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Kinetics of the Iron(II) Reduction of *trans*-Azidopyridine- and Azidoamminebis(dimethylglyoximato)cobalt(III). Evidence for Protonation

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The kinetics of the Fe^{2+} reduction of trans-*azidopyridinebis(dimethylglyoximato)cobalt(III) and* trans-*azidoamminebis(dimethylglyoximato)cobalt(III) in aqueous perchlorate medium at* $I = 1.0$ *mol* dm^{-3} *ionic strength have been studied. The effects of* $[H^+]$ *and* $[Fe^{2+}]$ *on the rate were determined. The reaction was found to be second order and showed an inverse dependence on* $[H^+]$*. The second order rate constant could be expressed in the form* $k_{II} = k_1 + k_2 (1 + K_B [H^+])^{-1}$*. The kinetic data were found to be* $k_1 = 0.196 \pm 0.004$ dm^3 mol^{-1} s^{-1}, $k_2 = 2.6 \pm 0.5$ dm^3 mol^{-1} s^{-1} *and* $K_B = 1618 \pm 300$ dm^3 mol^{-1} *for* $Co(DH)_2(py)N_3$ *and* $k'_1 = 7.97 \pm 0.9 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, $k'_2 = 0.166 \pm 0.04$ dm^3 mol^{-1} s^{-1} *and* $K'_B = 312 \pm 50$ dm^3 mol^{-1} *for* $Co(DH)_2(NH_3)N_3$*. The inverse dependence on* $[H^+]$ *and the trend in the activation parameters suggest an inner-sphere mechanism involving protonated and unprotonated species of the complex.*

Introduction

Reports on the kinetic studies of the electron-transfer reactions of the *trans*-bis(dimethylglyoximato)cobalt(III) complexes are at present very few [1–3] in contrast to their pentaammine and ethylenediamine analogues [4, 5]. The Cobaloximes offer some interesting but scarcely explored possibilities for their electron-transfer reactions. (i) Due to the presence of the oxime function, the complexes may be protonated in acid media. Adin and Espenson [6] have reported the protonation constants of some alkylaquobis(dimethylglyoximato)cobalt(III) complexes. Crumbliss *et al.* [7] have reported the isolation of the protonated form of chloroethylbis(dimethylglyoximato)cobalt(III) hydrate. (ii) The oxime could function as a bridging ligand [2]. (iii) Studies with non-electrolyte complexes could minimize medium effects. In this report on the kinetics of the Fe^{2+} reduction of *trans*-azidopyridine- and azidoamminebis(dimethylglyoximato)cobalt(III), we aim to focus attention on some of these possibilities.

Experimental

Materials

$Co(DH)_2(py)N_3$ and $Co(DH)_2(NH_3)N_3$ (DH^- = dimethylglyoximate anion, py = pyridine) were prepared as reported in the literature [8]. The purity of the complexes was ascertained by their uv–visible spectra, ir spectra and also by elemental analysis. Iron(II) perchlorate was prepared [9] in solution by dissolving 99.9% pure iron powder (Electrolytic grade, Sarabhai Chemicals) in a slight excess of perchloric acid. Iron(II) was determined by spectrophotometry with 1,10-phenanthroline. Sodium perchlorate (Koch-Light) was used without further purification. Lithium perchlorate was prepared by addition of perchloric acid (reagent grade) to lithium carbonate followed by recrystallization. Dimethylsulphoxide ('Baker Analysed') and perchloric acid (E. Merck, reagent grade) were used as such. Doubly distilled water was used throughout the study.

Kinetic Measurements

Since the complexes were not soluble in pure water, the studies were carried out in 1 vol % dimethylsulphoxide–water mixture. Solutions of weighed amounts of the complexes in dimethylsulphoxide were prepared. Solutions of the complex and the Iron(II) reagent were thermostated separately and mixed at the time of the reaction. Aliquots were withdrawn and quenched by ice-water and the decrease in absorbance was measured at 303 nm for $Co(DH)_2(py)N_3$ and at 307 nm for $Co(DH)_2(NH_3)N_3$ in a Carl Zeiss recording spectrophotometer. All the experiments were carried out under pseudo first order conditions with 20 to 200 fold excess of $Fe(ClO_4)_2$. Rate constants were calculated from the slopes of the plots of $\log(A_0 - A_\infty) - \log(A_t - A_\infty)$ *vs.* time. All the reactions were studied up to at least three half-lives and the plots were linear. All reactions were studied in perchlorate medium and the ionic strength was adjusted to 1.0 mol dm^{-3} by sodium perchlorate.

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pH Studies on Protonation Equilibria

The pH measurements were carried out with a M/s. Bhagyanagar Electronics digital pH meter. pH's were measured for various hydrogen ion concentrations in the range 1.0×10^{-4}–1.0×10^{-2} mol dm^{-3} in the presence (h_1) and in the absence of the complex (h_2). K_B was determined as $[\text{Complex} - \text{H}]^+_{eq}$ $[\text{Complex}]^{-1}_{eq}$ $[\text{H}^+]^{-1}_{eq}$, where $[\text{Complex} - \text{H}]^+_{eq} = (h_2 - h_1)$, $[\text{Complex}]_{eq} = [\text{Complex}]_{total} - [\text{Complex} - \text{H}]^+$ and $[\text{H}^+]_{eq} = h_1$.

Stoichiometry

The stoichiometry of the reaction was determined by measuring the Fe(III) and Co(II) present in the product mixture. FeN_3^{2+} and Cobaloxime(II) were also detected among the products. Iron(III) was determined spectrophotometrically by Kitson's method [10]. Cobalt(II) was determined as $CoCl_4^{2-}$ in the presence of excess hydrochloric acid. The ratio of Fe(III): Co(II) was found to be 1:1 in the reactions studied, indicating the stoichiometry of 1:1.

Results

The reactions studied may be represented as

$$Co(DH)_2(amine)N_3 + Fe^{2+} + 2H^+ \longrightarrow Fe^{3+} + Co^{2+} + 2DH_2 + amine + N_3^- \qquad (1)$$

Cobaloxime(II) was also observed as a product at $[H^+] \leq 0.001$ mol dm^{-3}. A 1:1 stoichiometry was experimentally observed by spectrophotometry. Studies at various $[Fe^{2+}]$ indicate the rate law, rate = k [Complex] $[Fe^{2+}]$, the reaction being second order (Tables I and II). Tables I and II show the second order rate constants for the Fe^{2+} reduction of $Co(DH)_2(py)N_3$ and $Co(DH)_2(NH_3)N_3$ respectively at various hydrogen ion concentrations. The effect of hydrogen ion on the rate may be observed from the plot of the rate constants *vs.* $[H^+]$ shown in Fig. 1. The rate constants decrease with increasing hydrogen ion concentration in the range 0.001–0.1 mol dm^{-3} and reach a limiting value. The dependence on hydrogen ion concentration could be expressed in the form

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

suggesting a pre-equilibrium step. A linear plot of k_{obsd} *vs.* $[H^+]^{-1}$ would give a and b (Fig. 2). The data suggest the presence of an equilibrium mixture of the protonated and unprotonated forms of the complex.

TABLE I. Rate Constants for the Iron(II) Reduction of *trans*-$Co(DH)_2(py)N_3$ in Perchlorate Medium[a] of I = 1.0 mol dm^{-3} ($NaClO_4$).

$[H^+] \times 10^3$ mol dm^{-3}	Temp. °C	$[Fe(II)] \times 10^4$ mol dm^{-3}	k_{II} dm^3 mol^{-1} s^{-1}
1.23	60	8.67[c]	1.069
5.63	60	8.67[c]	0.445
5.63[b]	60	8.84[c]	0.447
8.57	60	8.67[c]	0.372
8.57[b]	60	8.84[c]	0.367
11.51	60	8.67[c]	0.331
15.00	60	8.67[c]	0.297
30.59	60	8.67[c]	0.241
45.27	60	8.67[c]	0.243
59.95	60	8.67[c]	0.221
74.60	60	8.67[c]	0.217
100.00	60	8.67[c]	0.203
58.98	60	8.67[c]	0.219
58.98	40	8.90[d]	0.043
58.98	45	9.67[d]	0.053
58.98	50	8.90[d]	0.096
58.98	55	8.90[d]	0.151
104.50	45	9.23[d]	0.055
104.50	45	22.97[d]	0.054
104.50	45	46.18[d]	0.056
104.50	45	101.59[d]	0.055
104.50	45	230.86[d]	0.052
104.50	45	415.57[d]	0.053

[a] Solvent: 1 Vol.% DMSO–H_2O mixture. [b] I = 1.0 mol dm^{-3} ($LiClO_4$). [c] [Complex] = 3.9031×10^{-5} mol dm^{-3}. [d] [Complex] = 3.9274×10^{-5} mol dm^{-3}.

TABLE II. Rate Constants for the Iron(II) Reduction of *trans*-$Co(DH)_2(NH_3)N_3$ in Perchlorate Medium[a] of I = 1.0 mol dm^{-3} ($NaClO_4$).

$[H^+] \times 10^2$ mol dm^{-3}	Temp. °C	$[Fe(II)] \times 10^3$ mol dm^{-3}	$k'_{II} \times 10^2$ dm^3 mol^{-1} s^{-1}
1.62	60	4.32[b]	3.53
1.99	60	4.32[b]	3.12
2.34	60	4.32[b]	2.88
3.12	60	4.32[b]	2.00
4.61	60	4.32[b]	1.58
6.10	60	4.32[b]	1.53
7.59	60	4.32[b]	1.60
11.52	60	4.32[b]	1.19
5.90	60	4.32[b]	1.53
5.90	50	8.98[b]	0.80
5.90	55	8.98[b]	1.21
5.90	65	8.98[b]	3.54
5.90	70	8.50[c]	3.96

[a] Solvent: 1 Vol.% DMSO–H_2O mixture. [b] [Complex]: 3.6547×10^{-5} mol dm^{-3}. [c] [Complex]: 3.9711×10^{-5} mol dm^{-3}.

Activation parameters were determined for the Fe^{2+} reduction of both $Co(DH)_2(py)N_3$ and $Co(DH)_2(NH_3)N_3$ at hydrogen ion concentrations chosen from the limiting region of Fig. 1 (Tables I and II). The data were obtained from rate constants measured at five temperatures in the range 40° – 60 °C for $Co(DH)_2(py)N_3$ and 50° – 70 °C for $Co(DH)_2(NH_3)N_3$. The values are, $\Delta H^{\ddagger} = 71.7 \pm 0.8$ kJ mol^{-1},

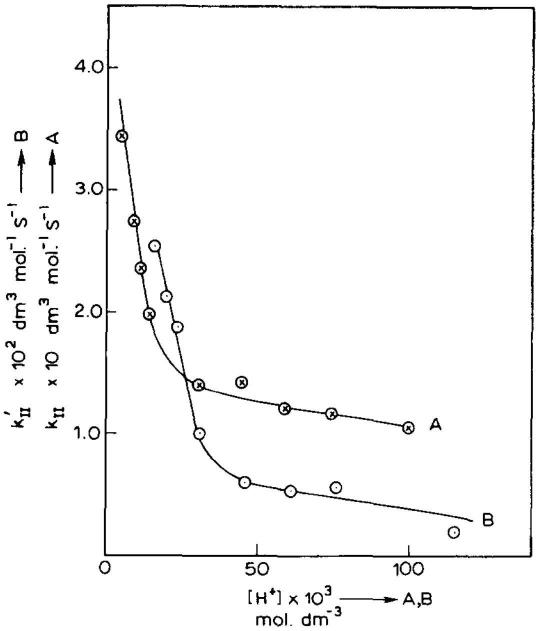

Fig. 1. Hydrogen ion dependence of rate constants for the Fe^{2+} reduction of $Co(DH)_2(py)N_3$ and $Co(DH)_2(NH_3)N_3$ at 60 °C and I = 1.0 mol dm^{-3} ($NaClO_4$). Plots of k_{II} *vs.* [H^+]. A = $Co(DH)_2(py)N_3$; B = $Co(DH)_2(NH_3)N_3$.

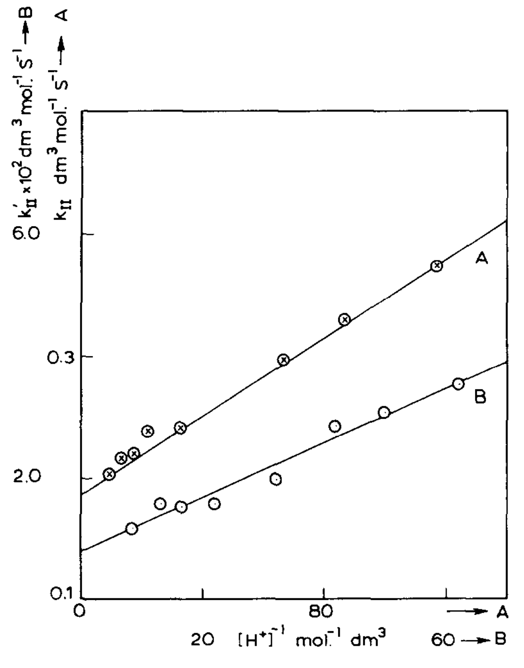

Fig. 2. Hydrogen ion dependence for the Fe^{2+} reduction of $Co(DH)_2(py)N_3$ and $Co(DH)_2(NH_3)N_3$ at 60 °C and I = 1.0 mol dm^{-3} ($NaClO_4$). Plots of k_{II} *vs.* [H^+]$^{-1}$. A = $Co(DH)_2(py)N_3$; B = $Co(DH)_2(NH_3)N_3$.

$\Delta S^{\ddagger} = -43.1 \pm 2.4$ J K^{-1} mol^{-1} for $Co(DH)_2(py)N_3$ and $\Delta H^{\ddagger} = 81.9 \pm 2.1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -32.2 \pm 4.1$ J K^{-1} mol^{-1} for $Co(DH)_2(NH_3)N_3$.

The possibility of aquation of the complexes under the experimental conditions was ruled out since a spectrophotometric study showed no aquation during the period of electron-transfer kinetic study.

Discussion

It may be seen from the data in Tables I and II, *i.e.*, the inverse dependence of rate on [H^+] leading to a limiting rate at high [H^+], that the reaction involves considerable protonation of the Cobaloximes, even at [H^+] $\simeq$ 0.01 mol dm^{-3}. The reproducibility of the rate constants in $NaClO_4$ (1.0 mol dm^{-3}) as well as in $LiClO_4$ (1.0 mol dm^{-3}) media shows that the hydrogen ion effect is genuine and not a medium effect. Besides, one would expect medium effects to be insignificant when the reactant is a non-electrolyte. The observed proton dependence and the second order kinetics suggest the following reaction sequence*:

$$Co(DH)_2(amine)N_3 + H_3O^+ \overset{K_B}{\rightleftharpoons} [Co(DH)(DH_2)(amine)N_3]^+ + H_2O \quad (3)$$

$$[Co(DH)(DH_2)(amine)N_3]^+ + Fe^{2+} \xrightarrow{k_1} Co^{2+} + Fe^{3+} + \text{free ligands} \quad (4)$$

$$Co(DH)_2(amine)N_3 + Fe^{2+} \xrightarrow{k_2} Co^{2+} + Fe^{3+} + \text{free ligands} \quad (5)$$

Accordingly, the rate equation may be written as

$$\text{Rate} = k_1 [Co(DH)(DH_2)(amine)N_3]^+ [Fe^{2+}] + k_2 [Co(DH)_2(amine)N_3] [Fe^{2+}] \quad (6)$$

and

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

where k_{II} is the second order rate constant. The first term in eqn. 7 would be independent of [H^+] for high K_B and [H^+], *i.e.*, at the limiting region of the curve in Fig. 1. A plot of k_{II} *vs.* [H^+]$^{-1}$ gives k_1 as inter-

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*An alternative explanation for the observed proton dependence may be found in the hydrolysis ($K_h \simeq 10^{-4}$) of Fe(II) ion as reported by Wells and Salaam [11]. However pK_h for Fe(II) has been estimated as 9.5 [12]. We attempted to study the hydrolysis of $Fe(ClO_4)_2$ by pH-metry and observed that the process at pH ~ 4 in the presence of air is the oxidation of Fe(II) and not hydrolysis.

cept (Fig. 2). From the linear plots of $(k_{II} - k_1)^{-1}$ *vs.* $[H^+]$, k_2 and K_B could be obtained. These values were, however, calculated by a least-squares method.

The following values were obtained for k_1, k_2 and K_B: (i) $Co(DH)_2(py)N_3$: $k_1 = 0.196 \pm 0.004$ dm^3 mol^{-1} s^{-1}, $k_2 = 2.6 \pm 0.5$ dm^3 mol^{-1} s^{-1} and $K_B = 1618 \pm 300$ dm^3 mol^{-1}; (ii) $Co(DH)_2(NH_3)N_3$: $k_1' = 7.97 \pm 0.9 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, $k_2' = 0.166 \pm 0.04$ dm^3 mol^{-1} s^{-1} and $K_B' = 312 \pm 50$ dm^3 mol^{-1}. It is noticed that $k_1 < k_2$ for both complexes *i.e.*, the unprotonated species reacts faster than the protonated species, a trend similar to that pointed out by Taube [13] for the chromium(II) reduction of $Co(NH_3)_5(H_2O)^{3+}$. A 10^6 fold increase in rate was observed for $Co(NH_3)_5OH^{2+}$ over the aquo complex. A higher rate for the conjugate base is a characteristic of the inner-sphere mechanism. This may be a consequence of the reduction of the overall basicity of the protonated complex towards formation of an inner-sphere complex with the Fe^{2+} ion. Of particular interest are the high values of protonation constants for the azido complexes. Using a spectrophotometric technique Adin and Espenson [6] have reported values of *ca.* 3.5–4.3 for K_B for some alkylaquobis(dimethylglyoximato)cobalt(III) complexes. Prince and Segal [1] have predicted a very approximate value of 0.25 dm^3 mol^{-1} for the $Co(DH)_2(NH_3)Br$–V^{2+} reaction from a kinetic study. In the present investigation we carried out pH measurements with the complexes to confirm protonation. The results agree with the K_B data from kinetics ($K_B = 1376 \pm 172$ dm^3 mol^{-1} for $Co(DH)_2(py)N_3$ and $K_B' = 535 \pm 76$ dm^3 mol^{-1} for $Co(DH)_2(NH_3)N_3$). However, the pH data should be taken as only approximate, because of the very low solubility of the complexes in water. The concentrations used were of the order of 10^{-4} mol dm^{-3}.

Accepting that an inner-sphere mechanism operates, the question as to the site of bridge formation may be considered. There are reports [2, 3] suggesting that the oxygen of the oxime ligand should be the bridging site. Recently Bakac and Espenson [14] have reported that Iron(III) binds at the oxime oxygen in methyl(aquo)cobaloxime, on the basis of spectrophotometric studies. It may be expected that the Iron(II) would also form the bridge at the oxime oxygen.

The activation parameters were determined from rate constants measured at sufficiently high $[H^+]$ that only the protonated forms of the complexes, *viz.*, $Co(DH)(DH_2)(amine)N_3^+$, would be present. The second term in the r.h.s. of eqn. 7 would vanish under these conditions and the first term would become k_1, as $K_B [H^+] \gg 1$. The activation parameters refer to the rate constant k_1.

The trend $Co(DH)_2(py)N_3 > Co(DH)_2(NH_3)N_3$ is observed for the reduction rates, consistent with previous reports on non-bridging ligand effects, *viz.*, py > NH_3. Linck [15, 16] has reviewed on the effect of non-bridging ligands in inner-sphere reactions. He explains the lower rates for NH_3 as being due to the σ^* orbital in the ammine complexes being at a higher energy level for electron-transfer than in the π-stabilized pyridine complexes. Accordingly, for non-bridging ligands the stronger their σ bonds with the metal, the slower should be the reduction of the corresponding complexes. The activation parameters obtained in our studies appear to confirm this. The values are: $Co(DH)_2(py)N_3$: $\Delta H^{\ddagger}$: 71.7 ± 0.8 kJ mol^{-1}, $\Delta S^{\ddagger}$: −43.1 ± 2.4 J K^{-1} mol^{-1} and $Co(DH)_2(NH_3)N_3$, $\Delta H^{\ddagger}$: 81.9 ± 2.1 kJ mol^{-1}, $\Delta S^{\ddagger}$: −32.2 ± 4.1 J K^{-1} mol^{-1}. The energy of the σ^* orbitals in the complexes appears to be reflected in the activation energy. However, further work needs to be done with a wider range of non-bridging ligands before applying this criterion.

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