A Kinetic Study of Iron(II) Reduction of Cobaloxime by Visible Spectrophotometric Method

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The kinetics of iron(II) reduction of aquoiodocobaloximes, *viz.*, $[Co(dmgH)_2(H_2O)I]$ where $dmgH^-$ = dimethylglyoximato mono anion, was studied spectrophotometrically at 484 nm in 4% (v/v) DMSO-H_2O medium at $27 \pm 0.1°C$ at various hydrogen ion concentrations and ionic strength under pseudo-first-order conditions using an excess of the reductant. The inverse dependence of rate on $[H^+]$ suggests equilibrium between the protonated and unprotonated forms of the complexes, the protonated form reacting slower than the unprotonated form. Added Ni^{2+} and ionic strength have no effect on the rate of the reaction.

Key Words: Cobaloximes, Cobalt(III)-dioximes, Iron(II) reduction, Visible Spectrophotometric determination.

INTRODUCTION

Cobalt(III) complexes of dimethyl glyoxime of the type $[Co(dmgH)_2(B)X]$, where $dmgH^-$ = dimethylglyoximato mono anion, known as cobaloximes, have been studied extensively as model compounds for vitamin-B_{12} and coenzyme-B_{12} with several axial ligands[1]. Champloy *et al.*[2] have carried out an extensive survey on the structure, redox behaviour and the catalytic activities of coenzyme-B_{12} and its models. The chemical nature of cobalt(III) in oxime and dioxime environment was studied[3, 4] by their redox behaviour with reductants such as Fe(II), Cr(II), etc. The reactions were mostly influenced by oxime network and were monitored by the UV absorption of the complexes. Here, the visible spectrometric method of study of the kinetics of reduction of a cobaloxime containing axial iodide and water were reported.

EXPERIMENTAL

Preparation of the complex: The complex, used for the study, was prepared by a two stage method from *trans*-dichlorobis(dimethylgloximato)cobaltate(III), $H[Co(dmgH)_2Cl_2]$, as follows. The dichloro complex, *viz.*, $H[Co(dmgH)_2Cl_2]$ was prepared by a modified method reported in literature[5]. Cobaltous chloride (0.10 mol) (AR, E. Merck) was dissolved in 750 mL of acetone and mixed with dimethylglyoxime (0.2 mol). The mixture was agitated for 10 min and filtered to remove any undissolved materials. Dry air was passed for 30 min and the solution was allowed to stand overnight. The green crystals of the dichloro complex formed were collected and washed with acetone, methanol and ether.

Trans-dichlorobis(dimethylglyoximato)cobaltate(III) (0.01 mol) was gently warmed with 50 mL of water for 30 min. The completion of the reaction was indicated by the colour change from green to light brown indicating the formation of *trans*-aquochlorobis(dimethylglyoximato)cobalt(III), $[Co(dmgH)_2(H_2O)Cl]$.

The aquochloro complex, thus obtained, was filtered and treated with KI (0.01 mol) of in 50 mL of warm water[6] and stirred for 30 min. The solution turned dark brown. The brown coloured product, aquoiodobis(dimethylglyoximato)cobalt(III), *viz.*, [Co(dmgH)$_2$(H$_2$O)I], crystallized when allowed to stand over night. The purity of the complex was ascertained by elemental analysis, IR and NMR spectral data. Cobalt present in the complex was determined volumetrically using EDTA and xylenol orange as indicator.
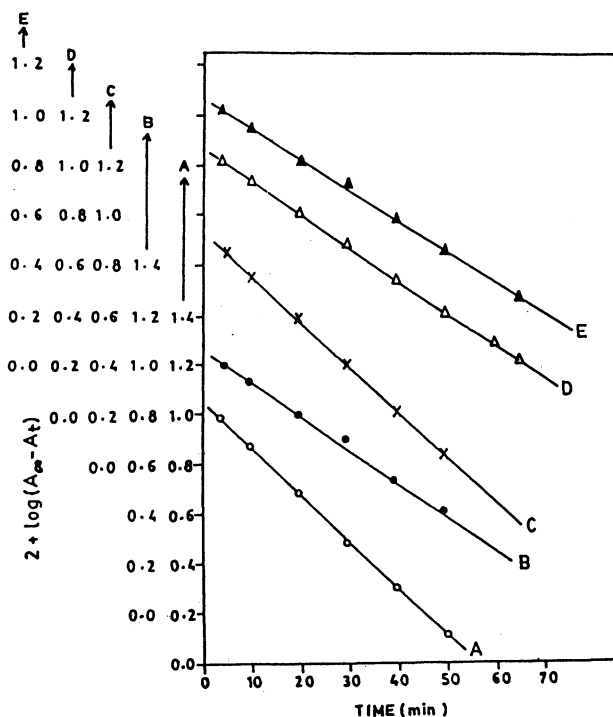

Fig. 1.   Iron(II) reduction of *trans*-[Co(dmgH)$_2$(H$_2$O)I] in 4.0% DMSO-H$_2$O (v/v) at 27 ± 0.1°C.
   [Complex] = 1.0 × 10^{-4} M; [Fe(II)] = 2.0 × 10^{-3} M
   B: [H$^+$] = 0.2 M,   I = 0.50 M
   C: [H$^+$] = 0.02 M, Ni(II) = 0.002 M, I = 0.50 M
   D: [H$^+$] = 0.2 M,   Ni(II) = 0.002 M, I = 0.50 M
   E: [H$^+$] = 0.2 M,   I = 0.05 M

Preparation of Iron(II) perchlorate: Iron(II) perchlorate, used as the reductant, was prepared by dissolving 99.9% pure iron powder (0.56 g) in 150 mL of 0.25 M perchloric acid in nitrogen atmosphere. The dissolution of iron was complete over a period of 12 h. The concentration of iron(II) in the solution was estimated by titrating it against standard potassium permanganate. The excess acid present in the solution was determined by titrating a known volume of the solution, after passing through Dowex 50W-X8, [H$^+$] cation exchange resin, against standard alkali. The solution was preserved in an airtight flask under nitrogen atmosphere. Fresh solutions were prepared frequently.

Kinetics of the Iron(II) reduction of the complexes: The iron(II) reduction of the complexes was followed using SPEKOL visible spectrophotometer. Solutions of required volumes of the complex in DMSO-H$_2$O, lithium perchlorate to provide the required ionic strength and perchloric acid to give the desired acid strength were thermostated at $27 \pm 0.1°C$. The reaction was initiated by the addition of a known volume of iron(II) solution. The rate of the reduction of the complexes was followed under pseudo-first-condition with excess of iron(II) from the increase in absorption of the ferric ions produced by estimating it as the thocyanate complex. Exactly 2 mL of the reaction mixture was mixed with 8 mL of 40% ammonium thiocyanate and the absorbance was measured at 484 nm. The pseudo-first-order rate constants, k_{obs}, were obtained from the slopes of the linear plots of log $(A_\infty - A_t)$ *vs.* time.

The stoichiometry of the reaction was determined by estimating Fe(III) and Co(II) present in the product mixture. Iron(III) was estimated as ferric thiocyanate and cobalt(II) as $[CoCl_4]^{2-}$ by Kitson method[7]. The ratio of Fe(III) : Co(II) was found to be 1 : 1.

Product Analysis: A known amount of complex solution in 10% aq. methanol was mixed with a known amount of Fe(II) solution and the reaction was allowed to stand for 6 h. The products formed in the reaction were separated by passing through Dowex 50W-X8, [H$^+$] cation exchange resin. The products were eluted using water and 0.5 M HClO$_4$. The first fraction obtained at the time of charging the column with the product mixture and subsequent elution with water contained free dimethylglyoxime (dmgH$_2$) which was estimated spectro-photometrically ($\lambda_{max} = 2.26$ nm, $\varepsilon_{max} = 15400\ M^{-1}\ cm^{-1}$) and iodide as silver iodide gravimetrically. The second fraction obtained by eluting with 0.5 M HClO$_4$ contained cobalt(II) which was estimated as $[CoCl_4]^{2-}$.

RESULTS AND DISCUSSION

Kinetics of the Iron(II) Reduction of the Complexes

The iron(II) reduction of aquoiodocobaloxime was studied by following the increase in the absorbance of the reaction mixture at 484 nm due to the liberation of Fe^{3+} as ferric thiocyanate complex at which the ligands have negligible absorbance. Pseudo-first-order plots of log $(A_\infty - A_t)$ vs time were found to be linear. The pseudo-first-order rate constants, k_{obs}, were obtained at different hydrogen ion and Ni^{2+} concentrations and ionic strength (Table-1).

A linear dependence of pseudo-first-order rate constant, k_{obs}, on Fe(II) was observed indicating the first-order dependence of rate with respect to Fe(II). Hence, the second-order rate constants, k, were obtained by dividing k_{obs} by the concentration of Fe(II) used for the red-ox reaction.

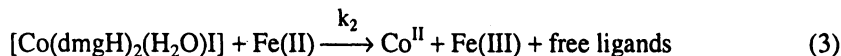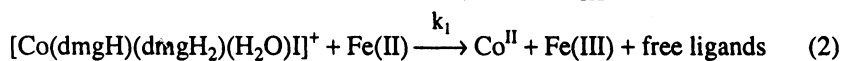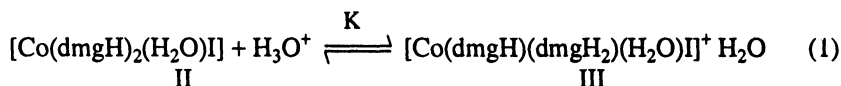The rate shows an inverse dependence on [H$^+$]. Such kind of trend is in good agreement with already reported work[3, 4]. It has been verified that [H$^+$] dependence is not a medium effect and is a consequence of acid-base equilibrium[8]. The magnitude of change in rate constant with [H$^+$] is too large to be attributed to medium effects.

TABLE-1

IRON(II) REDUCTION OF AQUOIODOCOBALOXIME: EFFECT OF [H$^+$], Ni(II)
AND IONIC STRENGTH

Pseudo-first-order rate constants k_{obs} (s^{-1}), second-order rate constants, k (M^{-1} s^{-1}) and the second-order rate coefficients, k_1 and k_2 (M^{-1} s^{-1}) for the iron(II) reduction of aquoiodocobaloxime in 4% (v/v) DMSO-H$_2$O at 27 ± 0.1°C. [Complex] = 4.0 × 10^{-4} M, [Fe(II)] = 2.0 × 10^{-3} M.

Line	[H$^+$] (M)	[Ni(II)] (M)	Ionic strength, I (M)	k_{obs} × 10^4 (s^{-1})	k (m^{-1} s^{-1})
A	0.20	—	0.50	7.259	0.3629
B	0.20	—	0.50	5.006	0.2503
C	0.20	0.002	0.50	7.0796	0.3540
D	0.20	0.002	0.50	4.971	0.2485
E	0.20	—	0.05	5.003	0.2502

The [H$^+$] dependence must arise due to acid-base equilibria, involving the oxime in the complex. Hence, the following reaction sequence may be proposed:

$$[Co(dmgH)_2(H_2O)I] + H_3O^+ \underset{}{\overset{K}{\rightleftharpoons}} [Co(dmgH)(dmgH_2)(H_2O)I]^+ H_2O \quad (1)$$
$$\text{II} \qquad\qquad\qquad\qquad\qquad\qquad\quad \text{III}$$

$$[Co(dmgH)(dmgH_2)(H_2O)I]^+ + Fe(II) \xrightarrow{k_1} Co^{II} + Fe(III) + \text{free ligands} \quad (2)$$

$$[Co(dmgH)_2(H_2O)I] + Fe(II) \xrightarrow{k_2} Co^{II} + Fe(III) + \text{free ligands} \quad (3)$$

Accordingly, the rate equation may be written as

$$\text{Rate} = k_1[Co(dmgH)(dmgH_2)(H_2O)I] + [Fe(II)] + k_2[Co(dmgH)_2(H_2O)I][Fe(II)] \quad (4)$$

Hence, the second-order rate constant, k, for the reduction of cobaloximes may be expressed in the form:

$$k = \frac{K[H^+]k_1}{K[H^+] + 1} + \frac{k_2}{K[H^+] + 1} \quad (5)$$

where K is the protonation constant and k_1 and k_2 are the second-order rate coefficients for the reduction of the protonated (III) and unprotonated (II) forms of the complex, respectively.
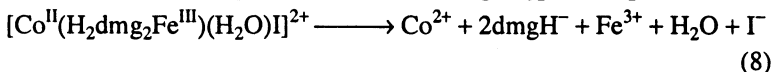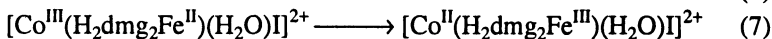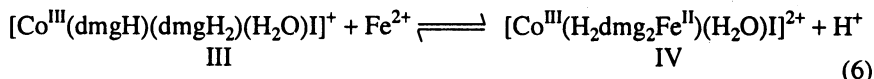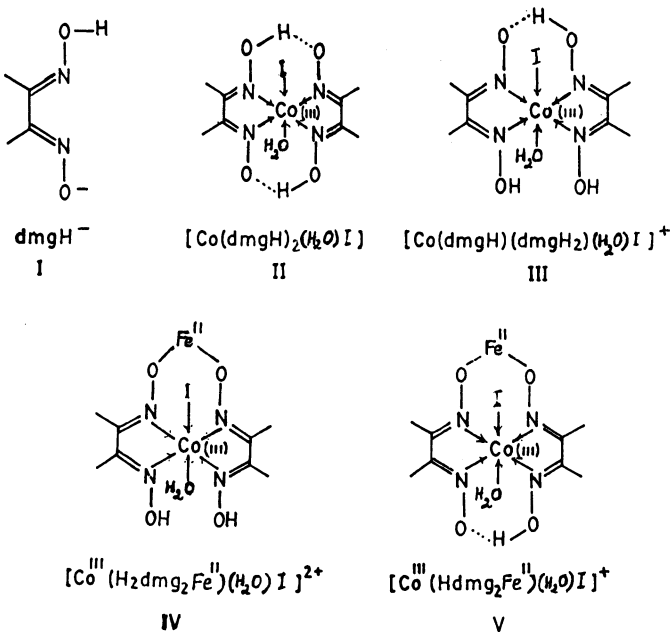
The value of the protonation constant, K, for the complex was obtained as 235 M^{-1} by pH titration and by the Irving and Rossoti method[9] of computation. Hence, the rate coefficients k_1 and k_2 can be obtained by feeding the values of k at different hydrogen ion concentrations. Accordingly, the rate coefficients k_1 and k_2 were found to be 0.2355 ± 0.0016 and 0.9401 ± 0.0286 M^{-1}s^{-1}, respectively.

It may be noted that equation-5 represents the extent to which the second-order rate coefficients k_1 and k_2 contribute to the overall second-order rate constant, k for the reaction at different [H$^+$]. For example, the fractional contribution of k_1 to the second-order rate constant k in the [H$^+$] range 0.02–0.2 M vary from 0.825 to 0.971 and that of k_2 in the reverse order *viz.*, 0.0175 to 0.029 for the same [H$^+$] range. Moreover, the magnitude of the second-order rate coefficients k_1 and k_2 follows the
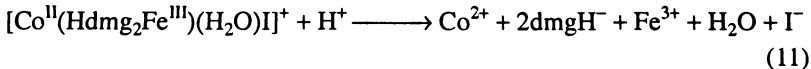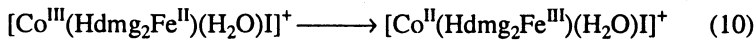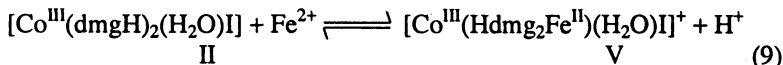
order $k_1 < k_2$. The observed $[H^+]$ dependence of k and the values of k_1 and k_2 indicate that the unprotonated form (II) is reduced at a faster rate than the protonated form (III). Such behaviour is characteristics of an inner-sphere reaction.

Hence, the iron(II) reduction of the cobaloximes may be considered stepwise as oxime bridged iron(II) reduction of protonated and the unprotonated forms of the complexes:

Oxime bridged iron(II) reduction of the protonated complexes:

$$dmgH^-$$
$$I$$

$$[Co(dmgH)_2(H_2O)I]$$
$$II$$

$$[Co(dmgH)(dmgH_2)(H_2O)I]^+$$
$$III$$

$$[Co^{III}(H_2dmg_2Fe^{II})(H_2O)I]^{2+}$$
$$IV$$

$$[Co^{III}(Hdmg_2Fe^{II})(H_2O)I]^+$$
$$V$$

$$[Co^{III}(dmgH)(dmgH_2)(H_2O)I]^+ + Fe^{2+} \rightleftharpoons [Co^{III}(H_2dmg_2Fe^{II})(H_2O)I]^{2+} + H^+$$
$$\text{III} \qquad\qquad\qquad\qquad\qquad\qquad \text{IV}$$
$$(6)$$

$$[Co^{III}(H_2dmg_2Fe^{II})(H_2O)I]^{2+} \longrightarrow [Co^{II}(H_2dmg_2Fe^{III})(H_2O)I]^{2+} \quad (7)$$

$$[Co^{II}(H_2dmg_2Fe^{III})(H_2O)I]^{2+} \longrightarrow Co^{2+} + 2dmgH^- + Fe^{3+} + H_2O + I^-$$
$$(8)$$

Oxime bridged iron(II) reduction of the unprotonated complexes:

$$[Co^{III}(dmgH)_2(H_2O)I] + Fe^{2+} \rightleftharpoons [Co^{III}(Hdmg_2Fe^{II})(H_2O)I]^+ + H^+$$
$$\text{II} \qquad\qquad\qquad\qquad\qquad \text{V}$$
$$(9)$$

$$[Co^{III}(Hdmg_2Fe^{II})(H_2O)I]^+ \longrightarrow [Co^{II}(Hdmg_2Fe^{III})(H_2O)I]^+ \quad (10)$$

$$[Co^{II}(Hdmg_2Fe^{III})(H_2O)I]^+ + H^+ \longrightarrow Co^{2+} + 2dmgH^- + Fe^{3+} + H_2O + I^-$$
$$(11)$$

Since, dimethyl sulphoxide has a strong absorption in the region 220–230 nm, the product analysis was carried out in 10% (v/v) CH_3OH-H_2O medium to identify and to estimate the free oxime liberated in the reduction of the cobaloxime. The first fraction eluted with water contained 90–95% of the total oxime and iodide, supporting the liberation of the ligands in their free states.

Generally, nickel(II) is a powerful donor to dimethylglyoxime. Hence, it was thought that it could influence the reaction mechanism. But, the observed trend in the reaction in the presence and in the absence of Ni(II) shows that it has no effect or negligible effect on rate of the reaction. Moreover, ionic strength also has very little effect on the rate of the reaction confirming that the reduction of the unprotonated neutral complex contributes more to the overall reaction rate than the reduction of the protonated form of the complex, which is very well illustrated by their rate coefficient, *viz.*, k_1 and k_2.

The effect of $[H^+]$ on the rate of the reaction and the product analysis suggests that the cobaloxime undergoes reduction by iron(II) by bridging mainly through oxime oxygen. The preference to equatorial oxime is somewhat surprising compared to axial halogen bridging. The reason could be that the oxime bridging must provide a pathway of lower barried than bridging by the axial ligands. The available data[10] on Co—N bond lengths in cobaloximes may be considered to support this observation. For example, the Co^{III}—N equatorial bond length in cobaloximes is 1.87 Å while it is also of same value for Co^{II}—N *viz.*, 1.89 Å in cobalt(II) salicylaldehyde ethylenediamine. Thus, the bond length to the equatorial ligand in the tetraaza macrocyclic complexes of cobalt(III) differs little from those of the cobalt(II) analogues. Hence, the change from Co(III) to Co(II) in their complexes will involve minimum energy barrier if bridging involves equatorial oxime may be expected.

ACKNOWLEDGEMENTS

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