10^4. This rate enhancement may explain the absence of a Cl^- effect on the $Ru(H_2O)_5NO^{3+}$–Cr^{2+} reduction.

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Registry No. I, 64294-49-1; II, 64294-50-4; $[(NH_3)_5Ru\text{-}NH\text{-}Cr(H_2O)_5]^{5+}$, 64294-51-5; $[Ru(NH_3)_5NO](TFMS)_3$, 64200-43-7; $K_2[RuCl_5(H_2O)]$, 14404-33-2; $Ru(H_2O)_6^{2+}$, 30251-71-9; $Ru(H_2O)_6^{3+}$, 30251-72-0; $Ru(H_2O)_5NO^{3+}$, 56586-57-3; $K_2[RuCl_5NO]$, 14854-54-7; $[Ru(NH_3)_5OH_2]^{3+}$, 25590-52-7; $[Cr_2(OH)_2]^{4+}$, 12323-96-5; $Ru(NH_3)_5Cl_3$, 18532-87-1; *trans*-$[Ru(NH_3)_4NO(Cl)]^{2+}$, 20094-12-6; *trans*-$[Ru(NH_3)_4NO(OH)]^{2+}$, 52720-69-1; *cis*-$[Ru(NH_3)_4NO(Cl)]^{2+}$, 52707-08-1; $Cr(H_2O)_6^{3+}$, 14873-01-9; $Cr(H_2O)_6^{2+}$, 20574-26-9.

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Contribution from the Departments of Chemistry, Georgetown University, Washington, D.C. 20057,
and George Mason University, Fairfax, Virginia 22030

Kinetics of Reduction of $Ru(NH_3)_6^{3+}$ and of $Ru(NH_3)_5Cl^{2+}$ by Ti(III)

PURUSHOTHAMAN CHALILPOYIL, KEITH M. DAVIES, and JOSEPH E. EARLEY*

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Both $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ (in Cl^- and $CF_3SO_3^-$ media) are reduced by Ti(III) in second-order reactions. Rate constants for both reactions are inversely proportional to $[H^+]$, indicating that $TiOH^{2+}$, not Ti^{3+}, is the reductant. Rate constants (at 25 °C) for reduction by $TiOH^{2+}$ are 35 and 12 M^{-1} s^{-1}; corresponding activation enthalpies are 41 and 33 kJ/mol. Outer-sphere electron transfer is indicated for both reactions. The relative values of the rate constants accord with expectations based on the free-energy changes involved.

Since Ti^{3+} is a d^1 ion and Ru(III) complexes are low-spin d^5, Ti(III)–Ru(III) redox reactions involve t_{2g} orbitals both as donor and as acceptor orbitals. In the expectation that this circumstance would lead to interesting redox behavior, we have studied reduction of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ by Ti^{3+}. Since both Ti^{3+} and Ru(II) reduce ClO_4^-, we used Cl^- and $CF_3SO_3^-$ media.

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* To whom correspondence should be addressed at Georgetown University.

Experimental Section

Materials. Reagents were generally prepared as previously described.[1] Chloride and bromide salts of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ were prepared by the method of Ferguson and Love.[2] Spectra agreed with those in the literature. Anal.[3] Calcd for $Ru(NH_3)_6Br_3$: Ru, 22.8; N, 19.0; Br, 54.1. Found: Ru, 22.4; N, 19.5; Br, 52.7.

Kinetic Measurements. Rates of reaction were measured spectrophotometrically using a Gilford 2400 spectrophotometer with a thermostable 10-cm cell compartment. For reduction of $Ru(NH_3)_5Cl^{2+}$, the decrease of absorbance at the absorbance maxima of the oxidant (328, 345 nm) was followed. For $Ru(NH_3)_6^{3+}$, the increase in absorbance at 275 nm, where both $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ have maxima (ϵ 475, 624), was followed. Reactions were initiated by injecting Ti^{3+} by means of Pt needles. Ti^{3+} was normally in large excess. Pseudo-first-order rate plots were linear for at least 2 half-times unless otherwise noted. Increase of absorbance below 300 nm occurred during the reaction. Rate constants for replicate runs agreed within 5%.

Spectral changes during the reaction between $Ru(NH_3)_6^{3+}$ and Ti^{3+} in $CF_3SO_3^-$ media were more complex than those for the same reaction in Cl^- media. In $CF_3SO_3^-$ media, an additional absorbance peak developed around 400 nm and intense absorbance in the UV changed the ruthenium peaks into shoulders. When reactions in $CF_3SO_3^-$ media were followed at 275 nm, rate plots were linear for only about 1 half-time. In the case of $Ru(NH_3)_5Cl^{2+}$, autocatalysis was observed in $CF_3SO_3^-$ media, but not in Cl^- media. Estimates of initial rates from runs in $CF_3SO_3^-$ media gave rate constants consistent with those observed from rate plots in Cl^- media.

Results and Discussion

In chloride media, with either Ru(III) oxidant in excess, spectral changes during reaction indicated a 1/1 ratio between amounts of Ru(III) reduced and of Ti(III) oxidized. The kinetic data, shown in Table I, show that the observed first-order rate constant, k_1, is proportional to [Ti(III)] and that the second-order rate constant ($k_2 = k_1/[\mathrm{Ti(III)}]$) is inversely proportional to $[H^+]$ ($k_2 = k/[H^+]$). Activation parameters for the temperature variation of the acid-independent rate constant, k, are shown in Table II.

Since Ti^{3+} reduces perchlorate ion, media other than those usually used for kinetic studies of redox reactions had to be used. Media involving the noncomplexing trifluoromethanesulfonate ion gave complex kinetics, but Cl^- media gave simpler results. It appears[1,4] that the stability of complexes formed between Ti^{3+} and Cl^- is quite low. The kinetic complications which are observed in reduction of $Ru(NH_3)_6^{3+}$ by Ti^{3+} in $CF_3SO_3^-$ media seem to be due to subsequent reactions of the Ti(IV) products of the initial redox reaction. The changes in the UV region of the spectrum are best understood as resulting from Ti(IV) polymerization which can be retarded by high concentrations of Cl^-. The peak around 400 nm which appears when $Ru(NH_3)_6^{3+}$ is reduced in $CF_3SO_3^-$ (but not in Cl^-) media appears to be due to products formed after loss of NH_3 by the initial Ru(II) product.[5] Deviations from first-order kinetic plots for reduction of $Ru(NH_3)_5Cl^{2+}$ in trifluoromethanesulfonate media are in a direction that indicates autocatalysis. The following sequence explains[6] this complication:

$$Ru(NH_3)_5Cl^{2+} + Ti(III) \rightarrow Ru(NH_3)_5Cl^{+} + Ti(IV) \qquad (1)$$

$$Ru(NH_3)_5Cl^{+} + H_2O \rightarrow Ru(NH_3)_5(H_2O)^{2+} + Cl^- \qquad (2)$$

$$Ru(NH_3)_5Cl^{2+} + Ru(NH_3)_5(H_2O)^{2+} \rightarrow Ru(NH_3)_5(H_2O)^{3+} + Ru(NH_3)_5Cl^{+} \qquad (3)$$

$Ru(NH_3)_5Cl^+$ produced through process 1 can be reused in the step described by (3), in a catalytic conversion of $Ru(NH_3)_5Cl^{2+}$ to $Ru(NH_3)_5(H_2O)^{3+}$. The aquation of $Ru(NH_3)_5Cl^+$ (eq 2) can be driven to the left by the presence of a high concentration of Cl^- in solution, thus forestalling

Table I. Rate Constants for Reduction of Ru(III) Cations by Ti(III) (μ = 1.0 M)[a]

$[H^+]$, mM	[Ti(III)], mM	T, °C	$10^3 k_1$,[g] s^{-1}	k_2,[h] M^{-1} s^{-1}	$10^2 k$,[i] s^{-1}
		$Ru(NH_3)_6^{3+}$ [b]			
46.8	5.4	25.0	18.6	3.44	16
46.8	10.8	25.0	37.3	3.45	16
69.9	5.4	25.0	13.1	2.42	17
69.9	21.7	25.0	52.5	2.42	17
80.4	21.7	25.0	55.0	2.54	20
100.1	5.4	25.0	9.43	1.74	17
112.7	5.4	25.0	7.55	1.39	16
132.2[c]	10.8	25.0	14.3	1.32	17
156.6	5.4	25.0	6.08	1.12	17
178.8	10.8	25.0	9.96	0.920	16
205.9	11.0	25.0	9.43	0.855	18
222.8	10.8	25.0	9.47	0.874	19
245.2[c]	21.7	25.0	14.0	0.647	16
299.4	5.4	25.0	3.70	0.683	20
322.0	21.7	25.0	11.5	0.531	17
77	4.9	25.0[d,e]	$30._4$	6.2	~48
101	6.1	25.0[d,e]	$30._9$	4.5	~45
125	4.9	25.0[d,e]	$36._3$	7.4	~93
46.8	5.4	17.0	7.30	1.35	63
69.9	5.4	17.0	4.78	0.883	62
100.1	5.4	17.0	4.05	0.749	75
112.7	5.4	17.0	3.59	0.663	74
156.6	5.4	17.0	2.42	0.448	70
178.8	10.8	17.0	3.61	0.333	59
200.8	10.8	17.0	4.33	0.400	80
222.8	10.8	17.0	2.30	0.212	47
245.2	21.7	17.0	5.98	0.276	68
299.4	5.4	17.0	1.48	0.272	81
46.8	5.4	10.0	3.04	0.560	26
69.9	5.4	10.0	2.19	0.404	28
112.7	5.4	10.0	2.10	0.388	43
156.5	5.4	10.0	1.08	0.199	31
200.8	10.8	10.0	1.43	0.132	26
245.2	21.7	10.0	2.39	0.110	27
299.4	5.4	10.0	0.564	0.104	32
		$Ru(NH_3)_5Cl^{2+}$ [f]			
10.0	0.989	25.0	5.55	5.61	5.6
17.5	0.980	25.0	2.89	2.95	5.2
22.4	8.13	25.0	30.9	3.80	8.5
32.7	1.26	25.0	2.14	1.70	5.6
40.1	2.15	25.0	2.96	1.38	5.5
55.4	8.13	25.0	11.0	1.35	7.5
70.4	2.04	25.0	1.64	0.804	5.7
88.2	5.05	25.0	3.57	0.707	4.4
105	8.13	25.0	4.95	0.609	6.4
113	4.16	25.0	2.08	0.500	5.6
137	10.1	25.0	4.71	0.467	6.4
154	3.86	25.0	1.41	0.305	5.6
179	10.3	25.0	3.50	0.340	6.1
204	8.13	25.0	2.14	0.263	5.4
255	10.1	25.0	2.07	0.205	5.2
24.8	2.22	33.2	11.4	5.13	12.7
50.5	2.22	33.2	5.92	2.67	13.4
75.1	2.22	33.2	3.98	1.79	13.4
101	2.31	33.2	3.04	1.32	13.3
149	4.17	33.2	3.90	0.935	13.9
200	4.32	33.2	3.04	0.704	14.0
20.0	5.56	15.5	8.08	1.45	0.029
39.8	2.35	15.5	1.20	0.511	0.020
58.0	5.56	15.5	2.18	0.392	0.023
75.9	5.56	15.5	1.50	0.270	0.020
97.2	5.76	15.5	1.13	0.196	0.019
118	4.70	15.5	0.755	0.161	0.019
180	5.56	15.5	0.611	0.110	0.020
195	4.88	15.5	0.491	0.101	0.020

[a] LiCl unless otherwise noted. [b] [Ru(III)] = 0.1–0.3 mM. [c] Bromide salt of oxidant. [d] $CF_3SO_3^-$ medium. [e] Initial rate measurement. [f] [Ru(III)] = 0.06–0.12 mM. [g] k_1 is the observed pseudo-first-order rate constant. [h] $k_2 = k_1/[Ti^{3+}]$. [i] $k = k_2[H^+]$.

Table II. Activation Parameters for Reduction of Ru(III) by Ti(III)

Oxidant	$10^2 k$, s^{-1} (25 °C)	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/(deg mol)	$10^{-1} k_2$, $M^{-1} s^{-1}$ (25 °C)	$\Delta H^{\ddagger\prime}$,[a] kJ/mol	$-\Delta S^{\ddagger\prime}$,[a] J/(deg mol)
$Ru(NH_3)_6{}^{3+}$	17.5 ± 1.0	82 ± 4	17 ± 12	$3._5$	41 ± 10	~70
$Ru(NH_3)_5Cl^{2+}$	6.1 ± 4	75 ± 4	−17 ± 12	$1._2$	33 ± 10	~100

[a] For reduction by $TiOH^{2+}$, on the assumption that K_a for acid dissociation of Ti^{3+} (at 25 °C) is 5×10^{-3} M and the corresponding $\Delta H°$ is 42 kJ/mol.

autocatalysis in Cl^- media. For both $Ru(NH_3)_6{}^{3+}$ and $Ru(NH_3)_5Cl^{2+}$, the redox rate constants, which are estimated from the more complicated rate plots observed for reactions carried out in $CF_3SO_3{}^-$ media, agree well with the more precisely determined values corresponding to reductions in Cl^- media. In Cl^- media, the spectrum of the ruthenium product obtained on reduction of $Ru(NH_3)_6{}^{3+}$ is that of $Ru(NH_3)_6{}^{2+}$, not that of $Ru(NH_3)_5Cl^{2+}$. It may be concluded that Cl^- is an innocent medium anion for these systems. It seems likely that the base catalysis which we observe results from $TiOH^{2+}$, rather than Ti^{3+}, being the reducing agent for these reactions, so that $k = k_2K_a$, where K_a is the acidity constant of Ti^{3+}, about 5×10^{-3} M under our conditions. Part of the temperature dependence of the overall redox rate constant is due to change in K_a with change in temperature.

Pecsok and Fletcher[7] studied the effect of temperature on the K_a of Ti^{3+} by potentiometric titration, but they stated that their results are not precise enough to determine $\Delta H°$ and $\Delta S°$ for the acid dissociation. The value of $\Delta H°$ for the acid dissociation of V^{3+} is ca. 42 kJ mol^{-1},[8] and other M^{3+} ions are similar in this respect. If we assume that this value applies to Ti^{3+} as well,[9] then the activation parameters, $\Delta H^{\ddagger\prime}$ and $\Delta S^{\ddagger\prime}$, which pertain to reduction by $TiOH^{2+}$, would be those shown in the last two columns of Table II. After the correction, the values of $\Delta H^{\ddagger\prime}$ fall in the usual range for electron-transfer reactions and those of $\Delta S^{\ddagger\prime}$ are not far from the usual range.

Using the present results, published kinetic and redox potential data, and Marcus' cross relationship,[10] the self-exchange rate constant for the $TiOH^{2+}$–TiO^{2+} couple at 25 °C was estimated to be 0.01 M^{-1} s^{-1}, which is the same as the corresponding value for the V(II)–V(III) couple.[11]

The observation that the rate of reduction of $Ru(NH_3)_6{}^{3+}$ is somewhat faster than the rate of reduction of $Ru(NH_3)_5Cl^{2+}$ is consistent with the fact that the reduction potential of the former ion is somewhat more positive than that of the latter.[12] The magnitude of the rate difference is close to what would be expected for $\Delta\Delta G^{\ddagger}/\Delta\Delta G° = 0.5$.[13]

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Registry No. $Ru(NH_3)_6{}^{3+}$, 18943-33-4; $Ru(NH_3)_5Cl^{2+}$, 21560-19-0; Ti(III), 22541-75-9.

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