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Description of Tyrosine-Histidine Cycle to Transport Electron from Water in Photosystem II

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Abstract: *The actual role of tyrosine Z (D1-Y161) and histidine Z (D1-His190) in water splitting during photosynthesis is covered under debate. Some experimental data can reveal few proposed ideas or opinion in this respect till now. But there are also exist such of limitations which can oppose to clear the way of functional activities of tyrosine-histidine working system in reality. However it is tried to remove all limitations and explained to fulfill all proposed data at the situation of activities of tyrosine-histidine functional system here on the basis of more logical solution.*

Key Words: *Electrostatic Attraction, Electron Transfer, Proton-Couple Electron Transfer, Proton Transfer, Resonance Effect, Polarization.*

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I. Introduction

It is already known that electrons (e) of oxygen-evolving complex (OEC) through water (H2O)-splitting can not be transferred directly into active (excited) chlorophyll P_{680}^{+} from OEC. Rather the transport is occurred via tyrosine Z (D1-Y161) by help of histidine Z (D1-His190). Although tyrosine radical formation after absorption of an electron by P_{680}^{+} is accepted by scientists; but the entire procedure of activity of tyrosine with function of histidine in this respect is under debate. However it is cleared that tyrosine is an electron carrier with bearing of proton and histidine is a proton acceptor (works as a base) according to their fuctional activities from few experimental results till now. The spectroscopic analysis reveals that the phenolic proton (H^{+}) of tyrosine is in a strong attraction of base histidine as well as tyrosine is in an ionic form. As a result, P_{680}^{+} can easily absorb electron (e) from tyrosine faster to form tyrosine radical. This fact also shows that tyrosine and histidine are closely bound by a several attraction or vice versa. Again proton-couple electron transfer (PCET) from OEC towards tyrosine radical is an essential proposal to reform the phenol group (—OH) in tyrosine. Beside it, there are some evidences in favour of releasing proton into the bulk from entire functional activities of tyrosine and histidine in photosystem II.

II. Tyrosine-Histidine Cycle

The following remarks are drawn after analysis of all obtained experimental data about functional activities of tyrosine and histidine during photolytic water-splitting and proposed ideas or opinions developed from structural analysis of photosystem II:

(i) The entire system of function of tyrosine and histidine is working as a cyclic process.
(ii) Tyrosine and histidine are bound together with a several binding of specific attraction at the preliminary stage.
(iii) Electron transfer (ET) is occurred into P_{680}^{+}.
(iv) Proton-couple electron transfer (PCET) is happened from oxygen-evolving complex (OEC).
(v) Proton transfer (PT) is proceeded into the bulk.
And (vi) tyrosine and histidine are rebound with each other by a several attraction at the last stage.

Moreover it is perceived that tyrosine and histidine can jointly work to transport electron from H_2O with OEC into P_{680}^{+} and can help for releasing proton into the bulk side by side. The substance of each step of tyrosine-histidine cycle is originated through a special fact.

The entire cycle is proceeded by four particular steps. Each step denotes a definite reason with its formation. At the preliminary stage, tyrosine Z (D1-Y161) and histidine Z (D1-His190) are located as Tyr—O^{-} and His—NH^{+} by transferring phenolic proton (H^{+}) of tyrosine into histidine in photosystem II with influence of resonance effect (RE) to gain stability. These two are bound together with electrostatic attraction (in an almost strong binding (SB)), which is nothing but the several binding expressed above to form [His—NH^{+}….Tyr—O^{-}]. It is the primary substance of tyrosine-histidine cycle. All steps of the cycle are described below:

A. *Step-I:* Electron Transfer (ET)

Electron (e) is transported from the preliminary substance [His—NH^+….Tyr—O^-] into P_{680}^+. The electron absorption is faster because of ionization of tyrosine as well as the more photo-electron affinity (electron affinity created by photon(hν)) of P_{680}^+. As a result, tyrosine radical (Tyr—$O^\cdot$) is formed and tyrosine-histidine binding is almost broken (very weak binding (WB)). The substance becomes expressed as [His—NH^+….Tyr—$O^\cdot$].

B. *Step-II:* Proton-Couple Electron Transfer (PCET)

Proton-couple electron transfer (e and H^+) is performed from oxygen-evolving complex (OEC) into [His—NH^+….Tyr—$O^\cdot$] to form the substance [His-NH^+….Tyr-OH] by the way of redox criteria.

C. *Step-III:* Proton Transfer (PT)

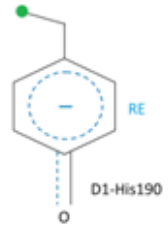
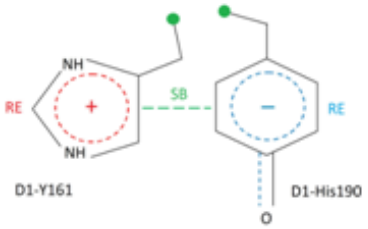
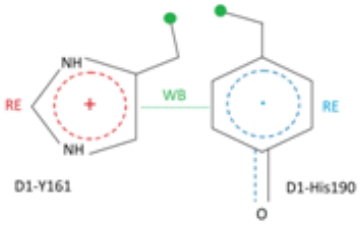
Proton (H^+) is transferred from histidine of the substance [His—NH^+….Tyr—OH] into the bulk to develop polarized bond (PB) formation in between tyrosine and histidine through hydrogen bonding (HB) due to unfavourable resonating structures of phenolic resonance in tyrosine. For that reason, the substance [His—N….H(δ+)—O(δ-)—Tyr] is obtained.

D. *Step-IV:* Tyrosine-Histidine Rebinding (THR)

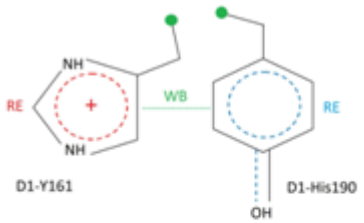
Finally by transferring phenolic proton (H+) of tyrosine into histidine, tyrosine and histidine can be expressed as Tyr—O^- and His—NH^+ with resonance effect to gain stability. These are bound together again by electrostatic attraction and the substance [His—NH^+….Tyr—O^-] is reformed. It is happened most probably by the influence of a metal ion (perhaps non-heme Fe^{2+}).

The structure of each substance is written in *Table-1* and the entire tyrosine-histidine cycle is described in the way of *Diagram-1* below:

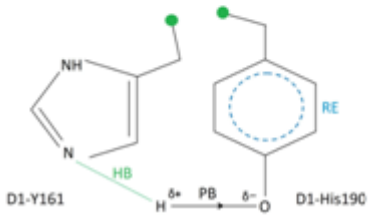
TABLE-1: Structure of substances with symbol

Tyr—O^-	
His—NH^+	
[His—NH^+….Tyr—O^-]	
[His—NH^+….Tyr—$O^\cdot$]	

[His—NH⁺....Tyr—OH]



[His—N....H(δ+)—O(δ-)—Tyr]



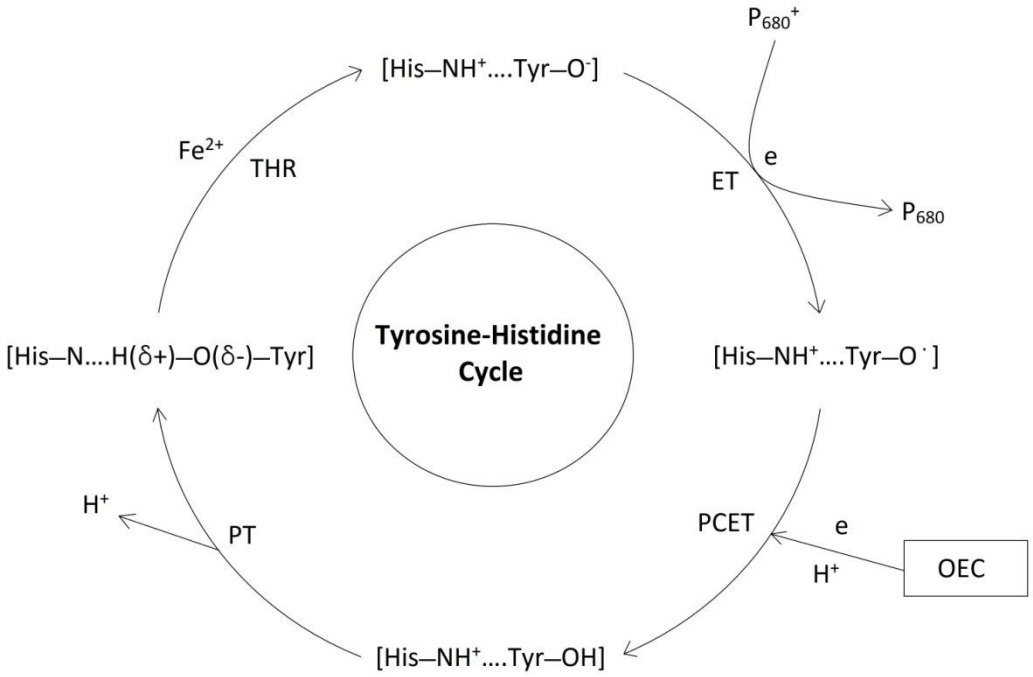


DIAGRAM-1: Tyrosine-Histidine Cycle

III. Summary

This cycle describes almost all features collected from modern research about the functional activities of tyrosine and histidine during photosynthetic water-splitting i.e. (a) ionic condition of tyrosine at the preliminary stage to donate electron (ET) into P_{680}^{+} more fast, (b) proton-couple electron transfer (PCET) from OEC, (c) proton transfer into the bulk, (d) location of opposite charge near tyrosine radical to accept electron more easily, (e) role of hydrogen bonding to reset up tyrosine-histidine substance for rolling their activities in water-splitting, (f) probability of influence of metal ion (non-heme Fe^{2+}) inside the activity of this procedure etc. However it is noted that the function of tyrosine-histidine cycle can depend on pH gradient of the bulk.

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