

An efficient copper(III) catalyst in the four electron reduction of molecular oxygen by L-ascorbic acid.

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Streszczenie

The anionic $[\text{Cu}^{\text{III}}(\text{LH}_{-4})]^{-}$ complex ($\text{L} = 8,17\text{-dioxo-}1,2,5,6,10,11,14,15\text{-octaaza-tricyclo}[13.3.1]$ eicosane-3,4,12,13-tetrone) is one of the rare copper(III) compounds, which exhibits high stability in basic aqueous solution. This copper(III) compound catalyses the reduction of molecular oxygen by L-ascorbic acid at pH 7.97, in Tris-HCl buffer solution at the ionic strength of 0.1 M (NaCl). Stoichiometry of the reaction (2:1.07 for L-ascorbic acid:dioxygen) indicates formation of water and dehydroascorbic acid as primary products. Based on detailed kinetic measurements, the rate equation— $d[\text{AscH}^{-}]/dt = k_{\text{obs}}[\text{AscH}^{-}]^{0.5}[\text{Cu}^{\text{III}}(\text{LH}_{-4})][\text{O}_2]^{0.5}$ —was obtained. The proposed mechanism includes a fast redox pre-equilibrium between the copper(III) centre and its reduced, copper(II) form, induced by the presence of L-ascorbate. The equilibrium constant K_1' at pH 8 ($8.78 \pm 3.11 \times 10^{-3}$) and k values for the forward and backward reactions ($1.18 \pm 0.68 \times 10^6$ and $1.46 \pm 0.82 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$, respectively) were determined by stopped-flow technique, following the decrease in absorbance of the copper(III) form at 550 nm. In the presence of molecular oxygen, re-oxidation of the copper(II) form of the catalyst takes place, based on cyclic voltammetry (CV) measurements. The decrease of the $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{III})$ oxidation and the subsequent increase of the $\text{Cu}(\text{III}) \rightarrow \text{Cu}(\text{II})$ reduction current peaks in the CV spectrum, when argon is exchanged to dioxygen atmosphere, indicate a relatively fast oxidation rate for $[\text{Cu}^{\text{II}}(\text{LH}_{-4})]^{2-}$. The determined $\Delta S^{\ddagger}$ ($-41 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$) for the catalytic reaction indicate an associative mechanism for the formation of the catalytically active copper-oxygen species that will react with the L-ascorbate to yield dehydroascorbate as product.

Słowa kluczowe

copper(III), l-Ascorbic acid, Catalytic oxidation, Dioxygen reduction

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