

SOME ADDITIONAL REMARKS ON THE MECHANISM OF
OXIDATIVE PHOSPHORYLATION

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This brief note amplifies my paper on the mechanism of mitochondrial oxidative phosphorylation (Bieber, 1964) and also constitutes a response to numerous queries that were directed to me.

A. Phosphorylation coupled to one-electron transfer, rather than to two-electron transfer, is most likely to occur in such a region of the respiratory chain where electrons are transferred singly due to the chemical character of the transport sites. This situation obtains in the region of the cytochromes. The multiplicity of cytochromes along the respiratory chain is a rather perplexing phenomenon which may find a partial explanation in the suggestion I now advance that some cytochromes play the role of regular one-electron carriers, while the others (or just one other) play the role of transformers in the coupling of one-electron transfer to phosphorylation. Chemically the cytochromes appear to be equally well suited for the latter role, the porphyrin system providing the requisite unsaturation ($H-Y=Z$) and the porphyrin-bound iron furnishing the electron depot for the partial short circuit (see Fig. 2 of my previous paper). These two structural features, it will be noted, are situated in close and permanent proximity as required for the proper timing of the various steps of the coupling operation. Cytochrome a may be a special case. Since it contains a protein-bound cuprous-cupric system in addition to the porphyrin-bound ferrous-ferric system, it may conceivably perform both of the above-mentioned roles simultaneously.

B. The light-energized phosphorylation occurring in photosynthetic organisms may also be due, in large part, to

the coupling of one-electron transfer to phosphorylation. If so, the previously postulated general mechanism for such coupling should apply here as well.

C. ATP hydrolysis may be coupled to electron promotion by the reverse operation of the cycles of Fig. 1 or Fig. 2. The electrical potential thus generated and the ensuing electrical current may serve a variety of useful functions in the life process. Since the promotion of a single electron requires half as much energy as the equivalent promotion of two electrons, the coupling of ATP hydrolysis to one-electron promotion (counterclockwise cycle of Fig. 2) is apt to be more common than the coupling of ATP hydrolysis to two-electron promotion (counterclockwise cycle of Fig. 1).

REFERENCE

Bieber, T.I., *Biochem. Biophys. Res. Comm.*, 16, 501 (1964).