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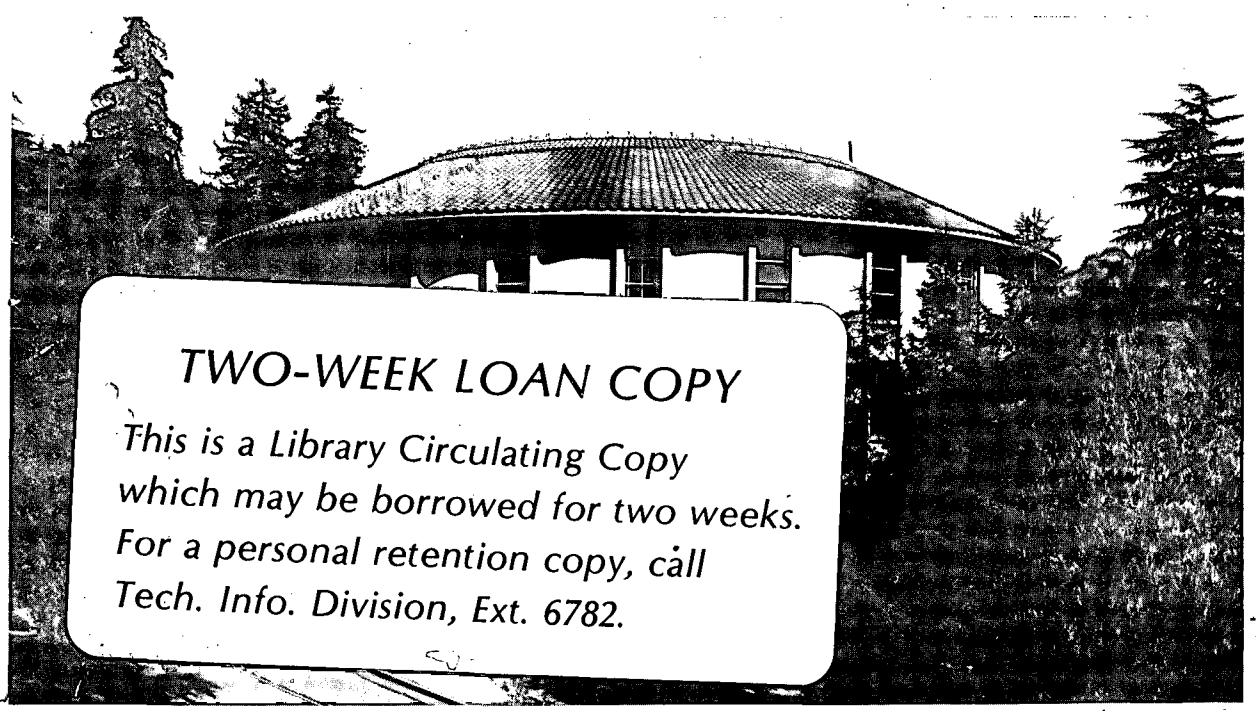

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DISCLAIMER

KINETICS OF PHOTOSENSITIZED ELECTRON TRANSPORT ACROSS A MEMBRANE BOUNDARY

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Abstract: A generalized system is described which accomplishes a photosensitized oxidation and reduction and the separation of the resultant oxidized and reduced species across a membrane boundary. A complete reaction mechanism is described and all of the corresponding kinetic steps are defined. A general rate law and an initial rate law are derived by a steady-state analysis. Based upon the rate laws, experimental conditions which should optimize the reaction efficiency are discussed.

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Introduction: The utilization of solar energy requires a photochemical conversion of the photon energy to another form: heat, electricity, or a useful chemical reaction, for example. Photosynthesis in plants is a photochemical solar energy conversion of great utility and relatively good efficiency. "Artificial photosynthesis" describes our attempts to mimic this natural process, with the aim of efficiently utilizing solar energy for the production of fuel, most desirably hydrogen from water.

Imitation of natural photosynthesis has at least three aspects: imitation of the molecules used in nature, imitation of the apparatus used in nature, and ultimately imitation of the reactions used in nature. The fundamental photochemical conversion step in photosynthesis is an electron transfer from photoexcited chlorophyll to a series of electron acceptors located across the photosynthetic membrane; the electron transfer sequence terminates at a previously photooxidized chlorophyll on the opposite side of the membrane (the two-photon Z scheme). Thus in artificial photosynthetic schemes, the molecules typically used are chlorophyll analogs (porphyrins), the apparatus typically used is a membrane and the reactions are typically photoinduced electron transfers. The electron transfer process can be coupled to the oxidation and reduction of water in the cyclic scheme shown below (Figure 1). S represents the photosensitizer, and D and A represent appropriate electron donor and acceptor systems with oxidation and reduction potentials suitable to carry out the reactions shown. Catalysts are typically required for the actual evolution of H_2 and O_2.

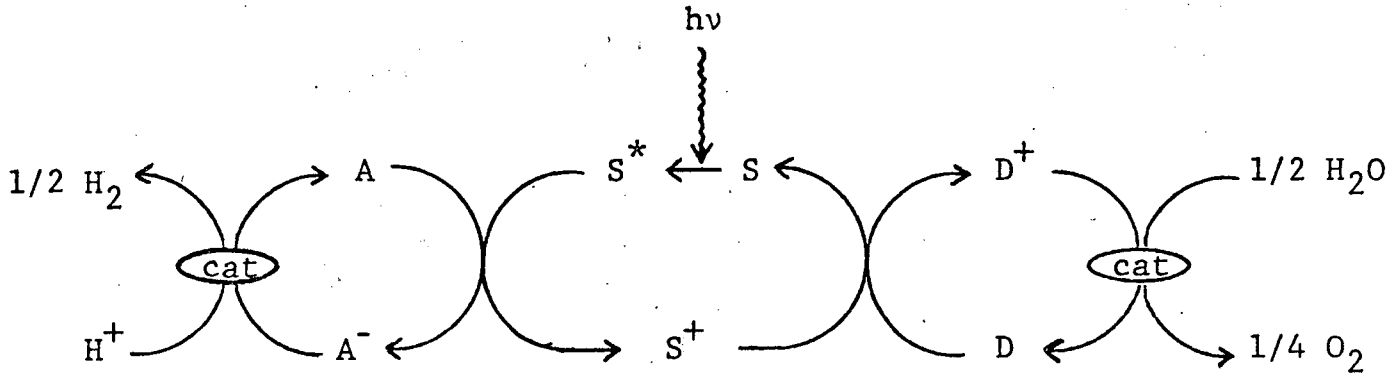

Figure 1 - Cyclic photochemical scheme for decomposition of water

The fundamental conversion accomplished in the above cycle is the chemical separation of oxidizing power and reducing power, which first appear as D^+ and A^-, respectively. For simplicity, the later conversions to O_2 and H_2 will be considered as separate processes. In such a scheme, the use of a membrane would provide a boundary to keep the oxidizing and reducing agents (D^+ and A^-) physically separated. Thus the sensitizer should be incorporated into the membrane (as chlorophyll is in the photosynthetic membrane), with the donor and acceptor systems located on opposite sides.

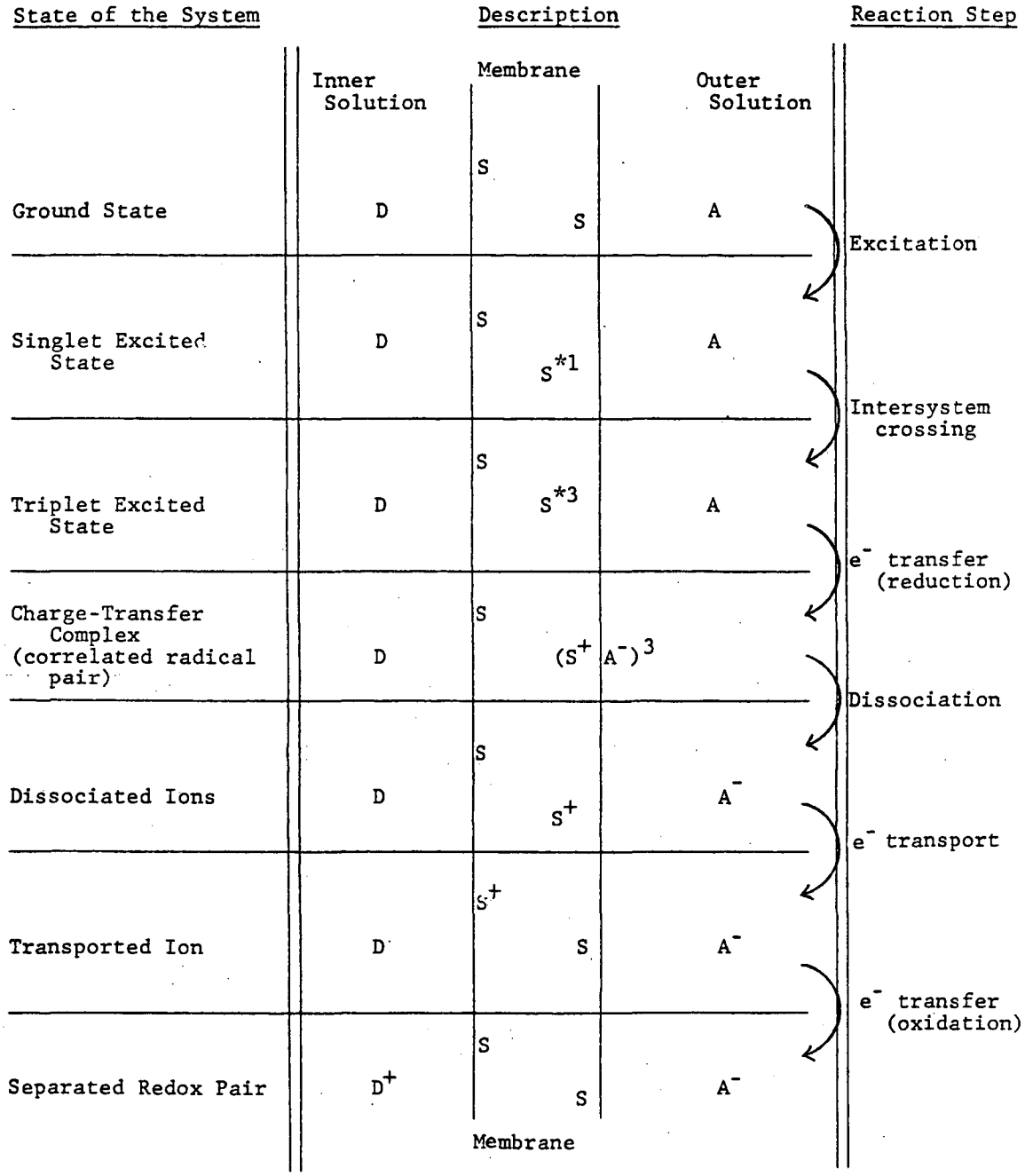

Figure 2
Photosensitized Electron Transfer
Across a Membrane Boundary

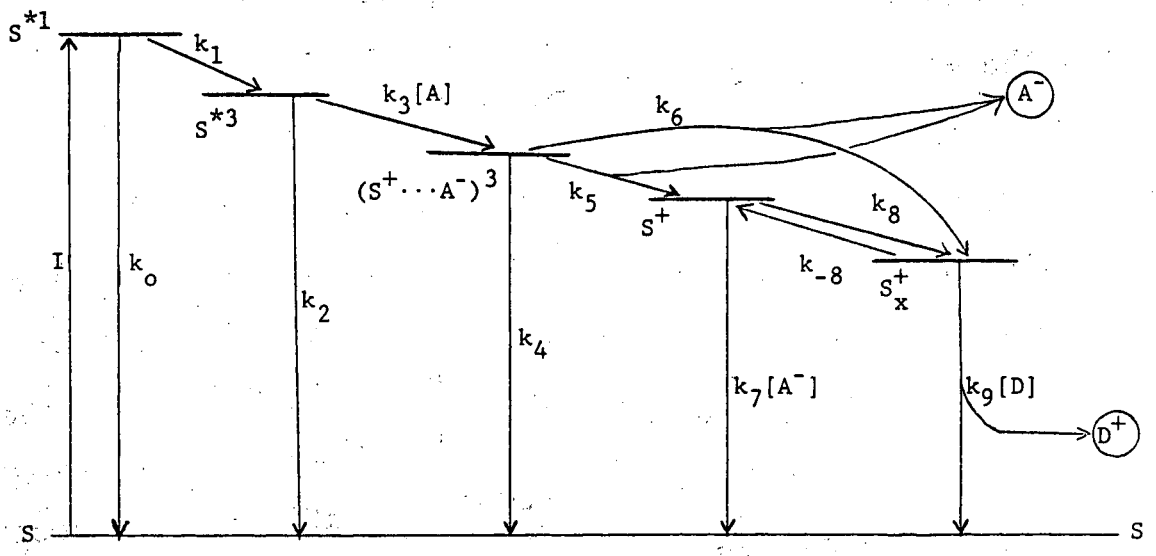

Figure 3

Kinetic Scheme

Definitions

S - photosensitizer (e.g., a porphyrin)

A - acceptor (e.g., a viologen)

D - donor (e.g., EDTA)

S^{*1} - singlet excited sensitizer

S^{*3} - triplet excited sensitizer

$(S^{+}\cdots A^{-})^{3}$ - charge-transfer (CT) complex

A^{-} - reduced ac eptor

S^{+} - oxidized sensitizer

S_x^{+} - transported oxidized sensitizer

D^{+} - oxidized donor

I - rate of light absorption

k_o - natural deactivation of S^{*1}

k_1 - intersystem crossing

k_2 - natural deactivation of S^{*3}

k_3 - bimolecular encounter, $S^{*3} + A$

k_4 - deactivation of CT complex

k_5 - separation of CT complex by A^{-} loss

k_6 - separation of CT complex by S^{+} transport

k_7 - bimolecular back reaction, $S^{+} + A^{-}$

k_8 - transport of S^{+} (e^{-} transport)

k_{-8} - reverse e^{-} transport

k_9 - bimolecular oxidation, $S^{+} + D$

Description of the System: Figure 2 illustrates each of the mechanistic steps required in order to accomplish the photosensitized separation of oxidizing and reducing power. Figure 3 locates the various states on a relative energy diagram and defines the kinetic steps which interconvert the states. The membrane is visualized as containing the sensitizer S in two distinct populations: molecules of S on the the outer surface of the membrane which are capable of direct interactions with the acceptor A in the outer solution, and molecules of S on the inner surface of the membrane which can interact with the donor D in the inner solution. In the case of a lipid bilayer membrane and a hydrophilic, membrane-bound sensitizer, the two distinct populations of sensitizer are easily visualized. In the case of a much thicker membrane with an unknown distribution of sensitizer throughout the membrane (such as a hollow fiber membrane), the two populations of sensitizer will be differentiated based upon the ability to interact with D or A in the inner or outer solutions, respectively.

Step 1 - Excitation: Absorption of a photon by the membrane-bound sensitizer produces initially an excited singlet state (S^{*1}). Under conditions of high sensitizer concentration in the membrane, significantly more light will be absorbed by the molecules on the outer surface. (For 10^{-2} M sensitizer with $\varepsilon = 10^{4}\ M^{-1}\ cm^{-1}$, 90% will be absorbed in the first 10μ). Nevertheless, it is important to consider that some absorption will take place by sensitizer molecules within the membrane. In these cases, energy transfer to the molecules on the outer

surface would be required within the lifetime of the sensitizer excited state. This energy transfer whould also be facilitated by high sensitizer concentrations in the membrane.

Step 2 - Intersystem Crossing: For completeness, the possibility is considered that the photoreaction of interest occurs from a different excited state (S^{*3}) than that originally produced upon excitation. In general, a photoreaction from a triplet state would be more desirable for several reasons: (1) the typically longer excited state lifetime of a triplet state would facilitate energy transfer throughout the membrane, as mentioned above: (2) the triplet radical pair produced upon electron transfer would be less likely to recombine than a singlet radical pair; (3) triplet radical pairs may be subject to a magnetic field effect (described in an accompanying report). It is also possible that the photoreaction of interest may arise from two different excited states, in which case the kinetics could become substantially more complicated than what is considred here.

Step 3 - Reductive Electron Transfer: Encounter of an acceptor (A) with an excited sensitizer (presumably on the outer surface of the membrane) leads to electron transfer quenching of the excited state. The initial product of this quenching will be called a charge-transfer complex. It will be a radical pair, since one electron has been transferred from S^{*} to A, and it may also be an ion pair, depending upon the original charges of S and A. (For simplicity, all molecules have been assumed to be neutral in their original states).

Step 4 - Dissociation: The charge-transfer complex is a crucial junction point in the overall mechanism. To accomplish an effective photoreaction, the initial radical pair must be separated before deactivation takes place by a simple reverse electron transfer. The deactivation step (k_4) is typically very rapid - it is energetically favored and the partners are still within the same encounter solvent cage. The competing separation processes may be either removal of A^- by diffusion away from the membrane surface (k_5) or removal of S^+ from the outer surface (k_6), by processes described next.

Step 5 - Membrane Electron Transport: The second crucial junction point is the transport of the oxidizing power (originally as S^+) across the membrane. The competing process is the reencounter of S^+ with A^- from the bulk outer solution (the back reaction). This process is typically nearly diffusion-controlled; thus removal of S^+ from the outer surface must be rapid. Physical transport of S^+ itself across the membrane is conceivable but probably very slow, at least in comparison to an alternative mechanism of electron transport, which accomplishes the equivalent. In a bilayer system, the electron transport can be a single electron transfer from a sensitizer on the inner surface (S_x) to an oxidized sensitizer on the outer surface (S^+); this effectively exchanges the two (to become S_x^+ and S). Over distances typical for lipid bilayers (4-5 nm), electron transport by tunneling is a feasible process. For thicker membranes, multiple electron transfers (electron hopping) would be required. This process also

would be facilitated by high concentrations of sensitizer in the membrane. Alternatively, additives could be incorporated into the membrane to assist in conductivity properties, or the membrane itself could be conductive. Regardless of the mechanism, k_8 is taken to be the net rate constant for removal of S^+ from the outer surface, and k_{-8} represents the reverse process.

Step 6 - Oxidative Electron Transfer: Once oxidized sensitizer appears on the inner surface (S_x^+), it can interact with the donor (D). Besides the reverse electron transport (k_{-8}), no processes competing with oxidation of D are considered. With this step, all sensitizers are returned to the ground state, and an effective separation of D^+ and A^- across the membrane has been achieved.

Kinetic Equations:

The following analysis utilizes the definitions shown in Figure 3 to develop steady-state equations for each of the reactive intermediates involved in the mechanism and then a rate law for the overall reaction.

Steady-State Equations:

For $[S^{*1}]$:

$$I = (k_o + k_1)[S^{*1}]$$

$$[S^{*1}] = \frac{I}{(k_o + k_1)}$$

For $[S^{*3}]$:

$$k_1[S^{*1}] = (k_2 + k_3[A])[S^{*3}]$$

$$[S^{*3}] = \frac{k_1}{(k_2 + k_3[A])}[S^{*1}]$$

$$[S^{*3}] = I\left(\frac{k_1}{k_o + k_1}\right)\left(\frac{1}{k_2 + k_3[A]}\right)$$

For $[(S^+ \cdots A^-)^3]$:

$$k_3[A][S^{*3}] = (k_4 + k_5 + k_6)[(S^+ \cdots A^-)^3]$$

$$[(S^+ \cdots A^-)^3] = \frac{k_3[A]}{(k_4 + k_5 + k_6)}[S^{*3}]$$

$$[(S^+ \cdots A^-)^3] = I\left(\frac{k_1}{k_o + k_1}\right)\left(\frac{k_3[A]}{k_2 + k_3[A]}\right)\left(\frac{1}{k_4 + k_5 + k_6}\right)$$

For $[S^+]$:

$$k_5[(S^+\cdots A^-)^3] + k_{-8}[S_x^+] = (k_8 + k_7[A^-])\ [S^+]$$

For $[S_x^+]$:

$$k_6[(S^+\cdots A^-)^3] + k_8[S^+] = (k_{-8} + k_9[D])\ [S_x^+]$$

Two equations with two unknowns:

Let $x = [S^+]$

$y = [S_x^+]$

$C = [(S^+\cdots A^-)^3]$

$$k_5C + k_{-8}y = (k_8 + k_7[A^-])\ x$$

$$k_6C + k_8x = (k_{-8} + l_9[D])\ y$$

$$x = \frac{k_5C + k_{-8}\ y}{(k_8 + k_7[A^-])}$$

$$y = \frac{k_6C + k_8\ x}{(k_{-8} + k_9[D])}$$

$$y = \frac{k_6C(k_8 + k_7[A^-]) + k_8(k_5C + k_{-8}\ y)}{(k_{-8} + k_9[D])(k_8 + k_7[A^-])}$$

$$[S_x^+] = y = \frac{C(k_5k_8 + k_6k_8 + k_6k_7[A^-])}{k_8k_9[D] + k_{-8}k_7[A^-] + k_7k_9[D][A^-]}$$

$$\text{Rate} = k_9[D][S_x^+]$$

$$\text{Rate} = I\left(\frac{k_1}{k_o + k_1}\right)\left(\frac{k_3[A]}{k_2 + k_3[A]}\right)\left(\frac{k_9[D]}{k_4 + k_5 + k_6}\right)\left(\frac{k_8(k_5 + k_6) + k_6k_7[A^-]}{k_9[D](k_8 + k_7[A^-]) + k_7k_{-8}[A^-]}\right)$$

Consideration of Limiting Cases:

1. Initial Rate Law (where $[A^-] = 0$)

$$\text{Initial Rate} = I \left(\frac{k_1}{k_o + k_1}\right)\left(\frac{k_3[A]}{k_2 + k_3[A]}\right)\left(\frac{k_5 + k_6}{k_4 + k_5 + k_6}\right)$$

$$\Phi_{isc} = \left(\frac{k_1}{k_o + k_1}\right) \qquad \text{(intersystem crossing)}$$

$$\Phi_{ct} = \left(\frac{k_3[A]}{k_2 + k_3[A]}\right) \qquad \text{(charge transfer)}$$

$$\Phi_{sep} = \left(\frac{k_5 + k_6}{k_4 + k_5 + k_6}\right) \qquad \text{(separation)}$$

$$\text{Initial Rate} = I \cdot \Phi_{isc} \cdot \Phi_{ct} \cdot \Phi_{sep}$$

2. Effect of high concentration of A

(where $k_3[A] >> k_2$)

$$\Phi_{ct} \approx 1$$

3. Effect of high concentration of D

(where $k_9[D] >> k_{-8}$)

No effect on the initial rate.

$$\text{Rate} = I \ \Phi_{isc} \ \Phi_{ct}\left(\frac{k_8(k_5 + k_6) + k_6k_7[A^-]}{(k_4 + k_5 + k_6)(k_8 + k_7[A^-])}\right)$$

4. Effect of high concentration of S

   a. increased light absorption at outer surface

   b. increased energy transfer rates (to outer surface)

   c. increased electron transport rates (k_6 and k_8)

   Initial Rate = $I \cdot \Phi_{isc} \cdot \Phi_{ct} \cdot \Phi_{sep}$

   As k_6 increases, an increase should be observed in

$$\Phi_{sep} = \left(\frac{k_5 + k_6}{k_4 + k_5 + k_6} \right)$$

In cases in which increased sensitizer produces an increase in initial rate (W.E. Ford Ph.D. Thesis), this points out that a process such as k_6 must be an important kinetic step. Specifically, electron transport to the charge-transfer complex (k_6) occurs as well as the normal electron transport (k_8), since k_8 does not appear in the initial rate law.

Optimization of the Reaction Efficiency:

1. Sensitizer with high triplet yield; $\Phi_{isc} \approx 1 \quad (k_1 >> k_o)$
2. High concentration of A; $\Phi_{ct} \approx 1 \quad (k_3[A] >> k_2)$
3. Remove A^- as formed; $k_7[A^-] \approx 0$
4. High concentrations of D; $k_9[D] >> k_{-8}$

It seems likely that each of the four processes above can be reasonably well optimized by simple adjustments of experimental conditions. The net effect of all of these would give a total quantum efficiency limited only by Φ_{sep}.

$$\Phi_{total} \approx \Phi_{sep} = \left(\frac{k_5 + k_6}{k_4 + k_5 + k_6} \right)$$

Optimization of Φ_{sep} seems to be the major difficulty at the present time. Efforts to optimize Φ_{sep} will have three aspects:

1. Minimization of k_4, the rate of deactivation of the charge-transfer complex by a reverse electron transfer. This is an extremely rapid reaction and the competing processes apparently have only limited success in competing with it. This reverse electron transfer should be slower in the case of a triplet radical pair than a singlet radical pair, since a spin inversion would be required. Furthermore, the application of an external magnetic field could decrease the rate of such a spin inversion, as discussed in an accompanying report.

2. Maximization of k_6, the rate of electron transfer across the membrane. This rate should increase with higher concentration of sensitizer in the membrane, to facilitate an electron hopping mechanism for electron transport. It would also be expected that a thinner membrane would give a more rapid rate of electron transport. Furthermore, additives or the membrane itself could be designed to facilitate electron transport.
3. Maximization of k_5, the rate of separation of the charge-transfer complex by removal of A^-. The electrical charges on the acceptor, the sensitizer, and the membrane surface can be arranged to facilitate the ejection of A^- as soon as it is formed. Initial experiments by Itamar Willner have been extremely promising in this regard. In fact, the magnitude of the effects he has observed serve to illustrate that the primary limitation on the experimental quantum yields has been due to Φ_{sep}, the separation of the initially-formed radical pair.

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