity inhibits π-complex formation while a concomitant increase in basicity[24] of uncoordinated oxygen favors inner sphere reaction of Ti^{III}.

The first stage in the two-electron reduction of Ru(trien)-BQ$^+$ involves an *increase* in absorbance in the MLCT region. This suggests that, in the absence of stabilization of a radical, an electron is transferred *through* the ring to reduce Ru^{III} to Ru^{II}. The second stage of reaction involves a *decrease* of absorbance, indicating *reoxidation* of Ru^{II} to Ru^{III}: a second electron is transferred to the ring from Ti^{III}, in a process that also involves insertion into the ring of an electron deriving from Ru^{II}, to produce a hydroquinone product.[25] Quinonate and hydroquinonate ligands differ in geometry. Two-electron reduction of a quinonate ligand should encounter a substantial barrier.

Ru(trien)(Cl_2BQ)$^+$, and Ru(trien)BQ$^+$ in the presence of α-CD, follow a kinetic pattern that indicates *inner-sphere* ET. The hydrophobic cavity of α-CD is large enough for encapsulation of the quinone group of Ru(trien)(BQ)$^+$.[26] Molecular models indicate that oxygen atoms that are not ruthenium-bound protrude[27] from the CD cavity and are available for complexation with Ti^{III}. When Ru(trien)BQ$^+$ is encapsulated by α-CD, the outer-sphere path involving Ti^{III} attack on the ring is blocked, only the inner-sphere ET pathway is available. The substantially larger value of intramolecular ET rate for Ru(trien)BQ$^+$-α-CD, as compared to Ru(trien)(Cl_2BQ)$^+$, indicates[28] that the activation barrier is reduced by encapsulation.[29] The apolar interior of α-CD requires less reorganization accompanying ET than would solvent water surrounding an unencapsulated complex.[30] As expected, this effect is greater for the first (k') step than for the second (k) step. Considering the BQ^{2-} ligand as a conductor, we are now reporting the world's shortest *insulated* wire.

Supporting Information Available: Tables of data on spectrophotometric titrations, kinetics, cyclical voltammetry of ligands and complexes, and cyclodextrin complex formation, and ln k vs $1/T$ plots. This material is available at http://pubs.acs.org.

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(19) A mechanism in which a Ru^{III}−Ti^{III} complex undergoes outer-sphere reduction by Ti^{3+} but not by $TiOH^{2+}$ could account for the lack of $[H^+]^{-1}$ dependence observed in the reduction of the Ru(trien)BQ$^+$−α-cyclodextrin inclusion complex. Such a mechanism is unlikely. If outer-sphere reduction occurs, reaction by both $TiOH^{2+}$ and Ti^{3+}, or only by $TiOH^{2+}$, is expected. Encapsulation by α-cyclodextrin blocks attack by Ti^{III} on the quinone ring.

(20) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 9393−9404.

(21) Heats of formation (kJ mol^{-1}) are as follows: X CH_3, 147; X CCl_3, 79; X CH_2OCH_3, −11.7. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: Washington, DC, 1987; p 747.

(22) Foster, R.; Foreman, M. I. Quinone Complexes. In *The Chemistry of the Quinonoid Compounds, Part I*; Patel, S., Ed.; John Wiley and Sons: New York, 1974; p 275.

(23) Rathore, R.; *et al. op. cit.*

(24) The formation constant of the Ru^{III}−Ti^{III} complex is at least three times larger for Ru(trien)(Cl_2BQ)$^+$ than for the other two oxidants.

(25) (a) Attia, A.; Pierpont, C. *Inorg Chem.* **1995**, *34*, 1172. (b) Attia, A. S.; Jung, O.; Pierpont, C. G. *Inorg. Chim. Acta* ***1994***, *226*, 91.

(26) The hydrophobic cavity has dimensions of 5.7 Δ in diameter and 7.8 Δ in length. α-Cyclodextrin is known to form inclusion complexes with benzene derivatives. Szejtli, J. *Cyclodextrins and Their Inclusion Complexes*; Akadémiai Kiadó; Budapest, 1982.

(27) The complex was modeled using ZINDO-1 on the Hyperchem Release 3 (Hypercube).

(28) We are grateful to an anonymous referee for pointing out that alternative interpretations of the mechanism of action of cyclodextrin, including change of free energy of the redox reaction and blocking of proton transfer to the quinonate ligand, are possible

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