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Hydroxide Ion as a Bridging Ligand for Inner-Sphere Electron-Transfer Between Co(III) and Ti(III)

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In M *LiCl at 25 °C,* $Co(NH_3)_5Br^{2+}$ *reacts with* $TiOH^{2+}$ *with* $k_2 = 0.18$ M^{-1} s^{-1}. $Co(NH_3)_5F^{2+}$ *reacts with* Ti^{3+} *with* $k_2 = 1 \times 10^3$ M^{-1} s^{-1}. *For* $Co(en)_2(H_2O)(OH)^{2+}$ *ions, rate constants for reaction with* Ti^{3+} *are* 50 M^{-1} s^{-1} *for* trans *and* 20 M^{-1} s^{-1} *for* cis*: for the same oxidants, rate constants for reaction with* $TiOH^{2+}$ *are* 3×10^3 M^{-1} s^{-1} *for* cis *and* 4×10^3 M^{-1} s^{-1} *for* trans. *The reactions with rate constants near* 10^3 M^{-1} s^{-1} *are interpreted as substitution-limited inner-sphere processes. Bromide ion is a poor bridging ligand for Co(III)-Ti(III) electron transfers while hydroxide ion and (especially) fluoride ion are efficient bridging ligands; cross-bridge interactions are more important for reactions of Ti(III) than for reactions of Cr(II).*

Introduction

Cr^{2+} reduces Co(III) complexes by means of both outer-sphere and inner-sphere mechanisms: which reaction-path is followed is determined by which ligands are present in the Co(III) coordination sphere. The same two mechanisms also operate in the case of reductions of Co(III) complexes by Ti^{3+}, but the detailed nature of the influence of potential bridging ligands is different. For instance Cl^- is an efficient bridge for Cr(II)–Co(III) electron transfer, but not for the corresponding Ti(III)–Co(III) processes. We now report results of experiments [1, 2] which bear on this effect, particularly as it applies to OH^- as an electron-transfer ligand.

Experimental

Reagents were generally prepared as previously described [3]. Paratoluenesulfonic acid (hereafter HTos) was recrystallized from water. $[Co(NH_3)_5F](NO_3)_2$ was prepared by a published method [4] and converted to the iodide by treating a solution with a KI/HI solution. *Anal.* [5] %Found/%Calcd. for $[Co(NH_5)_5F]I_2$: Co, 14.3/14.2; N, 16.7/16.8; H, 3.5/3.6; F, 4.4/4.6; I, 61.1/60.9. $[Co(NH_3)_5Br]Br_2$ [6] gave the analysis (%Found/%Calcd.) Co, 15.4/15.4; N, 18.3/18.3; H, 3.9/3.9; Br, 62.3/62.5. *Trans*-hydroxoaquobis(ethylenediamine)cobalt(III) perchlorate was prepared as described [7]. *Anal.* %Found/%Calcd. for t-$[Co(en)_2(H_2O)(OH)](ClO_4)_2$: C, 11.8/11.6; H, 4.6/4.6; N, 13.6/13.6; Cl, 17.1/17.0. A solution of this salt was passed through a Dowex 50 ion-exchange column, washed free of ClO_4^- by 0.1 *M* HTos and eluted with 0.3 *M* HTos-2 *M* LiTos solution. The product, in 0.35 *M* HTos and 0.68 *M* LiTos, gave a visible spectrum [λ, nm(ε)]; 450 (37); 443 (42); 350 (68.6-sh). This solution of *trans*$[Co(en)_2(H_2O)_2]^{3+}$ was stored in the frozen state. *Cis*-aquohydroxobis-ethylenediaminecobalt(III) bromide monohydrate was prepared [7] and gave a spectrum agreeing with the literature [λ, nm(ε)]: 492 (78); 355 (65). *Anal.* [5] (%Found/%Calcd.): C, 12.5/12.2; H, 5.1/5.4; N, 14.2/14.3. A suspension of freshly-prepared $[Co(en)_2CO_3]Br$ [7] was treated with HTos and the product freed from Br^- using Dowex 50. In 0.3 *M* HTos-0.7 *M* LiTos, the product *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ showed two peaks in its spectrum: [λ, nm(ε)]; 492 (78); 356 (66).

Ti(III) solutions, in chloride media, were prepared as described [4]. Titanium sponge was dissolved in deaerated 2 *M* HTos by heating for one week. The resulting solution was placed on a deaerated Dowex 50 column and washed free of $SO_4^=$ using 0.1 *M* HTos: a solution of Ti(III) in 0.3 *M* HTos-2 *M* LiTos was obtained by elution, and stored frozen. Ti(III) solutions were generally handled using platinum needles and nitrogen atmospheres.

Kinetics were measured spectrophotometrically as previously [3] described by following change in absorbance at a wavelength of maximum absorbance of the Co(III) salt in the region 350–360 nm. Either first or second order rate plots were used, as appropriate. When $[H^+]$ >0.05 M rate plots were linear

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for two half-times, for less-acidic solutions complications due to polymerization of Ti(IV) were encountered, and initial slopes (to ~25% reaction) were used to compute rates

Results

Each reaction gave a 1/1 ratio of Co(III) consumed per mole of Ti(III) reactant (within 10%) when studied under second-order conditions Deviations from that stoichiometry occurred in some experiments when small amounts of perchlorate ion were present Some such deviations were found to be due to trace contamination caused by the use of stainless steel needles Complications were absent when platinum needles were used, unless trace amounts of Ni^{2+} were also added Table I shows results of kinetic experiments

TABLE I Rates of Reduction of Co(III) Complexes by Ti(III) in Aqueous Media

$[H^+]$, mM	[Ti(III)], mM	$k_2 \times 10^3$ m^{-1} s^{-1}
A) $Co(NH_3)_5Br^{2+}$, (0 2 to 0 5 mM), μ = 1 0 (LiCl), 25 °C		
50 2	86 6	1 17
91 3	21 7	8 43
91 3	43 4	9 86
70 0	43 4	11 8
46 5	21 7	15 7
46 5	43 4	16 1
18 9	8 67	39 0
12 3	5 42	48 0
B) $Co(NH_3)_5F^{2+}$, (1 to 2 mM), μ = 1 (LiCl), 25 °C		
32 5	15 4	714[b]
65 0	30 9	599[b]
129	61 7	395[b]
255	123 5	283[b]
255	30 9	282[b]
255	61 7	279[b]
450	123 5	130[b]
630	61 7	11 9[b]
720	30 9	76 1[b]
815	30 9	125[b]
C) *cis*-$Co(en)_2(H_2O)_2^{3+}$, (0 3 to 1 mM), 1 0 *M* LiCl, 25 °C		
46 8	5 42	10 3
55 2	5 42	7 49
55 2	10 8	7 47
55 2	21 7	7 56
67 2	21 7	5 70
80 4	21 7	4 00
125 2	43 3	2 04
167[c]	7 59	1 47
136[c]	7 59	1 85
D) *cis*-$[Co(en)_2(H_2O)_2]^{3+}$, LiTos, 2 *M*, 24 °C		
173	11 0	1 88
266	11 0	0 990
358	11 0	0 676
451	11 0	0 486
514	1 68	4 41
205	3 04	9 92
186	3 04	9 69
205	4 88	7 25
205	3 09	8 82
E) *trans*-$[Co(en)_2(H_2O)_2]^{3+}$, μ = 1 0 (LiTos), 24 °C		
195	5 97	22 2
358	6 18	8 2
254	6 18	17 8
223	6 18	26 0
117	3 09	60 7

[a] Observed pseudo-first-order rate constant divided by [Ti(III)] [b] These rate constants not multiplied by 10^3, as all the others in this column are [c] LiTos, 24 °C

Oxidation of Ti(III) by both $Co((NH_3)_5Br^{2+}$ and by $Co(NH_3)_5F^{2+}$ follow the rate law given by eqn (1)

$$\text{rate} = \frac{kK}{K + [H^+]} [Co(III)] [Ti(III)] \qquad (1)$$

For $Co(NH_3)_5Br^{2+}$, the acid-dissociation of $Ti(H_2O)_6^{3+}$ provides a sufficient interpretation of the acid-dependence of the rate Using 5×10^{-3} *M* as the equilibrium constant for that process [3], leads to the value of 0 18 (±0 02) M^{-1} s^{-1} for the second-order rate constant for reaction between $TiOH^{2+}$ and $Co(NH_3)_5$-Br^{2+}

In the case of $Co(NH_3)_5F^{2+}$, however, this interpretation is not sufficient to rationalize the data, which require K = 0 07 *M* and k = 1 1 $\times$ 10^3 M^{-1} s^{-1}

Both *cis* and *trans*-diaquo ions follow an acid dependence which is qualitatively different from that followed by the $Co(NH_3)_5X^{2+}$ ions A plot of $k[H^+]$ *vs* $[H^+]^{-1}$ is linear in both cases, indicating a rate law of the form of eqn (2)

$$\text{rate} = \left(\frac{k''}{[H^+]} + \frac{k'''}{[H^+]^2}\right) [Co(III)] [Ti(III)] \qquad (2)$$

For the *cis*-ion, k″ is 1 4 $\times$ 10^{-4} s^{-1} (at both μ = 1 and μ = 2) and k‴ is 1 6 $\times$ 10^{-5} *M* s^{-1} for μ = 1 0 and 5 5 $\times$ 10^{-5} *M* s^{-1} for μ = 2 0 For the *trans*-ion k″ is 2 $\times$ 10^{-3} s^{-1} and k‴ is 6 $\times$ 10^{-4} M^{-1} s^{-1} for μ = 1

Discussion

The reduction of $Co(NH_3)_5Br^{2+}$ is best interpretated as an outer-sphere electron-transfer between

$Co(NH_3)_5Br^{2+}$ and $TiOH^{2+}$. The second-order rate constant reported here is somewhat larger than previously reported values, but is still consistent with the rate to be expected for such a process on the basis of linear free-energy correlations [9]. The large value of K observed for $Co(NH_3)_5F^{2+}$ might be due to a prior deprotonation of the conjugate acid of the oxidant [10], or to a two-step mechanism involving a deprotonated intermediate.

If $Co(NH_3)_5FH^+$ had an acid-dissociation constant near 0.1 *M*, this species should have been detected in other kinetic or spectrophotometric studies. Absence of any evidence of protonation of the oxidant strongly favors the mechanism:

$$Ti(H_2O)_6^{3+} + Co(NH_5)_5F^{2+} \xrightleftharpoons[k_{-1}]{k_1} (H_2O)_5TiFCo(NH_3)_5^{5+}$$

$$(H_2O)_5TiFCo(NH_3)_5^{5+} \xrightleftharpoons{K'} HO(H_2O)_4TiFCo(NH_5)_5^{4+} + H^+$$

$$(HO)(H_2O)_4TiFCo(NH_3)_5^{4+} \xrightarrow{k_3} TiO^{2+} + Co^{2+} + HF + 5NH_4^+$$

The low-acid limiting rate is close to that observed for reaction of Ti(III) with [10] $Ru(NH_3)_5OOCCH_3^{2+}$ and with [11] $Ru(NH_3)_5NCS^{2+}$. This indicates that the factors which reduce the rates of Co(III) reductions, relative to those for Ru(III) reductions [12], are not important in these cases. This indicates that all three reductions are rate-limited by the same process, displacement of water from $Ti(H_2O)_6^{3+}$. A value of 10^3 M^{-1} s^{-1} then corresponds to k_1. The value of K is a combination of k_{-1}, K′ and k_3. Since it has been reported that TiF_2^+ has unusually high stability [13], it would be expected that K′ would be large.

The first term in rate law 2 might be interpreted as either reaction of $TiOH^{2+}$ with the diaquo ion or reaction of the hydroxo-ion with Ti^{3+}. The most reasonable mechanism for the second term is reaction of the aquo-hydroxy ions with $TiOH^{2+}$. This ratio of rates of reaction of *trans* and *cis* $Co(en)_2Cl_2^+$ with $TiOH^{2+}$ is about 4.5 in contrast to the ratio of 30 found for both rate constants of eqn. (2). The pK_a values for the diaquo ions are [14] 6.0 for *cis* and 4.5 for *trans*. The most coherent interpretation is to consider both terms of eqn. (2) to correspond to reactions of aquohydroxo-oxidants, with Ti^{3+} and $TiOH^{2+}$ respectively. On this basis, rate constants for reaction of aquohydroxo-ions with Ti^{3+} are 50 M^{-1} s^{-1} for *trans* and 20 M^{-1} s^{-1} for *cis*, and rate constants for reaction with $TiOH^{2+}$ are 3 X 10^3 M^{-1} s^{-1} for the *cis* ion and 4.10^3 M^{-1} s for the *trans* ion. The rate differences between the *cis* and *trans* ions are rationalized by the differences in acidity of the two ions, within experimental error.

All four rate constants are larger than would be expected for outer-sphere processes. The rate constants for the reaction of the aquohydroxy-oxidants with $TiOH^{2+}$ are close to those for the substitution-limited reactions of Ti(III) discussed above. It is apparent that hydroxide ion is an efficient bridging ligand for Co(III)–Ti(III) electron transfer. (It should be noted that a doubly-deprotonated intermediate could be formulated as a μ-oxo species, which would lead to strong cross-bridge interaction of the metal ions [15]). For Co(III)–Cr(II) reactions F^- is a relatively poor bridging ligand but OH^-, and especially Br^-, are rather efficient. For Co(III)–Ru(III) reactions, Br^- does not function as a bridging ligand but OH^-, and especially F^-, are effective. It seems that the closer approach of the metal atoms (in the intermediate) to one another, permitted by fluorine and oxygen (as compared to bromine), is more important when Ti(III) is reductant than when Cr(II) is reductant.

References

1 The experiments with Co(III) aquo-ions were reported in: S. Z. Ali and J. E. Earley, Paper No. 160, 167th Meeting of the Inorganic Division, American Chemical Society, Los Angeles, Ca., April, 1974.
2 The experiments involving the other oxidants were reported in: P. Chalilpoyil and J. E. Earley, Paper No. 179, Inorganic Division, 169th American Chemical Society Meeting, Philadelphia, April, 1975.
3 (a) M. Orhanovic and J. E. Earley, *Inorg. Chim. Acta, 12,* L16 (1975). (b) M. Orhanovic and J. E. Earley, *Inorg. Chem., 14,* 1478 (1975). (c) P. Chalilpoyil, K. M. Davies and J. E. Earley, *Inorg. Chem., 16,* 3344 (1977).
4 F. Basolo and R. K. Murmann, *Inorg. Synth., 4,* 171 (1953).
5 Galbraith Laboratories, Knoxville, Tennessee.
6 H. Diehl, H. Clark and H. H. Willard, *Inorg. Synth., 4,* 171 (1953).
7 R. D. Cannon and J. E. Earley, *J. Am. Chem. Soc., 88,* 1872 (1966).
8 J. Bjerrum and S. C. Rasmussen, *Acta Chem. Scand., 6,* R65 (1952).
9 G. A. K. Thompson and A. G. Sykes, *Inorg. Chem., 15,* 638 (1976).
10 A. Adegite, J. E. Earley and J. F. Ojo, *Inorg. Chem., 18,* 1535 (1980).
11 R. A. Lee and J. E. Early, *Inorg. Chem.,* in press.
12 P. I. Premovic and P. R. West, *Can. J. Chem., 53,* 1593 (1975).
13 H. C. Stynes and J. A. Ibers, *Inorg. Chem., 10,* 2304 (1971).
14 R. D. Cannon and J. E. Earley, *J. Am. Chem. Soc., 88,* 1872 (1966).
15 P. M. Smith, T. Fealey, J. E. Earley and J. V. Silverton, *Inorg. Chem., 10,* 1943 (1971).
16 G. A. Thompson and A. G. Sykes, *Inorg. Chem., 18,* 1731 (1979).