Energy Conversion in Bioluminescent Reactions

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Bioluminescence phenomenon is based on enzymatic reactions transforming chemical energy to visible light with high quantum efficiency (1-100%). There exist several types of bioluminescent reactions corresponding to several types of luminous organisms; they differ in chemical structure of components and enzymes. Purpose of the work was to reveal general similarities and peculiarities of energy conversion in different types of bioluminescent reactions – marine bacteria, coelenteramides, and fireflies. Variation of color of bioluminescence due to energy conversion is a question of special interest in this study.

Among similarities of the bioluminescent reactions are: (1) oxidative type of the reactions (with molecular oxygen included) and (2) type of electronic structure of the emitting molecules: emitters of the bioluminescent reactions are characterized by effective fluorescence of $\pi\pi^*$- type and upper electron-excited states of $n\pi^*$- type. The type of electronic structure of the emitters suggests activity of the upper states, which can be formed as primary excited states in the oxidative bioluminescent reactions.

The hypothesis on activity of the upper electron-excited states in bioluminescent process was experimentally verified using fluorescent molecules as energy acceptors. The hypothesis was confirmed experimentally in bacterial and coelenterate bioluminescence. However, activity of the upper electron-excited states was not found in firefly bioluminescence, probably because of highest efficiency of intramolecular energy transfer in the firefly emitter.

The upper excited states can be responsible for blue shifts of the bioluminescence in the presence of proper fluorescent acceptors. Examples of red shifts of the bioluminescence due to Forster energy transfer are discussed.

Another mechanism for variation of bioluminescence color takes place in coelenterate bioluminescence. It deals with chemistry in the fluorescent states of the emitting molecule (coelenteramide). This molecule can change its acidity in the fluorescent states since the lifetime of these states is longer than time of proton transfer. Several fluorescent forms of coelenteramide can be formed depending on its ionization degree. That is why the spectra of coelenterate bioluminescence are broad and complex; they include spectral components of various forms of coelenteramide in a broad spectral region.

The spectral components of coelenterate bioluminescence (from jellyfish *Aequorea victoria* and hydroid *Obelia longissima*) were determined and characterized. The results are discussed taking into consideration the proton transfer in the fluorescent states of the emitting molecule and amino acid surrounding of the emitter in the enzymes.