Iron(II) Reduction of *trans*-Bis(dimethylglyoximato)halogenopyridinecobalt(III) Complexes: Kinetics and Mechanism

Arunachalam Dayalan and Venkatapuram R. Vijayaraghavan*
Department of Physical Chemistry, University of Madras, Guindy Campus, Madras - 600 025, India

The iron(II) reduction of cobaloximes of the type *trans*-[Co(Hdmg)$_2$L(X)] [Hdmg = dimethylglyoximate(1−); L = pyridine (py), nicotinamide (na) or isonicotinamide (isna), X = Cl, Br or I] was studied in 1% (v/v) dimethyl sulfoxide–water at 27 ± 0.1 °C and I = 0.25 mol dm^{-3} ($LiClO_4$) in the range [H^+] 0.007–0.100 mol dm^{-3} under pseudo-first-order conditions using an excess of the reductant. The inverse dependence of rate on [H^+] suggests an equilibrium between the protonated and unprotonated forms of the complex, the protonated form reacting slower than the unprotonated form. The rate constants are in the order $Cl^- < Br^- < I^-$ and py < na ≈ isna for the axial ligands.

Studies on the chemistry of cobaloximes have been extensively carried out during the last three decades.[1,2] Interest in this class of compounds has grown since it was recognised that cobaloximes simulate the reactions of vitamin B_{12} and could be model compounds[1–3] which could help in understanding the mechanism of biological reactions involving vitamin B_{12}.

The kinetics of the iron(II) reduction of azidoammine- and azidopyridine-bis(dimethylglyoximato)cobalt(III) complexes, studied in this laboratory,[4] featured a rate dependence on [H^+] of the form $k = a + b(c + [H^+])^{-1}$ indicating equilibrium protonation of the oxime, and a faster reduction of the unprotonated than the protonated form. Such a kinetic behaviour suggested an inner-sphere reduction, possibly with bridging at the oxime oxygen.

However, the question still remains as to which would be the bridging site when additional ligands with proven bridging efficiency[5] are in the axial position of the substrate. Hence, it should be of interest to investigate the kinetics of reduction of cobaloximes which carry ligands like halides and pyridinecarboxamides. We report here a study of the iron(II) reduction of the complexes *trans*-[Co(Hdmg)$_2$L(X)] [Hdmg = dimethylglyoximate(1−); L = pyridine (py), nicotinamide (na) or isonicotinamide (isna); X = Cl, Br or I] in 1% (v/v) dimethyl sulfoxide (dmso)–water in the range 0.007 < [H^+] < 0.100 mol dm^{-3}.

Experimental

Materials.—Complexes of the type *trans*-[Co(Hdmg)$_2$(py)X], *trans*-[Co(Hdmg)$_2$(na)X] and *trans*-[Co(Hdmg)$_2$(isna)X] were prepared using a procedure similar to that reported in the literature.[6–8] The purity of the complexes was confirmed by elemental analysis and UV/VIS, IR and ^{1}H NMR spectral studies.[9]

Dimethyl sulfoxide (S. Merck) was dried over calcium hydride and distilled fractionally at reduced pressure. The distilled solvent was stored over 4 Å molecular sieves and used for all the kinetic studies.

Preparation of Iron(II) Perchlorate.—Iron(II) perchlorate solution was prepared[10] by dissolving 99.9% pure iron powder (Electrolytic grade, Sarabhai Chemicals) (2.6 g) in previously deaerated *ca.* 0.2 mol dm^{-3} perchloric acid (250 cm^3). The concentration of iron(II) ion formed was determined spectrophotometrically using 1,10-phenanthroline.[11] The excess of acid present in the iron(II) stock solution was estimated by passing a known volume of the solution through a cation-exchange resin column (Dowex 50W-X8, H^+) and titrating the eluate against standard alkali.

Kinetic Measurements.—The kinetic studies were carried out in 1% (v/v) dimethyl sulfoxide–water. A stock solution of the complex was prepared by dissolving a weighed amount of the complex in 10% (v/v) dmso–water. Required volumes of the solutions of the complex, lithium perchlorate (to provide 0.25 mol dm^{-3} ionic strength) and perchloric acid (to give the desired acid strength) were thermostatted at 27 ± 0.1 °C. The reaction was initiated by the addition of a known volume of iron(II) solution. The decrease in absorbance with time was measured at 300 nm using a Carl Zeiss (SPECORD) recording spectrophotometer. All the experiments were carried out under pseudo-first-order conditions with a 20–40 fold excess of Fe^{II} over the complex in an inert atmosphere. The pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of the linear plots of $\log(A_t - A_\infty)$ *vs.* time.

Stoichiometry.—The stoichiometry of the reaction was determined by estimating the Fe^{III} and Co^{II} present in the product mixture. Iron(III) was determined as the thiocyanate complex and cobalt(II) as $[CoCl_4]^{2-}$ in an excess of hydrochloric acid.[12] The ratio of Fe^{III}:Co^{II} was found to be 1:1.

Results and Discussion

Kinetic Data.—The kinetics of the iron(II) reduction of all the complexes was studied at 300 nm (shoulder) where the complexes showed appreciable absorbance which decreased in the presence of Fe^{II} and finally became negligible (*ca.* 10% of the initial absorbance). A linear dependence of k_{obs} on [Fe^{II}] was observed for all the complexes.

Studies were also carried out in the absence of Fe^{II} where the absorbance of the complex was monitored as a function of time during the same period as for the redox studies, and no change in absorbance was noted. Hence, the second-order rate constants, k, were obtained by dividing the pseudo-first-order rate constants k_{obs} by the concentration of Fe^{II} used (Table 1).

The dependence of the second-order rate constant k on [H^+] may be expressed in the form (1) where a, b and c are empirical

$$k = a + \frac{b}{(c + [H^+])} \quad (1)$$

Table 1 Second-order rate constants, k/dm^3 mol^{-1} s^{-1}, for the iron(II)[a] reduction of the cobalt(III) dimethylglyoximato complexes as a function of hydrogen-ion concentration at 27 ± 0.1 °C

	[H$^+$]/mol dm^{-3}					
Complex	0.007	0.010	0.025	0.050	0.075	0.100
[Co(Hdmg)$_2$(py)Cl][b]	0.161	0.151	0.086	0.068	0.062	0.046
[Co(Hdmg)$_2$(py)Br][c]	0.166	0.157	0.104	0.082	0.073	0.067
[Co(Hdmg)$_2$(py)I][d]	0.396	0.345	0.198	0.112	0.078	0.068
[Co(Hdmg)$_2$(na)Cl][b]	0.157	0.143	0.128	0.118	0.117	0.109
[Co(Hdmg)$_2$(na)Br][c]	0.165	0.152	0.134	0.126	0.122	0.111
[Co(Hdmg)$_2$(na)I][b]	0.443	0.327	0.221	0.178	0.148	0.130
[Co(Hdmg)$_2$(isna)Cl][b]	0.153	0.146	0.129	0.125	0.114	0.106
[Co(Hdmg)$_2$(isna)Br][b]	0.170	0.153	0.144	0.132	0.116	0.104
[Co(Hdmg)$_2$(isna)I][c]	0.697	0.484	0.273	0.166	0.149	0.132

[a] [Fe^{II}] = 4.0 × 10^{-4} mol dm^{-3}, I = 0.25 mol dm^{-3} ($LiClO_4$), solvent 1% (v/v) dmso–water. [b] [complex] = 1.5 × 10^{-4} mol dm^{-3}. [c] [complex] = 1.0 × 10^{-4} mol dm^{-3}. [d] [complex] = 5.0 × 10^{-5} mol dm^{-3}.

Table 2 Acid dissociation constants K and rate constants k_1 and k_2 for the iron(II) reduction of cobaloximes *

Complex	10^3K/ mol dm^{-3}	k_1/dm^3 mol^{-1} s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
[Co(Hdmg)$_2$(py)Cl]	5.1	0.042 (0.006)	0.304 (0.031)
[Co(Hdmg)$_2$(py)Br]	2.2	0.058 (0.003)	0.624 (0.017)
[Co(Hdmg)$_2$(py)I]	1.6	0.068 (0.013)	1.944 (0.033)
[Co(Hdmg)$_2$(na)Cl]	5.8	0.105 (0.003)	0.211 (0.009)
[Co(Hdmg)$_2$(na)Br]	2.4	0.107 (0.008)	0.312 (0.020)
[Co(Hdmg)$_2$(na)I]	1.6	0.124 (0.012)	1.998 (0.190)
[Co(Hdmg)$_2$(isna)Cl]	6.7	0.105 (0.004)	0.218 (0.015)
[Co(Hdmg)$_2$(isna)Br]	2.5	0.107 (0.009)	0.313 (0.023)
[Co(Hdmg)$_2$(isna)I]	1.7	0.109 (0.002)	3.154 (0.175)

* Standard deviations in parentheses.

Table 3 Trends in halide-bridged exchange and electron-transfer reactions

Reaction	Trend	Ref.
[CrX]$^{2+}$ + Cr^{II}	I > Br > Cl > F	14
[Cr(NH$_3$)$_5$X]$^{2+}$ + Cr^{II}	I > Br > Cl > F	15
[Rh(NH$_3$)$_5$X]$^{2+}$ + Cr^{II}	F > Cl > Br > I	16
[Ru(NH$_3$)$_5$X]$^{2+}$ + Cr^{II}	F > Cl > Br > I	17
[FeX]$^{2+}$ + Cr^{II}	I > Br > Cl > F	18
[Co(NH$_3$)$_5$X]$^{2+}$ + [Co(CN)$_5$(H$_2$O)]$^{3-}$	I > Br > Cl > F	19
[Co(NH$_3$)$_5$X]$^{2+}$ + Cr^{II}	I > Br > Cl > F	20
[Co(NH$_3$)$_5$X]$^{2+}$ + Fe^{II}	F > Cl > Br > I	21
[Co(Hdmg)$_2$L(X)] + Fe^{II}	I > Br > Cl	This work

parameters. This dependence suggests an equilibrium involving the protonated and unprotonated forms of the complex. The reaction sequence may be written as in equations (2)–(4) and the

$$[Co(Hdmg)_2L(X)] + H_3O^+ \overset{K_B}{\rightleftharpoons} [Co(H_2dmg)(Hdmg)L(X)]^+ + H_2O \quad (2)$$

$$[Co(Hdmg)(H_2dmg)L(X)]^+ + Fe^{2+} \xrightarrow{k_1} Co^{2+} + Fe^{3+} + \text{free ligands} \quad (3)$$

$$[Co(Hdmg)_2L(X)] + Fe^{2+} \xrightarrow{k_2} Co^{2+} + Fe^{3+} + \text{free ligands} \quad (4)$$

second-order rate constant k may be expressed as in (5) where

$$k = \frac{k_1[H^+]}{K + [H^+]} + \frac{k_2K}{K + [H^+]} \quad (5)$$

k_1 and k_2 are the rate constants for the reduction of the protonated and unprotonated forms of the complex respectively, and K ($=1/K_B$) is the acid dissociation constant of the protonated form. The values of K were measured potentiometrically by titrating the complex solution against standard alkali.[13]

Equation (5) is of the form $k = pk_1 + qk_2$ where p and q are constants for a given complex at a given [H$^+$]. Hence, for the reduction of a complex, six equations involving k_1 and k_2 were generated corresponding to [H$^+$] = 0.007, 0.01, 0.025, 0.05, 0.075 and 0.10 mol dm^{-3}. These when solved for k_1 and k_2, taken two at a time, gave 15 sets of solutions. Such calculations were done for all the complexes using a suitable program in BASIC. Rate constants k_1 and k_2 obtained in the range 0.007 < [H$^+$] < 0.05 were considered for estimating the standard deviation (Table 2).

The K values were also obtained from a linear least-squares treatment of equation (5) as follows. Equation (5) can be modified as (6). At high [H$^+$] equations (5) and (6) can be

$$k = \frac{k_1K_B[H^+]}{1 + K_B[H^+]} + \frac{k_2}{1 + K_B[H^+]} \quad (6)$$

written as (7) and (8). A plot of k *vs.* [H$^+$]$^{-1}$ gives k_1 as the

$$k = k_1 + \frac{k_2K}{H^+} \quad (7)$$

$$k = k_1 + \frac{k_2}{1 + K_B[H^+]} \quad (8)$$

intercept [equation (7)], and a plot of $(k - k_1)^{-1}$ *vs.* [H$^+$] gives $1/k_2$ and K_B/k_2 as intercept and slope respectively [equation (8)]. The agreement between the kinetic and equilibrium K values is satisfactory. For example K_{kin} and K_{eq} for *trans*-[Co(Hdmg)$_2$(ina)I] were found to be 1.5 × 10^{-3} and 1.7 × 10^{-3} mol dm^{-3} respectively.

It may be observed from Table 2 that $k_1 < k_2$ and that the k_2 values are more sensitive to halide variation than the k_1 values, suggesting a greater sensitivity to halide variation for the unprotonated form. The observed [H$^+$] dependence of k, and the values of k_1 and k_2, indicate that the unprotonated form is reduced at a faster rate than is the protonated form. Such a behaviour is characteristic of inner-sphere reactions.

Effect of Halide on the Rate of Reduction.—Studies on bridging by halide ions have been carried out [14–21] using several pairs of oxidants and reductants as well as in exchange reactions. Table 3 summarises these results. The trend $F^- < Cl^- < Br^- < I^-$ is known as the normal order and the reverse is known as the inverse order. Several aspects related to the oxidant and reducing agent appear to be significant in determining the trend. For example in the case of the chromium(II) reduction of both Rh^{III} and Ru^{III} an inverse order was found, while the corresponding reductions of Cr^{III}, Fe^{III} and

Co^{III} follow the normal order. It may thus be generalised that if the oxidant is a soft acid the inverse order applies and if hard the normal order, the reductant in both cases being a hard acid. Based on the above arguments one should expect an inverse trend for the iron(II) reduction of halogenocobaloximes which are soft acids, if the electron transfer is mediated by bridging through the halide ion. However, the observed normal order is inconsistent with electron transfer mediated by halide bridging.

Effect of Pyridine and Substituted Pyridines on the Rate of Reduction.—Considering the reduction of the pyridinecarboxamide complexes, there is an additional possibility, *viz.* bridging and electron mediation by the amide group. Similar reduction studies were carried out by Nordmeyer and Taube[5] using pentaammine(pyridinecarboxamide)cobalt(III) and Cr^{II}. The rate constants for the amide-bridged electron transfer are $(3.3 \pm 0.2) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} for $[Co(NH_3)_5(na)]^{3+}$ and 17.4 ± 0.5 dm^3 mol^{-1} s^{-1} for $[Co(NH_3)_5(isna)]^{3+}$ both reactions being independent of $[H^+]$. The higher rate constant for the isonicotinamide complex has been attributed to its greater conjugation effect.

In the light of the foregoing observations one should expect a much higher rate constant for the iron(II) reduction of $[Co(Hdmg)_2(isna)X]$ than $[Co(Hdmg)_2(na)X]$ for a given halogen, if the reductions are mediated through the amide group. However, the observed trend in rates, *viz.* py < na ≈ isna with the ratio of rates being 0.9–1.0:1 for the pyridinecarboxamide complexes, suggests that the reduction is not mediated by amide bridging.

Considering the bridging and electron-mediating efficiency of halide or pyridinecarboxamide, a preference for bridging at the oxime is somewhat surprising. The obvious reason would be that oxime bridging provides a pathway of lower energy than bridging by the axial ligands. The available data[22] 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 1.89 Å in *N,N'*-ethylenebis(salicylideneiminato)cobalt(II). Thus the bond length to the equatorial ligand in the tetraaza macrocyclic complexes of cobalt(III) differs little from those in the cobalt(II) analogues. Hence, we may expect that the change from Co^{III} to Co^{II} will involve the minimum Franck–Condon barrier if bridging involves equatorial oxime.

Acknowledgements

The authors thank Dr. T. Balakrishnan for his constant encouragement and the facilities provided.

References

1 G. N. Schrauzer, *Acc. Chem. Res.*, 1968, **1**, 97.
2 D. G. Brown, *Prog. Inorg. Chem.*, 1973, **18**, 177.
3 T. T. Tsoo, M. Loots and J. Halpern, *J. Am. Chem. Soc.*, 1982, **104**, 623.
4 P. N. Balasubramanian and V. R. Vijayaraghaven, *Inorg. Chim. Acta*, 1980, **38**, 49.
5 F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, 1968, **90**, 1162.
6 A. V. Ablov and N. M. Samus, *Russ. J. Inorg. Chem.*, 1960, **5**, 410.
7 A. V. Ablov and M. P. Filippov, *Russ. J. Inorg. Chem.*, 1959, **4**, 1004.
8 N. Mani, *Studies on Metal Complexes*, Ph.D. Thesis, University of Madras, 1986.
9 A. Dayalan and V. R. Vijayaraghaven, *J. Indian Chem. Soc.*, in the press.
10 R. D. Cannon and J. Gardinner, *J. Chem. Soc., Dalton Trans.*, 1972, 887.
11 J. G. Calvert and J. N. Pitts, jun., *Photochemistry*, Wiley, New York, 1967, p. 785.
12 R. E. Kitson, *Anal. Chem.*, 1959, **22**, 664.
13 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397.
14 D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, 1958, **80**, 1091.
15 A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, 1958, **80**, 1084.
16 G. T. Takaki and R. T. M. Fraser, *Proc. Chem. Soc.*, 1964, 116.
17 J. Stritar and H. Taube, *Inorg. Chem.*, 1969, **8**, 2281.
18 D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, 1969, **91**, 599.
19 J. P. Candlin, J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, 1963, **85**, 2517.
20 J. P. Candlin and J. Halpern, *Inorg. Chem.*, 1965, **4**, 766.
21 H. Diebler and H. Taube, *Inorg. Chem.*, 1965, **4**, 1029.
22 H. A. O. Hill, *Inorganic Biochemistry*, ed. G. L. Eichhorn, Elsevier, Amsterdam, 1973, p. 1067.

Received 4*th December* 1991; *Paper* 1/06340E