Reactivity of coordinated amido base in base hydrolysis of cis-(bromo)(2-aminothiazole)-bis-(ethylenediamine)cobalt(III) cation

Anadi C Dash* & Jyotsnamayee Pradhan
Department of Chemistry, Utkal University, Bhubaneswar 751 004
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Evidence is presented in support of cobalt(III) promoted NH-deprotonation of coordinated 2-aminothiazole in cis-[Co(en)_2(2-aminothiazole)Br]^2+ which undergoes base hydrolysis via S_N1 (CB) mechanism. The pK_{NH} of coordinated 2-aminothiazole is 12.8±0.1 at 25°C and I=0.1 mol dm^{-3}. The amido conjugate base undergoes H_2O or Br^- substitution at cobalt(III) centre 10^7 times faster than its conjugate acid analogue. This dramatic rate enhancement is predominantly due to considerably low activation enthalpy (ΔH^a = 46 ± 5 kJ mol^{-1}) for the substitution reaction of amido base. The negative value of ΔS^a (-39 ± 20 J K^{-1} mol^{-1}) is consistent with the fact that the solvation sphere of the transition state is relatively more ordered than that of the initial state.

Controversy continues to persist regarding the reaction mechanism of base hydrolysis of halogenoaminecobalt(III) complexes. Much evidence supports this view: that the rapid hydrolysis of acidoaminecobalt(III) complexes in alkaline medium is due to the generation of dissociatively activated amido conjugate base. The amido conjugates of aminecobalt(III) complexes remain as elusive intermediates due to the high pK of the most coordinated amines (pK_{NH} > 15) do not enable their direct detection even in strongly basic aqueous medium. Evidence for the NH-deprotonation of the coordinated aniline in cis-[Co(en)_2(C_6H_5NH_2)Cl]^2+ at pH > 3 was, nevertheless, reported by Nanda et al. and Chan et al. in their studies of aquation of this complex but the NH-deprotonation was not established firmly. To the best of our knowledge, Sargeson's estimated data of pK_{NH} = 10 for the coordinated aniline in cis-[Co(en)_2(C_6H_5NH_2)Cl]^2+ from a study of the base hydrolysis of this complex appears to be the only one for the halogenoaminecobalt(III) complexes. However, the facile cobalt(III) promoted NH-deprotonation of the coordinated imidazole and/or benzimidazole in cis-[N_4Co(imH/bzimH)X]^2+ ([N_4 = 2 en, 2(1,2-diaminopropane)] has been observed and the corresponding imido conjugate bases have been characterised. Herein we present kinetic evidence in favour of generation of an amido conjugate base in basic medium during our investigation of the base hydrolysis of cis-(bromo)(tzNH_2)-bis(ethylenediamine)cobalt(III) (tzNH_2 = 2-aminothiazole) (see structure I). The kinetic and thermodynamic parameters of this conjugate base are reported. Relevant data for the aquation of I has also been reported earlier from our laboratory.

Materials and Methods
The synthesis and characterisation of cis-[Co(en)_2(tzNH_2)Br](ClO_4)_2 have been described in our earlier paper. The kinetics of base hydrolysis was followed using a fully automated HITECH (UK) model SF 51 stopped flow spectrophotometer at 340 nm with [complex]=5×10^{-4} and I=0.10 mol dm^{-3} (adjusted with NaClO_4). Rate measurements were made under the pseudo-first order condition at 10.6, 15, 20 and 25°C temperature being controlled with an accuracy of ±0.1°C. The concentration of alkali was varied in the range of (4.45×10^{-3} to 99.45×10^{-3}) mol dm^{-3}.

Results and Discussion
The complex I undergoes fast base hydrolysis
in basic medium. The primary base hydrolysis can be represented by Eq. (1)
\[
\text{N}_5\text{CoBr}^{2+} + \text{OH}^- \xrightarrow{k_{cb}} \text{N}_5\text{Co} - \text{OH}^{2+} + \text{Br}^-
\]

The nonlinear variation of the pseudo-first order rate constant \(k_{\text{obs}}\) with \([\text{OH}^-]_T\) depicted in Fig. 1, is in keeping with the S_n1 (CB) mechanism as delineated in Eq. (2),
\[
\text{Co(en)}_2(\text{tzNH}_2)\text{Br}^{2+} + \text{OH}^- \xrightarrow{k_2} \text{Co(en)}_2(\text{tzNH})_{\text{Br}}^+ + \text{OH}_2
\]
for which \(k_{\text{obs}}\) takes the form give by Eq. (3)
\[
k_{\text{obs}} = \frac{k_1 k_2 [\text{OH}^-]}{k_1 [\text{OH}^-] + k_{-1} + k_2}
\]

For analogous complexes with primary amines in lieu of \(\text{tzNH}_2\), there was no conclusive evidence for the nonlinear variation of \(k_{\text{obs}}\) with \([\text{OH}^-]_T\). Hence selectively cobalt(III) promoted \(\text{NH}\)-deprotonation of \(\text{tzNH}_2\) is justified. With the assumption that the reprotonation rate constant \(k_{-1} \gg k_2\), Eq. (3) can be recast in terms of the equilibrium constant \(K_{cb} = k_1/k_{-1}\) and the rate constant \(k_2\) for the conjugate base as in Eq. (4),
\[
k_{\text{obs}} = \frac{K_{cb} k_2 [\text{OH}^-]}{1 + K_{cb} [\text{OH}^-]}
\]

The values of \(k_2\) and \(K_{cb}\) calculated from the slope and intercept of \(k_{\text{obs}}\) versus \([\text{OH}^-]_T\) plots by a weighted least squares procedure (\(k_{\text{obs}}\) was weighted inversely as its variance which was calculated from the known variance of \(k_{\text{obs}}\)) are collected in Table 1. The values of \(pK_{\text{NH}}\) \((K_{\text{NH}} = K_{cb} K_w)\) for the coordinated \(\text{tzNH}_2\) turn out to be \(12.8 \pm 0.1\) at \(25^\circ\text{C}\) \((I = 0.1\ \text{mol dm}^{-3})\) from the values of \(K_{cb}\) and \(K_w = 1.66 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}\) \((25^\circ\text{C}, I = 0.1, \text{mol dm}^{-3})\).

In our earlier study\(^2\) of the acid hydrolysis of complex I we also observed marked inverse acid dependence of its aquation rate constant in the \(pH\) range of 3.52 to 5.52 \((350 \text{ to } 50^\circ\text{C})\) which was attributed to the generation of the reactive amido conjugate base of the coordinated \(\text{tzNH}_2\). The extrapolated value of \(k_{cb} K_{\text{NH}} = 7.75 \times 10^{-11}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\) at \(25^\circ\text{C}, I = 0.3 \text{ mol dm}^{-3}\), note \(k_2 = k_{cb}\)\(^3\) yielded \(k_{cb} = 5.4 \times 10^2 \text{ s}^{-1}\) at \(25^\circ\text{C}\) using the ionic strength corrected value of \(K_{\text{NH}}\), which compared satisfactorily with the value of \(k_{cb}\) at the same temperature reported herein. This provides additional support to the fact that the amido conjugate base cis-\([(\text{en})\text{Co(tzNH} \text{Br}^+\text{)}\] is the reactive species in the base-catalysed hydrolysis reaction in the \(pH\) range of 3.5 to 13. A comparison of the rate constant of the amido base \(k_{cb}\) with that of its conjugate acid analogue \(k_{\text{aq}} = 2.65 \times 10^{-6}\ \text{ s}^{-1}\) at \(25^\circ\text{C}\)\(^4\) clearly reveals the dramatic labilising action of the amido base (calculated \(k_{cb}/k_{\text{aq}} = 1.4 \times 10^7\) at \(25^\circ\text{C}\)). This can not be attributed merely to the favourable electrostatic effect due to reduction of charge from \(+2\) to \(+1\). The activation enthalpy.

| Table 1 - Values of \(k_{cb}, K_{cb}\) and associated thermodynamic parameters |
|-----------------|-----------------|------------------|
|                  | \(I = 0.1\ \text{mol dm}^{-3}\) |                  |
| Temp. \(^\circ\text{C}\) | \(k_{cb}\ (\text{s}^{-1})\) | \(K_{cb}\ (\text{dm}^3\ \text{mol}^{-1})\) |
| 10.6            | 139 ± 22        | 6.8 ± 1.0        |
| 15.0            | 227 ± 71        | 6.1 ± 1.0        |
| 20.0            | 314 ± 73        | 7.3 ± 1.0        |
| 25.0            | 374 ± 66        | 10.0 ± 1.0       |

\(\Delta H^*\ (\text{kJ mol}^{-1}) = 46 \pm 5; \ \Delta H^\circ\ (\text{kJ mol}^{-1}) = 22 \pm 8; \ \Delta S^*\ (\text{J K}^{-1} \text{mol}^{-1}) = -39 \pm 20; \ \text{and} \ \Delta S^\circ\ (\text{J K}^{-1} \text{mol}^{-1}) = 95 \pm 29.\)

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\(\text{Fig. 1} - k_{\text{obs}}/\text{s}^{-1}\) versus \([\text{OH}^-]_T/\text{mol dm}^{-3}\) plot at 10.6°C (1), 15.0°C (2), 20.0°C (3) and 25.0°C (4) [Experimental points with standard errors are shown for the curves calculated from the values of \(k_{cb}\) and \(K_{cb}\) given in Table 1]
(\Delta H^\circ = 46 \pm 5 \text{ kJ mol}^{-1}) for the aquation of the amido base (see Table 1) is significantly lower than that for the aquation of its conjugate acid form \( \Delta H^\circ = 92 \pm 3 \text{ kJ mol}^{-1} \). This reduction in \( \Delta H^\circ \) might be suggestive of appreciable weakening of Co–Br bond in the ground state arising out of favourable electron displacement property of the amido nitrogen in the amido conjugate base. Also the \( \pi \)-bonded stabilisation of the transition state by the amido nitrogen might contribute to this large reduction in the value of \( \Delta H^\circ \). But it is difficult to make quantitative estimate of these two effects, i.e. \( \sigma \) and \( \pi \) bonding effects. The values of \( \Delta S^\circ \) \( ( - 39 \pm 20 \text{ JK}^{-1} \text{ mol}^{-1}) \) for the bromide release reaction of conjugate base satisfactorily agrees with that \( \Delta S^\circ = - 24 \pm 4 \text{ JK}^{-1} \text{ mol}^{-1} \) for the aquation of its conjugate acid form. Since both the values are comparable and appreciably negative, it is likely that no significant rearrangement occurs at the cobalt(III) centre in the actual act of substitution reactions of both the amido base and its conjugate acid form of the substrate. The \( \Delta S^\circ \) value reflects solvent participation in the transition state. Our earlier studies on the solvent effects on aquation of this complex has also revealed considerable solvent participation in this process. This point can be made clear by dissecting the transition state (ts) entropy on the basis of a dissociative activation model and applying the additivity principle, i.e.

\[ S^\circ_{\text{aq}}(\text{t.s.}) = S^\circ_{\text{aq}}(\text{Co(en})_2(tzNH))^{2+} + S^\circ_{\text{aq}}(\text{Br}^-). \]

Accordingly, the relative partial molar entropy of the dissociative transition state (i.e. l.h.s. of Eq. 5)

\[ S^\circ_{\text{aq}}(\text{Co(en})_2(tzNH)^{2+}) - S^\circ_{\text{aq}}(\text{Co(en})_2(tzNH)_2)\text{Br}^{2+} \]

\[ = \Delta S^\circ = S^\circ_{\text{aq}}(\text{Br}^-) \]

(5) turns out to be substantially large negative \( ( - 130 \pm 20 \text{ JK}^{-1} \text{ mol}^{-1} \) at 25°C using \( S^\circ_{\text{aq}}(\text{Br}^-) = 91 \text{ JK}^{-1} \text{ mol}^{-1} \). This clearly indicates that the net charge of cobalt(III) species remaining same, the solvent ordering in the Gurney cosphere of the transition state is substantially greater than that in the initial state.

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