

Short Communication

Kinetics and mechanism of the reduction of *trans*-dioxoruthenium(VI) by iron(II)

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Abstract

The kinetics of the reduction of *trans*-[Ru(TMC)(O)₂]²⁺ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) has been studied in aqueous acidic solution. The reaction has the following stoichiometry: *trans*-[Ru^{VI}(TMC)(O)₂]²⁺ + 2Fe²⁺ + 2H⁺ → *trans*-[Ru^{IV}(TMC)O(OH₂)]²⁺ + 2Fe³⁺. The rate law is $-d[\text{Ru(VI)}]/dt = k_2[\text{Ru(VI)}][\text{Fe}^{2+}]$ with $k_2 = 27.4 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C and 1.0 M ionic strength, and $\Delta H^\ddagger = 1.3 \pm 0.3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -(210 \pm 20) \text{ J mol}^{-1} \text{ K}^{-1}$. A mechanism that is consistent with the rate data is [Ru^{VI}(TMC)(O)₂]²⁺ + Fe²⁺ ⇌ [Ru^V(TMC)(O₂)]⁺ + Fe³⁺, followed by [Ru^V(TMC)(O₂)]⁺ + Fe²⁺ + 2H⁺ → [Ru^{IV}(TMC)O(OH₂)]²⁺ + Fe³⁺ (fast). Using the Marcus cross relation the rate constant for the outer-sphere electron transfer between Ru(VI) and Fe²⁺ is calculated to be 10 M⁻¹ s⁻¹, which compares favorably with the experimental value. However the low ΔH^\ddagger and the large negative ΔS^\ddagger is more consistent with an inner sphere mechanism

Introduction

Ruthenium oxo complexes have received much attention in recent years because of their remarkable abilities to act as stoichiometric and catalytic oxidants [1]. So far, most studies were concerned with the oxidation of organic molecules, with little emphasis on simple inorganic substrates [2–4]. As part of a program to study the reduction of ruthenium oxo complexes by simple inorganic species, we report here the kinetics of the reduction of *trans*-[Ru^{VI}(TMC)(O)₂]²⁺ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, structure is shown in Fig. 1) by Fe²⁺(aq). This complex is chosen for study because it is particularly stable compared to other *trans*-dioxoruthenium(VI) complexes; the presence of the macrocyclic ligand TMC

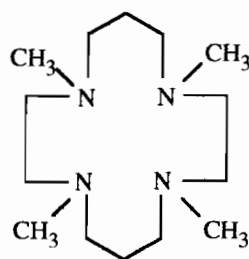


Fig. 1. Structure of TMC.

eliminates side reactions due to ligand loss or decomposition. The reduction of this complex with various Ru(II) complexes has recently been reported [3]. In the presence of excess Ru(VI), the complex is first reduced to Ru(V), which then undergoes acid-catalysed disproportionation. Because the Ru(II) reductants used (as well as the Ru(VI) oxidant) are substitutionally inert, the mechanism for the reduction of Ru(VI) to Ru(V) is restricted to the outer-sphere. In the present case the Fe²⁺ reductant is substitutionally labile, hence both outer-sphere and inner-sphere pathways are possible. It would be of interest to see which pathway would be preferred under this situation.

Experimental

Materials

trans-[Ru^{VI}(TMC)(O)₂](PF₆)₂ was prepared by a literature method [5]. Solutions of Fe²⁺ were freshly prepared before each set of kinetic runs by dissolving either iron wire (with warming) or ammonium iron(II) sulfate in perchloric acid or trifluoromethanesulfonic acid. The solutions were standardised with potassium permanganate [6]. No difference in rates was observed between the use of iron wire and ammonium iron(II) sulfate. Also there was no difference in rates between the use of perchloric acid and triflic acid. Most kinetic runs were done in perchloric acid using ammonium iron(II) sulfate. Ionic strength was maintained with either sodium perchlorate or sodium trifluoromethanesulfonate. All chemicals were of reagent grade. Water for kinetic experiments was distilled twice from alkaline permanganate.

Kinetic measurements

The kinetics of the reaction were determined using a Hewlett-Packard 8452A diode array spectrophotometer. The concentrations of Fe(II) were at least in 10-

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fold excess of Ru(VI). The rate of the reaction was measured by monitoring the disappearance of Ru(VI) at either 222 or 256 nm (λ_{\max} of Ru(VI)). Both wavelengths gave identical results and most runs were monitored at 256 nm. Pseudo-first-order rate constants, k_{obs} , were obtained by non-linear least-squares fits of A_t to time t according to the equation $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{\text{obs}}t)$, where A_0 and A_∞ are the initial and final absorbances, respectively. Second-order rate constants, k_2 , were obtained from linear least-squares fits of k_{obs} to $[\text{Fe(II)}]$. There was no difference in rate constants between reactions carried out in air or under argon, and most runs were done in air.

Products and stoichiometry

The amount of Fe^{3+} produced was determined by adding KNCS to the solution after reaction and measuring the absorbances of the resulting red $[\text{Fe}(\text{SCN})_n]^{3-n}$ complex [6]. Typically, 4 ml of 5×10^{-4} M of Fe^{2+} (2×10^{-6} mol) in 1 M HClO_4 were mixed with 4 ml of 1×10^{-4} M of Ru(VI) (4×10^{-7} mol) in 1 M HClO_4 . After 1 h, 1 ml of 2 M KNCS and 0.6 ml 4 M HCl were added, the solution was diluted to 10 ml and the absorbance at 480 nm was measured. By reading from a calibration curve, the concentration of Fe(III) produced was found to be 8.1×10^{-5} M (8.1×10^{-7} mol, average of two determinations). Control experiments showed that the excess Fe^{2+} and the Ru(IV) product did not interfere with the measurements. Thus 2 mol of Fe^{3+} were produced per mole of Ru(VI).

The product resulting from the reduction of Ru(VI) was determined as follows. Typically 1×10^{-6} mol of Ru(VI) was mixed with 2.2×10^{-6} mol of Fe(II) in 10 ml of 0.1 M HClO_4 . After 1 h the solution was loaded onto a Sephadex-SP C-25 cation-exchange resin. By eluting with 0.2 M HClO_4 and examining the UV-Vis spectrum of the solution 1.0×10^{-6} mol of *trans*- $[\text{Ru}^{\text{IV}}(\text{TMC})\text{O}(\text{OH}_2)]^{2+}$ (λ_{\max}/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 420 (150), 280 (1600), 210 (9800)) [7] was found to be present.

Results and discussion

Spectral change and stoichiometry

Rapid spectral changes were observed when a solution of Ru(VI) was mixed with an excess of Fe(II) in acidic solution. Well-defined isosbestic points at 216, 285 and 345 nm were maintained throughout the course of the reaction (Fig. 2). The final solution was found to contain 1 mol of Ru(IV) and 2 mol of Fe(III) per mole of Ru(VI) used (see 'Experimental'). Thus the overall reaction can be represented by eqn. (1).

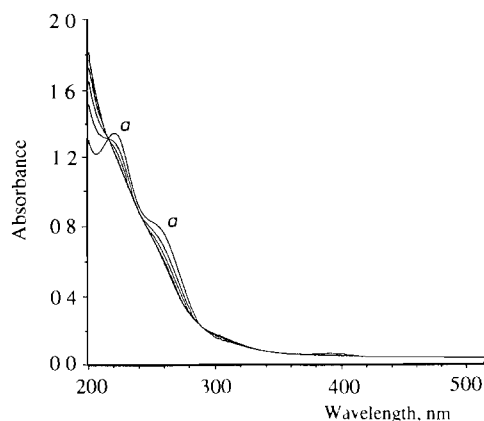
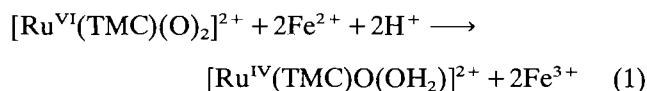


Fig. 2. Spectral changes during the reaction of $[\text{Ru}^{\text{VI}}(\text{TMC})(\text{O})_2]^{2+}$ (5×10^{-5} M) with Fe^{2+} (3.5×10^{-3} M) in 1 M $\text{CF}_3\text{SO}_3\text{H}$ at 25 °C a, Initial spectrum taken c 5 s after mixing. Spectra were recorded at 40 s intervals.



Kinetics

The kinetics of the reaction were followed at either 256 or 222 nm (λ_{\max} of Ru(VI)). In the presence of at least 10-fold excess Fe^{2+} , clean pseudo-first-order kinetics were observed for over three half-lives. The pseudo-first-order rate constants, k_{obs} , were obtained by non-linear least-squares fits of absorbance A_t to time t according to the equation $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{\text{obs}}t)$. Representative data are collected in Table 1. The pseudo-first-order rate constants were independent of $[\text{Ru(VI)}]$ from 2.5×10^{-5} M to 1×10^{-4} M, and this confirms that the decay of Ru(VI) is strictly first order. The rate constants were also independent of $[\text{H}^+]$ from 0.01 M to 1 M; the type of acid used (HClO_4 or $\text{CF}_3\text{SO}_3\text{H}$) and the presence or absence of air. A few studies were also made on the effect of added Fe^{3+} . Experiments were performed with 5×10^{-5} M Ru(VI), 5×10^{-4} M Fe^{2+} , and 1×10^{-4} M to 7×10^{-4} M Fe^{3+} . There was inhibition by Fe^{3+} ; k_{obs} decreased by about 14% on adding 7×10^{-4} M Fe^{3+} . Unfortunately, higher concentrations of Fe^{3+} could not be used due to its strong absorption at around 260 nm.

The pseudo-first-order rate constants were found to depend linearly on $[\text{Fe}^{2+}]$. Second-order rate constants, k_2 , were obtained from linear least-squares fits of k_{obs} to $[\text{Fe}^{2+}]$. Thus the experimentally determined rate law is

$$-\frac{d[\text{Ru(VI)}]}{dt} = k_2[\text{Ru(VI)}][\text{Fe}^{2+}] = k_{\text{obs}}[\text{Ru(VI)}] \quad (2)$$

The temperature dependence of k_2 at $\mu = 1.0$ and 0.1 is shown in Table 2. As can be seen, k_2 is rather insensitive to temperature as well as ionic strength. At

TABLE 1. First-order rate constants for the reaction of Ru(VI) with Fe(II)^a

| [H ⁺] (M) | 10 ³ [Fe(II)] (M) | 10 ² k _{obs} (s ⁻¹) |
|--------------------------|---------------------------------|--|
| 1.0 | 0.40 | 1.12 |
| 1.0 | 0.50 | 1.40 |
| 1.0 | 0.50 | 1.36 ^b |
| 1.0 | 0.50 | 1.42 ^c |
| 1.0 | 0.50 | 1.38 ^d |
| 1.0 | 0.50 | 1.30 ^e |
| 1.0 | 0.50 | 1.20 ^f |
| 1.0 | 1.50 | 4.18 |
| 1.0 | 2.60 | 7.23 |
| 1.0 | 3.50 | 9.65 |
| 0.10 | 0.40 | 1.20 |
| 0.01 | 0.40 | 1.22 |
| 0.01 | 0.40 | 1.24 ^g |

^a $\mu = 1.0$ M (NaClO₄), [Ru(VI)] = 5×10^{-5} M, $T = 25.0$ °C. Each data is the average of at least two determinations. Results are reproducible to within 5%. ^b[Ru(VI)] = 2.5×10^{-5} M. ^cCF₃SO₃H was used instead of HClO₄. ^d[Fe(III)] = 1×10^{-4} M added. ^e[Fe(III)] = 4×10^{-4} M added. ^f[Fe(III)] = 7×10^{-4} M added. ^gReaction carried out under argon.

TABLE 2. Temperature dependence of the second-order rate constants for the reaction of Ru(VI) with Fe(II)^a

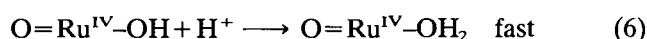
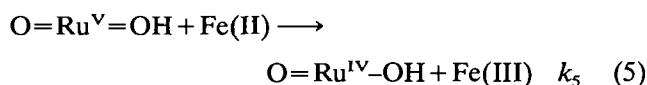
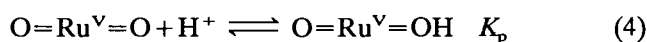
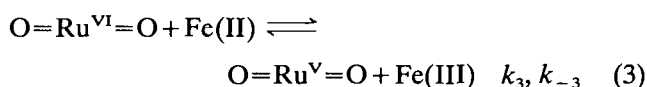
| μ | T (K) | k_2 (M ⁻¹ s ⁻¹) |
|-------|---------|---|
| 1.0 | 291 | 26.4 |
| 1.0 | 298 | 27.4 |
| 1.0 | 305 | 28.3 |
| 1.0 | 311 | 29.2 |
| 0.10 | 291 | 26.4 |
| 0.10 | 298 | 27.0 |
| 0.10 | 305 | 27.7 |
| 0.10 | 311 | 28.0 |

^aError $\pm 3\%$.

$\mu = 1.0$, $\Delta H^\ddagger = 1.3 \pm 0.3$ kJ mol⁻¹ and $\Delta S^\ddagger = -(210 \pm 20)$ J mol⁻¹ K⁻¹; at $\mu = 0.1$, $\Delta H^\ddagger = 0.5 \pm 0.5$ kJ mol⁻¹ and $\Delta S^\ddagger = -(210 \pm 20)$ J mol⁻¹.

Mechanism

A mechanism that is consistent with the simple rate law is shown in Scheme 1.



Scheme 1.

The initial step involves one-electron reduction of Ru(VI) to Ru(V). The dioxoruthenium(V) species then undergoes protonation with $K_p = 615$ at 299 K [3]. The protonated dioxoruthenium(V) species is a stronger oxidant ($E_{1/2} = 0.8$ V [3]) than dioxoruthenium(VI) ($E_{1/2} = 0.56$ V). (All potentials measured in this paper are versus NHE.) Using the steady-state approximation for $[\text{O}=\text{Ru}^{\text{V}}=\text{O}]$ and $[\text{O}=\text{Ru}^{\text{V}}=\text{OH}]$, the following rate law is obtained:

$$\frac{d[\text{Ru}(\text{IV})]}{dt} = \frac{k_3 k_5 K_p [\text{Ru}(\text{VI})][\text{Fe}(\text{II})]^2 [\text{H}^+]}{k_5 K_p [\text{H}^+][\text{Fe}(\text{II})] + k_3 [\text{Fe}(\text{III})]} \quad (7)$$

Under the conditions that $k_5 K_p [\text{H}^+][\text{Fe}(\text{II})] \gg k_{-3} [\text{Fe}(\text{III})]$, the rate law simplifies to that observed with $k_2 = k_3$.

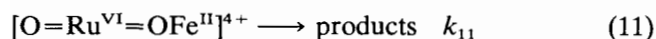
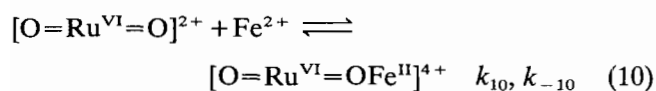
The main point of interest in this mechanism is whether the first step of the reaction, i.e. the electron transfer between Ru(VI) and Fe²⁺, is outer-sphere or inner-sphere. A calculation of k_{12} , the theoretical rate constant for the outer-sphere reaction between Ru(VI) and Fe²⁺, can be made using the Marcus cross relation [8]:

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} \quad (8)$$

where

$$\ln f_{12} = \frac{(\log K_{12})^2}{4 \ln(K_{11} k_{12}/z^2)} \quad (9)$$

The value of $K_{12} = 2.81 \times 10^{-4}$, the equilibrium constant for the reaction, is calculated from the reduction potentials for the Ru(VI)/Ru(V) (0.56 V) [9] and the Fe^{3+/2+} (0.77 V) [10] couples. A value of 1.5×10^5 [3] is used for k_{11} , the self-exchange rate for Ru(VI)/Ru(V). k_{22} , the self exchange rate for Fe^{3+/2+}, is $4 \text{ M}^{-1} \text{ s}^{-1}$ [11]. z , a collision frequency, is taken as $10^{11} \text{ M}^{-1} \text{ s}^{-1}$. The value of k_{12} obtained in this manner is $10 \text{ M}^{-1} \text{ s}^{-1}$. This calculated value compares favorably with the measured value of $27 \text{ M}^{-1} \text{ s}^{-1}$ at $\mu = 1.0$, and this is usually regarded as a good evidence for an outer-sphere mechanism. However, an outer-sphere mechanism cannot explain the observed activation parameters. The outer-sphere reduction of Ru(VI) by $[\text{Ru}^{\text{II}}(\text{NH}_3)_4 \text{bpy}]^{2+}$ (bpy = 2,2'-bipyridine) has $k_2 = 2.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, $\mu = 0.1$), with $\Delta H^\ddagger = (4.82 \pm 0.20)$ kJ mol⁻¹ and $\Delta S^\ddagger = -(117 \pm 20)$ J mol⁻¹ K⁻¹ [3]. In the present case, the reduction of Ru(VI) by Fe²⁺ has a lower ΔH^\ddagger even though k_2 is smaller by a factor of 10^5 . This is due to a much more negative ΔS^\ddagger . As pointed out by Taube [12], this observation can be rationalised by assuming a pre-equilibrium step as shown in Scheme 2.



Scheme 2.

ΔH^\ddagger overall would be low or even negative if the enthalpy change for the pre-equilibrium step is negative. This is possible if energy is released in the formation of the new $\text{Fe}^{2+}-\text{O}$ bond as well as from the interaction of the d-electrons of the two metal centers. For a reaction such as (8), ΔS^\ddagger would have large negative values. Hence, the observed activation parameters are more consistent with an inner-sphere mechanism. The lack of ionic strength dependence of k_2 is not surprising according to this mechanism since $k_2 = k_{10}k_{11}/(k_{-10}k_{11})$, a product of several terms.

The self exchange rate of $\text{Ru}(\text{VI})/\text{Ru}(\text{V})$ is rather rapid ($k = 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), so the outer-sphere pathway should be particularly favored for reactions with large driving force. In the present case, the reduction of $\text{Ru}(\text{VI})$ to $\text{Ru}(\text{V})$ by Fe^{2+} is uphill by 0.21 V (the overall reaction is, however, downhill by 0.23 V since $E_{1/2}$ for $\text{Ru}(\text{VI})/\text{Ru}(\text{IV}) = 0.90 \text{ V}$), and the inner-sphere pathway seems to be more favored. However, since k_2 is close to the rate constant for the theoretical outer-sphere pathway, it is likely that both inner-sphere and outer-sphere pathways are occurring simultaneously. For more uphill reactions it is possible that inner-sphere pathways will be predominant.

Acknowledgements

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