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Kinetics and Mechanism of the Iron(II) and Vanadium(II) Reductions of *trans*-diazido and Dithiocyanatobis(dimethylglyoximato)cobaltate(III) Complexes. Evidence for Oxime Bridging

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Introduction

Recently there have been many reports [1–9] on the linkage isomerization of *trans*-thiocyanatobis(dimethylglyoximato)cobalt(III) complexes. Norbury *et al.* [2–4] have reported the presence of an equilibrium mixture of S-bonded and N-bonded isomers of a series of *trans*-thiocyanatobis(dimethylglyoximato)cobalt(III) complexes of the general formula, $Co(DH)_2(CNS)L$ (where L = Cl^-, Br^-, NO_2^-, py, PPh_3, and *etc.*) and proposed that the variation of the ratio of the two isomers present in the solution is attributed to the dielectric constant of the solvents being used. Similar studies have been carried out on the bis(dimethylglyoximato)cobalt(III) complexes by Marzilli *et al.* [5–7] and Burmeister *et al.* [8, 9]. However, reports on the kinetics of the reduction of thiocyanatocobaloximes(III) are not available. It would be interesting to explore the consequences of such isomerization on the rates of reduction of these isomers. A comparative study of the reduction of thiocyanato and azidocobaloxime(III) would therefore provide some useful information on the reactivity order and the nature of the bonding in the thiocyanatocobaloxime(III). In this communication, we report the kinetics of the iron(II) and vanadium(II) reductions of *trans*-diazido and dithiocyanatobis(dimethylglyoximato)cobaltate(III) complexes.

Experimental

The complexes, $Co(DH)_2(NH_3)N_3$ [10], $Na[Co(DH)_2(N_3)_2]$ [10] and $K[Co(DH)_2(CNS)_2]$ [11] were prepared as reported in the literature. Iron(II) perchlorate [12] was prepared in solution by dissolving 99.9% pure Iron powder (Electrolytic grade, Sarabhai M. Chemicals) in a slight excess of perchloric acid. Iron(II) was estimated by spectrophotometry with 1,10-phenanthroline. Vanadium(II) perchlorate solutions were prepared by the reduction of vanadium(V) perchlorate solutions with zinc amalgam and stored over zinc amalgam in a nitrogen atmosphere. Vanadium(V) was estimated spectrophotometrically as reported in the literature [13]. The free perchloric acid in the vanadium(II) solutions was determined indirectly as reported in the literature [14].

All the kinetic experiments were carried out under pseudo first-order conditions using a large excess of the reductant under nitrogen atmosphere maintained by sealing the reaction vessels with serum caps. The reactions were followed spectrophotometrically at 330 nm using a Carl Zeiss recording spectrophotometer. For all systems, the ionic strength was adjusted by the addition of sodium perchlorate and perchloric acid.

Experiments were carried out to identify the bridging sites in the inner sphere reduction of the dianionic cobaloximes. Chromium(II) was used as the reductant in these experiments and the resulting Cr(III) species was analysed. Chromium(II) perchlorate solutions were prepared by dissolving pure chromium metal (Riedel) in a slight excess of perchloric acid ano stored under nitrogen. Chromium was estimated spectrophotometrically as chromate [15] after oxidizing the solution with alkaline hydrogen peroxide. The experiments are described below. $Co(DH)_2(NH_3)N_3$ (0.019 g, 56 μmol) was dissolved in 0.1 mol·dm^{-3} $HClO_4$ (10.0 ml) and the solution was deaerated completely with purified nitrogen before adding the chromium(II) solution (0.01 mol·dm^{-3}). The reaction was allowed to become complete and the mixture of products was transferred to a cation exchange resin column (5 cm × 1 cm) packed wih Dowex 50 W X8–H^+ form. The column was initially eluted with water followed by 0.1 mol·dm^{-3} $HClO_4$ to ensure that the column is free from any neutral and anionic species. CrN_3^{2+} species, identified spectrophotometrically [16] was eluted with 0.6 mol·dm^{-3} $HClO_4$ and another chromium(III) fraction, possibly $CrDH^{2+}$, and Co(II) were eluted successively with 1.0–1.5 mol·dm^{-3} $HClO_4$. Further, the chromium(III) fractions eluted were estimated quantitatively by the chromate analysis [15] and the values for the two fractions were (i) 20 μmol and (ii) 38 μmol respectively.

Similarly for the anionic complex, $Co(DH)_2(N_3)_2^-$ (0.016 g, 39 μmol), the various fractions eluted are in the following order: (1) CrN_3^{2+} (24 μmol) identified spectrophotometrically and estimated by chromate analysis was eluted with 0.6 mol·dm^{-3}

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TABLE I. Rate Constants for the Iron(II) Reduction of *trans*-Diazido- and Dithiocyanatobis(dimethylglyoximato)cobaltate(III).

$[H^+] \times 10^3$ mol·dm^{-3}	Temp. °C	I[c] mol·dm^{-3}	k_{II} dm^3·mol^{-1} s^{-1}
(i) $Co(DH)_2(N_3)_2^-$ [a]			
4	30.0	1.00	0.098
35	30.0	1.00	0.101
95	30.0	1.00	0.099
100	30.0	0.10	0.093
100	30.0	0.50	0.102
100	30.0	0.75	0.093
100	35.0	1.00	0.190
100	40.0	1.00	0.299
100	45.0	1.00	0.496
(ii) $Co(DH)_2(CNS)_2^-$ [b]			
100	30.0	1.00	0.023
100	36.5	1.00	0.044
100	45.0	1.00	0.116
100	50.0	1.00	0.180

[a] [Complex] ~ 4.3×10^{-5} mol·dm^{-3}; [Fe(II)] = 1.60×10^{-3} mol·dm^{-3}. [b] [Complex] ~ 3.8×10^{-5} mol·dm^{-3}; [Fe(II)] = 1.87×10^{-3} mol·dm^{-3}. [c] I = [$NaClO_4$].

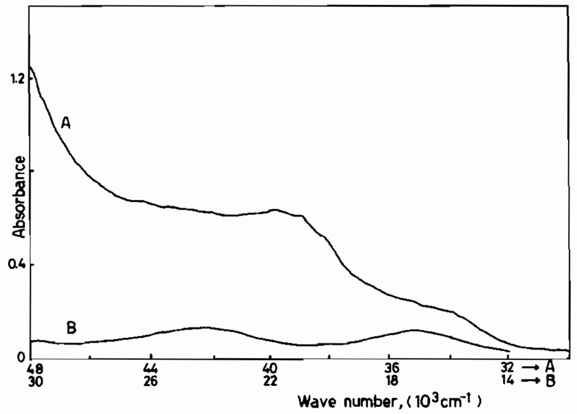

Fig. 1. UV–VIS absorption spectrum of $CrDH^{2+}$ species eluted using 1.0–1.5 mol·dm^{-3} $HClO_4$ for all the three complexes.

$HClO_4$, (ii) Co(II) with 1.0 mol·dm^{-3} $HClO_4$ and (iii) $CrDH^{2+}$ (16 μmol) was eluted with 1.0–1.5 mol·dm^{-3} $HClO_4$.

The product analysis for the complex $Co(DH)_2(CNS)_2^-$ (0.023 g, 52 μmol(with chromium(II) was carried out. The products obtained were characterized spectrophotometrically and estimated by chromate analysis. It was found that similar to the azidocobaloximes, $CrCNS^{2+}$ [17] (27 μmol) and $CrDH^{2+}$ (28 μmol) were spectrophotometrically identified. The spectrum of the second chromium(III) fraction which is identical for all the three complexes, most probably O-bonded $CrDH^{2+}$, is given in Fig. 1.

Results and Discussion

Studies on the iron(II) reduction of $Co(DH)_2(N_3)_2^-$ were carried out in the $[H^+]$ range 0.004–0.1 mol·dm^{-3} (Table I). The rate constant for the iron(II) reduction of $Co(DH)_2(CNS)_2^-$ measured at $[H^+]$ = 0.1 mol·dm^{-3} is also given in Table I. It may be seen from Table I that the rate constants for the iron(II) reduction of $Co(DH)_2(N_3)_2^-$ show no dependence on $[H^+]$. In the same $[H^+]$ range we observed an inverse $[H^+]$ dependence approaching a limiting value for the iron(II) reduction of the azidoamine-cobaloximes(III) [18] and the halogenopyridine-cobaloximes(III) [19]. The $[H^+]$ independence for $Co(DH)_2(N_3)_2^-$ reduction should therefore be due to completion of protonation of the complex even at $[H^+]$ = 0.004 mol·dm^{-3}. pH titration studies carried out independently for $Co(DH)_2(N_3)_2^-$ support this conclusion. However, rate data for the vanadium(II) reduction of $Co(DH)_2(N_3)_2^-$ indicate a very small direct dependence of rate on $[H^+]$ as seen from the values: k_{II} = 70.7 dm^3 mol^{-1}·s^{-1} at $[H^+]$ = 0.003 mol·dm^{-3} and k_{II} = 90.6 dm^3·mol^{-1}·s^{-1} at $[H^+]$ = 0.1 mol·dm^{-3}. Further the k_{II} values, exceeding the substitution controlled limiting rate constant for the vanadium(II), suggest that the reaction proceeds by an outer sphere mechanism [20].

It is interesting to compare the relative rates of the iron(II) and vanadium(II) reductions of $Co(DH)_2(N_3)_2^-$ and $Co(DH)_2(CNS)_2^-$. It is seen that for the iron(II) reduction, the rate trend is $Co(DH)_2(N_3)_2^- > Co(DH)_2(CNS)_2^-$, while it is reversed for the vanadium(II) reduction. In fact, the vanadium(II) reduction of $Co(DH)_2(CNS)_2^-$ is too fast to be measured by the technique employed here. It has been reported that $Co(DH)_2(CNS)_2^-$ is a mixture of isomers, $Co(DH)_2(SCN)_2^- \rightleftharpoons (Co(DH)_2(SCN)(NCS))^- \rightleftharpoons Co(DH)_2(NCS)_2^-$ in solution [6, 9] as well as in the solid state [1]. Epps and Marzilli [6] have reported from NMR studies that the various isomers are present in the ratio 1:2:2, suggesting that the rate of reduction is mainly controlled by the S-bonded isomer, which is understandable from the reactivity order. Reduction reactions of S-bonded thiocyanato complexes are known to be faster than the azido species [21–23]. For example k_{SCN}/k_{N_3} for the $Ru(NH_3)_6^{2+}$ reduction of $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5N_3^{2+}$ is *ca.* 200 while k_{N_3}/k_{NCS} for the $Ru(NH_3)_6^{2+}$ reduction of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$ is only 1.5 [21]. The presence of the S-bonded isomer in the mixture should therefore be responsible for the higher rate for the vanadium(II) reduction of $Co(DH)_2(CNS)_2^-$ than of $Co(DH)_2(N_3)_2^-$. For the iron(II) reduction, where the order $k_{N_3} > k_{NCS}$ is observed, the ratio k_{N_3}/k_{NCS} is *ca.* 4. This is very small compared with the value of $\sim 10^3$ observed for all inner sphere reactions involving N_3 and NCS bridges. The low value observed in the present study suggests the possibility of bridging sites other than N_3 and NCS, *viz.*, SCN and oxime oxygen. It has been reported that k_{SCN}/k_{N_3} for the iron(II) reduction (inner sphere) of $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5N_3^{2+}$ is 13.3 [22, 23].

The possibility of oxime bridging was tested by doing the product analysis with chromium(II), another inner sphere reductant. As observed, for the neutral complex, $Co(DH)_2(NH_3)N_3$, the ratio of the species, $CrDH^{2+}/CrN_3^{2+}$, is 2:1 whereas for the anionic complex $Co(DH)_2(N_3)_2^-$, the ratio is 1:2 suggesting that the higher percentage of the inner sphere reduction involves oxime bridging in the case of neutral complex and azide bridging for anionic complex. It is noteworthy to point out that Prince and Segal [24] have suggested the oxime bridged chromium(III) species for the chromium(II) reduction of the cationic complex, $Co(DH)_2(NH_3)_2^+$, wherein the only bridging site is the oxime ligand. The low value of k_{N_3}/k_{NCS} observed in the present study is thus a ratio of composite rate constants of reactions involving bridging partially through the oxime and the azide or thiocyanate. The ratios of concentrations of the two chromium(III) species formed, $CrDH^{2+}/CrX^{2+}$, for the two dianionic complexes are different; while the ratio is 1:2 for $Co(DH)_2(N_3)_2^-$, it is nearly equal to one for $Co(DH)_2(CNS)_2^-$. Weaver and Anson [25] have reported the equilibrium quotients for the equilibrium $Cr(H_2O)_6^{2+} + X^-(N_3^- \text{ or } NCS^-) \rightleftharpoons Cr(H_2O)_5X^+ + H_2O$ as 70 dm·mol^{-1} and 13 dm·mol^{-1} for $Cr(H_2O)_5N_3^+$ and $Cr(H_2O)_5NCS^+$ species respectively. Similarly the equilibrium quotients for the equilibrium $Cr(H_2O)_6^{3+} + X^-(N_3^- \text{ or } NCS^-) \rightleftharpoons Cr(H_2O)_5X^{2+} + H_2O$, are $\sim 10^3$ dm·mol^{-1} and 1.8×10^2 dm·mol^{-1} for the complexes $Cr(H_2O)_5N_3^{2+}$ and $Cr(H_2O)_5NCS^{2+}$ respectively [25]. Unfortunately, similar equilibrium constants for oxime coordinated chromium species are not available. However, the above results suggest that the stability of the oxime bridged species is at least equal to that of the thiocyanate bridges species, if not greater. The observed ratio $k_{N_3}/k_{NCS} \sim 4$ is better understandable in the light of the above results, *viz.*, partial bridging by the oxime as well as by the pseudohalides. When oxime bridging is involved, NCS, SCN and N_3 are nonbridging ligands and the reactivity order may be expected to parallel that of an outer sphere reduction, *viz.*, SCN > N_3 > NCS. The same order is expected when the pseudohalide is involved in bridging for iron(II) reduction [22, 23].

Activation parameters for the iron(II) reduction of the *trans*-diacidocobaloximes(III) were determined at $[H^+] = 0.1$ mol·dm^{-3}. The values are $\Delta H^\ddagger = 86.2 \pm 0.8$ kJ·mol^{-1} and $\Delta S^\ddagger = 18.8 \pm 2.5$ J·K^{-1} mol^{-1} for $Co(DH)_2(N_3)_2^-$ and $\Delta H^\ddagger = 85.4 \pm 1.3$ kJ·mol^{-1} and $\Delta S^\ddagger = 5.4 \pm 2.9$ J·K^{-1} mol^{-1} for $Co(DH)_2(CNS)_2^-$. The trend in the activation parameters suggests that both the complexes undergo reduction by an inner sphere mechanism. Positive $\Delta S^\ddagger$ values for the diacidocobaloximes(III) may be a consequence of the release of the solvent molecules from the activated complex in which the charge is reduced considerably compared to the other cationic oxidants.

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