The Mechanism of the Formation of the Cobalt(III) Products from the Reversible Oxygen Carrier, the μ-Dioxygentetrakis(histidinato)dicobalt(II) Ion

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SYNTHETIC molecular-oxygen carriers are of interest in part as a practical means of oxygen recovery and in part because of their potential relevance to biological molecular-oxygen carriers.[1] Hearon and his co-workers[2] have made extensive studies of the equilibria and stoicheiometry of the cobalt(II)–histidine oxygen carrier. Tanford[3] has studied the rate and mechanism of oxygen absorption by, and the ultimate oxidation of, the cobalt(II)–glycylglycine complex. Out of an interest in the role of polyfunctional, bridging ligands on the electron-transfer process, we decided to study the kinetics and mechanism of formation and oxidation of the cobalt(II)–L-histidine oxygen carrier. The formation of the oxygen carrier from the bis(histidinato)-cobalt(II) ion is very rapid,[2,4] and would have to be studied by special techniques, so our initial investigations were devoted to the decomposition (irreversible) of the oxygen carrier to give cobalt(III) complexes.

It was found that one mole of oxygen was absorbed for each two moles of bis(histidinato)-cobalt(II), hereafter CoL_2, in the formation of the reversible carrier. Slightly more than one additional mole of oxygen was required for the oxidation of the carrier, $Co_2L_4O_2$, to give Co^{III}.[2] In solutions with $4{\cdot}84 \times 10^{-3}$M-$Co^{II}$ and a 2·00 : 1 histidine to Co^{II} ratio, 1·14 moles of oxygen per $Co_2L_4O_2$ were consumed. At higher histidine : Co^{II} ratios greater amounts of oxygen were consumed (*e.g.*, 1·32 moles per $Co_2L_4O_2$ at 4·00 : 1). The presence of traces of unidentifiable organic residues after the reaction was complete suggests some of the oxygen, probably that in excess of 1·00 : 1 per $Co_2L_4O_2$, was used in the oxidation of histidine as has been suggested by Csaszar, Kiss, and Beck.[5]

Most of the ultimate product appears to be a mixture of three isomers of the bis(histidinato)-cobalt(III) ion. Ion-exchange experiments gave a violet, a red, and a red-orange solution. From the red solution a crystalline solid was isolated and analyses indicated it was bis(histidinato)cobalt(III) nitrate, $Co(C_6N_3H_8O_2)_2NO_3$. A solid separated from the violet solution was crystalline but satisfactory analyses could not be obtained. Caglioti, Silvestroni, and Furlani[6] have made polarographic studies of the irreversible products and have isolated a product $[Co(glycylglycine)_2OH]_2,H_2SO_4$, from the glycylglycine system. It is possible that the solids obtained from the red-orange and the violet solutions are similar to the above, but our red compound is different and contains nitrate.

The solids, bis(histidinato)cobalt(III) nitrate and the others, all gave identical i.r. spectra in mineral oil mulls. Electronic spectra of the three solutions showed maxima as follows; violet, 350 (ϵ 170), 545 (ϵ 81), shoulder 460 mμ; red, 500 mμ ($\epsilon \sim 87$); red-orange, 485 (ϵ 85), and shoulder 540 mμ. All of these solutions obeyed Beer's law upon dilution.

Rate studies were carried out at 25° with nitrate salts and in phosphate buffers at pH = 7·0 and 5·0 and at constant oxygen pressure (1 atm.). McDonald and Phillips[7] have concluded that Co^{II}–histidine solutions between pH = 4 and 7 contain octahedral cobalt(II) in 1 : 1 and 1 : 2 histidine complexes, hence we chose to work in that region of acidity. (K_1 and β_2 for the Co^{II}–histidine complexes were determined in the same media in which kinetics were measured and are in good agreement with the literature, which has recently been verified and extended by Perrin and Sharma.[8]) Total initial Co^{II} was of the order of 5×10^{-3} M, and the ionic strength 1·0 M. The reaction was followed by observing the appearance of the Co^{III}–L-histidine complexes at 500 mμ (ϵ 115 for the mixture of isomers in the proportions obtained) in quenched samples of the carrier. With solutions at pH = 7·0 a two-step process took place and the data could be fitted, by means of a first derivative least-squares computer programme, to two first-order steps of the type

$$A \xrightarrow{k_1} 2B \text{ and } B \xrightarrow{k_2} C$$

The second-step rate constant, k_2, was essentially constant for all histidine to Co^{II} ratios, but k_1 decreased as the histidine:Co^{II} ratio increased. For example, $k_1 = 3{\cdot}6 \times 10^{-5}$sec.$^{-1}$ for a 2·00 : 1 ratio and falls to $1{\cdot}9 \times 10^{-5}$ sec.$^{-1}$ at 8·00 : 1. The first step is pseudo-first-order in oxygen and the rate falls as the oxygen pressure is lowered. The exact kinetic order in oxygen has yet to be determined.

At constant oxygen pressure and all other experimental conditions unchanged, except pH 5·0, the oxidation also occurs with the absorption of a mole of oxygen by $Co_2L_4O_2$, but by a single first-order or pseudo-first-order rate law. The rate constant in this case equals $5{\cdot}45 \times 10^{-5}$ sec.$^{-1}$.

Since a minimum of one mole of oxygen per mole of $Co_2L_4O_2$ is required to produce the Co^{III} species, it seems reasonable to suppose that the first step (corresponding to k_1) results in the formation of two moles of a mononuclear peroxo-cobalt(II) species, perhaps something like $CoLO_2^+$. The second step would then correspond to the decomposition of the mononuclear oxygen species to give Co^{III} and peroxide plus oxygen, or superperoxide. The latter then either decomposes or oxidizes histidine. Since k_1 depends to some, yet to be determined, inverse order on the histidine concentration, it seems logical to assume that a rapid dissociation equilibrium occurs before the dinuclear oxygen carrier can react with the mole of oxygen, *i.e.*,

$$Co_2L_4O_2 = Co_2L_{(4-x)}O_2^{x+} + xL^-$$

The dissociated species can then react with a mole of oxygen to produce two moles of the mononuclear oxygen species which then decomposes to give cobalt(III).

At pH 5·0 the histidine complexes are more highly dissociated and probably attack of oxygen on the dinuclear species is more rapid, all or most of the carrier being partially dissociated, and a single first-order step is then rate determining.

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