

Iron(II) reduction of halogenopyridinecarboxylatocobalt(III)–dioxime complexes: Kinetics and mechanism

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Abstract. The iron(II) reduction of cobalt(III)–dioxime complexes of the type *trans*-[Co(DODOHbzo)(s-py)X]ClO₄, where DODOHbzo = 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioximate (1-), s-py = pyridine (py), nicotinic acid (nic-COOH) or isonicotinic acid (isonic-COOH) and X⁻ = Cl⁻, Br⁻ or I⁻, was studied in 1% (v/v) DMSO–H₂O at 27 ± 0.1°C and I = 0.25 M (LiClO₄) in the [H⁺] range 0.007–0.100 M 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 one. The rate constants reflect the trend Cl⁻ < Br⁻ < I⁻ and py < nic-COOH ≈ isonic-COOH for the axial ligands.

Keywords. Cobalt(III)–dioximes; iron(II) reduction; pyridinecarboxylic acids.

1. Introduction

The discovery (Schrauzer and Kohnle 1964) that the cobaloximes, *bis*(dimethylglyoximate)cobalt(III) complexes, bore chemical resemblance to vitamin-B₁₂, led to several studies on different aspects of vitamin-B₁₂ model complexes. Considerable structural modifications were made on the equatorial and axial ligands to understand the reactivity of the metal ion (Costa and Mestroni 1968; Costa *et al* 1969). Such studies also include the complexes of the ligand: 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime, (DOH)₂bzo which binds to the metal through its conjugate base (Mathur and Narang 1964; Mohapatra and Dash 1990).

Kinetics of the iron(II) reductions of some cobaloximes studied in this laboratory featured an inverse dependence of rate on [H⁺], which indicates the possibility of inner-sphere electron-transfer involving bridging by the dimethylglyoxime (Arunachalam *et al* 1981). However, it would be interesting to investigate the nature of the bridging site when additional ligands with proven bridging efficiencies are in the axial positions of cobalt(III)–dioximes. Hence, it is appropriate to investigate the kinetics of the reduction of cobalt(III)–dioxime complexes, which are similar to cobaloximes, carrying axial ligands like a halide, pyridine and pyridinecarboxylic acid. This report is a study of the iron(II) reduction of complexes of the type *trans*-[Co(DODOHbzo)(s-py)X]ClO₄.

* For correspondence

where DODOHbzo = 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione di-oximate (1-); s-py = pyridine (py), nicotinic acid (nic-COOH) or isonicotinic acid (isonic-COOH) and $X^- = Cl^-, Br^-$ or I^- . The studies have been carried out in 1% (v/v) DMSO-H₂O in the $[H^+]$ range 0.007–0.100 M.

2. Experimental

The ligand, (DOH)₂bzo, was prepared by the condensation of *o*-phenylenediamine and 2,3-butanedione monoxime as reported in the literature (Mathur and Narang 1964).

Complexes of the type *trans*-[Co(DODOHbzo)(py)X]ClO₄, *trans*-[Co(DODOHbzo)(nic-COOH)X]ClO₄ and *trans*-[Co(DODOHbzo)(isonic-COOH)X]ClO₄, were prepared using a procedure similar to that reported in the literature (Ramanujam and Alexander 1987). The purity of the complexes was confirmed (Dayalan and Vijayaraghavan 1992) by elemental analyses and UV-visible, IR and ¹H NMR spectral studies.

2.1 Preparation of iron(II) perchlorate

Iron(II) perchlorate solution was prepared (Cannon and Gardiner 1972) by dissolving 0.56 g of 99.9% pure iron powder (Electrolytic grade, Sarabhai Chemicals) in 250 ml of previously deaerated ≈ 0.2 M perchloric acid. The concentration of Fe(II), formed in solution, was determined spectrophotometrically using 1,10-phenanthroline (Calvert and Pitts 1967). The excess 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 50 W-X-8 H⁺) and titrating the eluate against standard alkali.

2.2 Kinetic measurements

Kinetic studies on the complex were carried out in 1% (v/v) DMSO-H₂O mixture. A stock solution of the complex was prepared by dissolving a weighed amount of the complex in 10% (v/v) DMSO-H₂O. Required volumes of the solutions of the complex, lithium perchlorate (to provide 0.25 M 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 Fe(II) solution. The change 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 an 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.

2.3 Stoichiometry

The stoichiometry of the reaction was determined by estimating the amounts of Fe(III) and Co(II) present in the product mixture. Iron(III) was determined as the thiocyanate complex having a maximum absorption at 480 nm by reference to the calibration curve and cobalt(II) was determined as $[CoCl_4]^{2-}$ at 690 nm ($\epsilon = 411 M^{-1} cm^{-1}$) in excess of hydrochloric acid (Kitson 1959). The Fe(III):Co(II) ratio was 1:1, indicating 1:1 stoichiometry with respect to the Fe(II) and Co(III) complexes.

3. Results and discussion

3.1 Kinetic data

Kinetics of the iron(II) reduction of all the complexes were studied at 300 nm (shoulder) where the complexes showed appreciable absorbance, which decreased in the presence of Fe(II) and finally became negligible ($\approx 10\%$ of the initial absorbance). A linear dependence of k_{obs} on $[\text{Fe(II)}]$ was observed for all the complexes studied. Hence, the second-order rate constant, k , was obtained by dividing k_{obs} by the concentration of Fe(II) used (table 1). The studies were also carried out in the absence of Fe(II) in which the absorbance of the complex was monitored as a function of time during the same period as for the redox studies – no change in absorbance was noted.

The observed dependence of the second-order rate constant, k , on $[\text{H}^+]$ may be expressed in the form

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

where a , b and c are empirical parameters. The experimental $[\text{H}^+]$ dependence suggests an equilibrium involving the protonated and unprotonated forms of the complex. The reaction sequence may be written as

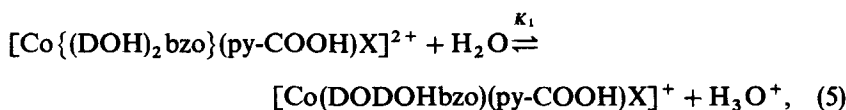
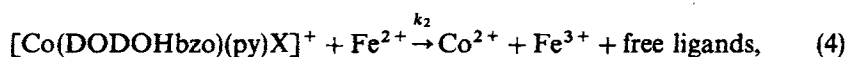
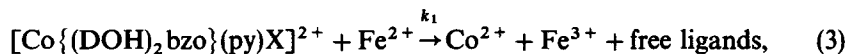
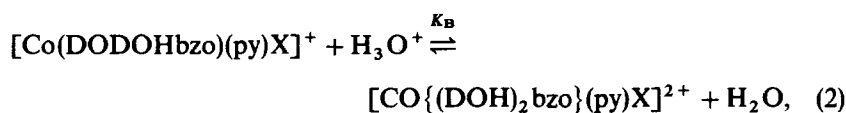
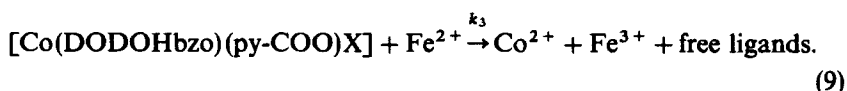
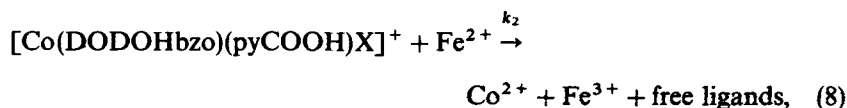
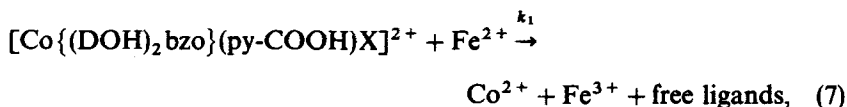
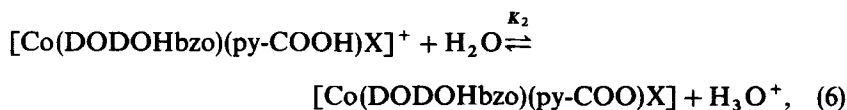


Table 1. Second-order rate constants, $k(\text{M}^{-1}\text{s}^{-1})$ for the iron (II) reduction^a of the cobalt(III) complexes as a function of hydrogen ion concentration at $27 \pm 0.1^\circ\text{C}$.

Complex	$k(\text{M}^{-1}\text{s}^{-1})$ at $[\text{H}^+]$ (M)					
	0.007	0.010	0.025	0.050	0.075	0.100
$[\text{Co}(\text{DODOHbzo})(\text{py})\text{Cl}]\text{ClO}_4^b$	0.144	0.126	0.086	0.060	0.052	0.048
$[\text{Co}(\text{DODOHbzo})(\text{py})\text{Br}]\text{ClO}_4^b$	0.176	0.144	0.090	0.064	0.053	0.049
$[\text{Co}(\text{DODOHbzo})(\text{py})\text{I}]\text{ClO}_4^c$	0.433	0.330	0.176	0.109	0.087	0.067
$[\text{Co}(\text{DODOHbzo})(\text{mic-COOH})\text{Cl}]\text{ClO}_4^b$	0.191	0.172	0.155	0.140	0.131	0.128
$[\text{Co}(\text{DODOHbzo})(\text{nic-COOH})\text{Br}]\text{ClO}_4^b$	0.195	0.176	0.164	0.159	0.140	0.136
$[\text{Co}(\text{DODOHbzo})(\text{nic-COOH})\text{I}]\text{ClO}_4^b$	0.608	0.465	0.280	0.182	0.156	0.140
$[\text{Co}(\text{DODOHbzo})(\text{isonic-COOH})\text{Cl}]\text{ClO}_4^b$	0.145	0.135	0.120	0.115	0.112	0.109
$[\text{Co}(\text{DODOHbzo})(\text{isonic-COOH})\text{Br}]\text{ClO}_4^c$	0.192	0.163	0.144	0.122	0.109	0.107
$[\text{Co}(\text{DODOHbzo})(\text{isonic-COOH})\text{I}]\text{ClO}_4^c$	0.525	0.403	0.270	0.185	0.155	0.139

^a $[\text{Fe(II)}] = 4.0 \times 10^{-3}\text{M}$; $I = 0.25\text{M}$ (LiClO_4); solvent: 1% (v/v) DMSO- H_2O ; ^b $[\text{complex}] = 1.0 \times 10^{-4}\text{M}$; ^c $[\text{complex}] = 5.0 \times 10^{-5}\text{M}$.



The second-order rate constant, k , for the Fe(II) reduction of pyridine and pyridinecarboxylic acid (py-COOH) complexes may be expressed as

$$k = \frac{k_1[\text{H}^+]}{K_1 + [\text{H}^+]} + \frac{k_2 K_1}{K_1 + [\text{H}^+]}, \quad (10)$$

$$k = k_1 \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} + k_2 \frac{K_1[\text{H}^+]}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} + k_3 \frac{K_1 K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2}, \quad (11)$$

respectively, where k_1 , k_2 and k_3 are the rate constants for the reduction of the protonated, unprotonated and deprotonated forms of the complex respectively, and K_1 and K_2 are the acid dissociation constants of the protonated form of the complex. The K_1 and K_2 values were measured potentiometrically by titrating the solution of the complex against standard alkali (Irving and Rossotti 1953).

Equations (10) and (11) are of the form, $k = pk_1 + qk_2$ and $k = pk_1 + qk_2 + rk_3$, respectively, where p , q and r are constants for a given complex at a given $[\text{H}^+]$. Hence, for the reduction of a complex, six equations involving k_1 , k_2 and k_3 were generated corresponding to $[\text{H}^+] = 0.007, 0.01, 0.025, 0.05, 0.075$ and 0.10 M. These six equations when solved for k_1 , k_2 and k_3 , taken three at a time, gave a set of solutions. Such calculations were done for all the complexes using a suitable program in BASIC. Values of rate constants, k_1 , k_2 and k_3 , satisfying all the six equations relating k were considered for estimating the standard deviation (table 2).

The K_1 values for the pyridine complexes were also obtained from a linear least squares treatment on (10) as follows.

$$k = \frac{k_1 K_B [\text{H}^+]}{1 + K_B [\text{H}^+]} + \frac{k_2}{1 + K_B [\text{H}^+]}, \quad (12)$$

where

$$K_B = 1/K_1.$$

Table 2. Acid dissociation constants, K_1 and K_2 , and the rate constants (k_1 , k_2 and k_3) for the iron(II) reduction of cobalt(III) complexes.^a

Complex	$K_1 \times 10^3$ (M)	$K_2 \times 10^4$ (M)	k_1 (M ⁻¹ s ⁻¹)	k_2 (M ⁻¹ s ⁻¹)	k_3 (M ⁻¹ s ⁻¹)
[Co(DODOHbzo)(py)Cl]ClO ₄	6.2	—	0.034(0.001)	0.269(0.005)	—
[Co(DODOHbzo)(py)Br]ClO ₄	3.0	—	0.036(0.002)	0.497(0.009)	—
[Co(DODOHbzo)(py)I]ClO ₄	1.9	—	0.042(0.001)	1.868(0.026)	—
[Co(DODOHbzo)(nic-COOH)Cl]ClO ₄	4.9	8.8	0.120(0.003)	0.229(0.003)	0.714(0.073)
[Co(DODOHbzo)(nic-COOH)Br]ClO ₄	2.4	4.2	0.130(0.001)	0.323(0.004)	1.120(0.045)
[Co(DODOHbzo)(nic-COOH)I]ClO ₄	1.5	3.6	0.105(0.002)	2.652(0.028)	6.411(0.320)
[Co(DODOHbzo)(isonic-COOH)Cl]ClO ₄	5.6	8.6	0.107(0.001)	0.164(0.005)	0.438(0.030)
[Co(DODOHbzo)(isonic-COOH)Br]ClO ₄	2.6	4.6	0.105(0.006)	0.316(0.007)	2.016(0.104)
[Co(DODOHbzo)(isonic-COOH)I]ClO ₄	1.5	3.7	0.108(0.005)	2.100(0.041)	8.548(0.230)

^aStandard deviation is given in parentheses.

At high $[H^+]$, (10) and (12) can be written as

$$k = k_1 + \frac{k_2 K_1}{[H^+]}, \quad (13)$$

$$k = k_1 + \frac{k_2}{1 + K_B [H^+]}. \quad (14)$$

A plot of k vs $[H^+]^{-1}$ gives k_1 as the intercept, (13). Hence, the linear plot of $(k - k_1)^{-1}$ vs $[H^+]$ gives $1/k_2$ and K_B/k_2 as intercept and slope respectively, (14). The agreement between the kinetic (K_1) and equilibrium (K_1) values is satisfactory.

It may be observed from table 2 that $k_1 < k_2 < k_3$, and that the latter values are more sensitive to halide variation than 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 , k_2 and k_3 indicate that the unprotonated form is reduced at a faster rate than the protonated form. Such behaviour is characteristic of inner-sphere reactions.

3.2 Effect of halide on the rate of reduction

Studies on bridging by halide ions have been carried out using several pairs of oxidants and reductants. 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 the reducing agent appear to be significant in determining the trend. For example, an inverse order is observed in the Cr(II) reductions of $[Ru(NH_3)_5X]^{2+}$ complexes (Stritar and Taube 1969), while the reductions of $[Co(NH_3)_5X]^{2+}$ complexes by Cr(II) follow the normal order (Candlin and Halpern 1965) and the corresponding reductions by Fe(II) follow the inverse order (Diebler and Taube 1965). We may thus generalise that if the oxidant is a soft acid, inverse order is followed and if hard, normal order, the reductant in both cases being a hard acid. Based on the above arguments, one should expect an inverse order for the Fe(II) reduction of halogeno-cobalt(III)-dioximes 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.

3.3 Effect of pyridine and substituted pyridine on the rate of reduction

In the case of the reduction of pyridinecarboxylic acid complexes, we find an additional possibility, viz., bridging and electron-mediation by the carboxylic acid group. A general trend in the rate of the Cr(II) reduction of pyridinecarboxylatopentaammine-cobalt(III) complexes was found to be: isonic-COOH > nic-COOH, with the ratio of rate constants 1:10 (Gould and Taube 1964). The higher rate constant for the isonicotinic acid complexes has been attributed to its greater conjugative effect.

In the light of the foregoing observations one should expect a much higher rate constant for the Fe(II) reduction of $[Co(DODOHbzo)(isonic-COOH)X]^+$ than for $[Co(DODOHbzo)(nic-COOH)X]^+$ for a given halogeno complex, if the reductions are mediated through the carboxylic acid group. However, the observed trend in rates, viz., py < nic-COOH \approx isonic-COOH with ratio of rates being 0.9-1.0 for the

pyridinecarboxylic acid complexes, suggests that the reduction is not mediated by carboxylic acid bridging.

4. Conclusion

Considering the bridging and electron-mediating efficiency of the halide or pyridine-carboxylic acids a preference to bridging at the oxime is somewhat surprising. The reason could be that the oxime bridging must provide a pathway of lower barrier than bridging by the axial ligands. The available data (Hill 1973) 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 cobalt(II)salicylaldehydeethylenediimine. Thus, length of the bond to the equatorial ligand in the tetraaza macrocyclic complexes of cobalt(III) differs little from those of the cobalt(III) analogues. Hence, we may expect that the change from Co(III) to Co(II) in their complexes will involve minimum Franck-Condon barrier if bridging involves the equatorial oxime.

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References

- Arunachalam M K, Balasubramanian P N and Vijayaraghavan V R 1981 *J. Inorg. Nucl. Chem.* **43** 753
Calvert J G and Pitts J N 1967 *Photochemistry* (New York: John Wiley and Sons) p. 785
Candlin J P and Halpern J 1965 *Inorg. Chem.* **4** 766
Cannon R D and Gardiner J 1972 *J. Chem. Soc., Dalton Trans.* 887
Costa G and Mestroni G 1968 *Tetrahedron Lett.* **41** 4005
Costa G, Mestroni G and Savorgnani E L 1969 *Inorg. Chim. Acta* **3** 323
Dayalan A and Vijayaraghavan V R 1992 *Indian J. Chem.* **31A** 800
Diebler H and Taube H 1965 *Inorg. Chem.* **4** 1029
Gould E S and Taube H 1964 *J. Am. Chem. Soc.* **86** 1318
Hill H A O 1973 *Inorganic biochemistry* (ed.) G L Eichhorn (Amsterdam: Elsevier) p. 1067
Irving H and Rossotti H S 1953 *J. Chem. Soc.* 3397
Kitson R E 1959 *Anal. Chem.* **22** 664
Mathur N and Narang C K 1964 *Talanta* **11** 647
Mohapatra M and Dash K C 1990 *Indian J. Chem.* **A29** 788
Ramanujam V V and Alexander V 1987 *Inorg. Chem.* **26** 3124
Schrauzer G N and Kohnle K 1964 *Chem. Ber.* **97** 3056
Stritar J and Taube H 1969 *Inorg. Chem.* **8** 2281