

Proton-coupled electron transfer reactions at Rieske [2Fe-2S] clusters: three oxidation states and four protonation states.

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Rieske clusters are unusual amongst [2Fe-2S] clusters because they are ligated by two cysteine and two histidine residues, and because their reduction potentials ($[2\text{Fe-2S}]^{2+/1+}$) are strongly pH dependent. The pH-dependence arises from deprotonation of the two histidine ligands, which coordinate the redox-active iron centre. Rieske clusters are important components of two respiratory enzymes, the cytochrome *bc*₁ and *b₆f* complexes, and it is possible that they are used for proton transfer, as well as electron transfer, during catalytic turnover.

Recently, we have used protein-film voltammetry to study the proton-coupled electron transfer reactions of Rieske clusters [1 - 3]. In addition to the $[2\text{Fe-2S}]^{2+}$ (all-ferric) and $[2\text{Fe-2S}]^{1+}$ states, Rieske clusters can exist in the $[2\text{Fe-2S}]^0$ (all-ferrous) state also [4]. Reduction to the all-ferrous state requires a very low potential, and is accompanied by protonation of the cluster. Therefore, Rieske clusters can adopt three oxidation states (+2, +1 and 0) and four protonation states (both histidine ligands can be protonated or deprotonated, and the cluster can also be protonated) [4].

This talk describes the different oxidation and protonation states of the Rieske cluster, and studies of them by voltammetric (protein-film voltammetry) and spectroscopic techniques.

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