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# Kinetics and Mechanism of the Acid-Catalysed Ring Opening of *cis*-$[Co(en)_2(\beta\text{-alaO})]^{2+}$

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*The preparation of* cis-$[Co(en)_2(\beta\text{-}alaO)]I_2$ *is described. Ring opening of the complex occurs in acidic solution. Kinetic studies establish that the reaction shows a first-order dependence on* $[H^+]$ *with rate* $= k_H[Complex][H^+]$. *Values of* $k_H$ *have been determined over a temperature range giving* $\Delta H^{\ddagger} = 59.9$ *kJ mol*$^{-1}$ *and* $\Delta S^{\ddagger}_{298} = -50$ *J K*$^{-1}$ *mol*$^{-1}$. *The solvent deuterium isotope effect* $k_{D_2O}/k_{H_2O}$ *for the ring opening process is 2.4, consistent with a mechanism involving a rapid pre-equilibrium protonation step followed by slow rate-determining ring opening. Mechanisms involving concerted attack by* $H^+$ *and* $H_2O$ *are excluded.*

## Introduction

The opening of chelate rings in cobalt(III) complexes in acidic solution is well documented. Detailed kinetic studies have been reported for phosphato [1], oxalato [2] and carbonato [3] complexes. Little kinetic and mechanistic information is available on the opening of amino-acid chelate rings in acidic media. Fastrez and Daffe [4] have recently studied the protonation equilibrium, $[Co(en)_2(glyO)]^{2+} + D^+ \rightleftharpoons [Co(en)_2(glyOD)]^{3+}$ in strongly acidic solution by $^1H$ nmr spectroscopy. A $pK_{BH^+}$ of *ca.* −1.5 to −1.6 can be obtained from the data. The complex has a similar basicity to 5-chloro-2-nitroaniline ($pK_{BH^+} = -1.52$) [5] indicating half protonation in 4.5–5 *M* $HNO_3$ [5]. Boreham and Buckingham [6] have recently investigated oxygen exchange and chelate ring opening in $[Co(en)_2(glyO)]^{2+}$. Some 6% of the ring opened aqua glycinate complex is present at equilibrium in 1 *M* $HClO_4$.

For other investigations we required information on the stability of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ in acidic media. The present paper describes kinetic and mechanistic work on the ring opening reaction.

## Experimental

The complex *cis*-β-alaninatobis(ethylenediamine)-cobalt(III) iodide, *cis*-$[Co(en)_2(\beta\text{-alaO})]I_2$ was prepared as follows. β-Alanine (0.04 mol) was dissolved in water (20 cm$^3$) containing sodium hydroxide (0.04 mol). The solution was heated to *ca.* 60 °C and *trans*-$[CoCl_2(en)_2]Cl$ (0.04 mol) in water (7 cm$^3$) added slowly. The solution was maintained at 60 °C for *ca.* 20 min with continuous stirring, then filtered. The filtrate was allowed to cool and a slight excess of NaI in water (1–2 cm$^3$) added. Crystals were obtained on refrigeration. The product was recrystallised three times from a dilute aqueous solution of NaI, then thoroughly dried *in vacuo.* Hydrates can be characterised depending upon the degree of drying. The complex was isolated as shining red crystals. *Anal.* Calc. for $C_7H_{22}N_5O_2CoI_2$ (M = 521.03) C, 16.14; H, 4.26; N, 13.44. Found C, 15.94; H, 4.20; N, 13.56%. The ir spectrum (KBr disc) has sharp $\nu$NH bands at 3190 and 3100 cm$^{-1}$. A sharp band at 1653 cm$^{-1}$ is assigned to $\nu$COO(asym) and a broader band at 1627 cm$^{-1}$ is probably $\delta$NH. A weaker band at 1363 cm$^{-1}$ is probably $\nu COO^-$-(sym). The visible spectrum has $\lambda_{max}$ 506 nm ($\epsilon$ = 186 $M^{-1}$ cm$^{-1}$) and 354 nm ($\epsilon$ = 171 $M^{-1}$ cm$^{-1}$) in aqueous solution. The complex $[Co(en)_2(glyO)]Cl$ has $\lambda_{max}$ 487 nm ($\epsilon$ = 98 $M^{-1}$ cm$^{-1}$) and $\lambda_{max}$ 346 nm ($\epsilon$ = 107 $M^{-1}$ cm$^{-1}$) [7]. *Cis*-$[CoCl(en)_2NH_2CH_2CH_2CO_2H]Cl_2$ was prepared as described for the corresponding glycine derivative [7].

### *Kinetics*

The reaction was monitored at 285 nm where a substantial decrease in absorbance occurs. Reactions were carried out using nitric acid solutions (due to the limited solubility of the complex in perchlorate media) and adjusted to I = 0.1 *M* with $KNO_3$. Values of the observed first order rate constants ($k_{obs}$) at constant hydrogen ion concentration were computed from plots of log ($A_t - A_\infty$) *versus* time. Each rate constant is the mean value of triplicate runs. All reactions were monitored using a Gilford 2400S spectrophotometer, thermostatted by circulating water.

Additional spectral measurements including interval scan spectra were made with a Perkin-Elmer 402 spectrophotometer. Infrared measurements were made with a Perkin-Elmer 457 instrument using KBr discs.

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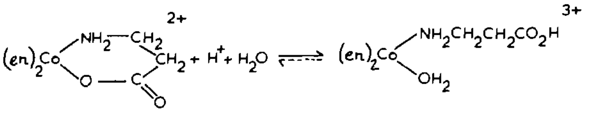
## Results and Discussion

Marked visible spectral changes occur on dissolution of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ in dilute $HNO_3$ solutions ($5 \times 10^{-3}$ *M* to $20 \times 10^{-3}$ *M*). Aqueous solutions of the complex have $\lambda_{max}$ 506 nm ($\epsilon = 186\ M^{-1}\ cm^{-1}$) and 354 nm ($\epsilon = 171\ M^{-1}\ cm^{-1}$). The 'infinity' spectrum in nitric acid has $\lambda_{max}$ 484 and 348 nm. Mercury(II) catalysed aquation of *cis*-$[CoCl(en)_2\text{-}NH_2CH_2CH_2CO_2H]$ in dilute nitric acid solution gives a product with $\lambda_{max}$ 493 and 350 nm.

The spectral changes observed with $[Co(en)_2(\beta\text{-}alaO)^{2+}]$ in nitric acid are consistent with ring opening of the $\beta$-alaninato ring (eqn. 1):

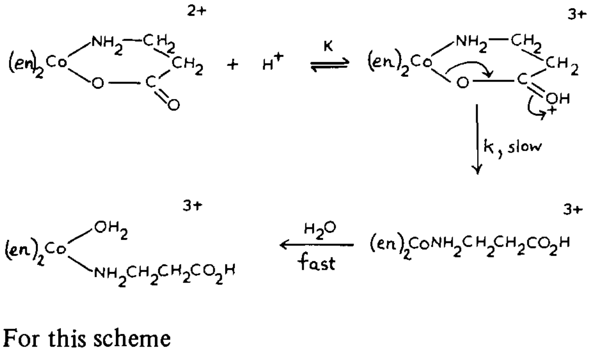


Opening of the six-membered chelate ring is apparently more favourable than opening of the five-membered glycinato ring. It has been estimated that only *ca.* 6% of the aqua glycinate complex is in equilibrium with $[Co(en)_2(glyO)]^{2+}$ in 1.0 *M* $HClO_4$ (K = 0.06) [6].

Ring opening of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ in dilute nitric acid solutions is a quite rapid process. Thus in 0.01 *M* $HNO_3$ at 25 °C, $t_{1/2}$ is 1.8 min. The kinetic data obtained is summarised in Table I.

Plots of $k_{obs}$ (the observed first order rate constant at constant hydrogen ion concentration) *versus* $[H^+]$ are linear passing through the origin, Fig. 1. The reaction shows a clean first order dependence on $[H^+]$ and values of $k_H$ were determined from the slope of such plots ($k_{obs} = k_H[H^+]$).

A possible reaction scheme is shown in the Scheme.



For this scheme

$$\text{rate} = \frac{kK[\text{Complex}][H^+]}{(1 + K[H^+])} \qquad (2)$$

Under the conditions of the present experiments $K[H^+] \ll 1$ (the $\beta$-alaO derivative is not expected to have a markedly different basicity to the glyO complex), so that equation (2) reduces to rate = $kK[\text{Complex}][H^+]$ and $k_H = kK$. The temperature dependence of $k_H$ was studied at the additional temperatures of 30, 35 and 40 °C giving $\Delta H^{\ddagger} = 58.8$ kJ $mol^{-1}$ and $\Delta S^{\ddagger}_{298} = -51$ J $K^{-1}$ $mol^{-1}$ (correlation coefficient = 0.9994 for the Eyring plot), Table I.

TABLE I. Acid Catalysed Ring Opening of *cis*-$[Co(en)_2(\beta\text{-alaO})]^{2+}$ at I = 0.1 *M* ($KNO_3$).[a]

| Temp. | $10^3\ [H^+]$ (*M*) | $10^3 k_{obs}$ ($s^{-1}$) | $k_H$ ($M^{-1}\ s^{-1}$) |
|---|---|---|---|
| 25 | 5.0 | 3.24 | 0.65 |
| | 6.0 | 3.94 | 0.66 |
| | 8.0 | 4.94 | 0.62 |
| | 9.0 | 6.04 | 0.67 |
| | 10.0 | 6.22 | 0.62 |
| | 12.0 | 7.94 | 0.66 |
| | 14.0 | 8.88 | 0.63 |
| | 16.0 | 10.70 | 0.67 |
| | 20.0 | 13.13 | 0.66 |
| 30 | 8.0 | 7.71 | 0.96 |
| | 10.0 | 9.76 | 0.98 |
| | 12.0 | 11.52 | 0.96 |
| | 14.0 | 11.96 | 0.85 |
| | 16.0 | 14.80 | 0.93 |
| 35 | 1.0 | 1.52 | 1.52 |
| | 2.0 | 2.60 | 1.30 |
| | 4.0 | 5.55 | 1.38 |
| | 6.0 | 9.06 | 1.51 |
| | 9.0 | 13.04 | 1.45 |
| 40 | 1.0 | 2.33 | 2.33 |
| | 2.0 | 3.37 | 1.69 |
| | 3.0 | 5.76 | 1.92 |
| | 4.0 | 8.99 | 2.25 |
| | 5.0 | 11.89 | 2.38 |

[a] Using the following values of $k_H$ ($M^{-1}\ s^{-1}$) 0.65 (25 °C); 0.94 (30 °C); 1.43 (35 °C) and 2.11 (40 °C) gives $\Delta H^{\ddagger}$ = 58.8 kJ $mol^{-1}$ and $\Delta S^{\ddagger} = -51.4$ J $K^{-1}$ $mol^{-1}$ with a correlation coefficient of 0.9994 for the Eyring plot.

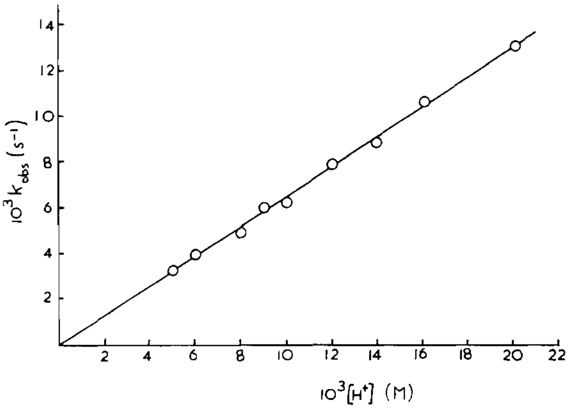


Fig. 1. The acid-catalysed ring opening of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ at 25 °C in $HNO_3$ solutions at I = 0.1 *M* ($KNO_3$).

Previous $^{18}O$ work has established that for the acid-catalysed exchange process between $H_2O^{18}$ and carboxylate groups bound to cobalt(III), discrimination between the two oxygen atoms is commonly observed [6]. Ring opening probably involves protonation of the 'carbonyl oxygen' in a rapid pre-equilibrium step followed by slow rate determining opening of the chelate ring with Co–O bond cleavage (Scheme). A further (if somewhat improbable) mechanism involving concerted attack by $H^+$ and $H_2O$ can also be considered. These two mechanisms can be differentiated by the use of solvent deuterium isotope effects [8]. As $D_2O$ is less basic than $H_2O$, the substrate will be able to compete with the solvent for the deuterion in $D_2O$ more effectively than for the proton in $H_2O$. For the stepwise pre-equilibrium mechanism (Scheme), $k_{D_2O}/k_{H_2O} > 1$. However, for a mechanism involving concerted attack by $H^+$ and $H_2O$ a rate-determining proton transfer step would be involved and $k_{D_2O}/k_{H_2O} < 1$.

The solvent deuterium isotope effect was determined at 25 °C, Table II, giving $k_{D_2O}/k_{H_2O} = 2.4$, a value completely consistent with the pre-equilibrium mechanism shown in the Scheme. Solvent deuterium isotope effects of 2.2–2.6 are observed for the decarboxylation of carbonato complexes of cobalt(III), which proceed by a similar pre-equilibrium mechanism and Co–O bond cleavage [8]. In addition there is quite a strong similarity in the activation parameters for the ring opening of carbonato and carboxylato complexes, Table III, suggestive of a similar mechanism.

## Acknowledgement

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TABLE II. Solvent Deuterium Isotope Effect at 25 °C and I = 0.1 *M*.

| Medium | $10^3k_{obs}$ ($s^{-1}$) | $k_H$ or $k_D$ ($M^{-1}$ $s^{-1}$) | $k_{D_2O}/k_{H_2O}$ |
|---|---|---|---|
| $9.92 \times 10^{-3}$ *M* DCl[a] | 14.69 | 1.48 | 2.4 |
| $10.0 \times 10^{-3}$ *M* HCl[b] | 6.22 | 0.62 | |

[a] $D_2O$ solvent. [b] $H_2O$ solvent.

TABLE III. Activation Parameters for the Acid Catalysed Ring Opening of Carboxylato and Carbonato Complexes of Cobalt(III).

| Complex | $\Delta H^{\ddagger}$ (kJ $mol^{-1}$) | $\Delta S^{\ddagger}_{298}$ (J $K^{-1}$ $mol^{-1}$) | Ref. |
|---|---|---|---|
| $[Co(en)_2(\beta\text{-alaO})]^{2+}$ | 58.8 | −51 | This work |
| $[Co(o\text{-phen})_2(ox)]^+$ | 92.8 | −78 | 2 |
| $[Co(o\text{-phen})_2(mal)]^+$ | 90.3[a] | −44[a] | 9 |
| $[Co(NH_3)_4CO_3]^+$ | 64 | −26 | 3 |
| $[Co(en)_2CO_3]^+$ | 57.7 | −31 | 3 |
| $[Co(tren)CO_3]^+$ | 46.4 | −110 | 3 |
| $[Co(\alpha\text{-trien})CO_3]^+$ | 62.8 | −21 | 3 |

[a] Values determined from $k_{obs}$ rate constants in 1 *M* HCl as a non-linear acid dependence is observed.

## References

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