ON THE EQUILIBRIUM BETWEEN THE REACTION CENTERS OF THE TWO PHOTOSYSTEMS IN PHOTOSYNTHESIS

THE EFFECT OF INDEPENDENT ELECTRON-TRANSPORT CHAINS

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ABSTRACT The equilibrium observed by Joliot et al. (2) between the reaction centers of photosystems I and II of photosynthesis, is explained by a kinetic model. The essential idea is that the electron transport chains are independent entities, and therefore the possibility arises that the reaction centers may exist in oxidized and reduced forms, respectively, and not react with one another because they belong to different chains. According to this idea the observed equilibrium is not a real one but a result of the kinetic effect. Facts which do not fit nicely with the equilibrium model (photophosphorylation between the two photosystems, observed oxidation potentials of the reaction centers) remain consistent with the present kinetic model.

INTRODUCTION

Recent papers of Eley and Myers (1) and Joliot, Joliot, and Kok (2) dealt with the interaction of photosystems I and II[1] of photosynthesis, and in particular the steady-state levels of the oxidized and reduced states of systems I and II traps. According to them, the oxidation states of the traps are governed by a dark equilibrium

$$T_1^+ + T_2^- \rightleftarrows T_1 + T_2$$

where T_1, T_2 denote the primary electron donor and acceptor of systems I and II respectively, $+$ and $-$ refer to oxidized and reduced states of T_1 and T_2 respectively. (see Fig. 1).

When light is given, there is a shift in the oxidation levels of T_1 and T_2 compared to the dark. In limiting light conditions, when all dark steps are much faster than the photochemical steps, we expect that this shift will always be restricted to obey

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[1] Abbreviations—PS-I, PS-II: photosystems I and II, respectively.

the equilibrium law:

$$K = \frac{[T_1][T_2]}{[T_1^+][T_2^-]}.$$

Joliot et al. (2) attempted to measure the reduction and oxidation levels by limiting light conditions, of the reactions centers of the two photosystems in isolated chloroplasts. From their results, they calculated a dark equilibrium constant of value between 4 and 7. This rather small value corresponds to an oxidation-reduction potential difference of only about 40–60 mv, in contrast to other independent estimates. For example, potential determination of fluorescence (3) and P_{700} (4) changes give at least a value of about 200 mv, corresponding to an equilibrium constant higher than about 2000. The main difficulty with a low equilibrium constant is to understand how noncyclic photophosphorylation, which is believed to be coupled to the electron transport somewhere between the two photosystems (5), may be driven with high efficiency despite the small potential difference. A possible argument is that the coupling to phosphorylation lowers by itself the apparent equilibrium constant according to the equation

$$T_2^- + T_1^+ + X \rightleftarrows T_2 + T_1 + X\sim$$

where X and $X\sim$ are low and high energy precursors of photophosphorylation. However, since addition of uncouplers did not change the results for the equilibrium constant (2), it appears that the small equilibrium constant is a property of the uncoupled system. This difficulty was considered at length by Joliot et al. (2), who suggested as one possibility that the site of phosphorylation is not between the two photosystems.

Since the point is of considerable importance, I would like to suggest a different explanation for this effect which has a kinetic origin rather than a thermodynamic one.

Table-of-Definitions

$[T_1]$, $[T_2]$ = concentrations of the "open" reaction centers in PS-I and PS-II respectively.

$[T_1^+]$, $[T_2^-]$ = concentrations of the oxidized form of T_1 and reduced form of T_2.

t_1, t_2 = fractions of the traps of PS-I and PS-II in the "open" form. $t_1 = [T_1]/([T_1] + [T_1^+])$; $t_2 = [T_2]/([T_2] + [T_2^-])$.

K = equilibrium or "apparent equilibrium" constant, defined by Equation 1.

R = rate of steady electron-transport.

x_i = fraction of possible oxidation-state of a chain between PS-I and PS-II. The oxidation state of a chain is defined by the particular model. (see text.)

I = total light intensity absorbed.

α_1, α_2 = the fraction of the absorbed light which is channeled to PS-I or PS-II, respectively.

ϕ_1, ϕ_2 = quantum yields for primary reactions in PS-I and PS-II, for a quantum absorbed in an "open" trap. (T_1 reduced or T_2 oxidized.)

β = $\alpha_1\phi_1/\alpha_2\phi_2$

THE EQUILIBRIUM MODEL, A SUMMARY

The general model of electron transport is presented in Fig. 1. T_1 and T_2 represent the components of the reaction centers which can be oxidized by PS-I or reduced by PS-II, respectively. Under light–limiting conditions, the trasnport of electrons from H_2O to PS-II and from PS-I to the electron-acceptor is so fast as not to limit the over-all rate. According to Eley and Myers (1), and to Joliot et al. (2), the steady state under light-limiting conditions, is given by considering the three processes:

$$T_1 \xrightarrow{h\nu_{\text{I}}} T_1^+ \tag{i}$$

$$T_2 \xrightarrow{h\nu_{\text{II}}} T_2^- \tag{ii}$$

$$T_1^+ + T_2^- \rightleftarrows T_1 + T_2 . \tag{iii}$$

The rate of reaction i is proportional to the light intensity absorbed into PS-I and to the fraction of "open" centers, t_1. It will therefore be given by $\alpha_1\phi_1 It_1$. In the same way the rate of the reaction ii is given by $\alpha_2\phi_2 It_2$.[2] It is assumed that the electron donor to T_2 and the electron acceptor to T_1 have constant activities since the dark reactions regenerating them are not limiting in weak light. Reaction iii, also relatively fast and not limiting in weak light, introduces a thermodynamic equilibrium K which restricts the values of t_1 and t_2.

$$K = \frac{[T_1][T_2]}{[T_1^+][T_2^-]} = \frac{t_1}{1 - t_1} \cdot \frac{t_2}{1 - t_2} \tag{1}$$

In the steady state the rate of reaction i must be balanced by the rate of reaction ii, therefore:

$$\alpha_1\phi_1 It_1 = \alpha_2\phi_2 It_2 . \tag{2}$$

From Equations 1 and 2, one may solve for t_1 and t_2. The results are:

$$t_1 = \frac{[T_1]}{[T_1] + [T_1^+]} = \frac{K(\beta + 1) - [K^2(\beta + 1)^2 - 4K(K - 1)\beta]^{1/2}}{2(K - 1)\beta} \tag{3a}$$[3]

$$t_2 = \frac{[T_2[}{[T_2] + [T_2^-]} = \frac{K(\beta + 1) - [K^2(\beta + 1)^2 - 4K(K - 1)\beta]^{1/2}}{2(K - 1)} . \tag{3b}$$[3]

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[2] Joliot et al. (2) used a more involved expression for the rate of reaction ii, considering the possibility of energy transfer between different pigment units of PS-II. (see also later in text). In principle the results are similar.

[3] The minus sign must be chosen alone for the square root in Equations 3 *a* and 3 *b*, for a positive sign will always lead to t_1 and t_2 larger than 1, as can be easily proved.

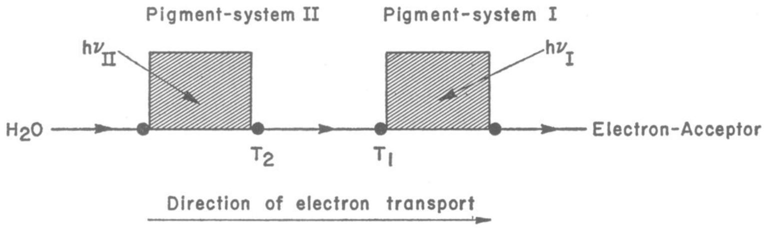

FIGURE 1 Schematic representation of the two photosystems and the associated electron transport. The full circles indicate primary electron carriers for each of the systems; intermediate electron carriers are not shown. The arrows indicate the direction of the electron flow, from H_2O to the electron-acceptor.

From the above results one can compute the steady-state rate and the quantum yield.

$$R = \alpha_1\phi_1 I t_1 = \alpha_2\phi_2 I t_2 \qquad (t_1 \text{ and } t_2 \text{ given by 3 } a, b) \tag{4a}$$

$$\text{quantum yield} = R/I = \alpha_1\phi_1 t_1 = \alpha_2\phi_2 t_2 \,. \tag{4b}$$

Equation 4 *b* gives the quantum yield as a function of t_1 or t_2, both of which can be substituted from Equations 3 *a* or 3 *b* and expressed in terms of K and β.[4]

Joliot et al. (2) computed the quantum yield R/I vs. β, assuming $K = 5$ and observed that, as β changes from 1 to 0.7 there is practically no change in the calculated yield. It was therefore stated (2) that the equilibrium between T_1 and T_2 explains the constancy of the quantum yield over the short-wavelength region (6) ($\lambda < 680$ mμ for green organisms) and eliminates the need for special assumptions such as the hypothesis of energy-transfer from PS-II to PS-I (spillover [7]). Qualitatively speaking, the equilibrium tends to oppose the effect of any difference in light absorption between the two photosystems, by adjusting the ratios t_1 and t_2; in this way it has a "buffering" effect, for moderate changes in β.

THE INDEPENDENT CHAINS MODEL

An alternative suggestion to the equilibrium model would be to assume that the electron transport system is not like a homogenous chemical system, but is com-

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[4] The results for t_1 and t_2 (Equations 3 *a*, *b*) do not depend on the light intensity, but only on the way of light distribution between the photosystems (viz. on $\alpha_1\phi_1$ and $\alpha_2\phi_2$). Therefore, when we gradually decrease the light intensity until the light is extinguished completely we must obtain the same values for t_1 and t_2 in the dark which we obtained in the previous illumination. This is correct in so far as we can neglect the slow side oxidation or reduction reactions of the electron-transfer components with the environment. Otherwise, but only at very low light intensity, these side reactions will predominate and fix a limiting value for t_1 and t_2 in the dark which will be independent of the previous illumination.

Suppose we continue to neglect the side reactions, so that there is no dependence on light intensity. In this case, even light of an infinitesimally small intensity would fix values for t_1 and t_2. We have just to remember that the transition to the steady state may take time, (infinitely long for an infinitesimal light intensity), so that there is never an abrupt change in changing illuminations as one might think superficially from the equations.

posed of definite independent chains of electron carriers. In this case, each electron carrier molecule is constrained to react only with a particular neighbor molecule *in the same chain.* Even if, for a single chain, the equilibrium is completely shifted in one reaction direction, it would be possible, in a collection of many chains, to find simultaneously, a certain concentration of T_1^+ and T_2^- which cannot react immediately since they are not connected to the same chain. The following diagram exemplifies the point:

$$T_1^+ - T_2 \tag{a}$$

$$T_1 - T_2^- \tag{b}$$

$$T_1 - T_2 . \tag{c}$$

Here, we draw three possible forms (oxidation states) of an electron transport chain. We may imagine that all three forms exist in a macroscopic collection of many chains. There would be no reaction between T_1^+ of chain *a* and T_2^- of chain *b*, simply because there is no physical connection between the two. In a single chain, however, and this will be assumed from now on, the equilibrium is very far toward the right of Equation iii. Therefore, the following oxidation state of a single chain

$$T_1^+ - T_2^-$$

has only a transitory significance and very rapidly will disappear to give form *c*, its concentration would be neglected, at least under light-limiting conditions.

Therefore, the experimental finding that T_1^+ and T_2^- exist simultaneously in an appreciable fraction *does not necessarily imply an effect of a thermodynamic equilibrium* between the two, but may be the result of the existence of independent electron transport chains.

We consider a few models in more detail to obtain more quantitative results. (*A*) The reaction centers are connected directly. This is a hypothetical case which will help to illustrate the point in the easiest way. In this case, the electron transport chains between the photosystems are composed of two members only, T_1 and T_2

$$T_1 \text{——} T_2 .$$

In the whole assembly of electron transport chains, one has to consider all the possible oxidation states of a chain, rather than of an individual electron carrier. Under limiting-light intensities, the following oxidation states have to be taken into account[5]:

$$T_1^+ \text{——} T_2 , \qquad T_1 \text{——} T_2 , \qquad \text{and} \qquad T_1 \text{——} T_2^- .$$

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[5] All calculations as well as measurements cited here apply to light limiting conditions only. As said already, intermediates like T_1^+——T_2^- react very fast, and therefore exist in negligible amounts, if, indeed the real equilibrium constant is very large. The same applies to models *B* and *C* (see later in text), where, for example $T_1CT_2^-$ will react very fast to give $T_1C^-T_2$ so that we can neglect its existence.

The scheme of reaction is written as follows:

$$T_1^+ \text{——} T_2 \underset{\alpha_1\phi_1 I}{\overset{\alpha_2\phi_2 I}{\rightleftharpoons}} T_1 \text{——} T_2 \underset{\alpha_1\phi_1 I}{\overset{\alpha_2\phi_2 I}{\rightleftharpoons}} T_1 \text{——} T_2^-. \tag{iv}$$

For simplification, we assume that the rate of any of the reactions in equation iv is proportional to the fraction of the relevant intermediate, so that we deal with a complex of first-order reactions. For example, the rate of the reaction:

$$T_1T_2 \xrightarrow{\alpha_2\phi_2 I} T_1T_2^-$$

is

$$\alpha_2\phi_2 I \frac{[T_1T_2]}{[T_1T_2] + [T_1^+T_2] + [T_1T_2^-]}.$$

This relation is justified if the absorbed photons are distributed in proportion to the concentrations of each species and the chance of energy transfer from unit to unit is zero.

Denoting by x_1, x_2, and x_3 the fractional concentrations of $T_1^+T_2$, T_1T_2, and $T_1T_2^-$, respectively, one obtains the following equations:

$$\frac{d[T_1^+T_2]}{dt} = \alpha_1\phi_1 I x_2 - \alpha_2\phi_2 I x_1 \tag{5 a}$$

$$\frac{d[T_1T_2^-]}{dt} = \alpha_2\phi_2 I x_2 - \alpha_1\phi_1 I x_3 \tag{5 b}$$

$$x_1 + x_2 + x_3 = 1. \tag{5 c}$$

Solving for the steady state, one obtains:

$$x_1 = \frac{\beta^2}{\beta^2 + \beta + 1} \qquad x_2 = \frac{\beta}{\beta^2 + \beta + 1}$$

$$x_3 = \frac{1}{\beta^2 + \beta + 1}. \tag{5 d}$$

From this one can calculate t_1 and t_2, the fractional concentrations of the reaction centers, respectively. These are expressed in terms of the x_i's of equation 5 *d*:

$$t_1 = 1 - x_1, \qquad t_2 = 1 - x_3. \tag{5 e}$$

Model *A* gives results most pertinent to illustration of our point. From Equations 5 *d* and 5 *e* it follows that for $\beta = 1$ (i.e., at such wavelengths where PS-I and PS-II have equal activity), $t_1 = t_2 = 2/3$. Therefore, a considerable fraction ($\approx 1/3$) of both reaction centers exists in the form T_1^+ and T_2^-, simultaneously. Intermediate electron carriers between T_1 and T_2 would decrease the effect, as is considered in the following models.

Although there is no significance in this model to the equilibrium constant, as defined by Equation 1, it is still a useful quantity for a comparison to the experiment, which may be referred to as the "apparent equilibrium constant." It is, of course, not really constant, but depends on β. From Equation 5 *d* and 5 *e* we obtain:

$$K = \frac{1 - x_1}{x_1} \cdot \frac{1 - x_3}{x_3} = (1 + \beta)(1 + \beta^{-1}) \qquad (5f)$$

(*B*) We consider the effect of an intermediate electron carrier, C between T_1 and T_2. We write C and C^- for the oxidized and reduced forms of C, respectively. The following series of possible reactions arises:

$$\underset{(x_1)}{T_1^+CT_2} \underset{\alpha_1 \phi_1 I}{\overset{\alpha_2 \phi_2 I}{\rightleftarrows}} \underset{(x_2)}{T_1\,CT_2} \underset{\alpha_1 \phi_1 I}{\overset{\alpha_2 \phi_2 I}{\rightleftarrows}} \underset{(x_3)}{T_1\,C^-T_2} \underset{\alpha_1 \phi_1 I}{\overset{\alpha_2 \phi_2 I}{\rightleftarrows}} \underset{(x_4)}{T_1\,C^-T_2^-} \qquad (5)$$

The fractions of the intermediate oxidation states are denoted by x_1 to x_4, respectively, from left to right. By analogy with the treatment of model *A* the steady-state solutions of the equations-system v is:

$$x_1 = \frac{\beta^3}{\beta^3 + \beta^2 + \beta + 1}, \qquad x_2 = \frac{\beta^2}{\beta^3 + \beta^2 + \beta + 1}$$
$$x_3 = \frac{\beta}{\beta^3 + \beta^2 + \beta + 1}, \qquad x_4 = \frac{1}{\beta^3 + \beta^2 + \beta + 1}. \qquad (6a)$$

The "apparent equilibrium constant" K is given by

$$K = \frac{1 - x_1}{x_1} \cdot \frac{1 - x_4}{x_4} = (1 + \beta + \beta^2)(1 + \beta^{-1} + \beta^{-2}). \qquad (6b)$$

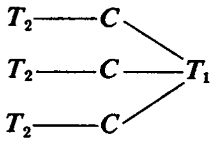
One can easily generalize the results of models *A* and *B* to include the possibility of any number, *n*, of electron carriers between T_1 and T_2. The resulting equation for K would be:

$$K = (1 + \beta + \beta^2 \cdots + \beta^{n+1})(1 + \beta^{-1} + \beta^{-2} \cdots + \beta^{-(n+1)}) \qquad (6c)$$

We denote such a model $B_n(n = 1.2 \cdots)$.

(C) We consider a model in which several chains starting with T_2 converge in T_1. This model takes into account the existing large pool (8) between PS-I and PS-II, the division of the pool into two equal parts (*Q* and *P* [9, 10] or A_1 and A_2 [11]), together with the assumption that T_1 is present in a relatively small amount.

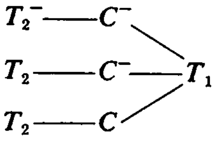
In this model, the scheme of reactions becomes complicated. We illustrate this for the case of three converging chains: the arrangement of a unit in the electron-transport chain is assumed to be:



where T_2 and C denote the two parts of the main pool. The schemes of reactions is as follows:

$$\begin{tikzcd}
\underset{(x_1}{T_1^{+}CT_2} \arrow[r, shift left, "k_1"] & \underset{(x_2)}{T_1\,CT_2} \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] & \underset{(x_3)}{T_1\,C^{-}T_2} \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] \arrow[d, shift right, "k_5"'] & \underset{(x_4)}{T_1\,C^{=}T_2} \arrow[l, shift left, "k_{-3}"] \arrow[r, shift left, "k_4"] \arrow[d, shift right, "k_6"'] & \underset{(x_5)}{T_1\,C^{\equiv}T_2} \arrow[l, shift left, "k_{-4}"] \arrow[d, shift right, "k_7"'] \\
 & & \underset{(x_6)}{T_1\,C^{-}T_2^{-}} \arrow[u, shift right, "k_{-5}"'] \arrow[r, shift left, "k_8"] & \underset{(x_7)}{T_1\,C^{=}T_2^{-}} \arrow[u, shift right, "k_{-6}"'] \arrow[l, shift left, "k_{-8}"] \arrow[r, shift left, "k_9"] \arrow[d, shift right, "k_{10}"'] & \underset{(x_8)}{T_1\,C^{\equiv}T_2^{-}} \arrow[u, shift right, "k_{-7}"'] \arrow[l, shift left, "k_{-9}"] \arrow[d, shift right, "k_{11}"'] \\
 & & & \underset{(x_9)}{T_1\,C^{=}T_2^{=}} \arrow[u, shift right, "k_{-10}"'] \arrow[r, shift left, "k_{12}"] & \underset{(x_{10})}{T_1\,C^{\equiv}T_2^{=}} \arrow[u, shift right, "k_{-11}"'] \arrow[l, shift left, "k_{-12}"] \arrow[d, shift right, "k_{13}"'] \\
 & & & & \underset{(x_{11})}{T_1\,C^{\equiv}T_2^{\equiv}} \arrow[u, shift right, "k_{-13}"']
\end{tikzcd}$$

where, for example, $T_1\,C^{=}\,T_2^{-}$ is a short notation for:



The constants of reactions, k_i, for this scheme, are given from $\alpha_1\phi_1$ and $\alpha_2\phi_2$ as for the previous schemes. However, here we have to consider that the converging chains compete for oxidation and reduction. To compute the k's we add two assumptions: (*a*) each branched chain which contains C^- has an equal probability of being oxidized by PS-I. (*b*) The probability of light absorption in T_2 is equal for each of the branched chains.

For example, $T_1C^-T_2^-$ has an equal probability to be converted by oxidation, either to $T_1C^-T_2$ or to $T_1C{-}T_2^-$, and $T_1C{-}T_2$ has twice the probability of being converted by reduction to $T_1C^-T_2$ than to $T_1C{-}T_2^-$. Taking the above into account, the rate constants referring to reactions of $T_1C^-T_2^-$ are written as an example:

$$\begin{array}{llll} k_9 = \tfrac{1}{3}\,\alpha_2\phi_2\mathrm{I} & & k_{-9} = \tfrac{2}{3}\,\alpha_1\phi_1\mathrm{I} \\ k_{10} = \tfrac{1}{3}\,\alpha_2\phi_2\mathrm{I} & & k_{-10} = \alpha_1\phi_1\mathrm{I} \\ k_{-6} = \tfrac{1}{2}\,\alpha_1\phi_1\mathrm{I} & & k_6 = \tfrac{2}{3}\,\alpha_2\phi_2\mathrm{I} \\ k_{-8} = \tfrac{1}{2}\,\alpha_1\phi_1\mathrm{I} & & k_8 = \tfrac{2}{3}\,\alpha_2\phi_2\mathrm{I}. \end{array}$$

The net rate of change of $T_1C^-T_2^-$ is $-\ (k_9 + k_{10} + k_{-6} + k_{-8})x_7 + k_{-9}x_8 + k_{-10}x_9 + k_6x_4 + k_8x_6$, which in the steady state is equated to zero, forming one of the equations for the whole scheme.

Other similar schemes can be written for any number of branches T_2C per T_1. We may denote C_n for the general model with n branched chains T_2C per T_1. Several such schemes were computed with the aid of a digital computer.

DISCUSSION

The results of some calculations on models $A - C$ are given in Fig. 2. It illustrates quantitatively the effect of existence of electron transport chains, and may explain the results of Joliot et al. (2).

A direct comparison of the calculations with the data of Joliot et al. (2) is also given in Fig. 2. In this work (see reference 2), β, t_1, and t_2 are given as functions of the wavelength separately, from which it is possible to calculate t_1 and t_2 as a function of β. Two sets of comparison are made, one using the analysis of Joliot et al. (2) that the rate of PS-II is not a linear function of the concentration of "open" reaction centers; the other uses a linear relation, as used in the present calculations (cf. legend Fig. 2). The second comparison is more relevant, since our calculations were based on a linear relation. A rigorous derivation, however, would require a revision of our calculations to include the effect of energy-transfer between different units. This does not seem to be too critical at present in view of our over-all rough understanding of the system, and crude calculations may suffice.

From Fig. 2 it seems that models A, B_1, or C_2 may explain the data. More intermediates in model B or a larger number of branched chains in model C tend to increase K to much higher values than indicated by the experiment. This fact is incompatible with the picture of about 10 chains, starting in PS-II and converging to one center (9) (P_{700}) at PS-I.

The convergence of about 10 chains on one center was conceived of to explain the following: (*a*) the ratio pool of electron carriers/P_{700} was about 20, (*b*) the "pool" consisted mainly of two components in equal amounts, one serving as

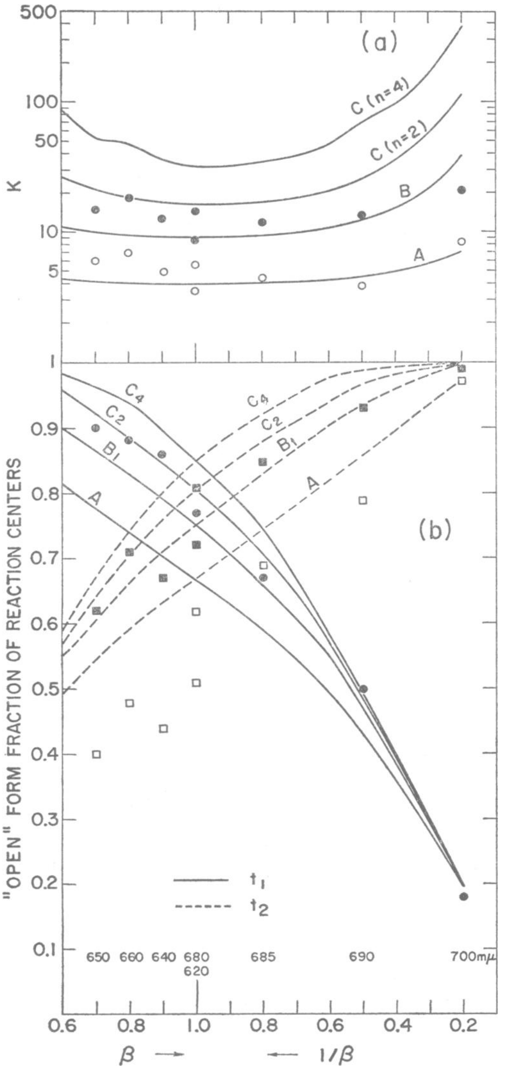


FIGURE 2 t_1, t_2, and K, calculated as function of β (or $1/\beta$) for the various models discussed. Points indicate the data of Joliot et al. taken from Fig. 6 of reference 2 for β vs. wavelength, and Fig. 9 of reference 2 for t_1 and t_2 vs. wavelength. In the linear relation $Vs1/Vp1$ and $Vs2/Vp2$ were taken as a measure for t_1 and t_2 respectively. In the nonlinear relation only $Vs1/Vp1$ was taken as a measure of t_1, t_2 is taken as $E/E_{\max}$. See reference 2 for the meaning of these symbols. (*a*) For curve B, read B_1. ○, Nonlinear relation between rate and the fraction of "open" reaction centers. ●, Linear relation. (*b*) ●, Data for t_1; ■, data for t_2, linear relation; □, data for t_2, nonlinear relation. Wavelength numbers indicate the corresponding wave-lengths taken from reference 2.

electron donor to the other (9), and (*c*) all the chains of the "pool" must terminate in P_{700}.

Experiments now in progress (12) on the kinetic changes of P_{700} indicate that perhaps one should question the accepted hypothesis that P_{700} is the only electron donor to PS-I. The kinetics indicate that the amount of chain convergence is much smaller than 10; thus most of the chains must terminate in components other than P_{700}. Such a picture may be in agreement with the present arguments.

Fig. 2 also shows that the variation in the apparent K as a function of β is small around $\beta = 1$. A change of β from 1 to 0.8 yields a change in K of only 1% for model A, 3% for model B, and 14% in model C for two branched chains. Therefore, one may mistake K for a true constant.

The conclusions of Joliot et al. (2) on the influence of K on the quantum yields, and especially on the constancy of the yield in the region of preferential absorption into PS-II, remain therefore valid and need not be changed as a result of the interpretation offered here.

In order to check experimentally whether it is possible that K represents a true thermodynamic equilibrium constant or whether it is just an apparent ratio caused by kinetic reasons, as suggested here, the value of K should be checked as a function of wavelength for values of β, or $1/\beta$ close to zero (From Fig. 2 it seems that a useful range would be $1/\beta < 0.2$) where it should vary considerably according to the second hypothesis. Also, the dependence or independence on temperature may serve as a possible check.

The independent chains hypothesis finds support also in the kinetic analysis of the fluorescence induction (10) which is accounted for in detail by the use of a similar model. The model seems therefore reasonable. It accounts for the observed "equilibrium constant" and its nondependence on phosphorylation factors and uncouplers. In any single chain of electron carriers, the reaction $T_2^- T_1^+ \rightarrow T_2 T_1$ progresses virtually in one direction only, and could be sufficiently energetic to drive a coupled phosphorylation.

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