Chromium(II) reduction of cobalt(III) complexes of 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime: Kinetics and mechanism

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Kinetics of chromium(II) reduction of 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; s-py is pyridine(py) or a substituted pyridine like nicotinamide (nic-CONH₂), isonicotinamide (isonic-CONH₂) nicotinic acid (nic-COOH) or isonicotinic acid (isonic-COOH), and X=Cl, Br or I has been studied in DMSO-H₂O (1% v/v) at 27 ± 0.1°C and I=0.25 mol dm⁻³ (LiClO₄) in the [H⁺] range 0.001-0.1 mol dm⁻³ under pseudo-first order conditions using an excess of the reductant. The inverse dependence of rate on [H⁺], trends in the rate constants, viz. Cl<Br<I and py<s-py for the axial ligands and product analysis suggest an inner-sphere reaction with bridging by Cr(II) at the oxime oxygen or halide.

Cobalt(III) complexes of dioximes, like dimethylglyoxime (cobaloximes), have been studied extensively¹,² as model compounds for vitamin-B₁₂. Kinetics of iron(II) reduction of some cobaloximes featured a rate dependence on [H⁺] indicating the possibility of an inner-sphere electron-transfer involving bridging at dimethylglyoxime³⁻⁵.

However a different redox behaviour may be expected when cobalt(III) complexes of macrocyclic dioximes, containing additional ligands with proven bridging efficiency⁶,⁷ are reduced by powerful reducing agents like Cr(II). Hence, it should be of interest to investigate the kinetics of reduction of cobalt(III)-dioxime complexes carrying axial ligands like halide, pyridine, pyridine carboxamide or pyridine carboxylic acid. This report is a study of the chromium(II) reduction of the complexes of the type trans-[Co(DODOHbzo)(s-py)X]ClO₄.

Preparation of the complexes
Cobalt(III)–dioxime complexes of the type trans-[Co(DODOHbzo)(s-py)(X)]ClO₄ (Structures I and II) where s-py = pyridine(py), nicotinamide (nic-CONH₂), isonicotinamide (isonic-CONH₂), nicotinic acid (nic-COOH) or isonicotinic acid (isonic-COOH) and X=Cl, Br, or I were synthesised and characterised⁸ by elemental analysis, UV-visible, IR and ¹H NMR spectra.

Preparation of chromium(II) perchlorate
Chromium(II) perchlorate solution was obtained by zinc-amalgam reduction⁹ of an aqueous solution of Cr(ClO₄)₃ obtained by dissolving an electrolytic grade chromium powder (E. Merck, 0.51 g) in 2.0 mol dm⁻³ HClO₄ (25 ml) in nitrogen atmosphere in a round bottom flask fitted with serum cap. Nitrogen was passed into the solution through a steel needle. The

Materials and Methods
Cobalt(II) chloride (E. Merck) 1,2-diaminobenzene (BDH), 2,3-butanedione monoxime (Loba Chemie), pyridine (AR,SD Fine Chemicals) pyridine carboxamides and pyridine carboxylic acids (E. Merck) were used as such for the synthesis of the complexes. Cobalt(II) bromide was prepared by the addition of a calculated amount of 40% aq HBr (E. Merck) to cobalt(II) carbonate (V.V. Chemicals, India) and evaporating the resulting solution to dryness.
outgoing nitrogen along with hydrogen formed was also made to escape through a steel needle fitted with rubber tube leading to a cold water bath so that the solution was not in contact with atmospheric oxygen. The reduction was complete in 3 hr, giving a sky blue solution of Cr(CIO\(_4\))\(_2\). Required volumes of the Cr(II) solutions were withdrawn using de-aerated hypodermic syringes fitted with stainless needle. The needle holes on the serum cap were sealed using rubber solution. The concentration of Cr(II) formed in solution was estimated by reaction with excess Fe(III), in nitrogen atmosphere, and estimating the Fe(II) produced using KMnO\(_4\). The concentration of the free acid present in the Cr(II) solution was determined by measuring the pH of a known volume of the solution diluted suitably.

**Kinetic studies**

The kinetics of chromium(II) reduction of cobalt(III) complexes in 1% (v/v) DMSO-H\(_2\)O was studied using applied photophysics Model 1705 stopped flow spectrophotometer. Solution of the complex, perchloric acid (of the required concentration) and lithium perchlorate (to adjust the ionic strength to 0.25 mol dm\(^{-3}\)) were de-aerated and thermostatted in one compartment. The air in the other compartment was flushed out by passing nitrogen for about 30 min and then filled simultaneously with Cr(II) solution by transferring it from the stock solution using de-aerated hypodermic syringe fitted with stainless needle. All needle holes were sealed using rubber solution. The solutions were injected into the mixing chamber at a pressure of 40 psi. The reaction was followed by monitoring the decrease in absorbance of the complex at 360 nm and at 27 ± 0.1°C in the time scale sampling interval 2-50 ms for the reaction. The absorption output was digitised with a Data Lab Model 902 transient recorder equipped with a variable input sensitivity and variable sampling interval, and was monitored by Trio-Model CS-1562 A oscilloscope. About 500-700 data points were collected for each run, and at least six kinetic runs were made for each value of the rate constant. The data were stored and analysed by a CBM 3032 personal computer. The kinetic data were stored and analysed by a CBM 3032 personal computer. The kinetic data were stored and analysed by a CBM 3032 personal computer. The kinetic data were stored and analysed by a CBM 3032 personal computer. The kinetic data were stored and analysed by a CBM 3032 personal computer. The kinetic plots were done on a Hewlett-Packard 7470 graphic plotter to get the pseudo-first order rate constants, \(k_{obs}\).

**Stoichiometric studies**

The stoichiometry of the chromium(II) reduction of the cobalt(III)-dioxime complexes was determined spectrophotometrically, by estimating the amount of pyridine, pyridine carboxamide or pyridine carboxylic acid and cobalt(II) liberated, for every mole of Cr(II) added. The ratio of Cr(II) added to pyridine, pyridine carboxamide or pyridine carboxylic acid and Co(II) liberated was found to be 1:1:1 suggesting the 1:1 stoichiometry of the reaction with respect to the reductant and the cobalt(III) complex (vide product analysis).

**Product analysis**

The nature of the products formed in the chromium(II) reduction of the complexes, in 10% CH\(_3\)OH-H\(_2\)O medium, was studied spectrophotometrically. A de-aerated complex solution (1.0 \(\times\) 10\(^{-3}\) mol dm\(^{-3}\), 25 ml in 0.01 mol dm\(^{-3}\) HClO\(_4\)) and chromium(II) (1.0 \(\times\) 10\(^{-3}\) mol dm\(^{-3}\), 25 ml) were allowed to react for 30 s in an atmosphere of nitrogen. The reaction mixture was exposed to air and then passed through Dowex 50 W-X8, H\(^+\) cation exchange resin (5 cm long and 1 cm diameter), maintained at 5°C by circulating ice-cold water. The products formed were absorbed on the resin. Gradient-elution technique \(^{10}\), using water (50 ml), 0.5 mol dm\(^{-3}\) HClO\(_4\) (100 ml) and 1.0 mol dm\(^{-3}\) HClO\(_4\) (100 ml) was employed to separate the products. Typical UV spectra of the various fractions, obtained at different intervals are shown in Fig. 1. Higher quantities of the complexes and chromium(II) (50 μ mol each) were used for the quantitative study of the product analysis.

The first fraction containing free dioxime, (DOH)\(_2\)bzo, eluted at the time of charging the column with the product mixture (obtained in 10% (v/v) CH\(_3\)OH-H\(_2\)O medium) followed by washing with water, was estimated spectrophotometrically (\(\lambda_{max} = 226\) nm; \(\epsilon_{max} = 43,000\) dm\(^{-3}\) mol\(^{-1}\) cm\(^{-1}\)). The halide present in this fraction was estimated gravimetrically as silver halide.

Similarly, free pyridine, pyridine carboxamide or pyridine carboxylic acid (detected in the second fraction, eluted with 0.5 mol dm\(^{-3}\) HClO\(_4\)) were estimated from their characteristic measured UV absorptions in 0.5 mol dm\(^{-3}\) HClO\(_4\). \(\lambda_{max}\) nm ((\(\epsilon_{max}\) dm\(^{-3}\) mol\(^{-1}\) cm\(^{-1}\))): py=256(5,500); nic-CONH\(_2\) = 263 (5,420); isonic-CONH\(_2\) = 265 (5,200); nic-COOH=262 (5,340); isonic-COOH = 272(4,660).
Cobalt(II) present in this fraction was estimated as follows: The solution was neutralised with solid NaOH and evaporated to dryness. About 2 ml of 50% ammonium thiocyanate was added. The cobalt thiocyanate complex formed was extracted and made up to 100 ml with acetone. The absorbance of the solution was measured at 625 nm (ε = 1864 dm$^3$mol$^{-1}$cm$^{-1}$). Chromium(III), present in the third fraction as Cr-dioxime, was estimated by chromatography. Analysis and nitrogen was estimated by micro-Kjeldahl method.

**Results and Discussion**

**Kinetic studies**

The kinetics of chromium(II) reduction of all the complexes was studied in 1% (v/v) DMSO-H$_2$O at 360 nm (where the complexes showed appreciable absorbance, and the products showed negligible absorbance) under pseudo-first order conditions, with an excess of chromium(II) over the complex. All reactions were studied as a function of hydrogen ion concentration in the range 0.001 - 0.100 mol dm$^{-3}$ in an atmosphere of nitrogen. A linear dependence of the pseudo-first order rate constant, $k_{obs}$ on [Cr(II)] was observed. A plot of $k_{obs}$ versus [Cr(II)] was linear without any appreciable intercept indicating the absence of self decomposition or back reaction. Hence, the second order rate constants, were obtained by dividing $k_{obs}$ by the concentration of Cr(II) used (Table 1).

Chromium(II) reduction of all complexes shows an inverse dependence on [H$^+$] reaching a limiting value at [H$^+$]=0.100 mol dm$^{-3}$. The decrease in second order rate constant with an increase in [H$^+$] from 0.001 to 0.100 mol dm$^{-3}$ is about 60-70% of the initial value at [H$^+$] = 0.001 mol dm$^{-3}$. For example, the second order rate constant for the chromium(II) reduction of trans-[Co(DODOHbzo)(py)Cl]ClO$_4$ decreases from 22.5 dm$^3$mol$^{-1}$s$^{-1}$ at [H$^+$]=0.001 mol dm$^{-3}$ to 9.5 dm$^3$mol$^{-1}$ s$^{-1}$ at [H$^+$]=0.100 mol dm$^{-3}$. The magnitude of the change in rate constant with [H$^+$] is too large and

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**Table 1**—Second order rate constants, k dm$^3$mol$^{-1}$s$^{-1}$ for chromium(II) reduction of cobalt(III)-dioxime complexes as a function of [H$^+$] in DMSO-H$_2$O (1%, v/v) at 27 ± 0.1°C

<table>
<thead>
<tr>
<th>Complex</th>
<th>[H$^+$], mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.001</td>
</tr>
<tr>
<td>[Co(DODOHbzo) (py)Cl]ClO$_4$</td>
<td>22.5</td>
</tr>
<tr>
<td>[Co(DODOHbzo) (nic-CONH$_2$)Cl]ClO$_4$</td>
<td>23.0</td>
</tr>
<tr>
<td>[Co(DODOHbzo) (nic-CONH$_2$)Br]ClO$_4$</td>
<td>28.5</td>
</tr>
<tr>
<td>[Co(DODOHbzo) (nic-CONH$_2$)I]ClO$_4$</td>
<td>79.5</td>
</tr>
<tr>
<td>[Co(DODOHbzo) (isonic-CONH$_2$)Cl]ClO$_4$</td>
<td>24.0</td>
</tr>
<tr>
<td>[Co(DODOHbzo) (isonic-CONH$_2$)I]ClO$_4$</td>
<td>33.0</td>
</tr>
<tr>
<td>[Co(DODOHbzo) (isonic-COOH)Cl]ClO$_4$</td>
<td>37.0</td>
</tr>
</tbody>
</table>
hence, it could not be attributed to medium effects. Medium effect causes a change in rate only about 10-20%.

This behaviour is similar to that reported in earlier studies for the iron(II) reduction of cobaloximes. It has been verified that the $[H^+]$ dependence is not a medium effect, and is a consequence of acid-base dissociation equilibria, involving the hydrogen bonded proton in the oxime. Hence, the following reaction sequence may be proposed:

\[
[\text{Co(DODOHbzo)}(s\text{-py})X]^+{\text{H}_2}\text{O} \leftrightarrow K_H ^{\text{AH}^{2+}} [\text{Co((DOH)}_2\text{bzo})(s\text{-py})X]^2+ + \text{H}_2\text{O} \quad (1)
\]

\[
[\text{Co((DOH)}_2\text{bzo})(s\text{-py})X]^2+ + \text{Cr(II)} \rightarrow \text{Co(II)} + \text{AH}^{2+} \text{Cr(III)} \text{-ligand} + \text{Free ligands} \quad (2)
\]

\[
[\text{Co(DODOHbzo)}(s\text{-py})X]^+ + \text{Cr(II)} \rightarrow \text{Co(II)} + \text{AH}^{+} \text{Cr(III)} \text{-ligand} + \text{Free ligands} \quad (3)
\]

Accordingly, the rate equation may be written as

\[
\text{Rate} = k_1[AH^{2+}][\text{Cr(II)}] + k_2[A^+]\text{[Cr(II)]} \quad (4)
\]

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

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

where $k_1$ and $k_2$ are second order rate coefficients for the reduction of the protonated, $AH^{2+}$; and unprotonated, $A^+$, forms of the complexes, respectively, and $K (1/K_H)$ is the acid dissociation constant of the protonated form of the complex. The values of $K$ were determined potentiometrically, by titrating the complex solution against standard alkali.

The plot of $k$ versus $[H^+]$ would produce a non-linear curve. The parameters $k_1$ and $k_2$ satisfying the above non-linear equation (Eq. 5) were calculated by the least squares method of best fit using a suitable program (Table 2).

It may be noted that the magnitude of the rate constants, $k_1$ and $k_2$, follows the order $k_1 < k_2$, with $k_2$ values being more sensitive to halide variation than the $k_1$ values, suggesting a greater sensitivity to halide variation for the unprotonated form. The $k_2$ values follow the trend in rates $Cl < Br < I$ for the halogeno complexes; and $py < py\text{-CONH}_2 < py\text{-COOH}$ for the substituted pyridine. The observed $[H^+]$ dependence of $k_1$ and the values of $k_1$ and $k_2$ indicate that the unprotonated form is reduced at a faster rate than the protonated form. Such a behaviour is characteristic of an inner-sphere reaction. Hence, the overall reaction of chromium(II) reduction of cobaloximes may be considered stepwise as in Eqs 6-8.

\[
[\text{Co(DODOHbzo)}(s\text{-py})X]^+ + \text{Cr(II)} \leftrightarrow [\text{Co}^{IIl}(\text{DOH})_2\text{bzoCr}^{IIl})(s\text{-py})X]^2+ + \text{H}^+ \quad (6)
\]

\[
[\text{Co}^{IIl}(\text{DOH})_2\text{bzoCr}^{IIl})(s\text{-py})X]^2+ \rightarrow [\text{Co}^{II}](\text{DOH})_2\text{bzoCr}^{IIl})(s\text{-py})X]^2+ + \text{slow} \quad (7)
\]

\[
[\text{Co}^{IIl}(\text{DOH})_2\text{bzoCr}^{IIl})(s\text{-py})X]^2+ \rightarrow [\text{Co}^{II}](\text{DOH})_2\text{bzoCr}^{IIl})(s\text{-py})X]^2+ + \text{fast} \quad (8)
\]

The formation constant, $K_F$, of the precursor complex should be greater for the unprotonated form than the protonated form of the complex. Such mode of binding of the metal ion, e.g., Fe(III), to the coordinated oxime has been reported in literature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$K \times 10^3$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
<th>$k_1$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
<th>$k_2$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(DODOHbzo)(nic-CONH$_2$)Cl]ClO$_4$</td>
<td>7.1</td>
<td>9.17</td>
<td>25.42</td>
</tr>
<tr>
<td>[Co(DODOHbzo)(nic-CONH$_2$)Br]ClO$_4$</td>
<td>5.0</td>
<td>10.89</td>
<td>33.34</td>
</tr>
<tr>
<td>[Co(DODOHbzo)(nic-CONH$_2$)I]ClO$_4$</td>
<td>3.1</td>
<td>11.83</td>
<td>98.90</td>
</tr>
<tr>
<td>[Co(DODOHbzo)(isonic-CONH$_2$)Cl]ClO$_4$</td>
<td>8.1</td>
<td>8.77</td>
<td>26.11</td>
</tr>
<tr>
<td>[Co(DODOHbzo)(nic-CONH$_2$)I]ClO$_4$</td>
<td>1.5</td>
<td>9.95</td>
<td>49.49</td>
</tr>
<tr>
<td>[Co(DODOHbzo)(isonic-COOH)Cl]ClO$_4$</td>
<td>1.5</td>
<td>10.00</td>
<td>55.99</td>
</tr>
</tbody>
</table>
Product analysis

Since dimethyl sulfoxide has a strong absorption in the region 220-230 nm, the product analysis was carried out in 10% (v/v) CH₃OH-H₂O medium to identify and to estimate the free oxime liberated in the reduction of the cobalt(III) - dioximes (first fraction). But, there was no difficulty in the identification and estimation of free pyridine, pyridine carboxamide or pyridine carboxylic acids and Cr-dioxime, which were eluted as subsequent fractions for products formed in 1% (v/v) DMDSO-H₂O and 10% (v/v) CH₃OH-H₂O media. Moreover, the results were almost identical in both solvent systems (Table 3).

The first fraction eluted with water, obtained for reactions carried out in 10% (v/v) CH₃OH-H₂O medium, contained 40 - 60% of the total dioxime in the [H⁺] range 0.01 - 0.1 mol dm⁻³, 50 - 60% of free halide and no chromium. Typical UV spectra of this fraction (10 ml aliquots collected at different intervals) are shown in Fig. 1(a).

The second fraction, obtained by eluting with 0.5 M HClO₄, contained 95-100% pyridine or pyridine carboxamide. The typical UV spectra of this fraction (10 ml aliquots collected at different intervals) are shown in Fig. 1(b). Cobalt analysis of this fraction showed about 95% Co(II), and chromatome analysis indicated 30 - 40% of halide (each with respect to complex) the latter could be attributed to CrX⁺.

The third fraction, eluted with 1.0 mol dm⁻³ HClO₄, showed a characteristic UV spectrum, which was found to be common for all the complexes, λₘₚₙₐₓ (nm): 208, 250 [Fig. 1(c)], which could be attributed to Cr-dioxime species. Hence, the inverse [H⁺] dependence on the rate of reduction, and the product analysis suggest that the chromium(II) reduction of the cobalt(III)-dioxime proceeds through oxime or halide bridging.

Pyridine carboxamides were shown to be potential bridging ligands in chromium(II) reduction of pyridinecarboxamidopentaaminecobalt(III). The rate constants for the amide bridged electron-transfer reaction are 3.3 ± 0.2 × 10⁻² dm³ mol⁻¹ s⁻¹ for [Co(NH₃)₅ (nic-CONH₂)]²⁺ and 17.4 ± 0.5 dm³ mol⁻¹ s⁻¹ for [Co(NH₃)₅ (isonic-CONH₂)]²⁺, both reactions being independent of [H⁺]. The greater rate constants for the reduction of cobalt(III) complexes of isonicotinamide, by two orders of magnitude has been attributed to its greater conjugation effect. Accordingly, one should expect a much higher rate constant, for the chromium(II) reduction of halogenocobalt(III)-dioximes containing axial isonicotinamide or isonicotinic acid than the corresponding nicotinamide or nicotinic acid complex, if the reductions were mediated through the amide or acid group. However, the observed similar trend in rates (Tables 1 and 2) and product analysis (Table 3) suggest that the reduction is not mediated by amide or acid bridging.

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References