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

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Streszczenie

The anionic $[Cu^{III}(LH_{-4})]^{-}$ complex (L = 8,17-dioxa-1,2,5,6,10,11,14,15-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 $-d[AscH^{-}]/dt = k_{obs}[AscH^{-}]^{0.5}[Cu^{III}(LH_{-4})][O_2]^{0.5}$ 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 $1.46 \pm 0.82 \times 10^{8}$ M^{-2} 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 Cu(II) → Cu(III) oxidation and the subsequent increase of the Cu(III) → Cu(II) reduction current peaks in the CV spectrum, when argon is exchanged to dioxygen atmosphere, indicate a relatively fast oxidation rate for $[Cu^{II}(LH_{-4})]^{2-}$. The determined $\Delta S^{\ddagger}$ (-41 ± 2 $Jmol^{-1}$ 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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