Inorganica Chimica Acta, *89* (1984) L21–L22

Enthalpy Changes in the Binding of O_2 to Co(II) Complexes with 1,4,8,11-Tetraazacyclotetradecane

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Received April 11, 1984

Much attention has been devoted to oxygen addition to Co(II) complexes for the interest they present as models of natural oxygen carriers [1a], for their possible applications in the oxygen storage [1b], and finally for the activation of molecular oxygen [1c]. In spite of this incidence there are relatively few thermodynamic studies on these complexes and in particular calorimetric data are lacking. Only recently calorimetric measurements have been carried out in order to determine the enthalpy changes associated to the binding of O_2 to Co(II) complexes with nitrogen ligands in aqueous solution. The considered ligands were open chain bi- [2], tetra- [3] or pentadentate- [4] polyamines. Here we report the values of the enthalpy changes, obtained calorimetrically, corresponding to the addition of molecular oxygen to complexes of Co(II) with the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (cyclam).

In anaerobic aqueous solutions the CoL^{2+} (L = cyclam) species is formed for which a value of stability constant, $K_{CoL} = 5 \times 10^{12}$ mol^{-1} dm^{-3} at 35 °C and ionic strength I = 0.2 mol dm^{-3} was reported [5]. We obtained from potentiometric measurements a value of $K_{CoL} = 2 \times 10^{14}$ mol^{-1} dm^3 at 25 °C and I = 0.1 mol dm^{-3}. Moreover, in our findings, at pH > 9 also the species $CoLOH^+$ is present for which a stability constant $K_{CoLOH} = 1.2 \times 10^{17}$ mol^{-2} dm^6 was calculated.

In aerobic conditions, at 25 °C and KNO_3 0.1 mol dm^{-3}, according to McLendon and Mason [6] the $Co_2L_2O_2{}^{4+}$ peroxo complex is formed ($K^{CoL}_{Co_2L_2O_2} = 10^8$ mol^{-2} dm^6). For this latter species, at 35 °C and I = 0.2 mol dm^{-3} Kodama and Kimura [5] quote $K^{CoL}_{Co_2L_2O_2} = 47$ mol^{-2} dm^6. Endicott [7] finally reports $K^{CoL}_{Co_2L_2O_2} = 6 \times 10^9$ mol^{-2} dm^6 at 25 °C and I = 0.1 mol dm^{-3}. From our spectrophotometric, polarographic and pH-metric measurements a value of $K^{CoL}_{Co_2L_2O_2} = 2 \times 10^8$ mol^{-2} dm^6 was calculated for the formation of $Co_2L_2O_2{}^{4+}$ for which $\epsilon = 9000$ dm^3 mol^{-1} cm^{-1} at $\lambda = 300$ nm has been found at pH = 6. The formation, at pH > 11, of the $Co_2L_2O_2(OH)_2{}^{2+}$ species was also recognized from pHmetric and spectrophotometric measurements ($\epsilon = 12300$ dm^3 mol^{-1} cm^{-1} at $\lambda = 280$ nm). For this latter bishydroxoperoxo compound $K^{CoL,OH}_{Co_2L_2O_2(OH)_2} = 10^{23}$ mol^{-4} dm^{12} has been calculated. Finally for the monohydroxoperoxo compound $Co_2L_2O_2(OH)^{3+}$ the value of $K^{CoL,OH}_{Co_2L_2O_2(OH)} = 3 \times 10^{16}$ mol^{-3} dm^9 has been evaluated.

Enthalpy changes for the formation of $Co_2L_2O_2{}^{4+}$ and $Co_2L_2O_2(OH)_2{}^{2+}$ starting from CoL complex were determined by using a calorimetric apparatus and a procedure described elsewhere [2]. Four operating procedures have been selected:

i) CoL^{2+} species is formed in anaerobic atmosphere at pH 7.5–8.1 and $C_L{}^\circ/C_o{}^\circ$ ratios ranging from 1.05 to 1.2. When the equilibrium is attained hydrochloric acid is added in order to realize pH values ranging from 3 to 4 and O_2 gas is bubbled into the solution. In these conditions the $Co_2L_2O_2{}^{4+}$ is formed but its decomposition is so fast that reliable values for the $\Delta H^{CoL}_{Co_2L_2O_2}$ quantity cannot be obtained.

ii) The experiments are carried out as described in (i), but hydrochloric acid is not added. The pH realized after the addition of oxygen is about 5.7–6.0. In such a medium the greatly prevailing reaction is:

$$2CoL^{2+} + O_2(aq) \longrightarrow Co_2L_2O_2{}^{4+} \qquad (1)$$

The enthalpy change obtained for this reaction was:

$$\Delta H^{CoL}_{Co_2L_2O_2} = -86.1 \pm 2.5 \text{ kJ mol}^{-1}$$

iii) The starting solution is still as (i) but now, together with O_2, NaOH is added in order to realize pH values from 11 to 11.3. The reaction is:

$$2CoL^{2+} + O_2(aq) + 2OH^- \longrightarrow Co_2L_2O_2(OH)_2{}^{2+} \qquad (2)$$

for which $\Delta H^{CoL,OH}_{Co_2L_2O_2(OH)_2} = -132.1 \pm 2.2$ kJ mol^{-1} is calculated.

iv) The $CoLOH^+$ species is allowed to form in anaerobic atmosphere at pH ranging from 10.7 to 11.7. Then O_2 gas is bubbled. The pH practically does not change in accordance with the reaction

$$2CoLOH^+ + O_2(aq) \longrightarrow Co_2L_2O_2(OH)_2{}^{2+} \qquad (3)$$

for which the value $\Delta H^{CoL,OH}_{Co_2L_2O_2(OH)_2} = -114.1 \pm 0.8$ kJ mol^{-1} was obtained.

Among the peroxocomplexes of Co(II) with saturated polyamines studied to date, only the $Co_2(tetren)_2O_2{}^{4+}$ is similar to $Co_2(cyclam)_2O_2{}^{4+}$ complex. In fact the addition of O_2 to Co–en or Co–trien systems produces also the formation of an olate bridge. The value of $\Delta H^{CoL}_{Co_2L_2O_2} = -178.9 \pm 1.5$ KJ mol^{-1} obtained for the O_2 addition to Co–tetren^{2+} ion is considerably larger than the value -86.1 KJ mol^{-1} found for the formation of Co_2-

0020-1693/84/$3.00

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$(cyclam)_2O_2^{4+}$ ion (eqn. 1). This large difference is probably due to the possibility of one nitrogen of the pentadentate tetren occupying the axial position. In effect, by comparing reactions 3 *vs.* 2 and reaction 2 *vs.* 1 it results that also for the Co–cyclam peroxoderivative the occupation of the axial position produces a very noticeable enthalpic effect. Against a value of $\Delta H^{CoL}_{CoLOH} = -9$ kJ mol^{-1} for the addition of the OH^- ion to Co–cyclam complex, a mean value of –23 KJ mol^{-1} is calculated for the enthalpy change relative to the addition of one OH^- ion to one Co atom of the peroxocomplex $Co_2(cyclam)_2O_2^{4+}$.

Acknowledgement

This work was supported by Ministero della Pubblica Istruzione (Rome).

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