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Chapter

Murburn Model of Photosynthesis: Effect of Additives like Chloride and Bicarbonate

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Abstract

Oxygenic photosynthesis essentially involves photo-lysis (splitting of water to release oxygen), photo-reduction (formation of NADPH), and photo-phosphorylation (synthesis of ATP) reactions. These reactions use photoactive pigments such as chlorophylls and carotenoids. Z-scheme and Kok-Joliot cycle, the acclaimed and deterministic model of photosynthesis, are founded on the classical enzyme reaction mechanisms that depend solely on affinity-based interactions of enzymes with the substrates at defined active sites, for explaining electron/moiety transfers. In contrast, the new murburn model is built on stochastic collisions between diffusible reactive species (DRS) and other milieu components (including enzymes, substrates and ions). This novel perspective explains fast kinetics and action spectrum, and affords a spontaneously probable/evolvable biochemical system. The murburn perspective proposes that the photo-excitation of pigments in the chloroplast leads to effective charge separation and DRS-formation. DRS are stabilized/utilized by a pool of redox-active components *via* disordered/parallel bimolecular interactions at the thylakoid membrane interface. Herein, we provide details of how murburn model is a thermodynamically, kinetically, and mechanistically viable mechanism for the formation of ATP, NADPH and oxygen. The murburn model also provides more viable explanations for several classical experimental observations in photosynthesis (Emerson enhancement effect, Jagendorf/Racker experiments, etc.) and the non-specific effects of diverse additives (such as chloride and bicarbonate).

Keywords: murburn concept, photosynthesis, photolysis, photophosphorylation

1. Introduction

Oxygenic photosynthesis is a biological process that uses sunlight to convert simple chemical precursors into usable biomolecules/energy currency, maintains the

level of oxygen, and ultimately sustains life on earth. Although, the term "photo-synthesis" was proposed by Charles Barnes in 1893, the scientific community was aware almost five decades earlier that green plants used sunlight and water to convert carbon dioxide into carbohydrates. Since then, researchers have made continued efforts to understand the intricate mechanism of photosynthesis, which has been a tantalizing and daunting endeavor [1, 2]. Earlier, scientists believed that light-induced processes result in elaborate rearrangements of atoms and groups in organic compounds. By 1930s, Cornelius van Niel had proposed a generic stoichiometry for photosynthesis as: $CO_2 + 2H_2A + h\nu \rightarrow CH_2O + 2A + H_2O$, wherein 'A' denotes an oxygen or sulfur atom [3]. It was perceived in the earlier times that O_2 formed originated from CO_2, but the use of radioactive isotopes led to the conclusion that oxygen was produced from water [4]. After 1950s, photosynthesis was divided into two separate components: the first part of light reaction included NADPH/ATP synthesis and oxygen evolution and the second part of dark reaction leads to CO_2 fixation. By the mid-twentieth century, leading photosynthesis researchers like Eugene Rabinowitch, Robin Hill, Bessel Kok, Lou Duysens, Jan Amesz, and Horst Witt came to a consensus that deterministic electron transfer/transport chain (ETC) was functional in chloroplasts. That is: it was perceived that electrons move in an uphill manner first (upon photo-activation by Photosystem II) and then downhill through a series of redox centers and then again go uphill (upon photo-activation by Photsystem I). This overall zig-zag movement of electrons from water, through a series of redox centers of varying potentials, all the way to reduce $NADP^+$, was called Z-scheme. This can be compared with how a battery of electric and magnetic fields are positioned to drive species like protons in real time and space, within a sophisticated linear or cyclic particle accelerator facility. This model was primarily/supposedly the collective outcome of: (i) the interpretation of experimental findings made by the researchers mentioned above, (ii) the perception on mitochondrial physiology afforded by the likes of David Kaelin, and (iii) key discoveries of Robert Emerson and Daniel Arnon in chloroplasts. Emerson had demonstrated that only a few among the thousands of chlorophylls donate electrons upon photo-impact and two distinct photosystems (PS) working at two different wavelengths synergistically function to enhance the physiological photosynthetic yields [5–7]. Arnon elucidated the cyclic/non-cyclic photo-phosphorylation processes of light reaction [8–10]. The discoveries of such pioneers were interpreted in conjunction with the outer sphere electron transfer theory of Rudolph Marcus [11] and the proton-motive-force (*pmf*) based ATP-synthesis hypothesis proposed by Peter Mitchell [12]. This was because Marcus theory could afford deterministic electron transfer 'wiring routes' within/between proteins and Mitchell's chemiosmosis proposal could purportedly enable a 'coupling rationale' between the e-transfer to ATP-synthesis via a supposed proton-pumping mechanism. In the early 1970s, Bessel Kok interpreted Pierre Joliot's observations to propose the 'oxygenesis cycle' in situ [13], which was subsequently deemed localized at MnComplex of PS II. Although modified subsequently, Mitchell had also originally floated the Q(uinone)-cycle [14]. But *pmf* alone had failed to tangibly connect the physiological phosphorylative coupling with the trans-membrane movement of protons using the protein of F_oF_1-ATPase. Paul Boyer's conformation-change-based rotary ATP-synthesis proposal [15] forged a connection with Mitchell's chemiosmosis and the mechanism of the phosphorylation process, filling the evident void. Although, structural details of the relevant proteins were unavailable during the conceptualization of these explanations, the subsequent

discovery of the ordered arrangement of photo-active/redox-active centers in bacterial "light-trapping/harvesting complexes" [16] re-enforced the earlier assumptions. Today, perceptions and publications across the globe employ the Z-scheme ETC and chemiosmotic rotary ATP synthesis (CRAS) paradigm to explain the various theoretical/experimental aspects of photosynthesis.

Over the last few decades, greater structural details of the proteins' structures and mechanistic insights on redox physiology have led to significant upheavals in biology. This necessitates a systemic appraisal regarding the status of photosynthesis research and new viewpoints in the field. In this regard, this write-up shall focus on some concerns regarding the classical perceptions and detail how a new mechanism (murburn concept) can better explain the overall phenomena of oxygenic photosynthesis, including the effects of diverse additives.

2. Concerns regarding the classical perceptions

As evidenced with the advancement of any sphere of human endeavors, photosynthesis research also faced several obstacles, confusions and perception changes. Even in the light of the classical perception, one of the most challenging and unclear aspect acknowledged was/is to explain how the diverse colored pigments found scattered in photosystems and light-harvesting complexes (LHC) trap the incident energy of the broad visible spectrum of sunlight to relay it to reaction center chlorophylls [17]. Herein, only the simpler aspects of classical biochemistry (non-quantum biology) are addressed in significant detail. Further, since the exhaustive critical review of various aspects of the classical textbook perception (Z-scheme ETC for NADPH synthesis, Kok-Joliot cycle for oxygen evolution, Q-cycle for quinones-roles, and CRAS for phosphorylation chemistry) is already available elsewhere [18–35], only the salient problems plaguing the traditional school of thought shall be presented. Also, the myriads of experimental observations that cannot be reasoned within the classical perspective are addressed and briefly resolved in a later part of this write-up (Sections 4 and 5).

2.1 Unavailability of 'free protons for pumping'

Several species of cyanobacteria present the examples of one of the smallest living beings utilizing chlorophylls and deriving their energy from the photosynthetic process. Its sub-micron dimension ensconces a maximal aqueous volume of $\sim 10^{-16}$ liter. Since the organisms thrive at pH 8, calculation using Avogadro number gives us: $(10^{-16}\,\text{L}) \times (10^{-8}\,\text{molecules/L}) \times (6 \times 10^{23}) \approx {<}1$. That is—such cells are practically aprotic! Quite simply, these cells possessing thousands of membrane proteins cannot be present to support proton pumping activity. This simple calculation/consideration brings down the whole edifice of the classical purview because without proton-pumping, the ETC is apparently purposeless in its mechanistic scheme [18, 19, 32].

2.2 Non-viability of elaborate/serial ETCs in chloroplasts

Daniel Arnon, whose observations were one of defining pillars of the Z-scheme, changed his views by the early 1980s. His works and several other researchers also had

reported the violation of the classical pathway in situ via multiple modalities and also shown that NADPH could be made at PS II level itself ([35–37]; and several works mentioned in [37]). The formulators/advocates of Z-scheme had overlooked a key fact that the highly mobile and molecular oxygen (1e/2e active) also served as an acceptor of electrons in the Hill reaction [38]. Also disregarded was the fact that diverse species of organic/inorganic ions/molecules could serve as donors/acceptors of electrons in chloroplasts [39–46]. This aspect does not fit with the deterministic roles of donors and acceptors in each of the four major steps of the classical perspective, as shown in **Figure 1**. It can be seen that the purported mobile electron transporters of quinols (PQ) and/or plastocyanin (PC) must jump thylakoid membranes for effective functioning as donors and acceptors in the erstwhile proposal. Further, it was recently demonstrated that the rationale for explaining the Emerson enhancement effect with the serial arrangement of components (Water-PS II-PQ-Cyt. $b_6 f$-PC-PS I-Fd-FNR-NADP) was erroneous at a very fundamental level [32]. This is because serial connectivity could have explained only lowered yields with combined excitation at the two wavelengths. (This concept is easily evident from comparing two resistances
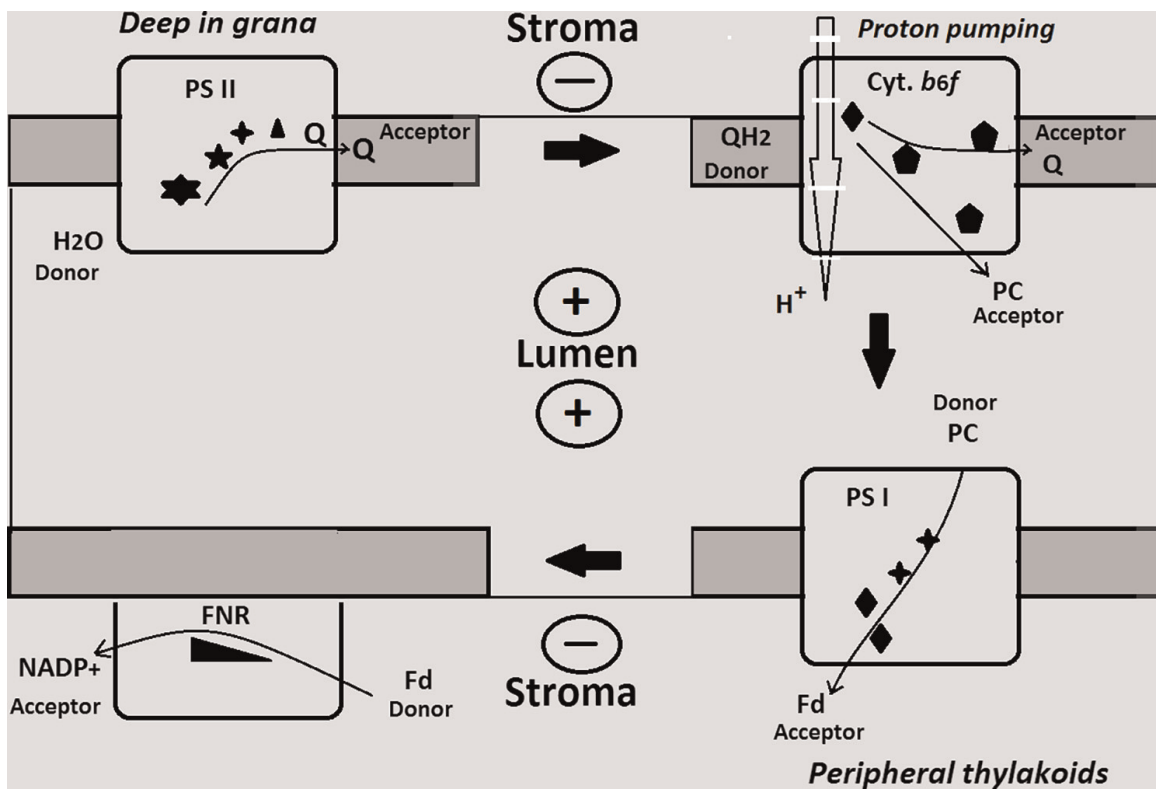

Figure 1.
A graphical representation of the spatio-temporal processes of Z-scheme. Within the classical purview, only certain molecules are supposed to serve as donors and acceptors of electrons at the various protein complexes. Not only is the electron route deterministic (within a given protein comprising of diverse types of redox/photo-active centers), unintelligent molecules are supposed to transport electrons as dedicated couriers, hopping across membranes and phases. Also, several redox/photo-active centers are present outside the purview of the purported ETC route (not shown). The blackened shapes within the proteins are the representations of a few of the different salient types of redox centers like MnComplex, tyrosine, RC chlorophyll, pheophytin, Fe-S, heme, flavin, etc. In the classical purview, the thylakoid membranes are supposed to be impervious to protons and yet, the quinones are somehow expected to acquire the protons when they get reduced at PS II. Cytochrome $b_6 f$ is supposed to carry out sophisticated bifurcation of electrons received from quinols, to recycle into quinone, but the reaction must also give electrons back to quinone itself. There is hardly any logic for PC ferrying electron to or binding with PS I. At steady state, a positive polarity is supposed to be established within the lumen, and yet, electrons are supposed to be drawn out of the lumenal phase by Fd. These aspects do not make any sound electrochemical or thermodynamic rationale, and when considering that cyanobacterial systems do not have protons in the inter-thylakoid spaces, the whole proposal is untenable.

connected in series or parallel. A higher current flow occurs with parallel connectivity.) Also, it did not make any evolutionary sense that an electron mobilized from a photosystem should go through several dozens of transfer steps, before the release of a molecule of oxygen or reduction of $NADP^+$. For example: a single 4e Q-cycle at Cyt. b_6f {(QH$_2$-FeS-Heme-PC = 3) $\times$ 2} + {(QH$_2$-Heme-Heme-Q = 3) $\times$ 2} alone would entail a dozen steps! Most importantly, mutation/knock-out studies had shown obligatory components of Z-scheme like PC and modules of Cyt. b_6f are totally dispensable in physiology [47–49]. Therefore, Z-scheme has little physiological relevance and has no means for ensuring any deterministic connectivity in chloroplasts.

2.3 Absence of a tangible chemical logic for phosphorylation

The RAS paradigm postulates that (quoting verbatim from Lehninger's acclaimed textbook of biochemistry) *"K_{eq} for ATP synthesis on the enzyme surface is near zero whereas the K_{eq} for the reaction in free solution is 10^{-5}. F_oF_1 binds ATP with very high affinity ($K_d \leq 10^{-12}$ M) and ADP with much lower affinity ($K_d \approx 10^{-5}$ M). The difference in K_d corresponds to a difference of about 40 kJ/mol in binding energy, and this binding energy drives the equilibrium toward formation of the product ATP. [50]"*. This reasoning is incorrect because a higher affinity for ATP does not provide any real mechanism or rationale for the formation of ATP, but only accounts for ATP breakdown! How F_oF_1 can fashion a phospho-anhydride bond between two negatively charged phosphate moieties is still left unaddressed because: (i) the enzyme is a known and demonstrable ATPase, with preference for ATP-binding (over ADP-binding), (ii) physiological steady-state ambiance in chloroplast has higher ATP concentration (as compared to ADP), and (iii) the thermodynamic dictate is highly tilted toward hydrolysis. Even if the realities are overlooked to imagine that protons were freely available in/around the thylakoids, the directionality of rotation in F_oF_1-ATPase would still be problematic. That is- assuming proton availability, they would be present within both lumenal and stromal phases across the c-ring. Since there is little pH gradient in physiology, there exists no reason why the c-ring should rotate only in the direction resulting in ATP-synthesis. (That is-once a proton comes across a c-ring, why cannot it go back across the c-ring of F_o? In Boyer's model, the proton is not consumed in the reaction at the active site of F_1!) Thus, the CRAS proposal was also a mere mirage, quite like chemiosmosis [21, 22].

2.4 Violation of the principles of thermodynamics and electrochemistry

When Mitchell proposed that pumping out protons enabled the conservation of energy in the 'crowding of protons' and this could be used for doing useful work by moving it back across the same membrane (and subsequently added a higher electrical energy term to make up for the deficiency in his equation), there was little thermodynamic accounting in the original proposal or its up-gradation thereafter [18–34]. For, this unrealistic exercise is similar to the following banking scenario: *once a sum of money was withdrawn from a customer's checking account, the system somehow credits the saving account of the same person with 4 folds the equivalent sum of money*! The classical mechanism fails because there is no known reproducible way that an ion pumped across a membrane can be used to commission work while returning to the same phase across the same membrane. There is little accountability when charged species are expected to move and counter the preset potential gradients [19, 32]. Further, seen from a holistic perspective, the classical purview proposes a deterministic

stoichiometry for the overall equation as: 2NADP$^+$ + 3ADPOH + 3POH → O$_2$ + 2NADPH + 2H$^+$ + 3ADPOP + H$_2$O; $\Delta_r G°_{aq} \approx$ 1464 kJ/mol. As per Z-scheme, 4 einsteins each of 680 nm and 700 nm can only give a total of ~1387 kJ/mol and this is inadequate to achieve the reaction mandate [17, 32]. Therefore, the classical perspective can only work by transgressing the established guiding principles of thermodynamics and electrochemistry.

2.5 Assembly/architecture/distribution/structure- function issues

The non-systematized and randomized assembly of the components of leaf/chloroplasts, thylakoid stacks therein and distribution of various proteins and small molecules in and around the highly convoluted lipid membranes hardly support the classical proposals. For example- while PS II dimers are found buried deeper in thylakoid stacks, PS I complexes are found in the peripheries of grana. It is unknown how plastoquinol traverses membranes to serve an electron-relay role in the deterministic ETC. Plastocyanin is found at very low concentrations, and it is present in both phases. The longer chain plastoquinol is more in abundance, which is not expected if quinols are mobile transporters of electrons in the membrane phase. Various pigments of chlorophyll *a* and *b*, carotenoids, etc. are found scattered in the membrane phase, with little scope for any intelligent or quantized modality for the collection and relay of energy by these molecules to the RC chlorophylls. The large extra-membrane extensions of various membrane-embedded proteins (photosystems, cytochrome complexes or NDH complexes, etc.) and the arrangement of redox centers in the redox proteins is not conducive to a leak-proof relay of electrons [25, 30, 32, 33]. Even the accessibility of the redox center of smaller proteins like plastocyanin does not make a good structure-function correlation to the ETC-CRAS paradigm [26]. In short, neither the architecture nor the components of chloroplasts (or their distributions) reflect the mandate set by the ETC-CRAS proposal. For more elaborate discussions in this regard, refer [32, 33].

3. The murburn model of photosynthesis

The quantitative and qualitative arguments listed in the section above conclusively discredit the Z-scheme (ETC)-CRAS explanation, which was proposed when adequate information of the chloroplast system was unavailable. Over the last two decades, murburn concept/model-based pursuits provide an alternative explanation to the photosynthetic process research [17, 25, 26, 28, 31–34]. In turn, this development was enabled and consolidated by insights derived from two decades of experimental findings and theoretical explorations in diverse redox enzymes and metabolic/physiological systems [18–24, 27, 29–31, 51–81].

3.1 Murburn concept

The term murburn is abstracted from 'mured burning' (confined oxidation) and invokes mild unrestricted reaction equilibrium dynamics OR electron/moiety transfer interactions among molecules, unbound ions and radicals. It is akin to combustion, but occurs in a more controlled manner because reactive species are generated in a 'sustained release' manner. Herein (as shown in **Figure 2**), although the scheme may not involve high affinity-binding based interactions, the reactions may show
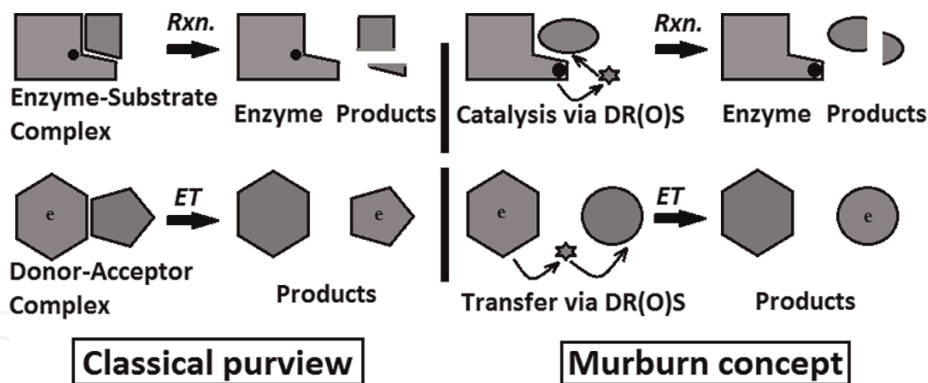
Figure 2.
Extension of classical enzyme-mediated catalysis paradigm with murburn concept. The left panel shows a classical understanding of enzyme-catalyzed reactions and electron transfers based on binary complex formation, owing to the affinity between them. The murburn mechanism does not disclaim the classical perception but is a larger paradigm that also permits useful roles for DR(O)S. therefore, the enzyme and substrate OR donor and acceptor may have a little mutual affinity (and need not bind). Such a reaction mechanism enables the explanation for the existence of a diverse array of substrates and inhibitors. Also, substrate inhibitions and activations by diverse additives need not invoke allosteric influence.

selectivity and specificity, and at times, a lower order of dependence on the substrate concentrations may be observed [32, 72, 78].

3.2 Details of the murburn scheme in chloroplasts

Murburn scheme sees chloroplasts as simple chemical engines (SCE) employing the principle of effective charge separation/stabilization (ECS), which is afforded by the membrane-embedded protein complexes [34]. Unlike the ordered/serial and highly inter-dependent reaction components within the deterministic classical purview, the murburn model deems each of the protein photosystems as independent elements that work in parallel within a reaction milieu (that has several non-specific interactive equilibriums). While the traditional view deems DR(O)S as toxic waste products, they are essential reaction components in the new model and they form a crucial/dynamic component of the reservoir of redox equivalents in the murburn model. Within the ETC-CRAS view, the events of photo-induced charge transfer-photolysis/oxygenesis-NADPH production-ATP synthesis are supposed to occur at distinct loci centered at PS II RC-MnComplex-FNR-F_oF_1ATPase respectively. In the murburn mechanism, these activities are delocalized and occur aided by DRS at diverse loci within the murzone (in or around the phospholipid membranes of thylakoids). To aid this function, it would be expected that the membrane proteins would have solvent/DR(O)S access channels to redox centers and also present low-affinity binding sites for ADP adjacently. This prediction is duly validated, as shown in **Figure 3**.

Figure 4 presents a salient snapshot of the events that transpire during the light reaction, centered at/around the various protagonists. All photo-active pigments (including LHC) are deemed as DRS producers and only the photosystems enable ECS, without which the lost charges are reversibly regained by the chlorophylls/carotenoids. The presence of various species like quinones in membrane and PC/Fd in milieu enables ECS, besides the integrally specific arrangement of a select few redox-active centers in the two Photosystems. While Cyt. b_6f recycles the electrons lost to the membrane (in QH_2), other intermediates are in direct equilibrium with diverse DRS and proteins (PC/Fd) or other molecules/ions of milieu. The membrane-anchor
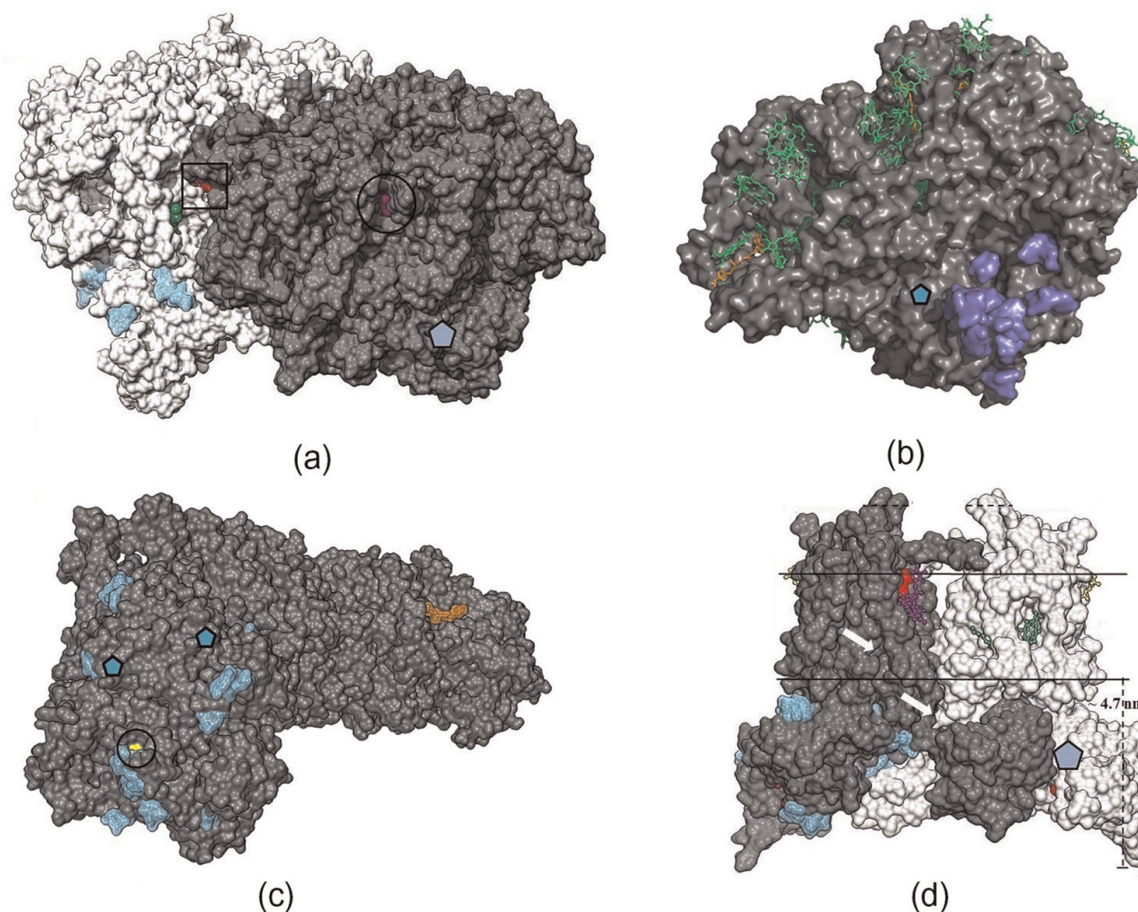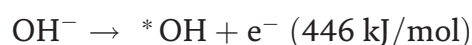
Figure 3.
ADP (blue) sites on chloroplast membrane-embedded protein complexes [32]. *In PS II (a), 3 ADP-sites (of a total of 6 per monomer) are shown in the pale monomer whereas a unique site is depicted with a pentagon in the dark monomer. Access to RC chlorophylls (red-orange) is shown in the square in the pale monomer whereas pheophytin (magenta) channel is circled in the dark monomer. Of the total 10 sites, 8 are depicted in blue whereas a hidden site is shown as a pentagon in PS I (b), with chlorophylls and carotenoids in color within the trans-membrane region. In NDH (c), 10 of the 12 ADP sites are visible (2 hidden sites are marked in the pentagon) and the solvent-accessible cysteine ligand (yellow) of the first Fe-S center is circled. A trans-membrane carotenoid is shown in red. Cyt. b_6f (d) has 6 ADP sites per monomer, of which 4 are visible on the black monomer and a hidden site is shown in the pentagon on the pale monomer. Easily accessible quinone (purple), carotene (yellow) and chlorophyll (green) are highlighted within the trans-membrane region (marked in horizontal lines). Arrows indicate channels enabling DR(O)S dynamics.*

of NDH aids in ATP synthesis and serves as a complexing hub for other protein like Cyt. b_6f.

Murburn reactions could be seen as continuously-fed single-pot, heterogeneous-phased equilibriums/systems that are auto-activated due to the presence of electron sources and sinks. This aspect is shown in **Figure 5**, followed by the examples of pertinent mass-charge balanced bimolecular equations and their overall free energy yields, as sourced from [31–33, 81].

Replenishment of photo-discharged pigments and DR(O)S generation
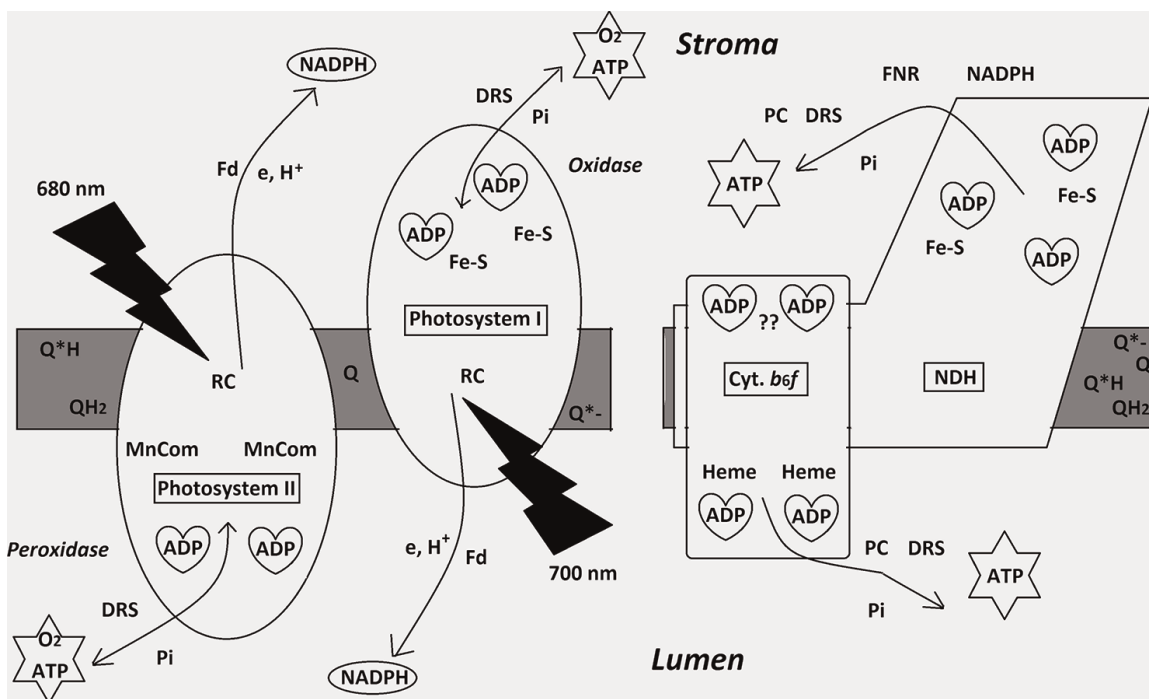
$$H_2O \rightarrow {}^*OH + H^+ + e^- \text{ (525 kJ/mol)}$$

$$OH^- \rightarrow {}^*OH + e^- \text{ (446 kJ/mol)}$$

$$H_2O_2 \rightarrow {}^*O_2{}^- + 2H^+ + e^- \text{ (426 kJ/mol)}$$

Figure 4.
The murburn model for overall events of light reaction. *The left side has the photo-active photosystems whereas the right side presents the two main auxiliary redox protein complexes. LHCs are not shown. All reactions are discretized, with stochastic routes for oxygen, NADPH and ATP formation in a delocalized fashion. Quinols are seen as stationary electron buffers within the membrane whereas PC/Fd serve the same roles in different regions of the redox spectrum, in the aqueous milieu around the membranes. Although, the peroxidative evolution of oxygen is higher at PS II, PS I can also produce some O_2. Similarly, NADP reduction can occur at both photosystems whereas ATP synthesis can occur at all the membrane-embedded complexes that subtend extensions into the aqueous phase. This can be contrasted or compared with the mitochondrial protein system wherein cytochrome oxidase (complex IV) is the major peroxidase and complex I (NADH dehydrogenase) is the major oxidase. Therefore, both chloroperoxidase and mitochondria work via oxidase-peroxidase cycles.*
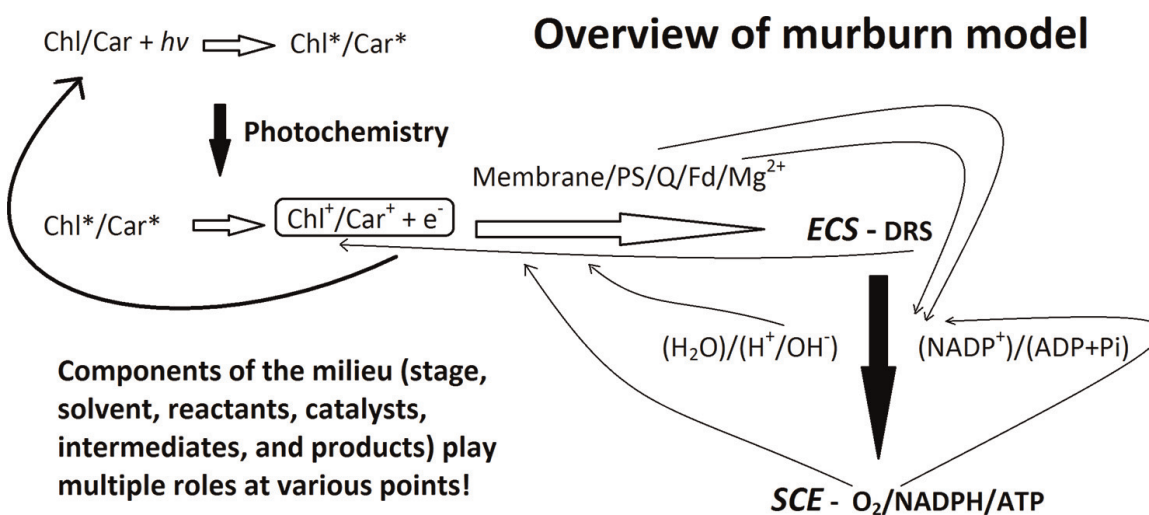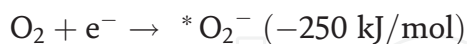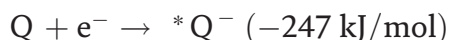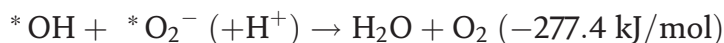

Figure 5.
The concepts of ECS, SCE and interactive networks in the murburn scheme for chloroplasts. *Once the photons activate the system, the achievement of ECS enables the generation of DR(O)S, which are dynamically turned over by the presence of suitable substrates. Complications of singlet/triplet states and inter-system cross-over are not shown. In the reaction scheme, oxygen is both a product and a catalyst. NADPH is a product in one sense but also a substrate for the ATP generation reaction that goes on simultaneously. Without the ECS afforded by photosystems, LHCs would go through futile cycles, as shown in the left. Chl/Car stands for chlorophyll/carotenoid.*

Other DR(O)S dynamics

$$H^+ + e^- \rightarrow \, ^*H \; (-39 \text{ kJ/mol})$$
$$Mg^{2+} + e^- \rightarrow Mg^+ \; (-69 \text{ kJ/mol})$$
$$Q + e^- \rightarrow \, ^*Q^- \; (-247 \text{ kJ/mol})$$
$$O_2 + e^- \rightarrow \, ^*O_2^- \; (-250 \text{ kJ/mol})$$
$$^*H + O_2 \rightarrow H^+ + \, ^*O_2^- \; (-211 \text{ kJ/mol})$$
$$Mg^+ + O_2 \rightarrow Mg^{2+} + \, ^*O_2^- \; (-181 \text{ kJ/mol})$$
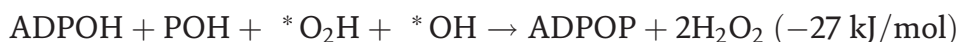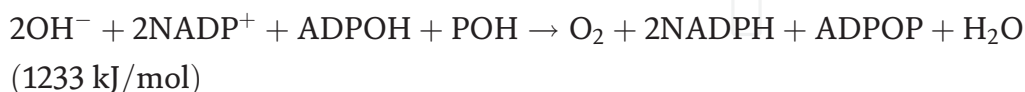$$^*Q^- + O_2 \rightarrow Q + \, ^*O_2^- \; (-2.9 \text{ kJ/mol})$$

O_2 evolution

$$2H_2O_2 \rightarrow 2H_2O + O_2 \; (-400 \text{ kJ/mol})$$
$$2\,^*O_2^- \, (+2H^+) \rightarrow H_2O_2 + O_2 \; (-158.8 \text{ kJ/mol})$$
$$^*OH + \, ^*O_2^- \, (+H^+) \rightarrow H_2O + O_2 \; (-277.4 \text{ kJ/mol})$$
$$^*O_2^- + H_2O_2 \, (+H^+) \rightarrow \, ^*OH + H_2O + O_2 \; (-91.8 \text{ kJ/mol})$$

NADPH formation

$$NADP^+ + H^+ + 2e^- \rightarrow NADPH \; (-93 \text{ kJ/mol})$$
$$NADP^+ + \, ^*H + e^- \rightarrow NADPH \; (-54 \text{ kJ/mol})$$

ATP synthesis

$$ADPOH + POH + \, ^*O_2H + \, ^*OH \rightarrow ADPOP + 2H_2O_2 \; (-27 \text{ kJ/mol})$$
$$ADPOH + POH + 2\,^*OH \rightarrow ADPOP + H_2O + H_2O_2 \; (-150 \text{ kJ/mol})$$
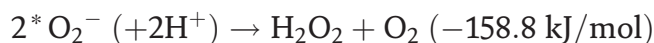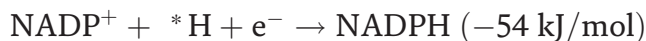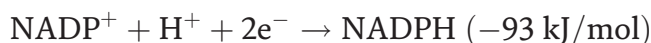
ATP synthesis cum O_2 evolution

$$ADPOH + POH + 2\,^*O_2H \rightarrow ADPOP + H_2O + H_2O_2 + O_2 \; (-92 \text{ kJ/mol})$$
$$ADPOH + POH + \, ^*O_2H + \, ^*OH \rightarrow ADPOP + 2H_2O + O_2 \; (-217 \text{ kJ/mol})$$

Simplest overall equation for a 4e reaction

$$2OH^- + 2NADP^+ + ADPOH + POH \rightarrow O_2 + 2NADPH + ADPOP + H_2O$$
$$(1233 \text{ kJ/mol})$$

All reactions (other than the photo-activations and some ATP-synthesis steps) are exergonic. Since they result from bimolecular collisions of small mobile species and radicals (which are known to have low activation energy barriers), they are practically diffusion-limited and very highly kinetically viable [20, 81–83]. The actual stoichiometry would vary with each system/setup, because this model is stochastic, depending on a diverse set of variables. The various components of the reaction systems can work independently and also work synergistically in tandem. Most importantly, the equilibriums permit the scope for a spontaneous evolution of the system over ages. There is no need for intelligent governance, as the presence of substrates switches the system to an activated state (owing to thermodynamic pull, enabled by electron-sinking and porting/

partitioning of products) [31, 32]. There are multiple routes and loci for any product formation, making the process highly viable. The phosphorylation reactions are actually the combination of two bimolecular reactions, with ADPOP, ADPOH, and POH standing for ATP, ADP, and Pi, respectively. Since oxygen is practically omnipresent, its intermediacy cannot be avoided in the steady-state, although it is not needed in the initial state. Therefore, a higher rate of oxygen evolution at MnComplex is primarily owing to a peroxidase type of activity, analogous to the role of cytochrome oxidase in mitochondria.

4. Murburn model explains various aspects of photosynthesis

The success of a model lies in its ability to explain and predict various aspects of the system. In this regard, the murburn concept is a ubiquitous principle of life (essentially—an interactive equilibrium of various molecules and ions that constitute the cell), which abides by the physics-biology continuum and is favored by Occam's razor (principle of parsimony) [72, 78]. In stark contrast, ideas such as elaborate deterministic ETCs of diverse components, proton motive force, chemiosmosis, rotary enzymatic synthesis, etc. are unheard of in any area of science, other than bioenergetics [27–30]. Such ideas were recognized because the research community had long searched for explanations, and these ideas provided an "out of the box" kind of explanation to the frustrated scientists. The findings were recognized before significant evidence was available and critical queries were adequately addressed. Earlier researchers had overlooked the importance of DRS in physiology because of an indoctrinated adherence to only Michaelis-Menten type mechanisms for catalysis. Also, the esthetic/deterministic orientation- *'DRS are too chaotic and cannot serve physiology with any constructive roles'* prevailed then [73]. Over the last two decades, ample evidence and arguments were presented for murburn concept [17–34, 51–81]. If labile DRS molecules like NO can serve as molecular messengers [84, 85], why cannot other such DRS serve in catalytic roles? There is no need to continue to deny the roles of DRS when researchers have repeatedly opined that DRS are also good for animal and plant physiology [86, 87]. Of course, the last statement does not negate the demonstrated harmful effects of large amounts of DRS in cells! What is implied is that all entities (stable or transient) have spatio-temporal and concentration-based contexts, which determine their utility or toxicity. With some salient examples below, the efficacy of the murburn model for explaining the light reaction is highlighted.

4.1 Chloroplast composition and structure-function relations of components

Unlike the time of 1960s–1970s (the times when Z-scheme ETC-CRAS proposals were forged) when the details of chloroplasts and its component proteins/pigments were lesser-known, currently, the system is much better explored [88, 89]. The facts that: (i) chloroplasts have highly convoluted thylakoid stacks of various tiers ensconcing sub-micro- to nano- dimensioned pools, (ii) the membranes are loaded with various protein complexes in a rather random manner, (iii) the protein complexes could aggregate in several supercomplex configurations, (iv) the distribution of low concentrations of plastocyanin and high concentration of ferredoxin across both lumenal and stromal phases, (v) preponderance of longer tail chain lengths of membrane quinols, (vi) multitudes of chlorophylls and carotenoids are found scattered

across the membrane phase and also adsorbed on to proteins, without any covalent tethering, (vii) the large membrane-protein complexes subtend extensions into the aqueous milieu presenting multiple low-affinity ADP sites, (viii) there is no special provision seen to localize water-binding or oxygen formation and limit these omni-present molecules, (ix) the structural features membrane-disc stacking seen in chloroplasts are also seen in rods/cones cells in retina, (x) existence of grooves/channels to redox centers in membrane and soluble proteins facilitate DROS-dynamics, etc. support the simple origin and ubiquitous functioning of the stochastic murburn model (and disclaim the sophisticated affinity-binding based electron-circuitry and proton-pumping facets demanded by ETC-CRAS model) [32, 33]. The clear strategy in nature is to minimize the availability of free protons (so that O—H bond formations are delayed), enabling photo-reduction and photo-phosphorylation chemistry at the membrane-interface.

4.2 Emerson enhancement effect: synergism between photosystems I and II

By the mid-1950s, Emerson had discovered that two distinct photosystems existed in chloroplasts and that oxygenesis/photophosphorylation (considered as the index of photosynthetic efficiency) were higher with the combined excitation of both photosystems (in comparison to the added outcomes of what was observed when each of the photosystems was excited independently) [5–7, 90]. This result can be easily visualized from online sources [91, 92]. In the backdrop of David Keilin's ETC concepts prevailing in the bioenergetic organelle of mitochondria, the researchers in the field reasoned it as an augmentation, from the serial arrangement of the two photosystems, and the Z-scheme was thus rooted. This was a fundamental theoretical error in deduction, as a serial arrangement of components cannot explain the synergism (enhancement of electron transfer and any other kind of mass transfer or reaction rate) [32, 33]. Murburn model's theorization of stabilization and utilization of DRS pool from common reservoirs (involving multiple reaction equilibriums) via parallel routes explains Emerson's original observation. Further, the fact that far-red illumination (excitation of PS I with 700 nm) also gave oxygenesis [90] is accommodated in the discretized murburn model whereas inadmissible in the Kok-Joliot and Z-scheme model.

4.3 Jagendorf experiment: chloroplasts presented with pH gradient

Yet another historically crucial detour in photosynthesis research was taken with the report and interpretation of this experiment [93]. The demonstration (driven by Mitchell's proposals) made was that even in dark, chloroplasts equilibrated at pH 4 gave ATP synthesis (noted with the provision of radiolabeled phosphate incorporated into ADP) when the external buffer pH was raised to pH 8. All this experiment demonstrates is that a pH gradient (low pH inside versus high pH outside) can give some ATP synthesis within confined aqueous pools, even without photochemistry. Clearly, this has little contextual physiological relevance because plant systems work at pH 8 (in/out) and the mechanism of photo-phosphorylation is to be understood! As per the currently prevailing consensus, both photosystems (I & II) are not proton pumps [32, 94]. Then, the role of trans-membrane proton pumping falls solely upon the remotely located Cyt. b_6f and F_oF_1-ATPase! Clearly, these components cannot connect the incompatibly distributed Photosystem II (in deep grana) and

Photosystem I (in peripheral thylakoids), and therefore, both ETC and proton-pumping connectivity breaks down (as advocated in the classical scheme, shown in **Figure 1**). Fundamental physiological reactions for NADPH synthesis and oxygenesis use protons in the left-hand side (as shown in Section 3.2) and in vitro proton-aided equilibrium driven phosphorylation also uses protons [32]. The pitfall of not including protons in the bioenergetic calculations in recent work is now clarified. Further, proton equilibriums or proton gradient-driven synthesis of ATP is quite different from physiological ATP synthesis [31, 32]. It must be seen that cyanobacteria have little free protons, thereby nullifying the proton-centric explanation in physiological contexts). Since Boyer's conformation change proposal for ATPase does not use protons at the F_1 active site, proton- involvement in the phosphoanhydride bond formation cannot be mechanistically/energetically correlated in sound theoretical terms. Currently, it is known that diverse anions and cations exist in intricate equilibriums within closed water pools [78]. Further, manipulation of potassium and hydroxide ion concentration was enough to give rise to superoxide (DRS) even in the bulk phase under ambient conditions [95]. Therefore, Jagendorf's observation is physiologically irrelevant and it is seen that the murburn concept is in a better position to explain such in vitro findings using chloroplasts [19].

4.4 Racker experiment: reconstituted liposomes with rhodopsin/ATPase

Racker had isolated and reconstituted a preparation of F_oF_1ATPase and photo-active rhodopsin in a vesicular system [96]. Based on the observation that photophosphorylation occurred within this in vitro reaction milieu, it was inferred that a proton-gradient was responsible for ATP synthesis and this was the way chloroplasts worked in physiology. It was pointed out that considering the high pK_a of the Schiff's base intermediate [17, 97], rhodopsin is unlikely to work as a proton-pump but is more of an interfacial DROS generator [98], owing to the photo-active nature of retinal [99]. Once a negatively charged species is produced in the inside due to photo-activation, protons are bound to enter and this could give equilibrium-assisted ATP synthesis within a closed water pool. Once again, the non-viability of proton-based rationale in rhodopsin system and theoretical aspects pointed out against equilibrium-driven ATP formation in the earlier point preclude the CRAS-type model in physiology. Also, it is a low probability event that the preps of proteins (the hydrophobic F_o and soluble F_1 fractions, and the membrane fraction of *Halobium* serving as a crude source for rhodopsin) could have assembled in a perfectly deterministic/asymmetric fashion necessary for the classical interpretation. The murburn explanation does not need the precise orientations or immaculate assembly and thus is a simpler rationale for the observed outcomes. This is confirmed by Table 1 of Racker's original paper itself [96], which shows that 19% of the activity of the test sample was retained in the negative control lacking F_oF_1ATPase, which points out that the protein is not the primary factor, it just enhances the reaction's efficiency! Also, while 29% activity of the test reaction was seen in a negative control incorporating F_o binding inhibitor oligomycin (alias rutamycin), premises dealing directly with DRS-dynamics like the incorporation of an electrophile (bis-hexafluoroacetonyl acetone) or absence of light or absence of the rhodopsin fraction gave 0% activity! If classical enzyme activity was operative, ADP + Pi and F_oF_1ATPase should have given some ATP-synthesis in the last negative control! Thus, the murburn concept is a better explanation for this key experiment [19] that was seen as a minimalist representation of physiological photosynthesis.

4.5 Justifying the action spectrum of light reaction

While the classical explanation confines only the Photosystem's reaction center chlorophyll as the source of photo-activated electrons, the murburn perspective allows all pigments to serve as the source of electrons. This permits an effective photo-activity ranging from 400 to 700 nm, with a relatively consistent quantum yield of 0.05 to 0.1 across this range. Else, it is difficult to see how photon or exciton transfers occur from several pigments to the reaction center chlorophyll of the photosystems. The murburn model obviates the unlikely premises where plants would need to resort to some mode of quantum computing [17] for such purposes [100]. Also, while the classical perception permits oxygen evolution only with 680 nm excitation of PS II, the murburn perspective allows for oxygenesis with even 700 nm excitation of PS I.

5. Murburn rationale for observations with diverse additives

Traditionally, the mechanism of biochemical reactions is deemed as 'black boxes' and the events transpiring within the 'boxes' are usually probed with the incorporation of additives. How an additive affects the system often gives profound insights regarding various aspects that govern the outcomes.

5.1 Inhibition by species like cyanide, uncouplers, etc

Cyanide presents very potent and debilitating effects on various physiologies of life. Through systematic investigation of a wide variety of factors, it was recently unraveled that the rationale for toxicity resulted from catalytic DRS-modulating action of the respiratory toxic principle of cyanide in mitochondria; and not due to a stoichiometric binding to the heme-center of cytochrome oxidase or any other heme centers of vital proteins, as conventionally perceived [21–24, 31, 65, 67, 68]. It is known for several decades now that even photosynthetic components and processes are inhibited by cyanide [101–107]. It is quite forthright to infer that the same murburn principles operational in oxidative phosphorylation would be relevant to photosynthesis too; and therefore, the modalities of inhibition by cyanide would also be common. This is because DRS is common to both respiratory and photosynthetic mechanisms whereas heme is not that crucial to the latter system. Further, redox-active interfacial DRS-modulators like disubstituted phenolics were seen as proton-shuttlers or active site inhibitors in mitochondrial and endoplasmic reticulum systems, respectively. In the liver microsomal (endoplasmic reticulum) systems with membrane-embedded cytochrome-P450 (CYP) and its reductase, the mandate is to metabolize xenobiotics. Therefore, there is a little evolutionary rationale for active site affinity binding-based interpretations for the vast array of ET-substrates and 'uncouplers' known. In the CYP system, there is also no scope for proton-pumping-based logic for inhibition, but the same uncoupling is seen in those systems too [58, 59, 64, 67, 70]. As a result, the classical perspective is inapplicable for explaining the effect of "uncoupling" [33]. Further, the shuttling explanation in mitochondrial/ chloroplast systems that prevailed in the bioenergetics community was a mere mirage. For, if protons (a small species with a unique positive charge) are not permitted to traverse the lipid membrane, it is unlikely that uncouplers (molecules with multiple

positive and negative charges) make repeated and deterministic trans-membrane flip-flop movements [31, 33].

5.2 Electron donation/acceptance by various molecules and ions

Reports in literature e.g., [41] show that amino acid like cysteine, sugar like 2-ketogluconate, vitamin like ascorbate, organics like arylamines, organic/inorganic anions like tetraphenylborate or ferrocyanide, small molecules like hydroxylamine/hydrazine, DROS like hydrogen peroxide, etc. all served as electron donors to PS II and some of them (like tetraphenylborate, ascorbate, hydroxylamine/hydrazine, etc.) could also serve as electron donor to PS I. While ferrioxalate, tetrazolium blue, DCPIP (dichlorophenol indophenol or Hill's reagent), massive ions like silicotungstate, etc. accept electrons from PS I, species like ferricyanide and $HgCl_2$ could accept electrons from both PS I & II. Quite interestingly, benzidines, flavins, quinones, etc. serve as electron donors and acceptors (both functions!) with both photosystems I & II. It is impossible to explain these findings in the context of classical photosynthetic chemistry of Z-scheme (**Figure 1**), which has a deterministic electron flow governed by affinity-binding driven logic, between definitive donors and acceptors. Affinity is based on molecular descriptors like dimensions, geometry, surface topography, electrostatics, hydrogen bonding, rotatable bonds, log P, etc. Since murburn model does not require the diverse species to directly access the redox centers, and the redox relay could be achieved via small soluble intermediates, the promiscuity and diversity of electron donors/acceptors are explicable. In molecular docking studies with several well-known herbicides/weedicides, there was neither conclusive nor marginal support derived for binding-based inhibitions of various chloroplast proteins [33]. In contrast, several mechanistic aspects supported murburn interpretations; e.g., the fact that iodinated inhibitors were more effective than chlorinated inhibitors (quite like the case in cytochrome P450 system [64]) suggested the conclusive involvement of DRS-based radical chemistry [33].

5.3 Maverick concentration-based effects proffered by diverse species

Researchers had reported unusual concentration-based modulation of chloroplast's photosynthetic activity upon the introduction of extraneous molecules [108, 109]. The unusual aspect of such an activity would be that a lower concentration of a molecule could show greater activity/impact than a higher concentration. Else, there could be more than one concentration regime of high impact. Since classical explanations for enzyme-substrate and receptor-ligand interactions can only afford simple mono- or biphasic reaction profiles (e.g., linear or hyperbolic asymptote) for non-inhibitory molecules, such observations cannot be explained by classical Michaelis-Menten supposition of the enzyme-substrate complex. Allosteric (binding-based) effects cannot reason this either because a lower concentration cannot give an allosteric effect that a higher concentration cannot. Species like azide gave activation effect at low concentrations owing to the formation of DRS, which may be stabilized at lower concentrations [60]. Since the outcome is catalyzed by such DRS, distinct/discrete concentration ranges of components may help stabilize a pertinent DRS in milieu (owing to multiple competing reaction equilibriums), which could lead to higher activity (i.e., detection of a molecule or product of interest). This finding helped clarify upon hormetic effects and unusual dose responses observed in diverse

ambiances by many researchers [61, 68, 71]. Clearly, the same inference applies in photosynthetic physiology also.

5.4 Effect of chloride ions

Otto Warburg, one of the greatest biochemists of the twentieth century, discovered that chloride ions were needed for reconstituting the oxygenesis function in plant tissues; and he proposed that chloride was an essential cofactor in photosynthesis [110]. This was against the general awareness of plant physiology during that time, which did not consider chloride ion as a dispensable ion in plant growth. Daniel Arnon followed through Warburg's work with adequate controls, and found that chloride was not essential for growth and the plants could photosynthesize quite effectively when grown on chloride-negative soil. However, he found that Warburg's observation was highly reproducible and also corroborated that bromide, surely a non-essential element, could also produce the same effect as chloride. Therefore, Arnon asked a key question [111]: *If the view that chloride or bromide is a coenzyme of photosynthesis in vivo is to be abandoned, how is the effect of these anions explained in vitro?* To solve this puzzle, Arnon formulated an interesting hypothesis that chloride protects a photo-labile substance in cells (which is essential for oxygenesis) from deactivation and supported it with experimental observation. Some researchers ardently tried to trace and solve the effect of chloride subsequently [39, 42]. Eventually, the experimental observations confirmed that chloride does enhance the light reaction in vitro. However, any Cl^- ions' physiological roles in photosynthesis or growth aspects resulting thereof were deemed questionable [112].

In the wake of the twenty-first century, the effects of chloride (and some other cations also) remained an enigma, in the photosynthesis chemistry [113]. Chloride ion has been considered both as a nutrient and toxicant [114]. In positive roles, it is seen as a micronutrient [115] and also a beneficial macronutrient [116]; considered relevant in photosynthetic [117], osmoregulatory [118] and growth [119] physiology. It was proposed that chloride *participates together with charged amino acid side chains in a proton-relay network, which facilitates proton transfer from the manganese cluster to the medium* [120]. Chloride ion was deemed important *to maintain the coordination structure of the Mn_4Ca cluster as well as the proposed proton channel, thereby keeping the oxygen-evolving complex fully active* [121].

While studying the activity of peroxidases, it was found that certain ions/molecules could enhance activities of electron abstraction from other electron donating ions/molecules e.g., [55, 60, 61, 63, 68]. This finding was the origin of pursuits that led to the murburn concept. This interactive electron/moiety transfer equilibriums originating due to the generation of a diffusible reactive intermediate from the active site of a protein could also give specific outcomes due to low-affinity interactions and/or spacing of kinetic windows in interactive equilibriums. It was seen that this mechanistic insight could explain the enhancement of peroxidative electron abstractions by chloride [55, 68]. Given the high distribution of one-electron active redox centers in thylakoid/stromal proteins and the report of high amounts of systems DRS in chloroplasts, it is natural to correlate that the observations in heme-peroxidase systems have contextual relevance in chloroplasts too. In the murburn model, the MnComplex has an electron sequestering peroxidase activity, which also reduces collateral damage. Therefore, the mechanistic enhancement of e-transfer by chloride ions is a direct testimony to the relevance of murburn concept in chloroplast physiology, regardless of its physiological significance. The point to note is that murburn model can explain both the positive and

negative effect of an ion like chloride, owing to the ion-radical equilibriums (whereas the classical model cannot, by virtue of being an overall deterministic 2e scheme).

5.5 The bicarbonate conundrum

Otto Warburg had originally discovered that bicarbonate enhanced the light reaction of photosynthesis [122]. Over the next half a century, researchers could not arrive at a consensus on this aspect (the veracity of this finding) and could not afford a convincing explanation for the same. While some supported bicarbonate as a source of electrons/oxygen [123–127], other opined against it and some even called such observations irrelevant or artifact [128–131]. It is in this context that murburn equilibriums aid in explaining the observed outcomes.

Four species coexist in a complex interactive equilibrium when gaseous CO_2 mixes with water: CO_{2aq}, H_2CO_3, HCO_3^- and CO_3^{2-}. Among these, bicarbonate is predominant in the physiological ranges. Carbonic anhydrase (CA), the enzyme is known to mediate this equilibrium is a Zn-containing protein. Although Photosystem II is quite distinctly different, it is also supposed to have some carbonic anhydrase-type activity [132, 133]. Also, literature shows that CA substituted with Mn works as a peroxidase, involving DRS [134]. Since CA is a *d*-block metal enzyme and PS II is a known DRS producer (owing to photo-redox chemistry and MnComplex), both qualify for murburn chemistry. From the equations below, it can be seen that the outcome involving charged species is pH-dependent whereas the neutral species is close to equilibrium:

i. $CO_2 + OH^- \rightarrow HCO_3^-$; -44.1 kJ/mol

ii. $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$; -35.9 kJ/mol

iii. $H_2CO_3 \rightarrow CO_2 + H_2O$; -0.1 kJ/mol

Now, if PS II abstracted an electron from bicarbonate,

$PS^+ + HCO_3^- \rightarrow PS + CO_2 + *OH$ or $\{\Delta_f G°(PS) - \Delta_f G°(PS^+) =\sim -612\ \text{kJ/mol}\}$

the energy term falls between that of hydroxide ion $\{-596\ \text{kJ/mol}\}$ and water $\{-676\ \text{kJ/mol}\}$. Two hydroxyl radicals formed can spontaneously coalesce to form a molecule of hydrogen peroxide. The reaction of these DRS with spontaneously formed superoxide from LHCs and other redox centers can easily generate oxygen, as shown in Section 3.2. This reaction could be catalyzed by MnComplex, and this peroxidase-type activity is more probable than the untenable Kok-Joliot cycle. Therefore, in the murburn scheme, besides water, bicarbonate could also potentially serve as a source of electrons and/or oxygen, thereby explaining the experimental findings/discussions of several researchers that worked on this intriguing problem [128, 129, 135–137], as discussed briefly below.

Provision of ^{18}O-labeled bicarbonate to chloroplasts (depleted of CA and bicarbonate) gave instantaneous evolution of ^{18}O-labeled CO_2 and unlabeled oxygen; and delayed evolution of small amounts of ^{18}O-labeled oxygen (Figure 1 of [136]). If bicarbonate is not involved in photosynthesis, there was no way for ^{18}O-labeled oxygen evolution. The low amount and delay in ^{18}O-label in oxygen can be explained by: (i) understanding the fast equilibriums of water (>55 M) and labeled bicarbonate (~mM, initially), which would lead to immediate loss of label in bicarbonate to water

and the loss to water cannot be driven back up into bicarbonate; (ii) noting that oxygen yield goes up significantly in the first cycle reactions (2nd flash also) when bicarbonate is presented (with respect to controls) [137]; (iii) seeing that kinetics for oxygen evolution from labeled water is almost an order slower than unlabeled water [137], which signifies that radical rebound reactions will be much slower for heavy labeled bicarbonate also; (iv) considering that after electron abstraction from labeled HCO_3^-, the formation of products ($^*OH + CO_2 + e^-$) results (which is the reason for immediate release of heavy-labeled CO_2 in the murburn model), the labeled oxygen atom in $^*OH$ (represented by bold **O**) may go through several reactions that may not lead to the formation of labeled O_2 (e.g., $^*OH + {^*O_2}^- + H^+ \rightarrow H_2\textbf{O} + O_2$ or $2HCO_3^- + 2^*OH + 2H^+ \rightarrow 2CO_2 + 2H_2O + H_2\textbf{O}_2$); (v) bicarbonate is a known activator of peroxide [138, 139] and carbonate/bicarbonate can aid 1e/2e catalysis in redox reactions mediated by porphyrins [140, 141].

The observations/considerations above, in conjunction with the clear finding in several researchers' experimental data that oxygen is evolved even in 2nd flash (post dark acclimatization) strongly support the murburn model [32, 137, 142]. Further, the murburn model's projection that bicarbonate could as well be a potential source of electrons or oxygen in the photosynthetic process is supported by the re-interpretation of other researchers' data/arguments [122–127, 143–147]. The elucidation of multiple access channels in the lumenal part of the PS II (of small dimensions of 1–2 Å) leading to MnComplex [148] further lends credibility to the roles of DRS advocated in the murburn scheme, as such a redox complex cannot be protected from making/using DRS. However, these channels cannot give direct access to the large molecules/ions purportedly donating electrons to PS II, as solicited in the classical purview. For detailed discussions, refer to other works [142].

6. Projections for photosynthesis research

As the ubiquity of murburn concept is evidenced in miscellaneous processes of nature and physiology (halogen ecology [55], aerobic respiration [31], xenobiotic metabolism [75], thermogenesis, and homeostasis & electrophysiology [31, 78], etc.), it is forthright to deduce that murburn precepts of photosynthesis [32, 33] would also prove to be enlightening and harness-able. Given the untenable nature of the classical explanation, attempting to use that as a basic pivot [149, 150] may end up limiting, rather than enhancing space-time yields. The new insights available now should enable more robust and cheaper experimental means for simulating oxygenic photosynthesis in synthetic systems.

7. Summation

From the historical progression of the current awareness in bioenergetics, it can be seen that the classical explanation was brought together as an amalgamation of ideas mooted by researchers of various backgrounds. It is also evident that some leading pioneers took the initiative to form a consensus, which did not account for several factual, theoretical and experimental aspects. Steadfast pursuit of evidence-based ideas over decades has birthed the murburn model of oxygenic photosynthesis. Herein, the various aspects of murburn scheme of light reaction were elaborated and applied for explaining several key aspects of the field. Importance was given to the

crucial criteria of reaction chemistry, thermodynamics, kinetics, structure-function correlations of proteins and architecture of organelles, evolvability of system, etc. Murburn concept endorses the utility of DR(O)S and affords a parallel connectivity among the various components like photosystems, light-harvesting complexes, cytochromes, oxidases, quinones, etc. It also affords a comprehensive global perspective, and maintains the continuum of chemico-physics to explain the theoretical/experimental aspects of biological observations.

8. Declarations

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