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The Kinetics of the Reaction Between tris-ethylendiamineruthenium(III) Cation and Titanium(III) Complexes

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Reactions between Ru(III) and Ti(III) complexes follow both outer-sphere [1] and inner-sphere [2] electron-transfer (hereafter ET) mechanisms. The kinetics of such reactions differ in important ways from kinetics of other well-studied redox systems (*e.g.* Co(III)–Cr(II) reactions) for reasons which include the unusual symmetry-match between the electron-donor and electron-acceptor orbitals involved. In The Ru(III)–Ti(III) case, both are t_{2g} orbitals and π–π overlap facilitates ET. We now report results of a study of the reaction of $Ru(en)_3^{3+}$ with Ti^{3+}, which provides detailed information on the outer-sphere mechanistic path.

Experimental

tris-Ethylendiamineruthenium(III) bromide was prepared by the method of Meyer [3], its properties (ϵ_{312} = 340) agreed with the literature. (ϵ_{312} = 360 ± 25) Ti(III) solutions were prepared by dissolving the metal in dioxygenated HCl, and standardized by usual methods [1]. Ru(III) solutions were used within one hour of preparation, to avoid complications due to hydrolytic decomposition of the complex (indicated by presence of a peak at 450 nm in the visible spectrum). Kinetic measurements were made at 302 nm using Durum and Aminco-Morrow stopped flow spectrometers. Pseudo-first-order rate plots were linear for at least two half-times and reproducible to within 5%. Reaction of $Ru(en)_3^{3+}$ with Ti(III) (under second-order conditions) results in an increase in absorbance at 302 nm which corresponds to 1.0/1.0 stoichiometry, using 1020 as ϵ_{302} of $Ru(en)_3^{2+}$. Kinetics of the reaction of $Ru(en)_3^{3+}$ with the Ti(III) complex of EDTA were measured at 302 nm using a Durum-Gibson stopped flow spectrophotometer thermostatted at 25 °C.

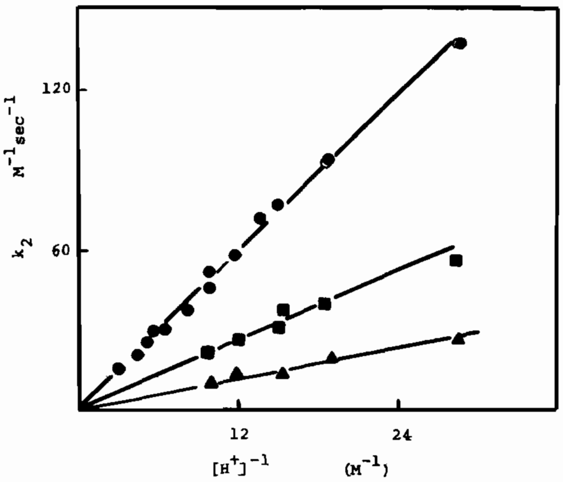

Fig. 1. Variation of k_2 with inverse acidity at 25.0, 15.0 and 5.0 °C (top to bottom). All measurements were made in 1 *M* LiCl media.

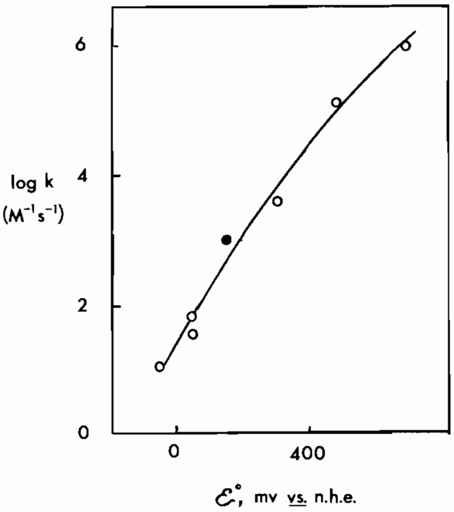

Fig. 2. Comparison of rate constants for reduction by $TiOH^{2+}$ with reduction potentials for a number of Ru(III) oxidants. The filled point represents $Ru(en)_3^{3+}$. The open points represent data reported in reference 1 for $Ru(NH_3)_5Cl^{2+}$, $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5H_2O^{3+}$ and related oxidants. The line corresponds to eqn. 2. Data refer to 1 *M* LiCl media at 25.0 °C.

Results

The kinetic data shown in Table I are adequately fitted by the rate law (1):

$$\text{rate} = k[Co(III)][Ti(III)][H^+]^{-1} \qquad (1)$$

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TABLE I. Rate Constants for the Reduction of $Ru(en)_3^{3+}$ Cation[a] by Ti(III) in Chloride Media (μ = 0.1 M LiCl).

$[H^+]$ mM	$[Ti^{3+}]$ mM	k_1 sec^{-1}	k_2[b] M^{-1} sec^{-1}	k[c] sec^{-1}
A 25 °C				
35.0	9.06	1.24	137	4.8
54.2	9.06	0.839	92.6	5.0
65.7	9.06	0.728	80.4	5.3
66.1	18.1	1.34	74.0	4.9
66.1	18.1	1.31	72.4	4.8
66.1	18.1	1.34	74.0	4.9
66.1	18.1	1.41	77.9	5.1
73.4	9.06	0.626	69.1	5.1
84.9	9.06	0.513	56.6	4.8
85.3	18.1	1.04	57.5	4.9
102	18.1	0.917	50.6	5.2
104	18.1	0.806	44.5	4.7
122	9.1	0.320	35.2	4.4
160	18.1	0.532	29.4	4.7
160	9.06	0.264	29.2	4.7
172	36.2	0.976	27.0	4.6
172	36.2	1.01	27.9	4.8
189	22.7	0.539	23.7	4.5
189	22.7	0.544	23.9	4.5
235	22.7	0.451	19.8	4.6
235	22.7	0.454	20.0	4.6
235	36.2	0.711	19.6	4.6
235	36.2	0.660	18.2	4.3
235	54.4	1.02	18.8	4.4
235	54.4	1.02	18.8	4.4
297	54.4	0.808	14.8	4.4
				5.0 ± 0.2 sec^{-1}
B 15.0 °C				
35.0	9.06	0.484	53.4	1.9
54.2	9.06	0.368	40.5	2.2
65.7	9.06	0.349	38.5	2.5
66.1	18.1	0.553	30.6	2.0
84.9	9.06	0.226	24.9	2.1
85.3	18.1	0.440	24.3	2.1
104	18.1	0.346	19.1	2.0
				2.1 ± 0.3 sec^{-1}
C 5.0 °C				
35.0	9.06	0.229	25.3	0.89
54.2	9.06	0.174	19.2	1.0
65.7	9.06	0.164	18.1	1.2
66.1	18.1	0.259	14.3	0.95
84.9	9.06	0.122	13.5	1.2
85.3	18.1	0.216	11.0	1.0
104	18.1	0.166	9.17	0.96
				1.1 ± 0.1 sec^{-1}
D 25.0 °C – EDTA present				
35.0	0.876[d]	68.5	78.2[e]	2.7[f]
54.2	0.994[d]	47.4	47.7[e]	2.6[f]
73.4	0.741[d]	29.5	39.8[e]	2.9[f]

[a] Concentration of $Ru(en)_3^{3+}$, 1 to 2 mM. [b] $k_2 = k_1/[Ti(III)]$. [c] $k = k_2[H^+]$. [d] Concentration of EDTA, $[Ti^{3+}]$ is 9.06 mM. [e] 10^{-3} k_2, where $k_2 = k_1/[EDTA]$. [f] 10^{-3} k where $k = k_2[H^+]$.

Figure 1 shows the variation of second-order rate constant with $[H^+]$ at three temperatures. These data are adequately fitted by eqn. 1 if the activation parameters associated with k are $\Delta H^* = 52 \pm 6$ kJ/mol and $\Delta S^* = -65 \pm 26$ J/mol-K.

The redox potential for the $Ru(en)_3^{3+/2+}$ couple was found to be 0.101 V *vs.* n.h.e. in sulfate media (μ = 1.0 M), $[H^+]$ = 0.02 *M*, sweep rate 0.006 V/sec. Since the potential found for $Ru(NH_3)_6^{3+}$, under the same conditions was +0.001 V *vs.* n.h.e., we take 0.15 V *vs.* n.h.e. as the value for ϵ^0 for the $Ru(en)_3^{3+,2+}$ couple on the same scale as previously used.

Discussion

The acid-dependence of rate indicates that $TiOH^{2+}$, rather than Ti^{3+}, is the reductant. In view of the lack of suitable lead-in group on the oxidants, the outer-sphere mechanism is expected. The kinetics follow the pattern observed for outer-sphere reactions, rather than that for inner-sphere reactions. Figure 2 shows the comparison of all outer-sphere Ru(III)–Ti(III) data now available with Ru(III) reduction potential. The free energy relationship is approximately linear, but some curvature is clearly seen. The data are adequately fitted by eqn. 2.

$$\log k = 1.40 + 8.50\,\epsilon\,(V) - 2.50(\epsilon(V))^2 \qquad (2)$$

The form of this equation is expected on theoretical grounds, but the curvature is less than predicted [6].

The data indicate that the second order rate constant for reduction of $Ru(en)_3^{3+}$ by $Ti(EDTA)H_2O^-$ ($k'_2 = k/K_a$, where $K_a = 5 \times 10^{-2}$) [5] is 3×10^5 M^{-1} s^{-1}. This value is much larger than would be expected on the basis of the corresponding Co(III)–Ti(III) reactions [5].

The value of ΔH^* reported here is lower than that for any other Ru(III)–Ti(III) outer-sphere redox reactions. The effect of this is offset by the entropy of activation, which is more negative than that for any other outer-sphere Ru(III)–Ti(III) reaction. For other Ru(III)–Ti(III) outer-sphere redox reactions ΔH° decreases as E° for reduction of Ru(III) becomes more positive indicating that variation in metal–ligand electronic interaction is dominant in determining variations in ΔH^*.

$Ru(en)_3^{+3}$ is an exception to this generalization, and its ΔH^* is at least 10 kJ/mol lower than would be expected, on the basis of previously-studied reactions. The most plausible interpretation of this result is that the presence of the chelate ring prevents approach of Ti(III) along certain directions, but restrains ligand vibrations such that approach along other directions (the octahedral face, say) is enhanced. This gives rise to lowered ΔH^*, but the former effect makes ΔS^* more unfavorable. If the interaction between electron-donor and electron-acceptor orbitals is an important determinant of ΔH^* then a small reduction in metal–metal distance should cause a large decrease in ΔH^*.

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