Evolutionary, kinetic and thermodynamic aspects on the bioenergetics of inorganic pyrophosphate (PPi) and adenosine triphosphate (ATP)

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Energy barriers for energy carriers are of fundamental significance for the successful operation of the bioenergetic reactions in living cells. PPi and ATP are outstanding "energy-rich" examples of molecular "energy currencies" in biological systems, with kinetic barriers preventing excessively fast thermodynamically feasible hydrolysis from occurring. The barriers may be considered to facilitate the energy coupling roles of these phosphate compounds, which are to secure growth and maintain numerous other energy requiring functions. The enzymes involved in overcoming the energies of acivation of the bioenergetic reactions have evolved to be very well tuned for their roles.

Three aspects will be discussed in some detail. The first is the fact that ATP at neutral pH is considerably more energy-rich than PPi, which thus has been called a "poor man´s ATP". This is exemplified by the kinetic and thermodynamic differences observed between the requirements for the photosynthetic formation of PPi and ATP in certain photobacterial chromatophores by varying levels of energy supply. At lower pH, PPi and ATP are equally energy-rich, which may be of significance for acidophiles. The second concerns the possible evolutionary significance of the finding that, in the dark, a pH gradient suffices to drive extensive PPi synthesis, whereas ATP synthesis requires both a pH gradient and a membrane potential (Strid *et al*, Biochim. Biophys. Acta 892 (1987) 236-244). Thirdly, PPi as the most plausible predecessor to ATP in the origin and early evolution of life, will be discussed.