THEORETICAL ANALYSIS OF THE ENHANCEMENT EFFECT IN PHOTOSYNTHESIS

EVIDENCE FOR THE "SPILL-OVER" MODEL

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ABSTRACT A quantitative examination of the "series" model of two distinct photosystems in photosynthesis is presented. Fractional absorptions and quantum yields of the two photosystems and energy transfer efficiency from photosystem II to photosystem I are introduced as parameters. Equations for the dependence of the enhancement functions and quantum yields on the wavelength are obtained. The predictions of the theory are compared to present literature data. There is, in general, an agreement of data to the form of the equations. Calculation of the energy transfer efficiency from photosystem II to photosystem I yields a significant value, ranging approximately from 0.5 to 1, in the different examples discussed, which include green, blue-green, and red algae.

Inconsistency with data obtained in the presence of the inhibitor DCMU and its significance is also discussed.

INTRODUCTION

According to present concepts photosynthesis in higher plants and algae requires a cooperation of two photoreactions (1, 2). One piece of evidence for this is the fall in quantum yield in certain ranges of the spectrum and its enhancement by the addition of light from other parts of the spectrum (Emerson enhancement effect) (1–23).

Other evidence, such as the spectroscopic observation of electron-carrier intermediates (24, 25), fluorescence transients (26–28), oxygen burst (13), and biochemical separation of the two photoreactions (29–31), leads to the "popular" series formulation of the two photoreactions (24, 32, 33). According to this formulation photoreaction I (terminology of Duysens) forms a strong reductant and weak oxidant while photoreaction II forms a strong oxidant and a weak reductant. The strong reductant reduces NADP,[1] which is further used for CO_2 reduction. The strong oxidant oxidizes H_2O and molecular oxygen is evolved. The other products of the two photoreactions react through a chain of several electron carriers, a reaction which possibly couples ADP phosphorylation (29).

[1] Abbreviations: NADP, nicotinamide adenine dinucleotide phosphate; ADP, adenosine diphosphate; ATP, adenosine triphosphate; DPIP, dichlorophenol indophenol; DCMU, 3,4-dichlorophenyl dimethyl urea.

The over-all reaction may be expressed as a transfer of electrons from H_2O to NADP, and then to CO_2, in series of processes which involve two light and several dark stages (see Fig. 1).

The manner in which the two photoreactions are sensitized is still an open subject. The most common model assumes the existence of two kinds of pigment aggregates, each of which is associated with its own photoreaction, I or II. The evidence for such a model comes from action spectra for partial photoreactions (13, 34, 35) and especially from enhancement spectra (3, 5, 14, 15, 20) which can be correlated to the absorptions of different photosystems I and II. More recent evidence is the fractionation of isolated chloroplasts into two kinds of fragments, each showing characteristics of photosystems I and II, respectively (36–38).

Fig. 1 represents the two photoreactions schematically demonstrating the physical separation of the two photosystems.

According to this concept, the quantum yield of photosynthesis should depend mainly on the way light is distributed between the two photosystems. In the steady

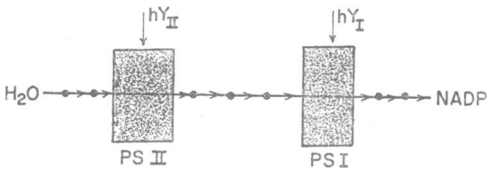

FIGURE 1 Schematic representation of redox reactions in photosynthesis. ⟶⟶, direction of electron (or H atom) flow. ●, intermediate electron carriers.

state the rates of electron flow sensitized by each photosystem must be equal, hence the over-all rate will be proportional to the light absorbed in the least absorbing photosystem which may depend strongly on the wavelength. Indeed one finds a universal drop in quantum yield in the far-red wavelength region ("red drop") which is explained by preferential absorption in photosystem I at these wavelengths. A similar drop is found in the blue region for the blue-green and red algae. From enhancement data and their interpretation it is possible to conclude that in the other regions photosystem II predominates in absorption. One expects therefore that the quantum yield should be maximal at the wavelength where the fractional absorption of the two pigment systems are equal, and drop where either one of them dominates. Contrary to this is the experimental observation that quantum yields are constant and maximal (7, 8, 11, 19, 30, 39) over the spectral region where system II absorption predominates.

In explanation Franck and Rosenberg (40) suggested that excitation absorbed in photosystem II is in fact used for both photoreactions while excitation absorbed in photosystem I is used only for photoreaction I. Their model involves discrimination of two types of excitation (singlet and triplet). Myers (22, 23) postulated the possibility of energy transfer from photosystem II to photosystem I, without any reference

to a specific model. He used the names "separate-package," for a model where the only interaction between the two photosystems is on the chemical level, and "spill-over," for a model where excess excitation in photosystem II is transferred to photosystem I in such a way as to obtain an optimal balance. From a macroscopic standpoint, if one does not care for the actual mechanism of balancing the two photosystems, the views of Franck and Rosenberg and of the "spill-over" mechanism of Myers are equivalent, at least when one considers steady-state electron transport [see Weiss (41)].

In order to obtain evidence for a "spill-over" mechanism Myers (22) tried to estimate the fractional absorption of the two systems from enhancement data and compare these with the quantum yields. In this way he hoped to eliminate the possibility that throughout the wavelength region where photosystem II predominates the fractional absorptions of the two systems remain practically constant. Myers' theoretical predictions and the experimental results of Emerson and Lewis (8) were plotted as function of wavelength (reference 22, Fig. 5). This comparison seems to favor the "spill-over" model, although the differences of quantum yields predicted by the "spill-over" and "separate-package" models were not sufficiently big compared to the precision in the experimental quantum yields for a definite conclusion.

In this paper I suggest a more definite test to discriminate the two hypotheses, based on quantum yields and enhancement data, which is valid also in the case where the absorptions of the photosystems may be constant in the region of predominance of photosystem II. It will be shown that by plotting the enhanced quantum yield vs. quantum yield (obtained at the same wavelength), a linear plot is predicted, from the slope of which one can deduce the quantitative importance of the "spill-over" mechanism. This test is especially accurate in the far-red region where the fractional absorption of the two photosystems has considerable variation.

The theoretical basis is similar, in fact, to the approach of Bannister and Vrooman (42). The novelty of the treatment lies in introducing an additional parameter for the energy transfer efficiency, thus treating both "separate-package" and "spill-over" models as well as intermediate situation, in one formula. The effect of quanta loss (by heat, fluorescence, and chemical reactions which are not directly related to the linear electron transport) is also accounted for by introducing the quantum yields for the primary reactions of each photosystem as additional parameters. In this way the effect of cyclic photophosphorylation will be also included. The following derivations will apply only to steady-state conditions and therefore no analysis of flash effects (4, 17, 21) will be made.

It is recognized that the theory is, in a sense, an oversimplification. However, it is essential at this stage to present a formal theory without entering too much into mechanistic details. The agreement of the essential features of the theory with the experiment will encourage a more rigorous treatment in the future.

THEORY

Definitions

I — Light intensity absorbed, of any spectral distribution, expressed in Einstein/unit of time.

I_1, I_2 — Light intensities absorbed into photosystem I and II, respectively, from the total intensity I.

α_1, α_2 — Fractions of monochromatic light absorbed into photosystems I and II, respectively.

λ_1, λ_2 — Two wavelength regions distinguished according to which photosystem, I or II, is dominant, respectively. They will be specified in parentheses. For example, $\alpha_1(\lambda_2)$ is α_1 measured for some wavelength in region 2. $I(\lambda_2)$ is the intensity of monochromatic light at some wavelength in region 2, etc.

I_D — Amount of excitation lost from photosystem II per unit of time in the case where this photosystem dominates.

I_c — Amount of excitation in photosystem I which is used for cyclic electron flow, per unit of time.

R — Rate of photosynthesis, expressed in electron equivalents/unit time.

$R(\lambda_1)$, $R(\lambda_2)$ — Rates obtained at λ_1 or λ_2.

$R(\lambda_1, \lambda_2)$ — Rate of two combined wavelengths from λ_1 and λ_2.

E_1, E_2 — Enhancement functions:

$$E_1 = \frac{R(\lambda_1, \lambda_2) - R(\lambda_2)}{R(\lambda_1)} \tag{1}$$

$$E_2 = \frac{R(\lambda_1, \lambda_2) - R(\lambda_2)}{R(\lambda_2)} \tag{1a}$$

$E_{1,max}$, $E_{2,max}$ — Maximum values of E_1 or E_2, obtained in a strong background of complementary light (λ_2 and λ_1, respectively).

Φ — Quantum yield of over-all steady-state photosynthesis, expressed in electron equivalents/Einstein abs. $= R/I$

Φ_{max} — Maximum quantum yield in the function Φ vs. wavelength.

Φ^E — Enhanced quantum yield, in light λ_1 or light λ_2, on a background of sufficiently strong complementary light

$$\Phi^E(\lambda_1) = \frac{R(\lambda_1, \lambda_2) - R(\lambda_2)}{I(\lambda_1)} = E_{1max}\Phi(\lambda_1) \tag{2}$$

and similarly

$$\Phi^E(\lambda_2) = \frac{R(\lambda_1, \lambda_2) - R(\lambda_1)}{I(\lambda_2)} = E_{2max}\Phi(\lambda_2). \tag{2a}$$

ϕ_1, ϕ_2 — The quantum yields for primary reactions in each photosystem, respectively.

$k = I_c/R$ — Stoichiometric factor between the light utilized in cyclic electron flow and the rate in the noncyclic flow.

ϕ'_1 — Apparent quantum yield of photosystem I primary act, considering "loss" of quanta to cyclic electron flow (see text)

$$\phi'_1 = \phi_1/(1 + k\phi_1). \tag{3}$$

γ — Efficiency of energy transfer from photosystem II to photosystem I.

S — Slope of the plot Φ^E vs. Φ [equations (19, 19a, 20)].

The quantum yields of the primary reactions ϕ_1 and ϕ_2 are introduced to take into account any loss processes of quanta other than required for the balancing of the photosystems. Very often these are neglected in any theory of photosynthesis, the assumption being made that the yield of a primary reaction is 1, which is not justified. In any real preparation there are certainly inactive photosynthetic units, or even whole chloroplasts or whole cells, and the ϕ's represent an average over the whole sample. The essential feature of ϕ_1 and ϕ_2 is the (assumed) wavelength independence, which is very usual for many single photochemical reactions. Another point for the inclusion at least of ϕ_1, is that by it one can take into account the effect of cyclic phosphorylation (29) (see later).

Calculation of the Rate of Photosynthesis. General Case

The following treatment will be general, applicable to light of any wavelength distribution. Special cases involve a monochromatic beam or two monochromatic beams. Equations for each special case will be obtained later by appropriate substitution. It is assumed that the intensity of the light is sufficiently low to limit the rate of photosynthesis and hence that the rate is a linear function of the light intensity. A light of intensity I, of arbitrary spectral distribution, is absorbed. A fraction of it, I_1, is absorbed by photosystem I, and a fraction I_2 is absorbed by photosystem II. At the beginning the rates of electron transport of the two photosystems are $\phi_1 I_1$ and $\phi_2 I_2$, respectively. However, since generally these rates are not equal, accumulation of products will occur between the systems in such a way to make some of the reaction centers of the "dominant" system "closed." In the steady state a certain fraction of quanta absorbed in the dominant system will be dissipated in the "closed" reaction centers. An additional assumption is made, for the case where photosystem II is dominant, that a quantum which arrives at a "closed" reaction center of photosystem II has a certain probability to be quenched by pigment system I. This probability is denoted by the parameter γ—the energy transfer efficiency; γ can take values from 0 to 1. A zero value implicates the impossibility of such energy transfer ["separate-package" in Myers' terminology (22)], while a unity

value implicates a full transfer efficiency and thus an optimal utilization of quanta ("spill-over" model). Values of γ less than 1 obviously represent an average over many photosynthetic units. For a single photosynthetic unit $\gamma < 1$ represents the competition between two possible processes, physical dissipation (as heat and fluorescence) and transfer to photosystem I. A reverse transfer from system I to system II seems improbable as the "red-drop" probably indicates.

Translating these considerations to a quantitative formulation two distinct cases are distinguished:

$$(a)\ \phi_1 I_1 > \phi_2 I_2 \qquad (b)\ \phi_1 I_1 < \phi_2 I_2$$

(system I or II dominant, respectively).

In case (*a*) some reaction centers of photosystem I will be "closed," and the balanced rate will be given by the smaller term $\phi_2 I_2$

$$R = \phi_2 I_2 \qquad (\text{for } \phi_1 I_1 > \phi_2 I_2). \tag{4}$$

In case (*b*), similarly, some reaction centers of photosystem II will be closed. Here, the balance between the two photosystems may be achieved in two ways, either by a dissipation loss (heat, fluorescence) of the excesr excitation, or by a transfer of the excess quanta to photosystem I. Both processes occur in the same time (on a macroscopic scale) and the relative importance of each is given by the parameter γ. We define[2] I_D as the amount of excitation per unit of time which arrives at the "closed" reaction centers and is lost from photosystem II. According to the definition of γ a part of I_D, γI_D, is transferred and utilized by photosystem I. In considering the balance between the photosystems one must substract from I_2 the amount lost, I_D, and add to I_1 the amount gained, γI_D. For a steady-state electron transport we obtain

Rate of electron transport through photosystem II: $\phi_2(I_2 - I_D)$

Rate of electron transport through photosystem I: $\phi_1(I_1 + \gamma I_D)$.

These rates must be equal, and be equal to the over-all rate. Hence

$$R = \phi_2(I_2 - I_D) = \phi_1(I_1 + \gamma I_D). \tag{5}$$

From (5) I_D can be solved in terms of the other parameters

$$I_D = \frac{\phi_2 I_2 - \phi_1 I_1}{\gamma\phi_1 + \phi_2}. \tag{6}$$

[2] I_D, as defined here, is a dynamic concept and is the result of the system adjustment rather than the cause of such adjustment. Therefore it cannot be calculated a priori from the parameters of the system. It is calculated from the assumption that the photosystems are balanced.

Substitution of I_D from (6) back to (5) yields[3] the rate R

$$R = \frac{\phi_1\phi_2}{\gamma\phi_1 + \phi_2}(I_1 + \gamma I_2) \qquad (\text{for } \phi_1 I_1 < \phi_2 I_2). \tag{7}$$

Consider for a moment the special case $\gamma = 0$: (6) and (7) give then $I_D = I_2 - (\phi_1/\phi_2)I_1$ and $R = \phi_1 I_1$ which is a similar result to equation (4). When $\gamma = 1$ one obtains $R = \phi_1\phi_2(I_1 + I_2)/(\phi_1 + \phi_2)$ which for $\phi_1 = \phi_2 = 1$ gives the "theoretical" maximum possible yield of $\frac{1}{2}$.

Inclusion of Cyclic Phosphorylation. It is well accepted that a linear electron flow is not sufficient to completely maintain CO_2 reduction. The Calvin cycle (43) requires 4 electron equivalents of NADPH and 3 of ATP. If one accepts a ratio ATP/2e = 1, only 2 ATP can be formed in the noncyclic electron flow. Additional ATP may be formed in a cyclic electron flow (29) sensitized presumably by photosystem I. Hence a certain fraction of light absorbed in system I must be utilized for cyclic electron flow. This of course might modify and change the previous arguments.

A possible approach is to consider the light utilization for a cyclic electron flow as a dissipation process (from the standpoint of noncyclic electron flow) and to take it into account by the parameter ϕ_1. However, this has to be justified formally: Since the cyclic electron flow is probably regulated and related to the linear electron flow ϕ_1 might change as a function of the balance between the photosystems, and especially change with wavelength. A priori therefore, it may not be a "good" parameter.

I shall prove, however, using a technique similar to that used to obtain equation (7), that the parameter ϕ_1 is still appropriate to include the effect of cyclic phosphorylation. The basic assumption is that the photosynthetic machinery is so regulated (at least under steady-state conditions) that the cyclic flow is always proportional to the noncyclic flow. This is required because of the constant stoichiometry between the products of the two.

Let us denote by I_c the amount of excitation per unit of time used for cyclic flow. The rate of cyclic phosphorylation is proportional to I_c and is assumed also to be proportional to the noncyclic electron transport rate R. Hence $I_c = kR$. The conconstant k is determined by the quantum yield of cyclic electron transport (with respect to I_c), the ATP/2e ratios in the cyclic and noncyclic phosphorylations, and the ATP requirements of the CO_2 fixation cycle and possibly other physiological requirements for ATP. In the case where system I dominates, there is enough excitation in system I for both cyclic phosphorylation and electron transport to system II, hence equation (4) is still valid. The case where system II dominates is more com-

[3] The way of derivation used to obtain equation (7) can be used in fact to derive also equation (4). For the case implicit to equation (4) define I_D as the amount of excitation (per unit time) lost from photosystem I, and take the efficiency of transfer from photosystem I to photosystem II to be zero.

plicated. Following previous arguments I_D is the light dissipated from system II and γI_D is the excitation received in system I. Now one must substract from the excitation of system I an amount I_c which is utilized for the cyclic flow. The balance expression of the noncyclic flow now takes the form

$$R = \phi_2(I_2 - I_D) = \phi_1(I_1 + \gamma I_D - I_c). \tag{5a}$$

I_c can be eliminated by the substitution $I_c = kR$. In this we obtain an analogous equation to equation (5) except that I_1 is replaced by $(I_1 - kR)$. Solving for I_D one obtains equation (6a), analogous to equation (6)

$$I_D = \frac{\phi_2 I_2 - \phi_1(I_1 - kR)}{\gamma\phi_1 + \phi_2}. \tag{6a}$$

Substitution of I_D back to (5a) yields an equation for R, whose solution is

$$R = \frac{\phi_1\phi_2}{\gamma\phi_1 + \phi_2 + k\phi_1\phi_2}\,(I_1 + \gamma I_2). \tag{7a}$$

The form of (7a) is of course different from (7), however, it is possible to define a new parameter $\phi'_1 = \phi_1/(1 + k\phi_1)$. In terms of ϕ'_1 (7a) transforms to

$$R = \frac{\phi'_1\phi_2}{\gamma\phi'_1 + \phi_2}\,(I_1 + \gamma I_2),$$

which is exactly identical in form with equation (7). ϕ'_1 may be interpreted as the apparent quantum yield of system I with respect to noncyclic electron flow. In further application the prime may be omitted from ϕ'_1, provided we recognize this interpretation. As an illustration we shall calculate this apparent yield for an ideal situation. Assuming ATP/2e = 1, both in the noncyclic and cyclic electron flows, quantum yield of 1 e/$h\nu$ for the cyclic electron flow, and a requirement of 2 TPNH and 3 ATP for 1 CO_2 fixation, one obtains that 1 electron is required in the cyclic flow per 2 electrons in the noncyclic flow and $k = I_c/R = \frac{1}{2}$. Therefore $\phi'_1 = \phi_1(1 + \frac{1}{2}\phi_1)$ which for the case $\phi_1 = 1$ gives $\phi_1 = \frac{2}{3}$.

Calculation of Quantum Yields and Enhancement Functions

The general equations (4) and (7) will now be used for the more specific cases of monochromatic light and the combination of two monochromatic lights. For monochromatic light one can define the distribution coefficients of absorbed light between the two systems, denoted by α_1 and α_2. They are the fractions from the total absorbed intensity that are absorbed in system I or system II, respectively. Later, in the application of the derived equations it will be assumed that $\alpha_1 + \alpha_2 = 1$. How-

ever, since this may not always be true (e.g., when an inactive pigment is present) a more general treatment will be carried out as far as possible.

Monochromatic Light. In this case I_1 and I_2 are given by $I_1 = \alpha_1 I$ and $I_2 = \alpha_2 I$. Two wavelength regions are defined, according to which of the two photosystems dominates: region 1 where $\alpha_1\phi_1 > \alpha_2\phi_2$ and region 2 where $\alpha_1\phi_1 < \alpha_2\phi_2$. Since the form of the following equations will depend on whether α_1 or α_2 is specified at region 1 or 2 it is advantageous to specify the wavelength region by means of parentheses, e.g., $\alpha_1(\lambda_1)$, etc. At wavelength region 1 equation (4) is relevant. The rate is given by

$$R(\lambda_1) = \phi_2\alpha_2(\lambda_1)I(\lambda_1) \tag{8}$$

and the over-all quantum yield is

$$\Phi(\lambda_1) = \phi_2\alpha_2(\lambda_1). \tag{8a}$$

At region 2 equation 7 is relevant. Therefore one obtains

$$R(\lambda_2) = \frac{\phi_1\phi_2}{\gamma\phi_1 + \phi_2}[\alpha_1(\lambda_2) + \gamma\alpha_2(\lambda_2)]I(\lambda_2) \tag{9}$$

and

$$\Phi(\lambda_2) = \frac{\phi_1\phi_2}{\gamma\phi_1 + \phi_2}[\alpha_1(\lambda_2) + \gamma\alpha_2(\lambda_2)]. \tag{9a}$$

Considering the variation of Φ vs. λ it is easy to prove that the maximum yield is obtained when $\alpha_1\phi_1 = \alpha_2\phi_2$, i.e., at the border between the two regions. Assuming $\alpha_1 + \alpha_2 = 1$, the maximum yield is given by

$$\Phi_{max} = \frac{\phi_1\phi_2}{\phi_1 + \phi_2}. \tag{10}$$

Φ_{max} is therefore independent of γ, and represents the optimal yield which can be achieved in a perfect balance of the two photosystems. If also $\gamma = 1$ (complete "spill-over") this maximum yield will be constant throughout the whole λ_2 region.

Two Monochromatic Lights. Lights of λ_1 and λ_2 of intensities $I(\lambda_1)$ and $I(\lambda_2)$ are added

$$I_1 = \alpha_1(\lambda_1)I(\lambda_1) + \alpha_1(\lambda_2)I(\lambda_2) \tag{11}$$

$$I_2 = \alpha_2(\lambda_1)I(\lambda_1) + \alpha_2(\lambda_2)I(\lambda_2). \tag{11a}$$

Again we distinguish two possibilities according to whether

$$\phi_1 I_1 \gtrless \phi_2 I_2 .$$

The two possibilities can be realized experimentally by varying the ratio $I(\lambda_2)/I(\lambda_1)$ from 0 to high values. The transition between them occurs at a certain ratio $I(\lambda_2)/I(\lambda_1)$ depending on the relevant α's.

(*a*) $\phi_1 I_1 > \phi_2 I_2$. This case is realized at low $I(\lambda_2)/I(\lambda_1)$ ratio. Substitution of (11) into (4) gives

$$R(\lambda_1, \lambda_2) = \phi_2\alpha_2(\lambda_1)I(\lambda_1) + \phi_2\alpha_2(\lambda_2)I(\lambda_2). \tag{12}$$

(*b*) $\phi_1 I_1 < \phi_2 I_2$. Substitution of (11) into (7) gives

$$R(\lambda_1, \lambda_2) = \frac{\phi_1\phi_2}{\gamma\phi_1 + \phi_2}\{[\alpha_1(\lambda_1) + \gamma\alpha_2(\lambda_1)]I(\lambda_1) + [\alpha_1(\lambda_2) + \gamma\alpha_2(\lambda_2)]I(\lambda_2)\}. \tag{13}$$

From equations (1), (8), (9), (12), and (13) we can calculate enhancement functions. For case (*a*), we obtain

$$E_1 = \frac{R(\lambda_1, \lambda_2) - R(\lambda_2)}{R(\lambda_1)}$$

$$= \frac{\phi_2\alpha_2(\lambda_1)I(\lambda_1) + \phi_2\alpha_2(\lambda_2)I(\lambda_2) - \phi_1\phi_2\{[\alpha_1(\lambda_2) + \gamma\alpha_2(\lambda_2)]/(\gamma\phi_1 + \phi_2)\}\, I(\lambda_2)}{\phi_2\alpha_2(\lambda_1)I(\lambda_1)},$$

which after a few algebraic manipulations gives

$$E_1 = 1 + \frac{\phi_2\alpha_2(\lambda_2) - \phi_1\alpha_1(\lambda_2)}{(\gamma\phi_1 + \phi_2)\alpha_2(\lambda_1)} \cdot \frac{I(\lambda_2)}{I(\lambda_1)} \qquad \left[\text{for small } \frac{I(\lambda_2)}{I(\lambda_1)}\right]. \tag{14a}$$

Since $\phi_2\alpha_2(\lambda_2) > \phi_1\alpha_1(\lambda_1)$, the second term is positive, indicating an increased enhancement as the ratio $I(\lambda_2)/I(\lambda_1)$ increases.

It is also useful to express E_1 as a function of $R(\lambda_2)/R(\lambda_1)$, which is easily obtained from the expressions for $R(\lambda_2)$ and $R(\lambda_1)$. The result is

$$E_1 = 1 + \frac{\phi_2\alpha_2(\lambda_2) - \phi_1\alpha_1(\lambda_2)}{\phi_1[\gamma\alpha_2(\lambda_2) + \alpha_1(\lambda_2)]} \cdot \frac{R(\lambda_2)}{R(\lambda_1)} \qquad \left[\text{for small } \frac{R(\lambda_2)}{R(\lambda_1)}\right]. \tag{14b}$$

For case (*b*) we get after a few manipulations

$$E_1 = \frac{\phi_1}{\gamma\phi_1 + \phi_2} \cdot \frac{\gamma\alpha_2(\lambda_1) + \alpha_1(\lambda_1)}{\alpha_2(\lambda_1)} = E_{1\,\max}\left[\text{for large } \frac{I(\lambda_2)}{I(\lambda_1)}\right]. \tag{14c}$$

According to equations (14), E_1 increases linearly with the ratio $I(\lambda_2)/I(\lambda_1)$, or $R(\lambda_2)/R(\lambda_1)$, until a point is reached from which E_1 remains constant $E_{1\,\max}$ for further increase in $I(\lambda_2)/I(\lambda_1)$ or $R(\lambda_2)/R(\lambda_1)$ (Fig. 2). The transition from linear increase of E_1 to a constant $E_{1\,\max}$ occurs when $\phi_1 I_1 = \phi_2 I_2$.

In the same way we calculate E_2. Here we note that the functions E_1 and E_2 are

interrelated, since from their definitions [equations (1), (1a)]

$$E_2 = 1 + (E_1 - 1)\frac{R(\lambda_1)}{R(\lambda_2)}. \tag{15}$$

It follows that in the range where E_1 is constant, E_2 is a linear function of $R(\lambda_1)/R(\lambda_2)$, and vice versa; where E_1 is a linear function of $R(\lambda_2)/R(\lambda_1)$, E_2 is constant and maximal (Fig. 2).

Using these relations or else calculating directly, we obtain for small ratios $I(\lambda_1)/I(\lambda_2)$ or $R(\lambda_1)/R(\lambda_2)$

$$E_2 = 1 + \frac{\phi_1\alpha_1(\lambda_1) + \phi_2\alpha_2(\lambda_1)}{\phi_1[\gamma\alpha_2(\lambda_2) + \alpha_1(\lambda_2)]} \cdot \frac{I(\lambda_1)}{I(\lambda_2)} \qquad \left[\text{for small } \frac{I(\lambda_2)}{I(\lambda_2)}\right] \tag{16a}$$

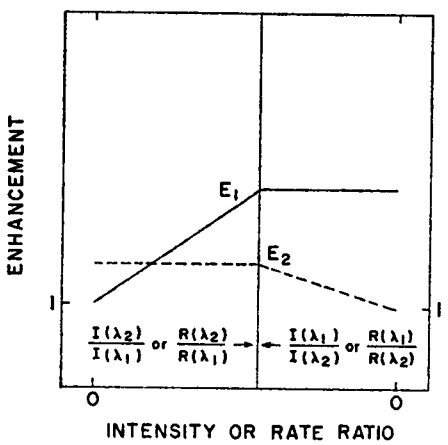

FIGURE 2 Theoretical representation of enhancement functions vs. ratios of rates or light intensities [Equations (14a-c), (16a-c)]. The abscissa is divided into two regions: from left to right $R(\lambda_2)/R(\lambda_1)$ [or $I(\lambda_2)/I(\lambda_1)$] increases linearly; from right to left $R(\lambda_1)/R(\lambda_2)$ [$I(\lambda_1)/I(\lambda_2)$] increases linearly; the breakpoint for E_1 or E_2 divides the two regions. One can view the abscissa as the $R(\lambda_2)/R(\lambda_1)$ axis, with a change of scale from linear to reciprocal right of the breakpoint. The breakpoint is common, in the magnitude of $R(\lambda_1)/R(\lambda_2)$ or $R(\lambda_2)/R(\lambda_1)$, to both regions.

or

$$E_2 = 1 + \frac{\phi_1\alpha_1(\lambda_1) + \phi_2\alpha_2(\lambda_1)}{(\gamma\phi_1 + \phi_2)\alpha_2(\lambda_1)} \frac{R(\lambda_1)}{R(\lambda_2)} \qquad \left[\text{for small } \frac{R(\lambda_1)}{R(\lambda_2)}\right] \tag{16b}$$

and for high ratios $I(\lambda_1)/I(\lambda_2)$ or $R(\lambda_1)/R(\lambda_2)$

$$E_2 = \frac{\gamma\phi_1 + \phi_2}{\phi_1} \cdot \frac{\alpha_2(\lambda_2)}{\gamma\alpha_2(\lambda_2) + \alpha_1(\lambda_2)} = E_{2\,\max} \left[\text{for large } \frac{I(\lambda_1)}{I(\lambda_2)}\right] \tag{16c}$$

In comparison to experimental data, any two independent experimental parameters may be extracted from the functions E_1 and E_2. The best choice is to use $E_{1\,\max}$ and $E_{2\,\max}$; $E_{1\,\max}$ depends only on the wavelength λ_1 [see equation (14c)], therefore the use of any wavelength for light λ_2 is of no importance, provided it is sufficiently intense. The same is true of $E_{2\,\max}$ which depends on λ_2 alone. Instead of $E_{1\,\max}$ it is possible to use the corresponding maximum enhanced quantum yield

defined in equation (2) (see definitions). From (2), (8a), and (14c) it follows that

$$\Phi^E(\lambda_1) = E_{1\,\max} \cdot \Phi(\lambda_1) = \frac{\phi_1\phi_2}{\gamma\phi_1 + \phi_2} [\alpha_1(\lambda_1) + \gamma\alpha_2(\lambda_1)] \tag{17}$$

and similarly from (2a), (9a), and (16c) it follows that

$$\Phi^E(\lambda_2) = \phi_2\alpha_2(\lambda_2). \tag{18}$$

$\Phi^E(\lambda_2)$ is therefore independent of γ and remarkably has a simple form, identical to $\Phi(\lambda_1)$ [see equation (8a)]. Use of equation (8a) for λ_1 and equation (18) for λ_2 allows us to map $\alpha_2\phi_2$ over the entire range of wavelengths, independent of any energy transfer assumption.

Simplifying Assumption. In order to make a practical use of equations (17) and (18) let us introduce the assumption $\alpha_1 + \alpha_2 = 1$. If this is substituted in equation (17) $\Phi^E(\lambda_1)$ is expressed as function of $\alpha_2(\lambda_1)$ and $\alpha_1(\lambda_1)$ is eliminated. One can then substitute $\phi_2 = \Phi(\lambda_1)/\alpha_2(\lambda_1)$ [see equation (8a)] and obtain a relation between $\Phi^E(\lambda_1)$ and $\Phi(\lambda_1)$

$$\Phi^E(\lambda_1) = \frac{\phi_1\phi_2}{\gamma\phi_1 + \phi_2} - \frac{\phi_1(1 - \gamma)}{\gamma\phi_1 + \phi_2} \Phi(\lambda_1). \tag{19}$$

In a similar way a substitution of $\alpha_2(\lambda_2)$ from equation (18) into equation (9a), assuming $\alpha_1 + \alpha_2 = 1$, gives a relation between $\Phi(\lambda_2)$ and $\Phi^E(\lambda_2)$

$$\Phi(\lambda_2) = \frac{\phi_1\phi_2}{\gamma\phi_1 + \phi_2} - \frac{\phi_1(1 - \gamma)}{\gamma\phi_1 + \phi_2} \Phi^E(\lambda_2). \tag{19a}$$

Note the close similarity of equations (19) and (19a), in fact they are identical except for the interchange of Φ and Φ^E. These equations predict a linear dependence between Φ and Φ^E for both wavelength regions. If both (19) and (19a) are plotted, as Φ^E vs. Φ, on the same diagram, two straight lines will be obtained, one for each wavelength region: These can be considered as two branches of one function. It is easy to prove that these two branches intersect at the point $\Phi^E = \Phi = \Phi_{max}$, which corresponds to the border between the two wavelength regions (see Fig. 3).

Such a plot of Φ^E vs. Φ provides a possibility to estimate γ from the slope. It follows from equations (19) that the slopes of the two branches, for λ_1 and λ_2, with respect to the $-\Phi$ and Φ^E axes, respectively, are equal, and given by

$$S = \frac{\phi_1(1 - \gamma)}{\gamma\phi_1 + \phi_2}. \tag{20}$$

For $\gamma = 1$ (complete "spill-over") $S = 0$ and both branches will parallel the two axes, respectively. For $\gamma = 0$, $S = \phi_1/\phi_2$ and the two branches will have a slope

ϕ_1/ϕ_2 with respect to the two axes, respectively. If also $\phi_1/\phi_2 = 1$ the slope will be 45° and the branches will merge to one (Fig. 3).

In order to make a reliable estimate of γ, γ is solved in terms of S, ϕ_1, and ϕ_2

$$\gamma = \frac{1}{1+S}\left(1 - S\frac{\phi_2}{\phi_1}\right). \tag{21}$$

One can estimate maximal and minimal values of ϕ_2/ϕ_1 from the expression for Φ_{max} [equation (10)], which for a given Φ_{max} may be considered as a formal relation between ϕ_1 and ϕ_2. It follows from this relation that ϕ_1 and ϕ_2 change in opposite directions so that the largest possible ratio of ϕ_2/ϕ_1 is obtained when $\phi_2 = 1$ (the maximum value), and the lowest ratio is obtained similarly when $\phi_1 = 1$. It follows

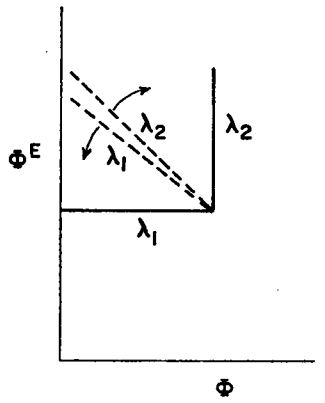

FIGURE 3 Theoretical representation of Φ^E vs. Φ, for the "separate-package" and the "spill-over" models. [equations (19) and (19a)]. Broken line, "separate-package" $\gamma = 0$; solid line, "spill-over" $\gamma = 1$. Both branches, λ_1 and λ_2, are indicated. As γ increases from 0 to 1 the lines rotate in the direction of the arrow.

therefore that the possible range of variation of ϕ_2/ϕ_1 is given by

$$\frac{\Phi_{max}}{1-\Phi_{max}} < \frac{\phi_2}{\phi_1} < \frac{1-\Phi_{max}}{\Phi_{max}}. \tag{22}$$

Substitution in (21) yields two limits for estimation of γ

$$\begin{aligned} \gamma &> \frac{1}{1+S}\left(1 - S\frac{1-\Phi_{max}}{\Phi_{max}}\right) \\ \gamma &< \frac{1}{1+S}\left(1 - S\frac{\Phi_{max}}{1-\Phi_{max}}\right). \end{aligned} \tag{23}$$

Physical Interpretation. The formal presentation expressed by equations (19) and (19a) has a very simple physical interpretation. In order to make it clear let us simplify and assume for a moment that ϕ_1 and ϕ_2 are equal to unity, so that the overall quantum yield is influenced only by the distribution coefficients of the light (α_1 and α_2) and γ. In any model the quantum yield of an amount ΔI of light λ_1 will

be equal to α_2. The effect of the same amount ΔI of light λ_1 in a strong background of light λ_2 will depend on the model: In the "separate-package" model photosystem I will be limiting and hence the quantum yield will be equal to the fraction of light absorbed in it, equal to α_1; the rest of the energy will be absorbed in photosystem II and add to the excess excitation in it, without additional effect on the electron transport rate. Hence, the sum of the quantum yield and enhanced quantum yield will be equal to 1, the enhanced yield will increase parallel to the decrease in the normal yield ($S = 1$). In the "spill-over" model, however, adding an amount ΔI of λ_1 changes the balance which existed before the addition. In order to retain the balance less light will be transferred from photosystem II. The effect will be equivalent to an equal distribution $\Delta I/2$ in each system. The enhanced quantum yield then will be $\frac{1}{2}$ and stay constant throughout λ_1 region ($S = 0$). This is the physical reasoning behind equation (19). In the same way one can also rationalize equation (19a).

COMPARISON WITH LITERATURE DATA

General Remarks

The purpose of this section is to provide a certain preliminary test of the theory. It is recognized that the literature data were not specifically designed for such a test. In some examples pieces of data from different works were tailored together, also the conditions for the enhancement measurements were not always specified. Therefore the results may not yet be conclusive and more critical experiments should be carried out. The key equations for an experimental comparison are the enhancement functions vs. the ratio of intensities or rates [equations (14a–c) and (16a–c)], and the enhanced yield vs. "normal" yield [equations (19, 19a)] with the equation for γ [equation (23)].

(*a*) *Dependence of Enhancement Functions on* $I(\lambda_2)$ *and* $I(\lambda_1)$ [*Test of Equations* (*14a–c*) *and* (*16a–c*)]

It was specifically shown by Bannister and Vrooman (42), that at low intensities, the enhancement functions depend on the ratio $I(\lambda_2)/I(\lambda_1)$ and not on their absolute intensities. This was shown by them by plotting $I(\lambda_2)$ against $I(\lambda_1)$ for various fixed enhancement values. The result is a series of lines radiating from the origin as expected from equation (14a). Deviations, obtained at high intensities, are attributed to light-saturation effects.

This result, although not rigorously established before, is also mentioned in several papers, and E_1 is frequently plotted against $I(\lambda_2)/I(\lambda_1)$ or $R(\lambda_2)/R(\lambda_1)$ (and similarly for E_2). The plot is a rising linear function which breaks at a certain point and then remains constant, following Fig. 2. Example data for such plots are Kok and Hoch, reference 25, Fig. 2; Govindjee, reference 16, Figs. 8, 9; Myers and

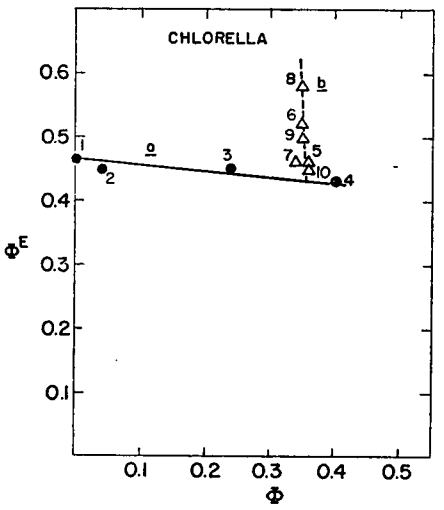

FIGURE 4 Plot of Φ^E vs. Φ for Chlorella pyrenoidosa: All absolute quantum yields are recalculated as equivalents/Einstein = 4 × mole O_2/Einstein in this and the following figures. ●, Points calculated for λ_1 region [Emerson et al. (9) recalculated by Govindjee (16)]. Since Φ^E is given greater than Φ by a factor of 1.25 even in the λ_2 region (Φ^E measured under λ_2 background) it was corrected by dividing it by this factor. △, Points calculated for λ_2 region [from Emerson and Lewis (8) and Govindjee and Rabinowitch (15)]. Numbers refer to the wavelength in this order: 1–4, 710, 700, 690, 680 mμ (λ_1); 5–10, 680, 670, 660, 650, 640, 630 mμ (λ_2).

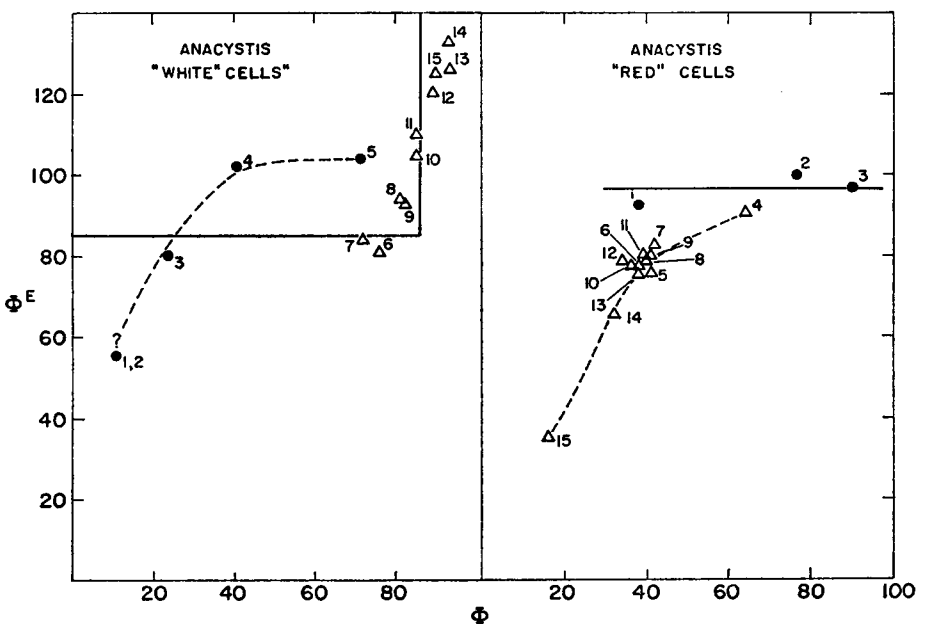

FIGURE 5 Φ^E vs. Φ for *Anacystis nidulans*: ●, λ_1 ; △, λ_2 [from Jones and Myers (20), their Figs. 4-7.] Action is measured arbitrarily in millimeters (on the original figures). Per cent absorption is calculated from the given relative OD curve and the given absorption at 620 mμ. Φ or Φ^E are given as action/absorption. Numbers refer to wavelength in this order: For "white" cells, 700, 690, 680, 670, 660, (λ_1); 650, 640, 630, 620, 610, 600, 585, 575, 560, 545, (λ_2) mμ. For "red" cells, 690, 680, 670, (λ_1); 660, 650, 640, 630, 620, 610, 600, 590, 580, 565, 540, 510, (λ_2) mμ.

Graham, reference 23, Figs. 5, 6; Jones and Myers, reference 20, Fig. 3. Some plots show a small region of curvature between the increasing region and the constant region of E_1. This may be partly due to the natural inclination to draw smooth curves, while the variation in the measurements is too high to locate the break point exactly. It may be a real effect, however, either because of nonhomogeneous light intensity distribution in the sample, as Myers and Graham (23) pointed out, or because of nonhomogeneity of the sample itself—say the cells have slightly different parameters α_1 and α_2 and therefore the point of break for each cell is different.

A point of divergence from the theory is the experimental drop of E_1 at high $I(\lambda_2)/I(\lambda_1)$ ratios after a range in which it is constant. This is almost undoubtedly due to light saturation effects, and is outside the scope of the present investigation.

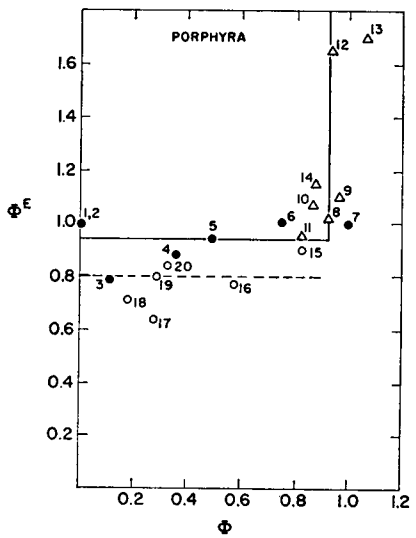

FIGURE 6 Φ^E vs. Φ for *Porphyra perforata*: ●, λ_1, red region; ○, λ_1, blue region; △, λ_2 region [from Fork (13, 19)]. Φ and Φ^E for λ_1 region and Φ for λ_2 region are given as action/absorption. Φ^E for λ_2 region is calculated as $E_{2\,max}\,\Phi$. Numbers refer to wavelength in this order: 1–7 (λ_1-red), 710, 700, 690, 680, 670, 660, 650; 8–14 (λ_2), 640, 620, 600, 580, 560, 540, 520; 15–20 (λ_1-blue), 520, 500, 480, 450, 440, 410 mμ.

(*b*) *Enhanced Quantum Yields vs. Quantum Yields* [equations (19) and (19a)]

Figs. 4–8 show plots of Φ^E vs. Φ for various samples. Generally, the plots are similar to the schematic plot of the "spill-over" model (Fig. 3).

Chlorella pyronoidosa (Fig. 4). The branch for λ_1 [equation (19)] is taken from Fig. 1 of reference 16 (recalculation from reference 9). The branch for λ_2 [equation (19a)] is calculated from quantum yield data of Emerson and Lewis (8) and enhancement data of Govindjee and Rabinowitch (15). Φ^E is calculated as $E_{2\,max}\cdot\Phi$.

The plot suggests a small slope of both branches. S for λ_1 is ≈ 0.1 and for $\lambda_2 \approx 0.05$. Calculation according to equation (23) gives the λ_1 branch, $0.78 < \gamma < 0.84$. and for the λ_2 branch, which is a different experiment, $0.86 < \gamma < 0.93$.

Anacystis nidulans (Fig. 5). As a source of data the work of Jones and Myers (20) was used. Relative Φ and Φ^E were calculated as action/absorption. For cells grown

on white light the plot seems to suggest the "spill-over" model ($\gamma \approx 1$) although the "noise" in the λ_1 branch is high. It seems that a possible error in this region may be caused by having taken the absorption curve from a different experiment. The λ_1 branch for cells grown on red light again suggests the "spill-over" model, ($\gamma \approx 1$). The λ_2 branch of the "red" cells shows much smaller yields than expected and cannot be explained simply by either one of the models. This may be explained by considerable absorption into inactive pigments.

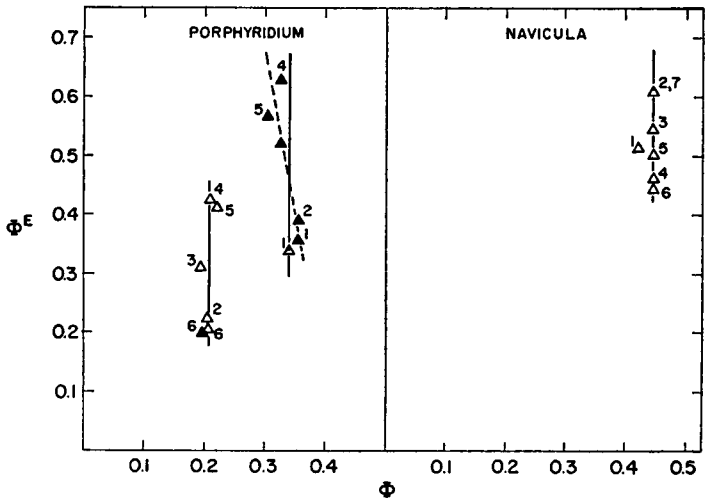

FIGURE 7

FIGURE 8

FIGURE 7 Φ^E vs. Φ for *Porphyridium cruentum*: Data are available only for the λ_2 region; △, "blue" cells; ▲, green cells [Brody and Emerson (6) and Emerson (10)]. Φ^E calculated as $E_{2\,max}$. Φ, median vertical; – – –, line drawn to suggest maximal slope. Numbers refer to wavelength in this order: 645, 580, 560, 545, 500, 485 mμ.

FIGURE 8 Φ^E vs. Φ for *Navicula minima*: Data is available only for λ_2 region [Tanada (19, 39) Govindjee and Rabinowitch (15)]. Φ^E calculated as $E_{2\,max} \cdot \Phi$. Numbers refer to wavelength in this order: 680, 670, 660, 640, 590, 545 mμ.

Porphyra perforata (Fig. 6). For this alga we used the data of Fork (13) and his enhancement given in reference 19, Fig. 16. As in the preceding example the yields are relative, calculated as action/absorption. $\Phi^E(\lambda_2)$ is calculated as $E_{2\,max} \cdot \Phi(\lambda_2)$. Both branches confirm the "spill-over" model ($\gamma \approx 1$) as well as the branch obtained in λ_1 blue region.

Porphyridium cruentum (Fig. 7). Only data on λ_2 region is available. Quantum yields are from Brody and Emerson's work (6). $E_{2\,max}$ is taken from another paper by Emerson (10). Brody and Emerson give data on two types of cells, namely those grown on green and those grown on blue lights. It is not clear whether the enhancement data of Emerson are relevant to "green" or "blue" cells, so that $\Phi^E(\lambda_2)$ is calculated as $E_{2\,max} \cdot \Phi(\lambda_2)$ for both types. The "green" cells have a constant yield in

λ_2 region from 660 mμ down to 545 mμ; the yield slightly decreases from 545 to 500 mμ. The "blue" cells have a peak yield at 645 mμ, a decreasing yield from 645 to 580 mμ and then a constant yield down to 485 mμ. The enhancement spectrum has a band from 485 to 580 mμ (10), a region where the yields for both types are constant. The plot of $\Phi^E(\lambda_2)$ vs. $\Phi(\lambda_2)$ for the "blue" cells is approximately parallel to the Φ^E axis ($\gamma \approx 1$). The same plot for the "green" cells was exaggerated to suggest a slope in the direction of small γ, from which γ is estimated to be $0.62 < \gamma < 0.78$. The reason for the drop in yield for the "blue" cells is not clear. It can be explained by absorption by an inactive pigment.

The enhancement data of Govindjee and Rabinowitch (15) for this alga are not used here. They give E_1 for a fixed wavelength of light 1 as a function of λ_2, so that $E_{2\,max}$ can be calculated. However, they use a ratio $R(\lambda_2)/R(\lambda_1) = 60$; at this high ratio E_2 may be lower than $E_{2\,max}$, at least at certain wavelengths.

Navicula minima (Fig. 8). Tanada's quantum yield values for this diatom are constant in the region between 539 and 680 mμ (19, 39). Govindjee and Rabinowitch (15) bring the wavelength dependence of E_1 for $R(\lambda_2)/R(\lambda_1) = 2$ from which $E_{2\,max}$ is calculated [$(E_{2\,max} = \frac{1}{2}(1 + E_1)$.]. $\Phi^E(\lambda_2)$ is calculated as $E_{2\,max} \cdot \Phi(\lambda_2)$. Assuming variation of 10% in the quantum yields, an upper estimate of the slope can be calculated as $\Delta\Phi(\lambda_2)/\Delta E_{2\,max} \cdot \Phi(\lambda_2)$, where $\Phi(\lambda_2)$ is the absolute noise in measuring $\Phi(\lambda_2)$ and $\Delta E_{2\,max}$ is the width of the range where $E_{2\,max}$ varies. Taking $\Delta\Phi(\lambda_2)/\Phi(\lambda_2) = 0.1, \Delta E_{2\,max} = 0.37$ (= peak of $E_{2\,max} - 1$) we get $S < 0.27$, hence from equation (23), taking $\Phi_{max} = 0.45$ (19, 39) we estimate $\gamma > 0.52$.

The constancy of the quantum yield in λ_2 region is demonstrated also for the blue-green alga Chroococcus (7). No enhancement data are available, but there is no indication that the yield is lower at the maximum of phycocyanine absorption, which presumably mainly contributes to photosystem II, as would be required by the "separate-package" model.

DISCUSSION

It is clearly seen that for many examples the literature data can be fitted to the framework of the presented theory. In all the examples which fit with the theory the parameter γ was significant. The plots were exaggerated to obtain a lower estimate for γ. In a few cases $\gamma \approx 1$, in others it may be lower than 1, but always higher than 0.5. The variations of γ in our examples are probably casual and represent variations in conditions rather than in species.

The energy transfer mechanism deserves some discussion. Physically such a mechanism depends on the specific interaction between the energy donor and energy acceptor molecules, which in the case of the Förster mechanism depends mainly on the mutual distance, orientation of the molecules, and overlap between the fluorescence spectrum of the donor with the absorption spectrum of the acceptor (44). If both two types of pigment aggregates exist in two parallel two-dimensional

layers (see Clayton (45) and Rabinowitch (46)] with a possible separation of several angstroms, one may come to a conclusion that such energy transfer may be physically feasible.

In considering the theoretical question of the back-transfer of energy from photosystem I to photosystem II, which is improbable according to the experimental data, two factors come into play: first, the overlap between the fluorescence spectrum of photosystem I (peaked around 730 mμ) to the absorption of photosystem II (peaked around 670–680 mμ) is much less compared to the former case. Second, it seems that in system I there are stronger competing quenching processes, as judged by the absence (or very small) fluorescence yield at room temperature, even in the condition when the primary reaction centers (P_{700}?) are bleached (47).

The present results may be applied also to the ideas of Franck and Rosenberg (40). In this case a possible interpretation of γ would be the efficiency of the singlet–triplet transition at the reaction center which is "prepared" for photoreaction I.

A possible inconsistency is the behavior of photosynthesizing samples in the presence of DCMU, as evident from the data of Hoch and Martin (30) for isolated chloroplasts. The quantum yield of NADP reduction catalyzed by an artificial electron donor in the presence of the inhibitor DCMU follows presumably α_1, as judged by the increase of yield at the far-red, and the fact that the sum of this yield with the "normal" Hill reaction yield is approximately 1. In the "spill-over" model one would expect a constant yield for this reaction (1 48, 49). On the other hand the same data suggest the "spill-over" mechanism for the "normal" reaction as judged by the good yield at short wavelengths ($\approx$ 0.5), compared to the yield with the artificial donor system ($\approx$ 0.2).

Similar results of Sauer et al. (48, 49), which however show good efficiency of the artificial donor system at short wavelengths, are fully consistent with the "separate-package" model.

The cytochrome oxidation data of Duysens and Amesz (50) for the alga *Porphyridium cruentum* in the presence of DCMU also suggest large wavelength dependence of the quantum yield contrast with the "spill-over" hypothesis. Normal quantum yields measurements for this alga [Brody and Emerson (6)] show that they may fall in the region λ_2 or stay approximately constant depending on growth conditions; thus a direct comparison to the cytochrome data is not possible.

It may be that DCMU is involved not only in blocking electron transport, but in changing somehow the physical parameters of the system in a way critical to the energy transfer mechanism. This may be true of the reaction mixture as such. Preliminary observations made in Dr. Avron's laboratory[4] show that the dependence of the quantum yield on wavelength might change in different reaction media. One might think that it would be possible to control γ by using different conditions for growth, and different reaction media in the case of isolated chloroplasts.

[4] Avron, N. Personal communication.

An independent supporting evidence for the possibility of energy transfer from photosystem II to I is the recent report of Murata et al. (51) on fluorescence measurements at low temperatures.

In conclusion it seems, at least from enhancement data, that energy transfer from photosystem II to photosystem I may be significant to the quantum yield of photosynthesis. The inconsistency with the data obtained in the presence of DCMU seems interesting and may provide a clue both to the mechanism of energy transfer and to the understanding of the inhibitory effect of DCMU.

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