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The Reductions of Azido-, Thiocyanato-, and Isothiocyanatopentacyanocobaltate(III) Anions by Titanium(III) in Aqueous Acidic Solution

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The reductions of azido-, thiocyanato-, and isothiocyanato-pentacyanocobaltate(III) anions by aquatitanium(III) have been studied in aqueous solution with I=1.0 mol dm^{-3} (LiCl) T=25 °C. The reactions are found to have inverse acid dependence of the form: $k_{\text{obsd}}=kK/(K+[\text{H}^+])$. The estimated values of k and K are 1.47 dm^3 mol^{-1} s^{-1} and 1.0×10^{-2} mol dm^{-3} for the azido complex and 4.85 dm^3 mol^{-1} s^{-1} and 6.0×10^{-3} mol dm^{-3} for the thiocyanato complex. Various criteria including the $k_{\text{N}_3^-}/k_{\text{NCS}^-}$ and $k_{\text{SCN}^-}/k_{\text{N}_3^-}$ ratios among others are used to suggest inner-sphere mechanism for these reactions.

The reductions of the three pentaamminecobalt(III) complexes of the general formula $[\text{Co(NH}_3)_5\text{X}]^{2+}$ (X= :N_3^-, :SCN^-, and :NCS^-) by various reductants (Cr(II), V(II), Fe(II), Eu(II), U(III), Ti(III), Ru(II), Cu(I)) have been widely investigated.[1-12]

The general reactivity trend that has been observed[1-12] for the reduction of these cobalt(III) complexes is $k_{\text{SCN}^-}>k_{\text{N}_3^-}>k_{\text{NCS}^-}$. In particular, the magnitude of the ratio $k_{\text{N}_3^-}/k_{\text{NCS}^-}$ has been used extensively in diagnosing mechanism of electron transfer. A very large ratio ($\geq 10^3$) is usually indicative of inner-sphere mechanism while a much smaller value (<10) implicates outer-sphere mechanism. The ratio $k_{\text{SCN}^-}/k_{\text{N}_3^-}$ also has been used (though less frequently) to diagnose electron transfer mechanism. A relatively large value $k_{\text{SCN}^-}/k_{\text{N}_3^-}$ (ca. 200) indicates outer-sphere mechanism while small values (<10) imply inner-sphere mechanism. Many of these authors[1-12] also employed the use of log-log plots, based on Marcus linear free energy (LFE) relationship as further evidence in the interpretation of the mechanisms of the reactions.

Unlike these pentaamminecobalt(III) complexes, the reductions of the pentacyano analogues are yet to be exhaustively studied. The ruthenium(II) reductions of $[\text{Co(CN)}_5\text{X}]^{n-}$ (X=H_2O, OH^-, NCS^-, N_3^-, n=2 or 3) reported recently,[13,14] and the vanadium(II) reductions of $[\text{Co(CN)}_5\text{X}]^{n-}$ (X=Cl^-, Br^-, I^-, SCN^-, N_3^-, and H_2O, n=2 or 3) reported by Espenson and Davies,[15] are the few examples of the redox behavior of pentacyanocobaltate(III) complexes. We here present a report of the reductions of $[\text{Co(CN)}_5\text{X}]^{3-}$ (X=N_3^-, SCN^-, and NCS^-) by aquatitanium(III) in aqueous acidic solution. The study is aimed at comparing the effects of the replacement of the nonbridging ammine (NH_3) ligands by the anionic cyano (CN^-) ligands and also investigating the coulombic effects in the reductions of the negatively charged anionic pentacyano complexes as compared to the positively charged cationic pentaammine complexes by cationic reductants.

Experimental

Materials. $\text{K}_3[\text{Co(CN)}_5\text{N}_3]$ was prepared according to the method described by Wilmarth and others.[16] It was purified and characterized by its electronic and infrared absorption maxima. Its absorption peaks and absorption coefficients agree with literature values.[16,17] The complexes $\text{K}_3[\text{Co(CN)}_5\text{SCN}]$ and $\text{K}_3[\text{Co(CN)}_5\text{NCS}]$ were prepared, purified and characterized by means of their infrared and electronic absorption spectra as reported in the literature.[17,18a] Hexaaquatitanium(III) solutions were prepared from titanium metal according to literature procedures.[19,21] Their electronic spectra agreed well with literature values.[19-21] The concentrations of the titanium(III) solutions were determined by both titrimetric and spectrophotometric dilution methods. Both methods agreed within 5%. The free acid concentrations in the titanium(III) solutions were determined by both ion-exchange titrations (using either Dowex 50W-X8 or IR120 Amberlite resin columns) and by substracting three times the titanium(III) concentration from the total hydroxyl concentration according to the equation:

$$[\text{H}^+]=[\text{OH}^-]-3[\text{Ti(III)}] \qquad (1)$$

assuming quantitative conversion of Ti(III) to $\text{TiO}_{2(s)}$ based on the equation:

$$4\text{Ti}^{3+}+\text{O}_2+12\text{OH}^-\rightarrow 4\text{TiO}_{2(s)}+6\text{H}_2\text{O} \qquad (2)$$

Kinetics. All the reactions were followed by conventional technique using a Pye-Unican SP 500 series 2 UV-Vis spectrophotometer. Absorbance changes were monitored at λ=380 nm for the $\text{Ti(III)}/[\text{Co(CN)}_5\text{N}_3]^{3-}$ systems and at λ=340 nm for $\text{Ti(III)}/[\text{Co(CN)}_5\text{X}]^{3-}$ (X= :SCN^-, :NCS^-) systems. All reactions were studied under pseudo-first-order conditions with the concentrations of the Ti(III) species in at least ten fold excess over those of the Co(III) oxidants. The cell compartment was well-thermostated to 25.0±0.1 °C. The reactions were studied at an ionic strength of 1.0 mol dm^{-3} (LiCl).

All the solutions used were thoroughly deoxygenated with pure nitrogen that has been previously scrubbed in chromous towers. Ti(III) solutions for use in kinetic runs were freshly prepared from a stock solution that had been stored under nitrogen in the refrigerator. During kinetic runs, nitrogen gas blanket was maintained over the solution mixtures in the serum-capped 4 cm spectrophotometric cell.

Results

Spectrophotometric titrations showed that the stoichiometry of all the redox reactions was 1 : 1, i.e. one mole of the oxidant was always consumed by one mole of the reductant. Pseudo-first-order plots using both infinity and Guggeinheim methods[18b)] were linear to more than three halflives in all cases. Several attempts made to study the titanium(III) reduction of $[Co(CN)_5NCS]^{3-}$ showed it to be very slow and no detailed kinetic study of this system was undertaken because of complications/errors accompanying such slow titanium(III) reactions. For the remaining two systems, the observed second-order rate constants, k_{obsd} decreased with increasing acidity as evidenced in Tables 1 and 2 thus showing that $TiOH^{2+}$ is the predominant Ti(III) reductant. Plots of k_{obsd} vs. $[H^+]^{-1}$ gave curves for both systems, while plots of $1/k_{obsd}$ vs. $[H^+]$ (Figs. 1 and 2) were linear for the two reactions. This is consistent with the rate equations:

$$k_{obsd}=\frac{kK}{K+[H^+]} \tag{3}$$

or

$$\frac{1}{k_{obsd}}=\frac{1}{k}+\frac{1}{kK}[H^+] \tag{4}$$

Table 1. Kinetic Data for the Reduction of $[Co(CN)_5N_3]^{3-}$ by Ti(III) at 25 °C and I=1.0 mol dm^{-3} (LiCl)

$[H^+]$	$10^4[Co(III)]$	$10^3[Ti(III)]$	10^4k_s	$k_{obsd}$$^{a)}$
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	s^{-1}	dm^3 mol^{-1} s^{-1}
0.005	1.005	3.06	35.56	1.064
	1.005	5.10	51.51	1.010
	1.005	7.14	84.25	1.180
0.020	1.005	2.04	8.67	0.425
	1.005	3.06	14.44	0.472
	1.005	5.10	22.49	0.441
	1.005	7.14	32.34	0.453
0.030	0.997	3.06	11.08	0.362
	0.997	5.10	18.05	0.354
	0.997	7.14	25.49	0.357
0.050	0.997	3.06	6.30	0.206
	1.000	5.10	12.80	0.251
	1.005	7.14	16.14	0.226
0.075	1.000	2.04	3.41	0.167
	1.000	3.06	5.18	0.169
	0.997	5.10	8.27	0.162
	0.997	7.14	11.99	0.168
	1.005	10.24	17.20	0.168
0.100	1.000	2.04	2.51	0.124
	1.000	3.06	3.76	0.123
	1.005	5.10	6.38	0.125
	1.005	7.14	9.07	0.127
	1.005	10.24	12.90	0.126

a) $k_{obsd}=k_s/[Ti(III)]$.

Table 2. Kinetic Data for the Reduction of $[Co(CN)_5SCN]^{3-}$ by Ti(III) at 25 °C and I=1.0 mol dm^{-3} (LiCl)

$[H^+]$	$10^4[Co(III)]$	$10^3[Ti(III)]$	10^3k_s	$k_{obsd}$$^{a)}$
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	s^{-1}	dm^3 mol^{-1} s^{-1}
0.010	2.20	2.22	3.79	1.706
	2.20	3.33	5.83	1.749
	2.94	4.44	8.63	1.941
	2.94	6.67	12.00	1.800
	2.94	11.11	19.51	1.756
0.020	4.12	4.44	5.20	1.170
	4.12	6.67	7.22	1.081
	4.12	8.89	9.96	1.119
0.050	2.20	2.22	1.17	0.525
	2.75	3.33	1.60	0.480
	2.97	5.50	2.69	0.489
	2.97	6.67	3.35	0.502
	2.97	8.89	4.45	0.500
0.075	2.20	2.22	0.79	0.356
	2.20	4.44	1.56	0.352
	2.75	7.78	2.80	0.360
0.100	2.20	3.33	0.90	0.270
	2.75	5.56	1.51	0.272
	2.75	6.67	1.83	0.274
	2.97	8.89	2.40	0.270

a) $k_{obsd}=k_s/[Ti(III)]$.

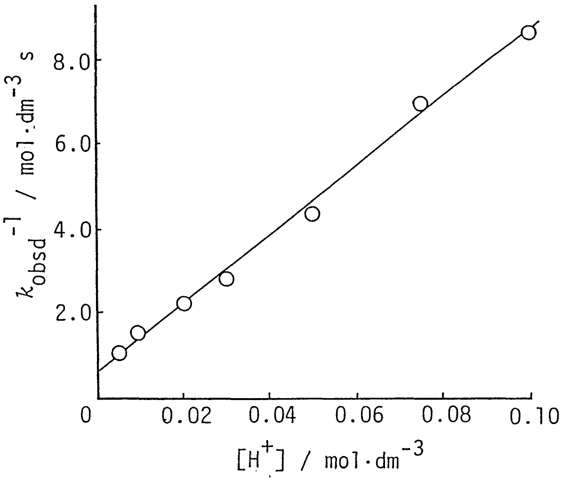


Fig. 1. Dependence of $1/k_{obsd}$ on $[H^+]$ for the Ti(III)/$[Co(CN)_5N_3]^{3-}$ reaction; I=1.0 mol dm^{-3}, t=25 °C.

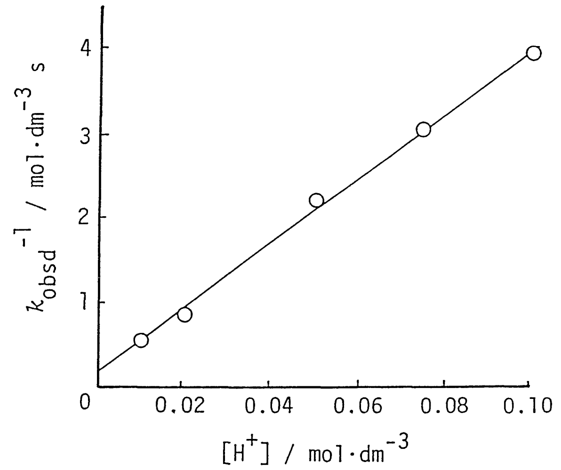


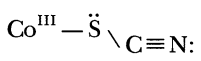
Fig. 2. Dependence of $1/k_{obsd}$ on $[H^+]$ for the Ti(III)/$[Co(CN)_5SCN]^{3-}$ reaction; I=1.0 mol dm^{-3}, t=25 °C.

From the plots of Figs. 1 and 2 and using least square analysis of the data in Tables 1 and 2 at 25 °C, K was estimated to be $(1.0\pm0.1)\times10^{-2}$ mol dm^{-3} with a correlation coefficient of 0.99 and $k=(1.47\pm0.16)$ dm^3 mol^{-1} s^{-1} for the reduction of $[\mathrm{Co(CN)_5N_3}]^{3-}$. For the reduction of $[\mathrm{Co(CN)_5SCN}]^{3-}$, similar treatment gave $K=(6.0\pm0.8)\times10^{-3}$ mol dm^{-3} with a correlation coefficient of 0.99 and a k value of (4.85 ± 0.62) dm^3 mol^{-1} s^{-1}.

Discussion

The second-order rate constants obtained in this study follow the trend $k_{\mathrm{SCN^-}}>k_{\mathrm{N_3^-}}>k_{\mathrm{NCS^-}}$ in agreement with the earlier reports.[1-12] Espenson[4] observed that the azido and the isothiocyanato ligands in complexes of the types M-N=N=N: and M-N=C=S: coordinate with metal-ion reductants in the activated complex states. In such cases, the attack from the usually hard reductant metal center is on the nitrogen atom for azido complex and on the sulfur atom for the isothiocyanato complex. The intermediate formed by the azido complex with the hard reductant is more stable and therefore reactions involving $:\mathrm{N_3^-}$ as the bridging ligand are expected to be much faster than those involving $:\mathrm{NCS^-}$ as bridging ligand. The fact that the reduction of $[\mathrm{Co(CN)_5NCS}]^{3-}$ was too slow to be measurable under our conditions shows that $[\mathrm{Co(CN)_5N_3}]^{3-}$ is reduced at a much faster rate. Birk[8] as well as Bakac and Orhanovic[9] also observed such very slow reactions in the Ti(III) reduction of $[\mathrm{Co(NH_3)_5NCS}]^{2+}$. The very slow rate observed for the reduction of $[\mathrm{Co(CN)_5NCS}]^{3-}$ in this study suggests a relatively high $k_{\mathrm{N_3^-}}/k_{\mathrm{NCS^-}}$ ratio which as earlier indicated by other authors[1-12] supports an inner-sphere mechanism. Similar high ratios have been used to classify many reactions as inner-sphere (Table 3) based on the higher stability of the $\mathrm{N_3^-}$ bonded intermediate over the $\mathrm{NCS^-}$ bonded one.

When $\mathrm{SCN^-}$ is the bridging ligand, the complex formed has been shown[1] to have a bent shape of the form



$$\mathrm{Co^{III}-\ddot{S}\backslash C{\equiv}N:}$$

For this complex, attack by the reductant can either be an adjacent one on the sulfur atom or a remote attack on the nitrogen atom. Shea and Haim[1] had observed that in the inner-sphere reductions of $[\mathrm{Co(NH_3)_5X}]^{2+}$ ($\mathrm{X=N_3^-}$ and $\mathrm{SCN^-}$) by $\mathrm{Cr^{2+}}$, the two oxidants are reduced at comparable rates. We may therefore in a similar manner propose again an inner-sphere mechanism in the present study in which $[\mathrm{Co(CN)_5SCN}]^{3-}$ and $[\mathrm{Co(CN)_5N_3}]^{3-}$ are reduced at comparable rates. Our observed low value of 3.3 for the $k_{\mathrm{SCN^-}}/k_{\mathrm{N_3^-}}$ ratio is therefore in agreement with inner-sphere mechanism (Table 3).

From our results, the values of K (Eq. 3) obtained in mol dm^{-3} are 6.02×10^{-3} and 1.01×10^{-2} for the thiocyanato and the azido oxidants respectively. While the K value for the reduction of the azido complex is much higher than the typical range of values of $(1.2-5.0)\times10^{-3}$ mol dm^{-3} often quoted[12,22,23] for the simple hydrolysis of Ti(III), the K value for the thiocyanato complex is only slightly higher than the upper limit of this hydrolytic constant of Ti(III). The higher values in both cases indicate that there are other preequilibria processes[19] including the formation of the precursor complexes along with that of the simple hydrolysis of Ti(III) in the reactions (i.e. the kinetically determined K is a composite equilibrium constant) which supports inner-sphere mechanism. A similar result was reported by Bakac and Orhanovic[9] in the Ti(III) reduction of the thiocyanato- and azido-pentaammine cobalt(III) complexes where the K values were given as 5.3×10^{-3} and 4.4×10^{-2} mol dm^{-3} respectively. A plausible explanation for the present observation and that of Bakac and Orhanovic[9] for cases where the K values are close to the normal values of K_a (hydrolytic constant of Ti(III)) is that the simple hydrolysis of Ti(III) plays a more significant role over that of other participating preequilibria processes in

Table 3. Relative Rates of Reduction of Azido, Thiocyanato, and Isothiocyanato Complexes at 25 °C

Oxidant	Reductant	$k_{\mathrm{N_3^-}}/k_{\mathrm{NCS^-}}$	$k_{\mathrm{SCN^-}}/k_{\mathrm{N_3^-}}$	Mechanism$^{a)}$	Reference
$[\mathrm{Co(NH_3)_5X}]^{2+}$	$\mathrm{Cr^{2+}}$	2×10^4	0.6	i.s	1
	$\mathrm{V^{2+}}$	43	2.3	i.s	2,3
	$\mathrm{Fe^{2+}}$	3×10^3	14.3	i.s	3,4
	$\mathrm{Eu^{2+}}$	4×10^3	16.0	i.s	5
	$\mathrm{U^{3+}}$	4×10^4	—	i.s	6
	$\mathrm{Cu^{+}}$	10^3	—	i.s	12
	$\mathrm{TiOH^{2+}}$	4×10^5	4.2	i.s	7,9
	$[\mathrm{Cr(bpy)_3}]^{2+}$	4	50	o.s	2,12
	$[\mathrm{Ru(NH_3)_6}]^{2+}$	1.5	200	o.s	11
	$[\mathrm{Ru(NH_3)_5H_2O}]^{2+}$	2.2	278	o.s	11
$[\mathrm{Co(CN)_5X}]^{3-}$	$[\mathrm{Ru(NH_3)_6}]^{2+}$	2.1	—	o.s	14
	$[\mathrm{Ru(NH_3)_5H_2O}]^{2+}$	2.1	—	o.s	14
	$\mathrm{TiOH^{2+}}$	$>10^3$	3.3	i.s	This work

a) i.s: inner-sphere, o.s: outer-sphere.

these reactions.

Sutin[24] as well as Poon and others[25] have put an upper limit of 50 $dm^3 mol^{-1} s^{-1}$ to the rate constants for the inner-sphere reductions of some cationic complexes by V(II). $[Co(CN)_5SCN]^{3-}$ and $[Co(CN)_5N_3]^{3-}$ are reduced by V(II)[15] with rate constants of 138 and 112 $dm^3 mol^{-1} s^{-1}$ respectively and are still classified as inner-sphere redox reactions. These exceptions have been linked with the anionic nature of the oxidants which confer higher stability on their precursor complexes in the transition states. V^{2+} has been shown[26] to be a more efficient reductant than $TiOH^{2+}$ in inner-sphere redox reactions. $TiOH^{2+}$ reduces[19] $[Co(CN)_5SCN]^{3-}$ and $[Co(CN)_5N_3]^{3-}$ with rate constants of 4.85 and 1.47 $dm^3 mol^{-1} s^{-1}$ respectively. These values are much lower than those of V^{2+} reductions[15] of the same complexes in agreement with Thompson and Sykes[26] observations for inner-sphere processes.

The pentaammine analogues of the present oxidants were reduced by Ti(III)[9] under similar conditions with rate constants of 1.0×10^3 and 45.6 $dm^3 mol^{-1} s^{-1}$ respectively. When the nonbridging ligand NH_3 is exchanged for CN^-, the respective rate costants are 4.85 and 1.47 $dm^3 mol^{-1} s^{-1}$. The higher reactivity of the pentaammine complexes over the pentacyano complexes can be explained in terms of nonbridging ligand effect. The NH_3 ligand is at a lower field strength in the spectrochemical series and therefore more weakly bound to the cobalt than the CN^- ligand. This makes the NH_3 ligand to provide a lower energy path for redox reactions and hence it is expected that the rates of Ti(III) reductions of the pentaammine oxidants would be faster than the corresponding pentacyano oxidants. The present result is in line with this expectation and is in agreement with what Benson and Haim[27] as well as Bifano and Linck[28] reported in their studies of nonbridging effects in reductions of some cobalt(III) complexes. Conversely, coulombic considerations resulting from the different nonbridging ligands require that the pentacyano complexes, which are anionic, be reduced at a faster rate by the positively charged Ti(III) species than the pentaammine complexes which are also positively charged as the Ti(III) species. The reverse is the case in this study and it therefore seems that the nonbridging ligand effect in this instance has a greater influence than the coulombic effect.

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