Enzymatic reactions of quinones in cytochrome complexes

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Cytochromes *bc* complexes are involved in mitochondrial or photosynthetic energy conversion systems. They transfer electron from membranous hydroquinone (QH_2) to water-soluble protein electron carrier in reactions that are coupled to proton translocation across the energy-conserving membrane[1]. The enzymatic cycle involves a joint action of two quinone binding sites catalyzing opposing reactions: oxidation of QH_2 at the Q_o site and reduction of quinone (Q) at the Q_i site. Here, we reflect on recent advances in understanding the molecular mechanism of these reactions.

In the Q_o site, the bifurcation reaction (BR) directs electrons into two cofactor chains: the Rieske cluster (FeS) in one chain and heme *b* in the other chain. The side reactions of BR may result in a generation of superoxide, thus *bc* complexes are considered as one of the producers of reactive oxygen species (ROS) in cells. In the Q_i site, the two electrons for Q reduction are transferred sequentially from the same cofactor (heme *b*) and the generation of ROS has not been reported.

For the Q_o site, the major advances include: a discovery of the state in which the semiquinone intermediate (SQ) is spin-coupled to reduced FeS[2,3], a formulation of the "*semireverse-Rieske off*" mechanism of ROS generation[4] and the observation that the spin-coupled state is non-reactive toward oxygen, thus might protect the site from generating elevated amounts of ROS[5]. For the Q_i site, the major advances include: a discovery of the existence of two forms of SQ intermediate differing in the relaxation properties and a formulation of the charge and spin polarization mechanism that controls the sequence of catalytic electron and proton transfers[6].

References

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