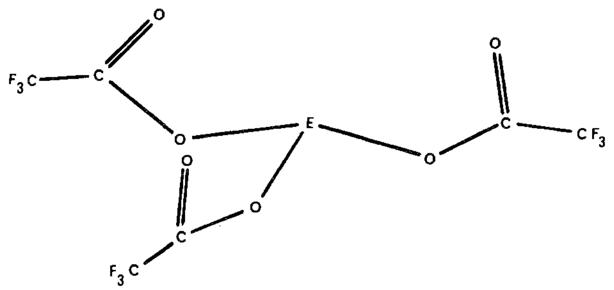

Figure 1. Suggested molecular structure of $E(O_2CCF_3)_3$ (E = P or As).

trasts with the reaction between $(H_2C{=}CH)_4Sn$ and CF_3CO_2H[11] and suggests that cleavage of vinyl atom bonds by trifluoroacetic acid is not a general route to trifluoroacetato complexes. The $(H_2C{=}CH)_3AsH^+$ ion does not appear to have been reported previously, although Forbes et al.[15] have prepared the related species $(H_2C{=}CH)AsEt_3^+$ and $(H_2C{=}CH)(C_{12}H_9)AsMe_2^+$.

Acknowledgment. We thank the S.R.C. for a research studentship to B.H.

Registry No. $P(O_2CCF_3)_3$, 54823-88-0; $As(O_2CCF_3)_3$, 3012-25-7; $Sb(O_2CCF_3)_3$, 54823-89-1; $Bi(O_2CCF_3)_3$, 37442-83-4; $[(H_2C{=}CH)_3AsH]O_2CCF_3$, 54823-90-4; $As(O_2CCF_3)_3{\cdot}N_2C_{10}H_8$, 54823-87-9; $(CF_3CO_2)_3As{\cdot}BBr_3$, 54823-91-5; $AsCl_3$, 7784-34-1; AgO_2CCF_3, 2966-50-9; CF_3CO_2H, 76-05-1; $(H_2C{=}CH)_3As$, 13652-20-5; 2,2'-bipyridyl, 366-18-7; boron tribromide, 10294-33-4.

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Mechanism of the Titanium(III) Reduction of Azido- and Isothiocyanatopentaamminecobalt(III)[1]

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Received November 5, 1974 AIC407642

Although the reduction of substituted cobalt(III)–ammine complexes by various metal ions has received considerable attention in the past, titanium(III) has been largely ignored as a reducing agent. Some work was done in sulfate media,[2,3] where considerable kinetic complications were observed due to the presence of sulfate, or in perchlorate media[2,3] with the halo-, aquo-, and sulfatopentaamminecobalt(III) complexes. The latter studies are complicated by the fact that the $Ti^{III}–ClO_4^-$ reaction,[3-5] although slower than the $Ti^{III}–Co^{III}$ reactions, could be kinetically significant by virtue of a possible intervention of one of the intermediate oxidation states of chlorine. More recently, interest in $Ti^{III}–Co^{III}$ reactions has been reawakened, with some studies being carried out in tosylate media.[6,7] The latter study involved the reaction of Ti(III) with *cis*- and *trans*-$Co(en)_2(H_2O)_2^{3+}$ and evidence was presented to suggest an inner-sphere mechanism for these reactions.[7] However, the question of the mode of electron transfer has remained largely unanswered. Among the several approaches used to attempt to distinguish between inner-sphere and outer-sphere mechanisms for reduction of Co(III) is a comparison of azide and isothiocyanate as potential bridging ligands.[8-11] It is this approach that we wished to investigate for Ti(III), carrying out experiments in chloride media, which we have previously found to be convenient for the study of Ti(III) reactions.[12,13] This criterion is based on the supposition that if the metal centers are hard, preferring N bonding with NCS^-, and if the reactions are inner sphere, involving the transfer of a bridging ligand, then the reaction should proceed much faster when the bridging group is azide than when it is isothiocyanate. For an outer-sphere reaction, the rates of the two reactions are expected to be approximately the same. Although a detailed analysis of this criterion requires that differences in stabilities of precursor complexes be taken into account,[11] the presence of such precursor complexes is an indication of an inner-sphere mechanism, so it should be possible to apply this criterion without regard for whether the rate effects are due to thermodynamic or kinetic factors. We have in fact been able to obtain evidence in favor of an inner-sphere mechanism by applying this criterion and by observing a rate law which suggests the presence of steady-state quantities of a precursor complex in the azide reaction.

Experimental Section

The preparation, storage, handling, and analysis of titanium(III) chloride in aqueous HCl solutions and of HCl, $HClO_4$, LiCl, and $LiClO_4$ solutions have been previously described.[12,14] Thermostating arrangements and procedures for kinetic studies have been described.[14] Kinetic measurements were carried out with a Cary 14 or a Varian Techtron 635 recording spectrophotometer, primarily at 302 nm for $Co(NH_3)_5N_3^{2+}$ (results were identical at 320 and 340 nm) and at 305 or 495 nm for $Co(NH_3)_5NCS^{2+}$. During the long time periods in which measurements were made on the $Ti^{III}–Co(NH_3)_5NCS^{2+}$ solutions at 305 nm, photochemically induced oxidation of Ti(III) apparently occurred,[15] so solutions were stored in the dark between measurements. Reaction solutions were purged with purified nitrogen at least 15 min prior to addition of Ti(III) to prevent possible oxidation by oxygen.

Pseudo-first-order plots of $\ln (D_t - D_\infty)$ vs. time (D = absorbance) were linear for at least 4–5 half-lives in solutions containing no ClO_4^-. When ClO_4^- was present, however, curvature was observed in proportion to the ClO_4^- concentration, due to the $Ti^{III}–ClO_4^-$ reaction.[3-5] The Guggenheim method[16] was used to treat the data in these experiments. Plots were linear for at least 3 half-lives.

The product of the reaction between Ti(III) and $Co(NH_3)_5N_3^{2+}$ was determined to be Co^{2+} by detection with NCS^- in mixed acetone–water solution.[17] No reaction between N_3^- or HN_3 and Ti(III) could be detected over periods long compared to normal reaction times when NaN_3 was added to a solution containing 0.047 *M* Ti(III) and 1.45 *M* HCl or to solutions of lower concentrations.

The complexes $[Co(NH_3)_5N_3]Cl_2$[18] and $[Co(NH_3)_5NCS]Cl_2$[19] were prepared according to published procedures. Stock solutions of these complexes were prepared fresh before each set of experiments.

Results

The kinetics of the $Ti^{III}–Co(NH_3)_5N_3^{2+}$ reaction were determined at 25.0° and 0.500 *M* ionic strength, maintained with LiCl and $LiClO_4$, over the concentration ranges $(0.5–4.0) \times 10^{-4}$ *M* Co(III), $(0.5–13) \times 10^{-3}$ *M* Ti(III), 0.034–0.50 *M* Cl^-, and 0.031–0.475 *M* H^+. Data presented in Table I

Table I. Rate Constants for the Ti^{III}–$Co(NH_3)_5N_3^{2+}$ Reaction at 25.0° and 0.500 *M* Ionic Strength

$[H^+]$, *M*	$[Cl^-]$, *M*	$10^4[Co(III)]_0$, *M*	$10^3[Ti(III)]_0$, *M*	$10^2 k_{obsd}$,[a] sec^{-1}	k_{ox},[b] M^{-1} sec^{-1}
0.0309	0.200	1.01	0.994	1.91	19.3
0.0309	0.500	1.03	0.994	2.12	21.3
0.0628	0.196	2.02	2.02	3.00	14.9
0.0628	0.498	2.05	2.02	3.35	16.6
0.126	0.200	2.02	4.04	4.28	10.6
0.126	0.489	2.05	4.04	4.53	11.2
0.198	0.0339	1.01	0.994	0.799	8.03
0.202	0.0689	2.02	2.02	1.63	8.05
0.202	0.138	2.02	4.04	3.25	8.05
0.200	0.198	1.95	3.90	3.15	8.07
0.200	0.299	2.02	4.04	3.21	7.94
0.200	0.397	2.02	4.04	3.25	8.05
0.200	0.485	2.02	4.04	3.25	8.05
0.200	0.485	2.05	4.04	3.15	7.80
0.298	0.198	2.02	4.04	2.47	6.11
0.300	0.488	2.02	4.04	2.57	6.35
0.300	0.488	2.05	4.04	2.53	6.26
0.300	0.488	4.04	4.04	2.52	6.24[c]
0.402	0.198	2.02	4.04	1.87	4.64
0.401	0.495	0.493	0.503	0.237	4.72
0.400	0.500	1.00	0.994	0.495	4.98
0.399	0.493	2.00	2.02	0.950	4.70
0.401	0.492	2.00	4.04	1.82	4.52
0.400	0.477	2.00	6.06	2.86	4.73
0.399	0.473	2.00	8.08	3.85	4.77
0.402	0.471	2.00	10.1	4.75	4.70
0.400	0.467	2.00	12.1	5.82	4.81
0.401	0.460	2.00	12.9	6.03	4.67
0.475	0.488	2.02	4.04	1.65	4.09[d]
0.475	0.488	2.02	4.04	1.47	3.65
0.475	0.488	2.05	4.04	1.60	3.95

[a] $k_{obsd} = -d \ln[Co(NH_3)_5N_3^{2+}]/dt$. [b] $k_{ox} = k_{obsd}/[Ti(III)]_0$; measured at 302 nm. [c] Measured at 340 nm. [d] Measured at 320 nm.

indicate a first-order dependence on [Ti(III)], no dependence on $[Cl^-]$, and a dependence on $[H^+]$ varying between zero order at low concentrations of acid and inverse first order at high concentrations, as shown by eq 1 and 2. A nonweighted linear

$$-d[Co(NH_3)_5N_3^{2+}]/dt = k_{ox}[Co(NH_3)_5N_3^{2+}][Ti(III)] \quad (1)$$

$$k_{ox} = a/(b + [H^+]) \quad (2)$$

least-squares fit of the straight line generated in a plot of k_{ox}^{-1} vs. $[H^+]$ yields the parameters $a = 2.21 \pm 0.07$ sec^{-1} and $b = 0.074_5 \pm 0.011$ *M* which reproduce the values of k_{ox} with an average deviation of 2.4% (Table II). Equations of the form of eq 2 have been found in our previous work on Ti(III) reductions[12,13] and have been interpreted as arising from the hydrolysis of Ti^{3+}

$$Ti^{3+} + H_2O \overset{K_a}{\rightleftharpoons} TiOH^{2+} + H^+ \quad (3)$$

Table II. Acid Dependence of the Rate Constants for the Ti^{III}–$Co(NH_3)_5N_3^{2+}$ Reaction

	k_{ox}, M^{-1} sec^{-1}		$k_{ox,cor}$, M^{-1} sec^{-1} [c]			
			$K_a = 0.0136$ *M*[d]		$K_a = 0.0118$ *M*[e]	
$[H^+]$, *M*	Obsd[a]	Calcd[b]	Obsd	Calcd[f]	Obsd	Calcd[g]
0.0309	20.3 ± 1.0	21.0	29.2	28.1	28.1	27.1
0.0628	$15.7_5 \pm 0.8_5$	16.1	19.2	19.8	18.7	19.3
0.126	10.9 ± 0.3	10.9	12.1	12.5	11.9	12.3
0.200	8.01 ± 0.06	8.06	8.56	8.73	8.48	8.65
0.300	6.24 ± 0.06	5.91	6.52	6.20	6.49	6.17
0.400	4.74 ± 0.09	4.66	4.90	4.81	4.88	4.79
0.475	3.90 ± 0.16	4.02	4.01	4.12	4.00	4.10

[a] Average values from Table I; uncertainties are average deviations. [b] Calculated from eq 2 with $a = 2.21$ sec^{-1} and $b = 0.074_5$ *M*. [c] $k_{ox,cor} = k_{ox}(K_a + [H^+])/[H^+]$. [d] K_a from ref 13. [e] K_a from ref 20 and 12. [f] Calculated from eq 4 with $c = 2.14$ sec^{-1} and $d = 0.0455$ *M*. [g] Calculated from eq 4 with $c = 2.15$ sec^{-1} and $d = 0.0484$ *M*.

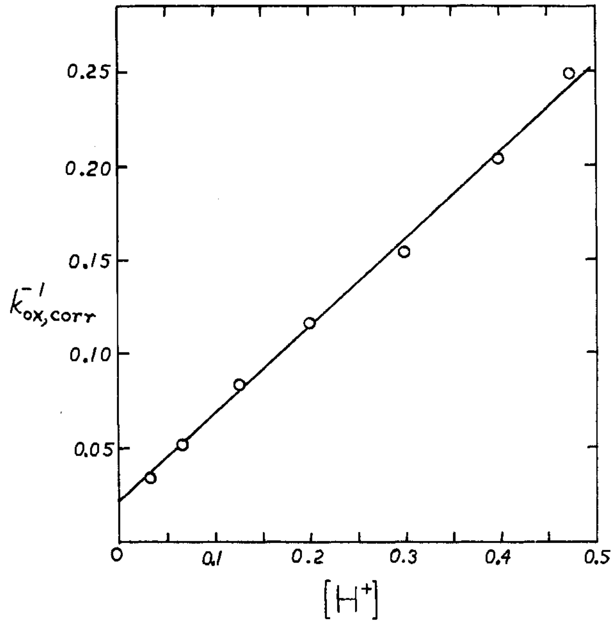

Figure 1. Plot of $k_{ox,cor}^{-1}$ vs. $[H^+]$ for the Ti^{III}–$Co(NH_3)_5N_3^{2+}$ reaction, showing the fit of the data to eq 4, using $K_a = 0.0136$ *M*. The line is based on the values $c = 2.14$ sec^{-1} and $d = 0.0455$ *M*.

This interpretation would require $b = K_a = 0.0745$ *M*, while the most reliable value we have obtained kinetically is 0.0136 ± 0.0035 *M*,[13] and a value obtained from careful spectral measurements[20] and corrected[12] to our conditions is 0.0118 *M*. The value of the parameter *b* is clearly too large to be equated to K_a. On the other hand, if $Co(NH_3)_5N_3^{2+}$ were protonated to a significant extent, then hydrolysis of $Co(NH_3)_5N_3H^{3+}$ could give rise to the observed eq 2. Careful spectral measurements were made with 2.02×10^{-4} *M* $Co(NH_3)_5N_3^{2+}$ in 0.50 *M* LiCl and in 0.50 *M* HCl. The spectra were identical to within 0.2% at wavelengths near the absorption maximum (302 nm). Staples[21] has obtained a value of 600 *M* for the acid dissociation constant of $Co(NH_3)_5N_3H^{3+}$ from the acid dependence of aquation of $Co(NH_3)_5N_3^{2+}$ in 3.7–12.4 *M* H_2SO_4. This value would indicate that less than 0.1% of the Co(III) species is present in the protonated form in 0.5 *M* HCl and is clearly incompatible with $b = 0.0745$ *M*. Our interpretation of the noncorrespondence of these constants is that eq 2 is a limiting form of a more complex equation which takes account of the hydrolysis of Ti(III), using the standard correction $[Ti^{3+}]/[Ti(III)] = [H^+]/(K_a + [H^+])$

$$k_{ox} = c[H^+]/(K_a + [H^+])(d + [H^+]) \cong c/(K_a + d + [H^+]) \quad (4)$$

This would require $K_a + d = 0.0745$ *M*, so $d \simeq 0.06$ *M*, and the term K_ad, which is dropped from the denominator on the far right, has a value of ca. 7×10^{-4} M^2. This term is sufficiently small to ignore except at the very low values of $[H^+]$, since it only contributes 18% to the denominator at $[H^+] = 0.0309$ *M* and 7% at $[H^+] = 0.0628$ *M*. To avoid the assumption that this term can be ignored, the linearized form of the equation in which $k_{ox,cor}^{-1} = k_{ox}^{-1}(K_a + [H^+])^{-1}[H^+]$ is plotted vs. $[H^+]$ (Figure 1) was treated by linear least squares to yield $c = 2.14 \pm 0.06$ sec^{-1} and $d = 0.0455 \pm 0.0088$ *M* with $K_a = 0.0136$ *M*, which reproduce the values of $k_{ox,cor}$ (Table II) with an average deviation of 3.1%. The values obtained with $K_a = 0.0118$ *M* are $c = 2.15 \pm 0.06$ sec^{-1} and $d = 0.0484 \pm 0.0088$ *M*, with an average deviation in $k_{ox,cor}$

of 3.1%. Mechanisms consistent with these results will be discussed below.

Attempts to study the kinetics of the Ti^{III}–$Co(NH_3)_5NCS^{2+}$ reaction were unsuccessful due to the slowness of this reaction. Interference from aquation of Co(III) or photochemically induced oxidation of Ti(III) by water[15] at long times limited studies to initial rates. Two studies at 25°, 0.500 *M* ionic strength, 4.04×10^{-3} *M* Ti(III), 3×10^{-4} *M* Co(III), 0.126 *M* H^+, and 0.489 *M* Cl^-, in which the absorbance at 305 nm was measured either intermittently or continuously, showed less than 1% reaction in 2 hr, setting a limit of $k_{ox} \leq 3 \times 10^{-4}$ M^{-1} sec^{-1}. Studies at longer times or at higher temperatures exhibited an absorbance increase rather than a decrease, as might be expected from oxidation of Ti(III) without concomitant reduction of Co(III).[15] An initial rate study at 25°, 1.01×10^{-2} *M* Ti(III), 4.76×10^{-3} *M* Co(III), 0.314 *M* H^+, 0.455 *M* Cl^-, and 495 nm established a value of $k_{ox} \simeq 2.3 \times 10^{-5}$ M^{-1} sec^{-1} for the redox rate constant, consistent with the earlier estimate.

Discussion

If we consider the rate constant ratios for azide and isothiocyanate as potential bridging ligands, we obtain values for $k_{ox,N_3^-}/k_{ox,NCS^-}$ of $>3.6 \times 10^4$ at 0.13 *M* H^+ and $\sim 2.7 \times 10^5$ at 0.3 *M* H^+. This discrimination in favor of the azide complex is greater than that observed for any other reducing agent examined,[9,10] including those such as Cr^{2+} which are known to be inner-sphere, so it appears to be safe to conclude that at least the reaction of Ti(III) with $Co(NH_3)_5N_3^{2+}$ is of the inner-sphere type and that Ti(III) is capable of acting as an inner-sphere reducing agent toward Co(III) complexes.

Further evidence for the operation of an inner-sphere mechanism in the Ti^{III}–$Co(NH_3)_5N_3^{2+}$ reaction is provided by the form of the rate equation. The mechanism cannot involve a simple one-step reaction between $Co(NH_3)_5N_3^{2+}$ and Ti^{3+} or $TiOH^{2+}$ because of incompatibilities between the measured kinetic parameters and known thermodynamic parameters, as discussed earlier. Two mechanisms (Mechanisms I and II) can be proposed which are consistent with the form of the rate equation given by eq 4 and which are kinetically indistinguishable, differing only in the order of formation of the activated complexes.[22] Each mechanism involves the equilibrium shown in eq 3 and the formation of a binuclear complex which is a precursor to the electron-transfer step and which is present only in steady-state concentrations.

Mechanism I

$$Ti^{3+} + Co(NH_3)_5N_3^{2+} \underset{k_2}{\overset{k_1}{\rightleftarrows}} Co(NH_3)_5N_3TiOH^{4+} + H^+ \qquad (5)$$

$$Co(NH_3)_5N_3TiOH^{4+} \xrightarrow{k_3} Co^{2+} + 5NH_3 + HN_3 + TiO^{2+} \qquad (6)$$

$$-d \ln [Co(NH_3)_5N_3^{2+}]/dt = k_1k_3k_2^{-1} [Ti(III)][H^+]/(k_3k_2^{-1} + [H^+])(K_a + [H^+]) \qquad (7)$$

$k_3k_2^{-1} = 0.045_5$ *M* and $k_1 = 47$ M^{-1} sec^{-1} if $K_a = 0.0136$ *M* (or 0.048_4 *M* and 44 M^{-1} sec^{-1} if $K_a = 0.0118$ *M*)

Mechanism II

$$TiOH^{2+} + Co(NH_3)_5N_3^{2+} \underset{k_5}{\overset{k_4}{\rightleftarrows}} Co(NH_3)_5N_3TiOH^{4+} \qquad (8)$$

$$Co(NH_3)_5N_3TiOH^{4+} + H^+ \xrightarrow{k_6} Co^{2+} + 5NH_3 + HN_3 + TiO^{2+} + H^+ \qquad (9)$$

$$-d \ln[Co(NH_3)_5N_3^{2+}]/dt = k_4K_a[Ti(III)][H^+]/(k_5k_6^{-1} + [H^+])(K_a + [H^+]) \qquad (10)$$

$k_5k_6^{-1} = 0.045_5$ *M* or (0.048_4 *M*) and $k_4 = 157$ M^{-1} sec^{-1} (or 182 M^{-1} sec^{-1})

Exchange of solvent water[23] with water bound to Ti^{3+} occurs with a rate constant of ca. 10^5 sec^{-1} (presumably equal to ca. $2 \times 10^3[H_2O]$) and the rate constant for complex formation between Ti^{3+} and NCS^- is ca. 4×10^3 M^{-1} sec^{-1}.[24] Since both studies indicate a rate of substitution on Ti^{3+} of ca. $(2-4) \times 10^3$ M^{-1} sec^{-1}, the values assigned to the rate constants k_1 and k_4 above are sufficiently small to be consistent with a process involving substitution on Ti(III). Thus these results provide evidence for the occurrence of an inner-sphere reduction of $Co(NH_3)_5N_3^{2+}$ by Ti(III).

Acknowledgment. Partial support of this work by the Faculty Grant-in-Aid Program at Arizona State University is gratefully acknowledged.

Registry No. Ti(III), 22541-75-9; $Co(NH_3)_5N_3^{2+}$, 14403-83-9; $Co(NH_3)_5NCS^{2+}$, 14970-18-4.

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Resonance Raman Spectrum of Matrix-Isolated Re_3Cl_9

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Received October 29, 1974 AIC40756L

Recent laser Raman studies of the orange matrix isolated $M^+Cl_2^-$ and $M^+O_3^-$ species have demonstrated that solid argon at 15°K is an effective medium for the study of resonance Raman spectra of unstable inorganic molecules.[1,2] In a study of polynuclear transition metal complexes, the Raman spectrum of solid Re_3Cl_9 has been reported.[3] Owing to a strong rhenium