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KINETICS OF THE Fe(II) REDUCTION OF *trans*-HALOGENOPYRIDINEBIS(DIMETHYLGLYOXIMATO)Co(III) COMPLEXES

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Abstract—The kinetics of the Fe(II) reduction of *trans*-chloro, bromo and iodopyridinebis(dimethylglyoximato)Co(III) have been studied at 30.0 ± 0.1°C and $I = 1.0\,\text{mol.dm}^{-3}(\text{NaClO}_4)$ in the $[\text{H}^+]$ range 0.0043–0.115 mol. dm^{-3}. The reaction showed an inverse dependence on $[\text{H}^+]$. The second order rate constant could be expressed in the form $k_{11} = k_1 + k_2(1 + K_B[\text{H}^+])^{-1}$. The kinetic data were found to be: Co(DH)$_2$(py)Cl–$k_1 = 0.051 \pm 0.003\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $k_2 = 0.76 \pm 0.04\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $K_B = 325 \pm 8\,\text{dm}^3\,\text{mol}^{-1}$; Co(DH)$_2$(py)Br–$k_1 = 0.071 \pm 0.004\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $k_2 = 1.21 \pm 0.04\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $K_B = 460 \pm 15\,\text{dm}^3\,\text{mol}^{-1}$; Co(DH)$_2$(py)I–$k_1 = 0.075 \pm 0.006\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $k_2 = 1.91 \pm 0.09\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, $K_B = 625 \pm 30\,\text{dm}^3\,\text{mol}^{-1}$. The inverse dependence on $[\text{H}^+]$ suggests an inner-sphere mechanism involving protonated and unprotonated species of the complex. The order of rates for the three complexes was found to be Co(DH)$_2$(py)I > Co(DH)$_2$(py)Br > Co(DH)$_2$(py)Cl.

INTRODUCTION

Electron-transfer reactions proceeding by the inner-sphere mechanism have been extensively studied[1–3]. Attempts to understand the intimate mechanism of these reactions have been made through studies on the effect of variation of bridging ligands[1, 3], non-bridging ligands[4, 5] and metal ion reducing agents on the rate. One particular aspect of these studies is the effect of variation of the coordinated halide ion, X^-, in the reduction of $\text{Co(NH}_3)_5\text{X}^{2+}$ by various reducing agents, Cr^{2+}[6], Fe^{2+}[7, 8], V^{2+}[7], Eu^{2+}[9], $\text{Cr(bipy)}_3{}^{2+}$[9], $\text{Co(CN)}_5{}^{3-}$[10], etc. While the order of reactivity of $\text{Co(NH}_3)_5\text{X}^{2+}$ in the reduction by Cr^{2+}, V^{2+} and $\text{Cr(bipy)}_3{}^{2+}$ is $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$, the order is reversed for reduction by Fe^{2+} and Eu^{2+}. The reversed order for the Fe^{2+} reduction has been attributed to the stability order $\text{FeF}^{2+} > \text{FeCl}^{2+} > \text{FeBr}^{2+} > \text{FeI}^{2+}$[11]. Applying the criteria of the Marcus equation to the FeX^{2+}–Fe^{2+} and CrX^{2+}–Cr^{2+} exchanges, the order of intrinsic barrier has been found to be $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ for the Fe^{2+} reduction and $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ for the Cr^{2+} reduction[11]. Haim[3, 12] has rationalized the results for the reduction of $\text{Co(NH}_3)_5\text{X}^{2+}$ by all the reducing agents mentioned, in terms of the stabilities of the transition states containing the bridging ligands, which is in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

A similar study of "halide effects" on the reduction of the *trans*-bis(dimethylglyoximato)Co(III) should be of interest. In this paper, we report our studies on the Fe^{2+} reduction of *trans*-chloro, bromo and iodopyridinebis(dimethylglyoximato)Co(III) complexes.

EXPERIMENTAL

Materials

Trans-Co(DH)$_2$(py)Cl, *trans*-Co(DH)$_2$(py)Br, and *trans*-Co(DH)$_2$(py)I (DH^- = dimethylglyoximate anion, py = pyridine) were prepared as reported in literature[13]. The purity of the complexes was ascertained by their UV-visible spectra, IR-spectra and also by elemental analysis. Fe(II) perchlorate was prepared[14] in solution by dissolving pure iron powder (Electrolytic grade, Sarabhai Chemicals) in a slight excess of perchloric acid. Fe(II) was determined by spectrophotometry with 1,10-phenanthroline. Sodium perchlorate (Koch-Light) was used without further purification. Dimethylsulfoxide (Baker Analysed) and perchloric acid (E. Merck, reagent grade) were used as such. Doubly distilled water was used throughout the study.

Kinetic measurements

The studies were carried out in 1 vol% dimethylsulfoxide–water mixture. Solutions of weighed amounts of the complex in dimethylsulfoxide were prepared. Solutions of the complex and Fe(II) perchlorate containing sodium perchlorate to provide 1.0 mol. dm^{-3} ionic strength were thermostated separately and mixed at the time of the reaction in the thermostated quartz cell placed in a Carlzeiss recording spectrophotometer at 30.0 ± 0.1°C. The changes in absorbance with time were measured at 274 nm for Co(DH)$_2$(py)Cl, 278 nm for Co(DH)$_2$(py)Br and 303 nm for Co(DH)$_2$(py)I. All the experiments were carried out under pseudo first order conditions with 20 fold excess of $\text{Fe(ClO}_4)_2$. Rate constants were calculated from the slopes of the linear plots of $\log(A_0 - A_\infty) - \log(A_t - A_\infty)$ vs time.

Stoichiometry

The stoichiometry of the reaction was determined by measuring the Fe(III) and Co(II) present in the product mixture. Fe(III) was determined as the thiocyanate complex and cobalt(II) as $\text{CoCl}_4{}^{2-}$ in excess hydrochloric acid. The ratio of Fe(III):Co(II) was found to be 1:1.

RESULTS

The reactions studied may be written as

$$\text{Co(DH)}_2(\text{py})\text{X} + \text{Fe}^{2+} + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{Co}^{2+} + 2\text{DH}_2 + \text{py} + \text{X}^- . \quad (1)$$

Bis(dimethylglyoximato)Co(II) was also a product in the higher pH range. A 1:1 stoichiometry was experimentally observed by spectrophotometry. Table 1 shows the second order rate constants for the Fe^{2+} reduction of Co(DH)$_2$(py)Cl, Co(DH)$_2$(py)Br and Co(DH)$_2$(py)I at various hydrogen ion concentrations. The rate constants decrease with increasing $[\text{H}^+]$ in the range 0.00434–

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Table 1. Rate constants for the Fe(II) reduction of *trans*-Halogenopyridinebis(dimethylglyoximato)Co(III) complexes in perchlorate medium[a] of I = 1.0 mol. dm^{-3} (NaClO$_4$) at 30.0 ± 0.1°C

Co(DH)$_2$(py)Cl [b]		Co(DH)$_2$(py)Br [c]		Co(DH)$_2$(py)I [d]	
[H$^+$] x 10^3 mol.dm^{-3}	k$_{II}$ dm^{3}mol^{-1}s^{-1}	[H$^+$]x 10^3 mol.dm^{-3}	k$_{II}$ dm^{3}mol^{-1}s^{-1}	[H$^+$] x 10^3 mol.dm^{-3}	k$_{II}$ dm^{3}mol^{-1}s^{-1}
5.11	0.366	4.51	0.438	4.36	0.620
6.97	0.309	5.53	0.393	6.03	0.568
8.85	0.244	10.49	0.283	9.52	0.355
13.46	0.196	19.52	0.198	16.73	0.240
29.00	0.105	27.32	0.146	31.17	0.149
57.97	0.066	37.56	0.090	46.52	0.115
60.03	0.059	60.00	0.085	62.42	0.098
80.42	0.060	82.50	0.079	88.92	0.083
100.00	0.059	100.00	0.075	100.00	0.077
115.00	0.059	114.50	0.073	115.20	0.076

a : Solvent : 1 vol % DMSO - H$_2$O mixture, [Fe(II)] : 8.649x10^{-4} mol.dm^{-3}

b : [Complex] : 4.958x10^{-5} mol.dm^{-3}

c : [Complex] : 3.763x10^{-5} mol.dm^{-3}

d : [Complex] : 4.373x10^{-5} mol.dm^{-3}

0.060 mol. dm^{-3} and reach a limiting value at [H$^+$] = 0.080 mol. dm^{-3} (Fig. 1). The rate dependence on [H$^+$] could be expressed in the form of eqn (2) suggesting

$$k_{\mathrm{obsd}} = a + b[\mathrm{H}^+]^{-1} \qquad (2)$$

a preequilibrium step. It may be seen from the table that the reduction rates follow the order Co(DH)$_2$(py)I > Co(DH)$_2$(py)Br > Co(DH)$_2$(py)Cl.

DISCUSSION

The inverse dependence of rate on [H$^+$] leading to a limiting rate at high [H$^+$] expressed by eqn (2) suggests the involvement of a preequilibrium step. This indicates the presence of an equilibrium mixture of the protonated and unprotonated forms of the complex over the range of [H$^+$] used. It has been demonstrated that this is a genuine hydrogen ion effect, by using LiClO$_4$ as the ionic medium[15]. The observed proton dependence and the second order kinetics suggest the following reaction sequence:

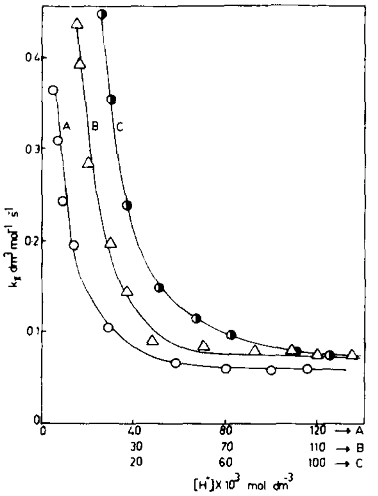

Fig. 1. Hydrogen ion dependence of rate constants for the Fe^{2+} reduction of *trans*-Halogenopyridinebis(dimethylglyoximato) Cobalt(III) complexes at 30°C and I = 1.0 mol · dm^{-3} (NaClO$_4$). Plots of k$_{II}$ vs [H$^+$]. A = Co(DH)$_2$(py)Cl; B = Co(DH)$_2$(py)Br; C = Co(DH)$_2$(py)I.

$$\mathrm{Co(DH)_2(py)X + H_3O^+ \overset{K_B}{\rightleftharpoons} Co(DH)(DH_2)(py)X^+ + H_2O} \qquad (3)$$

$$\mathrm{Co(DH)(DH_2)(py)X^+ + Fe^{2+} \xrightarrow{k_1} Co^{2+} + Fe^{3+} + py + X^- + 2DH_2} \qquad (4)$$

$$\mathrm{Co(DH)_2(py)X + Fe^{2+} \xrightarrow{k_2} Co^{2+} + Fe^{3+} + py + X^- + 2DH_2} \qquad (5)$$

The rate equation may then be written as

$$\begin{aligned}\text{Rate} &= k_1[\mathrm{Co(DH)(DH_2)(py)X^+}][\mathrm{Fe^{2+}}] \\ &\quad + k_2[\mathrm{Co(DH)_2(py)X}][\mathrm{Fe^{2+}}]\end{aligned} \qquad (6)$$

and

$$k_{\mathrm{II}} = \frac{k_1 K_B[\mathrm{H}^+]}{1 + K_B[\mathrm{H}^+]} + \frac{k_2}{1 + K_B[\mathrm{H}^+]} \qquad (7)$$

where k_{II} is the second order rate constant. At high [H$^+$], the first term in eqn (7) would be independent of [H$^+$] and be equal to k_1. A plot of k_{II} vs $[\mathrm{H}^+]^{-1}$ should give k_1 as intercept. From the linear plots of $(k_{\mathrm{II}} - k_1)^{-1}$ vs [H$^+$], k_2 and K_B could be obtained (Fig. 2).

The following values were obtained for k_1, k_2 and K_B respectively (i) Co(DH)$_2$(py)Cl: $k_1 = 0.051 \pm 0.003$ dm^3. mol^{-1} s^{-1}, $k_2 = 0.76 \pm 0.04$ dm^3. mol^{-1} s^{-1}, $K_B = 325 \pm 8$ dm^3. mol^{-1}; (ii) Co(DH)$_2$(py)Br: $k_1 = 0.071 \pm 0.004$ dm^3 mol^{-1} s^{-1}, $k_2 = 1.21 \pm 0.04$ dm^3 mol^{-1} s^{-1}, $K_B = 460$

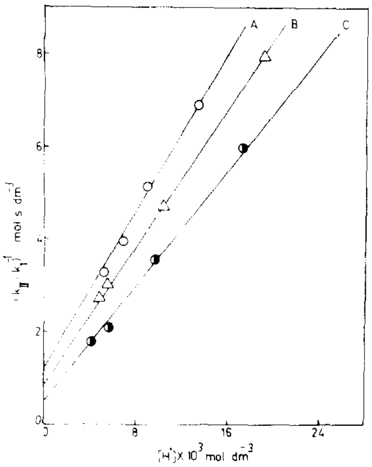

Fig. 2. Hydrogen ion dependence for the Fe^{2+} reduction of *trans*-Halogenopyridinebis(dimethylglyoximato) cobalt(III) complexes at 30°C and I = 1.0 mol · dm^{-3} ($NaClO_4$). Plots of $(k_{II} - k_1)^{-1}$ vs $[H^+]$. A = $Co(DH)_2(py)Cl$; B = $Co(DH)_2(py)Br$; C = $Co(DH)_2(py)I$.

± 15 dm^3 mol^{-1}; (iii) $Co(DH)_2(py)I$: $k_1 = 0.075 \pm 0.009$ dm^3 mol^{-1} s^{-1}, $k_2 = 1.91 \pm 0.09$ dm^3 mol^{-1} s^{-1}, $K_B = 625$ ± 30 dm^3 mol^{-1}. Similar reports on the protonation of cobaloximes have appeared in literature[16–18]. Our attempts to measure the protonation constant spectrophotometrically were unsuccessful since the spectral changes at different $[H^+]$ corresponding to pH 1–4 were very slight. However, it was attempted to measure the protonation constants by pH-metry. The weakly basic behaviour of the complexes was confirmed by pH-metry but reliable values of K_B could not be obtained by this method due to the very low solubility of the complexes in water. The trend $k_1 < k_2$ for all the complexes, suggesting that the unprotonated species reacts faster than the protonated species, is a characteristic of the inner sphere mechanism[1]. The same trend has been observed in the Fe^{2+} reduction of $Co(DH)_2(py)N_3$ and $Co(DH)_2(NH_3)N_3$ [15].

It is seen from Table 1 that the rate constants for the Fe(II) reduction follow the order $Co(DH)_2(py)I >$ $Co(DH)_2(py)Br > Co(DH)_2(py)Cl$. It is significant to note that this trend is reversed in the case of the Fe(II) reduction of the halopentaamminecobalt(III) complexes. This has been explained on the basis of the stabilities of the Fe(III)-halide complexes being in the order $F^- > Cl^- > Br^- > I^-$ for the reduction of the halopentaamminecobalt(III) complexes[11]. The order $I^- > Br^- > Cl^-$ observed for the cobaloximes appears to be the order of the ground state free energies of reduction of the halogenocobaloximes[19]. It is possible that the oxime oxygen functions as the bridging site. Suggestions to this effect are present in literature[20–22].

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