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Analysis of intramolecular electron transfer in tetraheme cytochrome c_3 by direct electrochemistry

Sim Sanghoon

Biological electron transfer, which is high efficient electron transfer observed in the electron transfer chain, was controlled by each redox protein. Redox protein selects a redox partner and maintains the electron transfer chain. There is an interesting the electron transfer mechanisms arising from redox protein.

Cytochrome c_3 from *Desulfovibrio vulgaris* (Miyazaki F), a redox protein, contains four hemes and has multiple redox state arising from conformational change during intramolecular electron transfer among hemes

Protein film voltammetry (PFV), a direct electrochemical measurement allowing direct observation of the redox reactions of a redox protein, was carried out to observe intramolecular electron transfer in cytochrome c_3

Direct electrochemical measurement shows higher redox potential (-0.095 V *vs.* SHE) than the other hemes, although the four hemes in cytochrome c_3 are bis-histidyl hemes (-0.350 V ~ -0.200 *vs.* SHE). The high redox potential of cytochrome c_3 was similar to that observed for the loss of an axial ligand at heme. To investigate the loss of the histidine ligand, the electrochemistry of four cytochrome c_3 Met mutants, in which the sixth coordinated histidine was replaced by methionine, was explored. The electrochemistry of the cytochrome c_3 mutants indicated that Heme III alone undergoes loss of its axial histidine ligand.

In addition, kinetic of an intramolecular electron transfer of cytochrome c_3 was investigated by high speed cyclic voltammetry, showing that conformational change of heme II was rate determining step.

Finally, redox potentials of each heme was successfully clarified by direct electrochemical measurement. To identify the redox potentials of the four hemes, the electrochemistry of four cytochrome c_3 Ala mutants, in which the sixth coordinated histidine was replaced by alanine, was carried out. The cyclic voltammograms arising from the four hemes are complicated but in the mutants, the redox potential of the one heme in which one histidine ligand is replaced with alanine is obviously higher. Thus, the redox potential of the bis-histidyl coordinated each heme can be determined.

In this study, mechanisms of intramolecular electron transfer of cytochrome c_3 were investigated and the roles of cytochrome c_3 during biological electron transfer were clarified.