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VECTORIALLY PHOTOINDUCED ELECTRON-TRANSFER PROCESSES
ACROSS WATER-IN-OIL INTERFACES OF MICROEMULSIONS

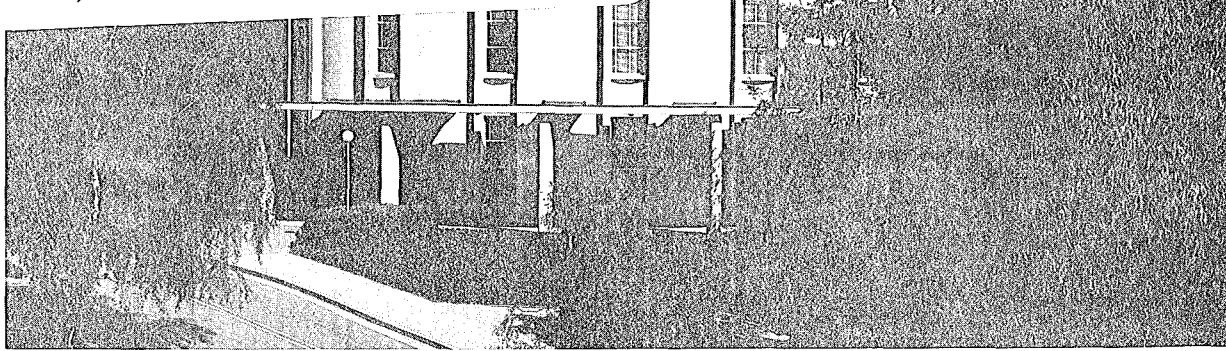
Itamar Willner, John W. Otvos, and Melvin Calvin

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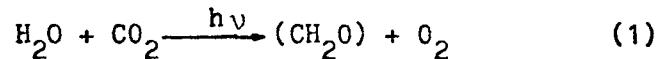
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Artificial photosynthetic devices are potential fuel sources. The basic idea in the design of such devices is a photosensitized electron-transfer that yields chemical species capable of reducing and oxidizing water to hydrogen and oxygen. A fundamental difficulty in effecting this transfer is the thermodynamically favored back reactions of the intermediary redox species. An interfacial model composed of a water-in-oil microemulsion is suggested to provide the separation of these redox species, thereby preventing back-reactions. This model is designed to accomplish the photodecomposition of water in two separate water-in-oil microemulsions coupled by a redox reaction. Phase-transfer of one of the redox products from the water-in-oil interface to the continuous organic phase is the principle by which separation is achieved. Two systems namely the oxidation and reduction sites of the general model, have been constructed. One system includes the photo-sensitized oxidation of a donor, EDTA, solubilized in the "water pool". In this system, benzylnicotinamide acts as a primary acceptor that mediates by the phase transfer principle the reduction of a secondary acceptor, dimethylamino-azobenzene, solubilized in the continuous organic phase. The second system involves the photosensitized reduction of methyl viologen, by tris(2,2'bipyridine)Ru(2+). In this system thiophenol is used as the donor and its oxidation product is phase transferred to the continuous organic phase. The

photoinduced processes accomplished in the two systems proceed along an uphill gradient of free energy. Two water soluble zinc-porphyrins, Zn-tetr phenylporphyrin sulfonate $[Zn\text{-TPPS}]^{4-}$ and $Zn\text{-tetramethylpyridiniumporphyrin}^{4+}$ $[Zn\text{-TMPyP}]^{4+}$ can substitute for the Ru(2+) complex in the second system. As the two Zn-porphyrins are oppositely charged, the effect of electrostatic interactions on the quantum yields of viologen reduction could be evaluated. The results suggest that the surface charge of the wateroil interface strongly influences the efficiency of electron-transfer.

INTRODUCTION

Devices that mimic the natural photosynthetic processes are of interest as fuel sources.¹⁻⁴ The net reaction of the photosynthetic pathway in green plants is the production of carbohydrates and oxygen from water and carbon dioxide using sunlight (1). This is a complex process of successive and simultaneous events that can be divided into photochemical and dark reactions.⁵⁻⁸ The photochemical reactions during which quantum conversion of



solar to chemical energy occurs, occur at two photoactive sites: photosystem I and photosystem II (Z - scheme, Figure 1). In photosystem II, an excited pigment transfers an electron to a chain of electron traps (plastoquinone, cytochrome f, etc.), leaving behind an electron "hole". The oxidized species thus formed oxidizes water to oxygen through mediation of catalyst(s) that accumulate oxidizing equivalents. In photosystem I, the excited pigment transfers an electron to a second electron trap, while electrons from trap II are supplied to the electron-deficient center of system I. Electrons trapped in photosystem I successively reduce ferredoxin and NADP (nicotinamide adenine di-nucleotide phosphate).⁶⁻⁸ The reduced NADP initiates the sequence of dark reactions,⁵ namely the Calvin cycle, in which CO_2 is reduced to carbohydrate.⁵ Photosystem II represents the oxidation of water to oxygen. The complementary photosystem I introduces a reducing power into the system. The electrochemical reduction potential of the primary acceptor in system I (ferredoxin) is about -0.4 vs. NHE, and this coincides with the potential of the redox couple H_2^+/H_2 at pH=7. Thus, from a thermodynamic point of view, the reducing potential introduced into photosystem I is equivalent to the potential required to reduce

Figure 1. Electron-transfer in photosynthesis-Z-scheme.

water to hydrogen. Thus the primary events of photosynthesis correspond in their redox properties to those required to decompose water and produce a potential fuel, hydrogen.

The bimimetic approach to designing artificial photosynthetic fuel devices is an attempt to simulate the essential features of the natural apparatus to the extent that water is decomposed. Since the photosensitization of electron-transfer reactions is the basic principle of photosynthesis, the artificial device (Figure 2) includes a sensitizer(s) that mimics the function of chlorophyll. The excited sensitizer induces an electron-transfer to an acceptor (A), which acts as an electron-trap. The oxidized sensitizer thus formed is reduced by a donor (D), and is regenerated. Consequently, the net result of this electron-transfer process corresponds to the photoproduction of a reduced species (A^-) and oxidizes species (D^+) along an endoergic pathway. Selection of the acceptor and donor in such a way that their reduced and oxidized forms are thermodynamically capable of reducing and oxidizing water to hydrogen and oxygen will allow one

Figure 2. General scheme for water photodecomposition.

to accomplish the photodecomposition of water. In this way, all the components of the system, except water, are recycled during the process.

The schematic cycle described in Figure 2 suffers from basic limitations due to the thermodynamically favored back reactions of the intermediates formed in the process (namely, back reactions between A^- and S_{ox} or D^+). As a result, the "useful" energy gained in the photochemical event producing the couple A^-/D^+ is degraded by the dark reactions (2) and (3). In the natural



process, membranes act as a kinetic barrier for the back reactions. It is believed that the two "half reactions" comprising the Z-scheme, Figure 1, are accomplished at opposite sides of a membrane separating two aqueous compartments. Such physical separation of the components of the two photoactive sites retards the back reactions^{10,11} and allows the subsequent utilization of the active species.

The problems involved in the construction of an artificial photosynthetic device can thus be resolved into the following parts:

- (a) Selection of synthetic sensitizers that mimic the function of chlorophyll;
- (b) Design of acceptors and donors capable of reducing and oxidizing water; and
- (c) Construction of molecular organizations that adopt the "membrane principle" whereby the separation of the redox intermediates is achieved and back reactions are prevented.

In the past few years we have attempted to solve these problems separately. Aspects of this research will be the subject of the following discussion.

Vectorial Photoinduced Electron-Transfer Across a Water-In-Oil Interface

A basic requirement in the construction of an artificial photosynthetic device is the need to separate reactive intermediates, formed photochemically, from back reacting with one another. One way of achieving this goal is to introduce an interface that controls unidirectional electron-transfer as well as physically separating the redox products. Several approaches to mimicking the "membrane principle" by artificial interfaces have been investigated. Micellar systems accomplish the physical separation of the redox products by their solubilization of components in two distinct environments: the continuous aqueous phase and the hydrophobic cavity of the micelles.¹²⁻¹⁴ In these systems the micellar surface charge can be utilized to control a vectorial electron-transfer and prevent back reactions using electrostatic charge repulsions.¹⁵ Another type of interface is the lipid bilayer membrane-vesicle.¹⁶⁻¹⁸ In this system, the lipid membrane separates two aqueous phases charged asymmetrically with the electron acceptor and donor. In such a way, the membrane functions as a barrier to the back reaction of the redox species accumulated in the aqueous compartments.

Recently, we proposed a water-in-oil microemulsion as a model system to control an electron-transfer in a vectorial fashion.¹⁹ Surfactant molecules aggregate in the form of reversed micelles in organic solvents similar to their aggregation to micelles in water. These reversed micelles can entrap water in their interior polar cavities, thus forming²⁰ a microemulsion of "water pools" in a continuous oil phase. The general model for the utilization of water-in-oil microemulsions in the photodecomposition of water is represented in Figure 3. The model consists of two half cells that include water-in-oil microemulsions, represented in Figure 3 as two water droplets. Using two sensitizers S_1 and S_2 , coupled redox reactions are induced photochemically to produce an oxidized donor (D_1^+) and a reduced acceptor (A_1^-) in the aqueous phases of the two separate half cells. The complementary redox products of this process (A_1^- and D_2^+) are confined by their solubilities to the continuous organic phase, so products are accumulated in the two distinct phases and back reactions are inhibited. The two half-cells are bridged by an electron and proton carrier (for example a quinone). As a result, the acceptor (A_1^-) and donor (D_2^+)

Figure 3. Model for the photodecomposition of water using water-in-oil microemulsions. The two water droplets represent two half-cells of water-oil microemulsions.

are recycled. By selecting the water soluble reduced acceptor (A_2^-) and oxidized donor (D_1^+) such that they can reduce and oxidize water, respectively, the original electron acceptor and donor are regenerated. In this way all the components of the system, except water, are recycled. The similarities of this model system to the natural photosynthetic system should be mentioned: the two half-cells of the model system substitute for the two photoactive sites of the natural process. The interface of the water-in-oil microemulsion is a synthetic approach to mimic the function of membranes in retarding back reactions. Coupling of the redox reactions in the two half-cells is essentially a duplication of the "in vivo" Z - scheme.

Photoinduced Electron-Transfer Across a Water-In-Oil Boundary, Separation of Redox Components by Phase-Transfer

The justification of the model system presented in Figure 3 requires demonstration of a photoinduced electrontransfer across the water-in-oil boundary, leading to the net separation of the photogenerated species in the two distinct phases. Solubilization of the sensitizer and one of the redox components in the aqueous phase, while confining the complementary redox component to the water-oil interface results in a compact structure (ca. 30 Å)²¹ that facilitates electron transfer.²² Designing the interface located redox component in such a way that its extraction to the continuous organic phase will occur subsequent to the electron-transfer process

is anticipated to separate the redox products in the two distinct phases. This idea is displayed in Figure 4. A sensitizer (S) and a donor (D) are solubilized in the aqueous phase and an acceptor (A_1), of amphiphilic character, is confined to the water-oil interface. The photoinduced electron transfer, mediated by the sensitizer (S), results in the production of a reduced acceptor ($A_1^{(red)}$) and oxidized donor (D^+). By selecting A_1 , so that its reduced form is extracted from the interface into the bulk organic phase, while the oxidized donor is confined to the aqueous phase, the net separation of products is achieved and back reactions are impeded. This phase transfer property of one of the redox products is essentially the basic principle for achieving the compartmentalization of the active species. In addition, by coupling of the reduced acceptor ($A_1^{(red)}$) extracted into the oil phase with a second acceptor (A_2), the interface located acceptor is recycled while the acceptor solubilized in the oil phase is reduced. Thereby, the phase-transferred acceptor ($A_1^{(red)}$) acts as a mediator for the electron-transfer across the interface.

These considerations have been guidelines for the construction of a microemulsion system in which an oxidized donor solubilized in the aqueous phase, was separated from a reduced acceptor confined to the bulk organic phase. In this system the donor, ethylenediamine- N,N,N',N' -tetraacetate (EDTA) and tris (2,2'-bipyridine)-ruthenium(II)-Ru(bipy)₃²⁺ as sensitizer, were dissolved in the

Figure 4. The separation of photoproducts by phase-transfer. Use of an interface located acceptor (A_1) as a mediator for the reduction of an acceptor (A_2) solubilized in the bulk organic phase.

aqueous droplets. Benzylnicotinamide (BNA^+) was used as a primary acceptor located at the interface. This acceptor was expected to fulfill the phase transfer requirements since its amphiphilic character insures initial localization at the water-oil interface, while upon reduction it would be extracted to the continuous organic phase due to charge removal.²⁴ In the organic phase, a second acceptor, 4-dimethylamino-azobenzene, was dissolved. The azo dye was expected to regenerate the interface-located acceptor, while being in turn reduced.²⁵ The oil soluble dye acceptor, 4-dimethylamino-azobenzene, absorbs in the visible spectrum ($\lambda_{\text{max}} = 402 \text{ nm}$ $\epsilon = 22000 \text{ M}^{-1} \cdot \text{cm}^{-1}$), while the corresponding hydrazo compound is colorless, so the reaction could be followed spectroscopically, and thus a probe for the complete electron transfer process was established.

A typical preparation of the microemulsion involved the addition of 0.15 ml of 0.3 M $(\text{NH}_4)_3\text{EDTA}$ aqueous solution ($\text{pH} = 8.5$) and 3 μl of a 0.01M $\text{Ru}(\text{bipy})_3\text{Cl}_2$ aqueous solution to a $5 \times 10^{-5} \text{ M}$ 4-dimethylamino-azobenzene-in-toluene solution (2.9 ml). Dodecylammonium propionate (220 mg, 0.3 M) and BNA^+ ($4.8 \times 10^{-3} \text{ M}$) were added, and the mixture was vortex stirred until clear. The solution was de-aerated with argon and illuminated with intervals of continuous blue light 440nm-550 nm, incident photon flux $\approx (13 \pm 3) \times 10^{-7} \text{ einsteins} \cdot \text{sec}^{-1}$). The illumination resulted in the reduction

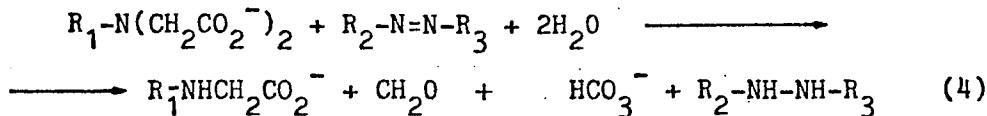
Figure 5. The reduction of 4-dimethylamino-azobenzene as a function of illumination time, monitored by the decrease of dye absorption at $\lambda = 402 \text{ nm}$ ($\epsilon = 22000 \text{ M}^{-1} \cdot \text{cm}^{-1}$).

of the dye and disappearance of its absorption at 402 nm (Figure 5). After four minutes of illumination, 80% of dye had been reduced ($\Phi_{\text{max}} = 0.13 \pm 0.04\%$). After the azo dye had been reduced, the concentration of the sensitizer appeared to be unchanged.

Control experiments, revealed that all the components included in the system were crucial for the azo dye reduction. By excluding $\text{Ru}(\text{bipy})_3^{2+}$, EDTA, or BNA^+ from the system, no reduction of dye was observed.²⁶ The fact that BNA^+ was required implies that it acted as mediating agent in the photoreduction of the dye. The amount of reduced azo dye, in comparison to the experimental mole ratio of dye: sensitizer (5:1), indicates that the sensitizer was recycled during the photochemical process. These results are rationalized by a photoinduced redox cycle presented in Figure 6. The excited $\text{Ru}(\text{bipy})_3^{2+}$ reduces the interface located acceptor, BNA^+ . The oxidized³ sensitizer, thus formed, is reduced by EDTA, thereby recycling the initial photoactive compound. The reduced acceptor produced at the interface is phase-transferred to the bulk organic phase and the azo dye is reduced.

Figure 6. Cyclic mechanism for photoinduced electron-transfer across the water-oil interface.

The reduced dye was identified as 4-dimethylamino-hydrazobenzene. Thus, the net reaction accomplished was the photoinduced reduction of 4-dimethylamino-azobenzene by EDTA. Based on the known oxidation products of EDTA^{17,18} the process is summarized in (4). The thermodynamic balance of this reaction, using glycine as a model for the oxidation

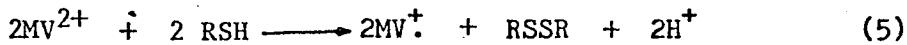


site of EDTA, reveals the process to be energy storing by approximately 37 Kcal/mole of EDTA consumed.

The results described so far demonstrate that an electron transfer across the water-oil interface along an endoergic pathway was accomplished. Recalling the original model displayed in Figure 3, this system represents the oxidation site half-cell, where, ultimately, oxygen is expected to be evolved.

Using a similar phase transfer principle as a means of separating redox components, we were able to construct the complementary reduction half-cell where hydrogen is expected to be evolved. In this system the acceptor dimethyl-4,4' bipyridinium dichloride (methyl viologen, MV²⁺), 6×10^{-3} M, was dissolved in the aqueous droplets (phosphate buffer, pH = 4.3) and Ru(bipy)₃²⁺ was used as sensitizer (1×10^{-4} M). Thiophenol (RSH), 0.1 M, was used as an electron-donor. This electron-donor was anticipated to be located at the interface of the water-in-oil microemulsion due to its amphiphilic character, but its oxidized product (RSSR²⁺) was expected to be extracted into the continuous organic phase. Illumination of the system with blue light ($\lambda = 400-550$ nm) resulted in the production of the blue methyl viologen radical MV⁺, ($\lambda_{\text{max}} = 603$ nm, $\epsilon_{\text{max}}^{2+} = 12400 \text{ cm}^{-1} \text{M}^{-1}$), $\Phi_{\text{max}} = 0.5\%$. Excluding the thiophenol or Ru(bipy)₃²⁺ from the system prevented the electron-transfer process and no MV⁺ was observed. The concentration of MV⁺ (16×10^{-5} M) produced photochemically demonstrated that the photosensitizer was recycled during the process. The photoinduced cycle conducted in the system is summarized in Figure 7. Photoexcited Ru(bipy)₃²⁺ transfers an electron to the acceptor producing MV⁺. The oxidized sensitizer oxidizes the interface located electron donor (RSH) and is recycled. The disulfide produced is extracted into the continuous organic phase and its separation from the water soluble reduced appear is

achieved. The net reaction induced photochemically represents the reduction of MV^{2+} by thiophenol (5). Based on the redox potential of the components involved in the



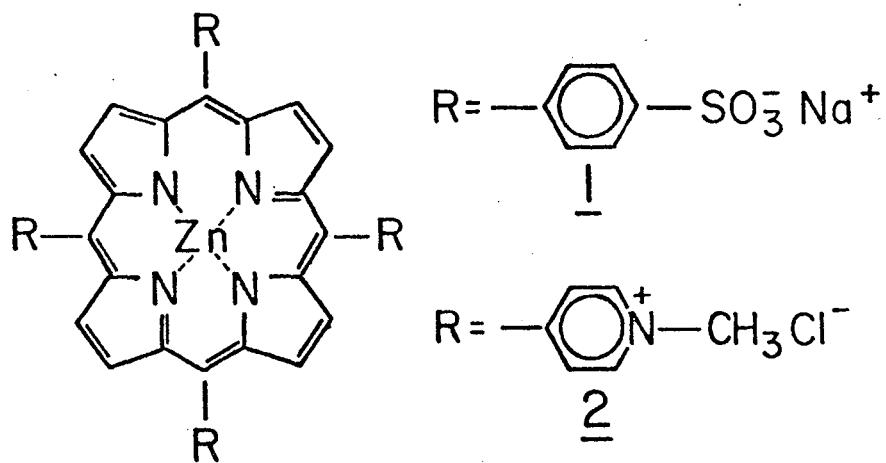
reaction: E° (thiophenol) = 0.11 V³¹, E° ($MV^{2+}/MV^{\cdot+}$) = -0.45 V³², and taking into account the pH-dependence of thiol oxidation and concentrations of components, the thermodynamic balance of the process is endoergic by ca. 7 Kcal/mole of thiol.

The use of thiophenol as donor should be emphasized. In the previously described system the electron donor, EDTA, was irreversibly decomposed during its oxidation. In the present system, thiophenol is a non-destructible electron donor²⁹ that allows further coupling with a redox cycle in the complementary half-cell (Figure 3). The reduced acceptor produced in the system, $MV^{\cdot+}$, can reduce water to hydrogen in the presence of solid catalyst such as Pt, PtO_2 or Au.³³⁻³⁵ Hence, the precursor for the hydrogen-evolving site has been constructed.

Figure 7. Photosensitized reduction of methylviologen (MV^{2+}). Separation of the redox products by phase transfer of the oxidized electron donor to the continuous organic phase.

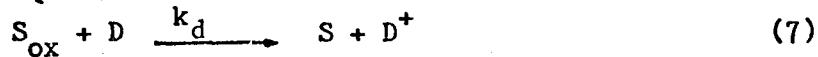
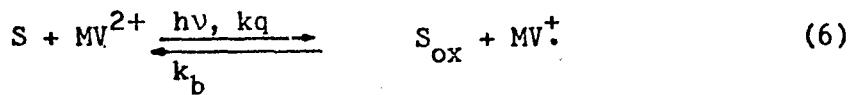
Effect of the Charged Interface on the Electron Transfer Process Across the Oil-Water Boundary

The systems described, so far, utilized $\text{Ru}(\text{bipy})_3^{2+}$ as the synthetic analogue of the natural chlorophyll to photosensitize the electron-transfer process. This synthetic dye absorbs only a limited fraction of the visible light ($\lambda_{\text{max}} = 460 \text{ nm}$). It is desirable to develop other sensitizers that absorb a wider range of the visible spectrum. Metalloporphyrins meet this requirement since they absorb in almost the entire visible light region and are known to induce photoredox reactions.³⁶ In particular, zinc-porphyrins are well established photosensitizers for inducing electron transfer reactions.³⁰⁻³⁸ Therefore, we investigated the previously described system, in which MV^{2+} is the water-soluble electron acceptor and thiophenyl is the interface-located electron donor, but $\text{Ru}(\text{bipy})_3^{2+}$ was replaced by water soluble Zn-porphyrins. The compounds used³ were Zn(II)-tetraphenylporphyrin sulfonate $[\text{Zn-TPPS}]^{4-}$ (1) and



$\text{Zn}(\text{II})$ -tetramethylpyridiniumporphyrin $[\text{Zn-TMPyP}]^{4+}$ (2). Illumination of the microemulsions including $[\text{Zn-TPPS}]^{4-}$ or $[\text{Zn-TMPyP}]^{4+}$ resulted in the production of MV^{\pm} . The quantum yields of MV^{\pm} production are displayed in Figure 8. It can be seen that $[\text{Zn-TPPS}]^{4-}$ was more efficient ($\Phi_{\text{max}} = 0.0067$) than $[\text{Zn-TMPyP}]^{4+}$ ($\Phi_{\text{max}} = 0.0025$) in inducing the redox cycle. The overall quantum yield of the electron-transfer process is determined by a sequence of reactions that include the rate of electron-transfer from the photoexcited sensitizer to MV^{2+} (k_a), the back-reaction (k_b), (6), and the reduction of S_{ox} by the donor (k_d), (7).

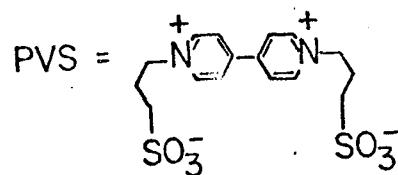
Figure 8. Quantum yields for photosensitized production of viologene radicals using Zn-porphyrins as sensitizers. Illumination with blue light 440 nm - 550 nm; incident photon intensity = $(13 \pm 3) \times 10^{-7}$ einsteins sec⁻¹. (A) [Zn-TMPyP]⁴⁺ as sensitizer, MV²⁺ (6×10^{-3} M) as acceptor. (B) sensitizer-[Zn-TPPS]⁴⁻; acceptor-MV²⁺ (6×10^{-3} M). (C) sensitizer-[Zn-TMPyP]⁴⁺, acceptor PVS° (6×10^{-3} M). (d) sensitizer-[Zn-TPPS]⁴⁻, acceptor PVS° (6×10^{-3} M).



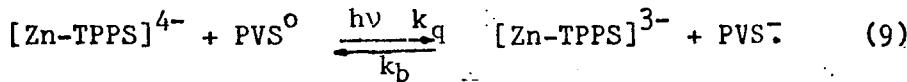
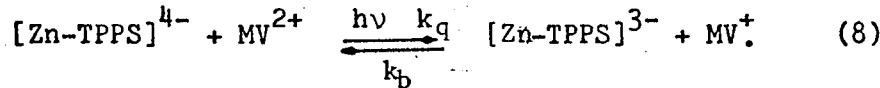
Recently, the kinetic parameters of electron-transfer from excited $[Zn-TPPS]^{4-}$ and $[Zn-TMPyP]^{4-}$ to MV^{2+} have been reported.³⁸ In aqueous solutions, the rate constant for electron-transfer from excited $[Zn-TPPS]^{4-}$ to MV^{2+} is higher by four orders of magnitude than that for $[Zn-TMPyP]^{4-}$. This difference has been attributed to electrostatic attractions between $[Zn-TPPS]^{4-}$ and MV^{2+} that facilitate the quenching process, and to differences in redox potentials of the two sensitizers that favor the electron-transfer from $[Zn-TPPS]^{4-}$. Thus, the enhanced quantum yield observed in the microemulsion system including (1) as photosensitizer, as compared to the microemulsion with (2), is in line with the properties of the two sensitizers.

The fact that the porphyrins 1 and 2 are oppositely charged allows examination of the influence of electrostatic effects on the efficiency of the photosensitized electrontransfer process. For this purpose propylviologen sulfonate (PVS⁰, 3) has been synthesized. The zwitterionic structure of (3) yields an overall neutral viologen whose reduced form is negatively charged PVS⁻. Thus, we anticipate that the quantum yields of the electron-transfer processes photosensitized by (1) or (2) and using MV^{2+} or PVS⁰ as acceptors, would be affected differently by electrostatic forces.

Illumination of a water-in-oil microemulsion composed of thiophenol, as electron donor, $[Zn-TPPS]^{4-}$ as photosensitizer, and propylviologen sulfonate, PVS⁰, (6×10^{-3} M) as electron acceptor resulted in the formation of viologen radical (PVS⁻) (Figure 8). The PVS⁻ production was four times as rapid as MV^+ formation. The difference in quantum yields can be attributed to electrostatic interactions of the positive interface of the microemulsion with the photoproduced species, resulting in prevention of back reactions.



Since structural changes in the alkyl substituents of viologens do not significantly affect their redox potentials,^{39,40} the enhanced efficiency in electrontransfer using PVS⁰ as acceptor cannot be attributed to differences in quenching of the excited sensitizer by the two acceptors.⁴¹ Furthermore, the mutual charge attraction of excited [Zn-TPPS]⁴⁻ and MV²⁺ would suggest an enhanced electron transfer to this acceptor (8).



Therefore, the effects of the interface on the reactants must predominate. The water-in-oil microemulsion system confines the encapsulated components to an aqueous microenvironment of ca. 20-30 Å. Hence, numerous collisions between either electron-acceptor and the sensitizer can occur during its excited state life time (1.5 ms)³⁸ independent of charge differences. Thus, the difference in quantum yields of viologen radicals production does not seem to originate from the primary electron-transfer event, but rather from prevention of the back-reactions between the reduced acceptor and oxidized sensitizer((8), (9.)

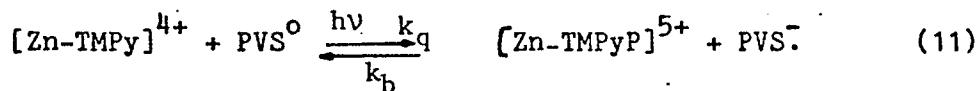
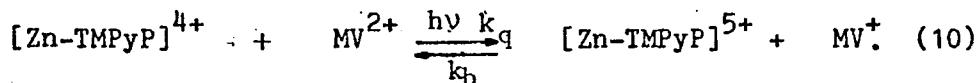
Figure 9. Photosensitized reduction of viologens by [Zn-TPPS]⁴⁻, using thiophenol as electron-donor: methylviologen (MV²⁺) as electron-acceptor (left), propylviologen sulfonate (PVS⁰) as electron-acceptor (right).

Electrostatic interactions between the positively charged interface of the water-oil microemulsion with the photoproduced redox species that results in control of their mutual back-reactions (9), are a rational explanation to the experiments result. The two negatively charged photoproducts using PVS^0 as acceptor, repel one another while being attracted by the positive interface. In this way, their separation is assisted and back reactions are prevented. With MV^{2+} as acceptor, the photoproducts are oppositely charged, and consequently the interface-charge effects are reduced by mutual electrostatic attractions (Figure 9).

Similarly, $[Zn-TPPS]^{4-}$ was replaced by the positively charged $[Zn-TMPyP]^{4+}$ (2) and the quantum yields of viologen radicals production using the two electron acceptors MV^{2+} and PVS^0 were compared. The quantum yields of the system are displayed in Figure 8. It can be seen that using $[Zn-TMPyP]^{4+}$ as photosensitizer the quantum yield of viologen radical production using PVS^0 as acceptor ($\Phi_{max} = 0.01$) is ca. four times that of the yield of MV^{2+} reduction ($\Phi_{max} = 0.0025$). The different efficiencies of viologen radical production imply that the positive water-oil interface is controlling the extent of back-reactions. With MV^{2+} as acceptor, the two positively charged photoproducts are repelled by the

Figure 10. Photosensitized reduction of viologens by $[Zn-TMPyP]^{4+}$, using thiophenol as electron-donor; methylviologen (MV^{2+}) as electron-acceptor (left), propylviologen sulfonate (PVS^0) as electro-acceptor (right).

positive interface and confined to the "water pools" (10). As a result, back-reactions appear to be significant. In the system with the zwitterionic viologen (PVS⁰), as electron acceptor, the photoproducts are oppositely charged (11). Although the formed species experience mutual electrostatic attractions, one of the products (PVS[·]) is attracted by the positive interface. Consequently, the redox species are separated and back-reactions are prevented (Figure 10).



In recent years the charge functionalization of micelles as a means of preventing back-reactions has been reported in several studies.^{14,15} Our results suggest that electrostatic interactions at the water-oil interface of microemulsions might similarly inhibit the back electron transfer. Eventually, further variations of the interface using neutral or negatively charged surfactants should be investigated. Meanwhile, the improved efficiency in the photoproduction of PVS[·] should be noted. Since viologen-radicals are capable of reducing water to hydrogen, our results suggest that derivatization of the viologen moiety could lead to improved hydrogen production.

CONCLUSION AND PERSPECTIVE

Several interfacial models that accomplish the separation of photoproduced redox species have been previously constructed. Micellar systems are capable of retarding back-reaction by utilizing surface potentials^{14,15} or self aggregation of one of the redox products.⁴¹ Also, lipid bilayer vesicles introduce a hydrophobic layer between two aqueous compartments as a barrier for back-reactions.^{16,18} In this paper a water-in-oil microemulsion is suggested as an additional approach to provide the separation of redox products. The phase transfer of one of the redox components into the continuous organic phase is the basic principle used to achieve the desired compartmentalization. The results presented suggest that the surface charge of the water-oil interface together with the electrostatic properties of the components can work cooperatively to improve quantum efficiencies. Utilization of these approaches in constructing rigid polymeric artificial membranes is a future goal.^{42,43}

Further attempts should be directed towards the development of hydrogen and oxygen evolving catalysts. Several hydrogen evolving mediators have been developed. Among them, the reduction of water by MV^+ in the presence of solid catalysts³³⁻³⁵ or natural hydrogenase enzymes³⁴ has been widely explored. It seems that developing homogeneous catalysts to evolve hydrogen might be advantageous.⁴⁵ The oxidation of water by $Ru(bipy)_3^{2+}$ in the presence of metal oxides has been reported^{46,47} and coupling to hydrogen evolution was achieved. Similarly, the use of manganese complexes, in particular manganese porphyrins is promising.⁴⁸⁻⁵⁰

Accomplishing the decomposition of water by a photoinduced redox cycle might lead to further developments of systems capable of CO_2 and N_2 fixation by similar photoinduced redox processes. The fact that nature has accomplished these processes encourages our attempts to construct artificial devices.

ACKNOWLEDGEMENT

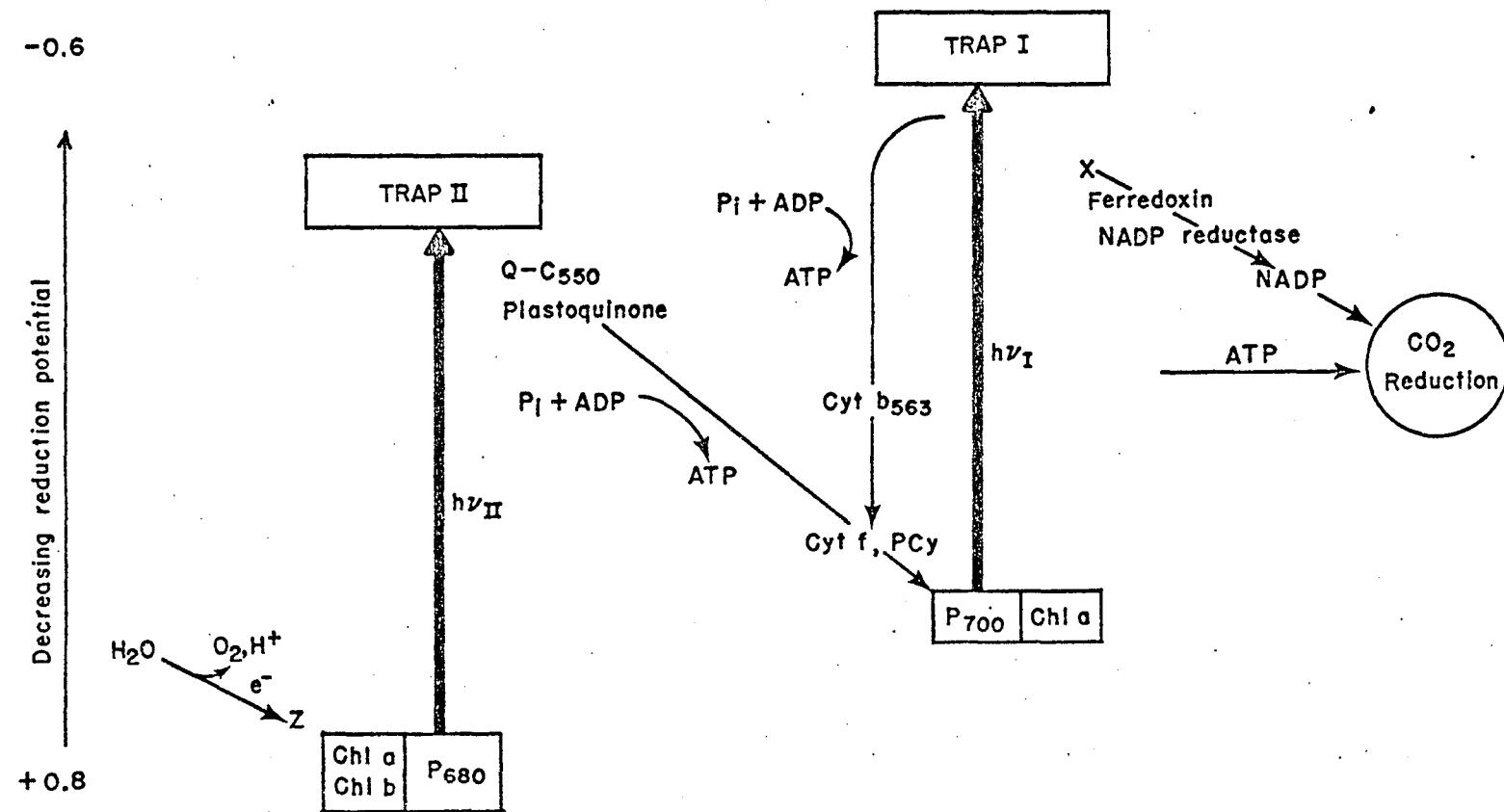
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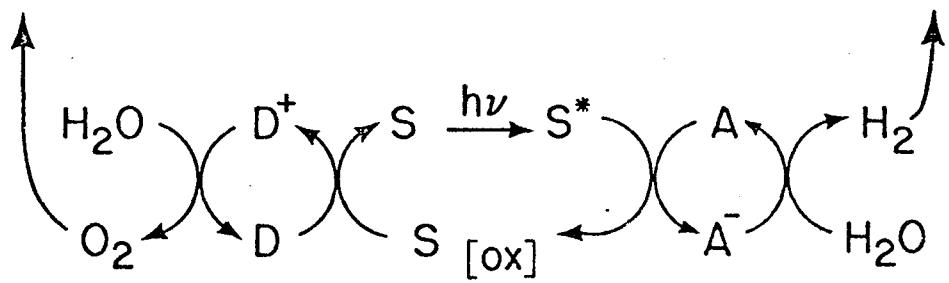


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Figure 1

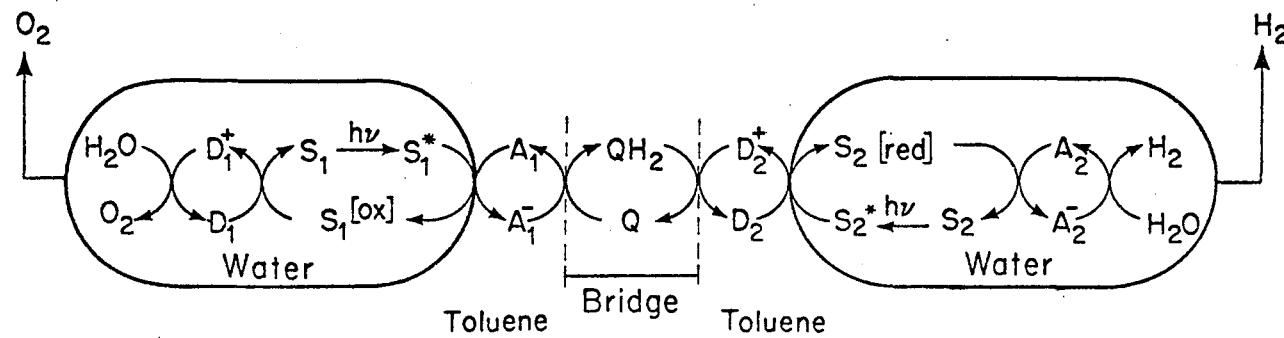
Willner, et al.



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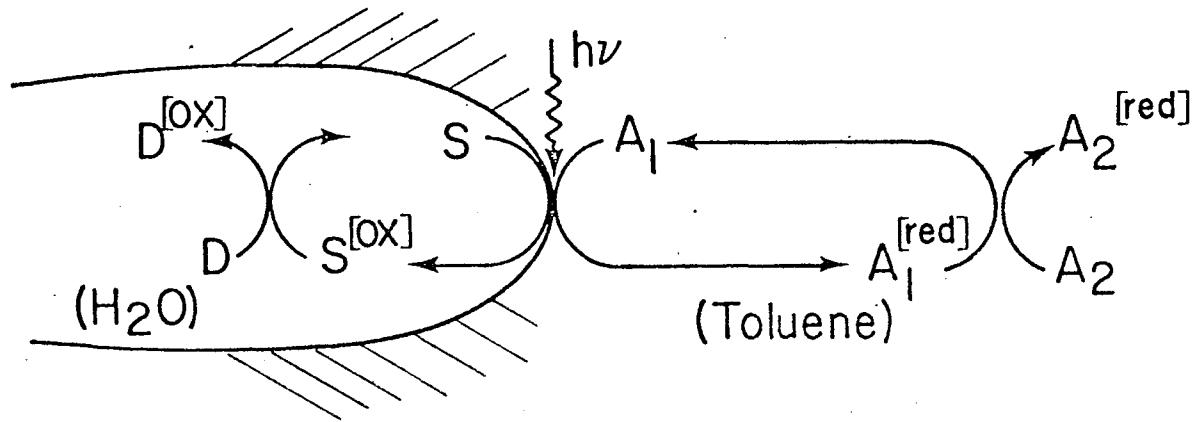
Figure 2

Willner, et al.



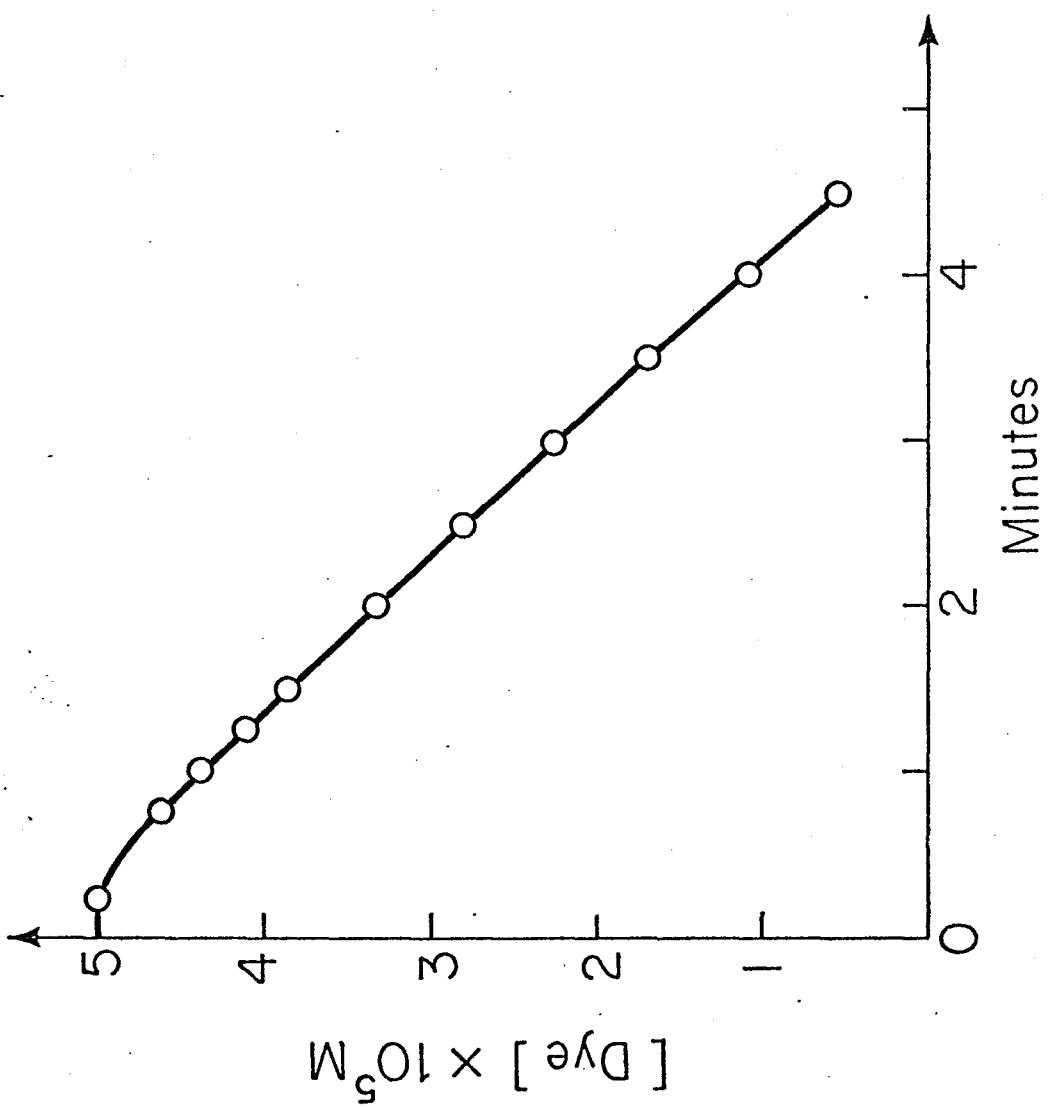
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Figure 3
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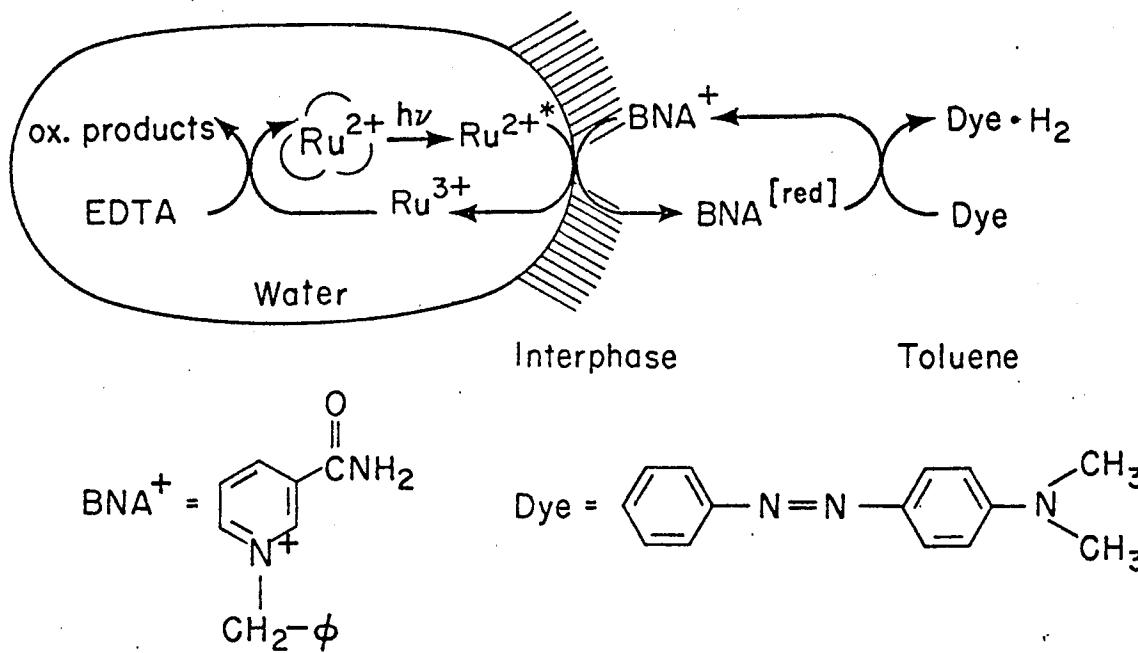
Figure 4
Willner, et al.



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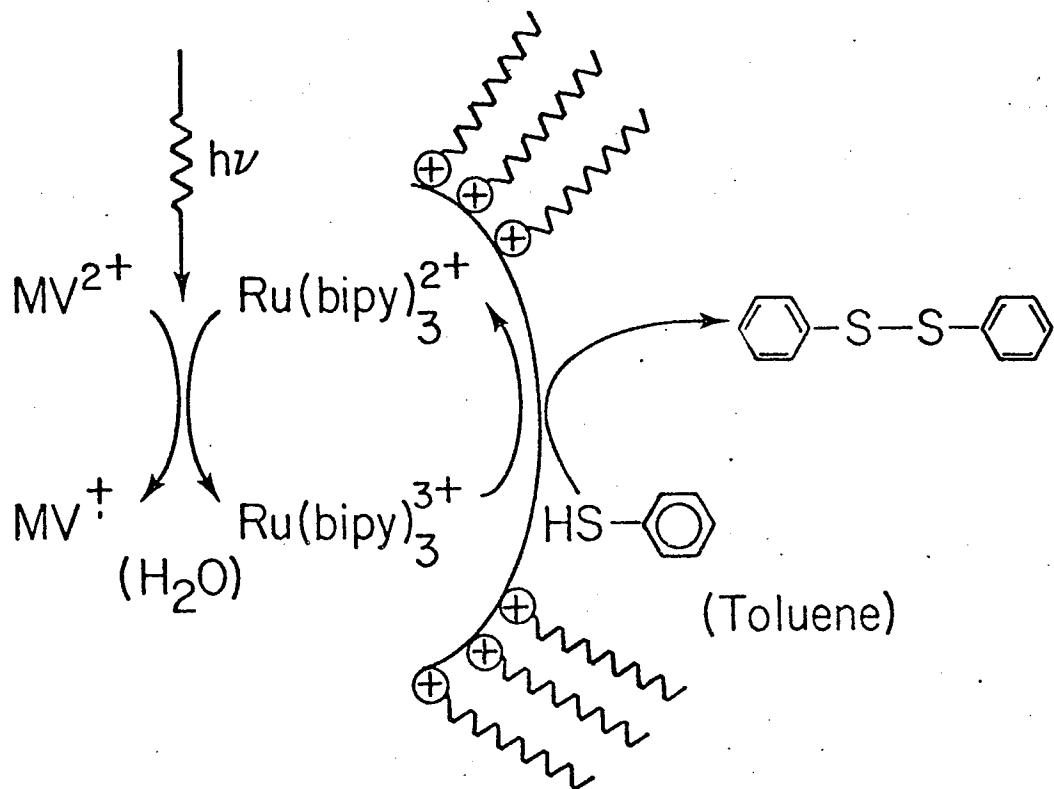
Figure 5

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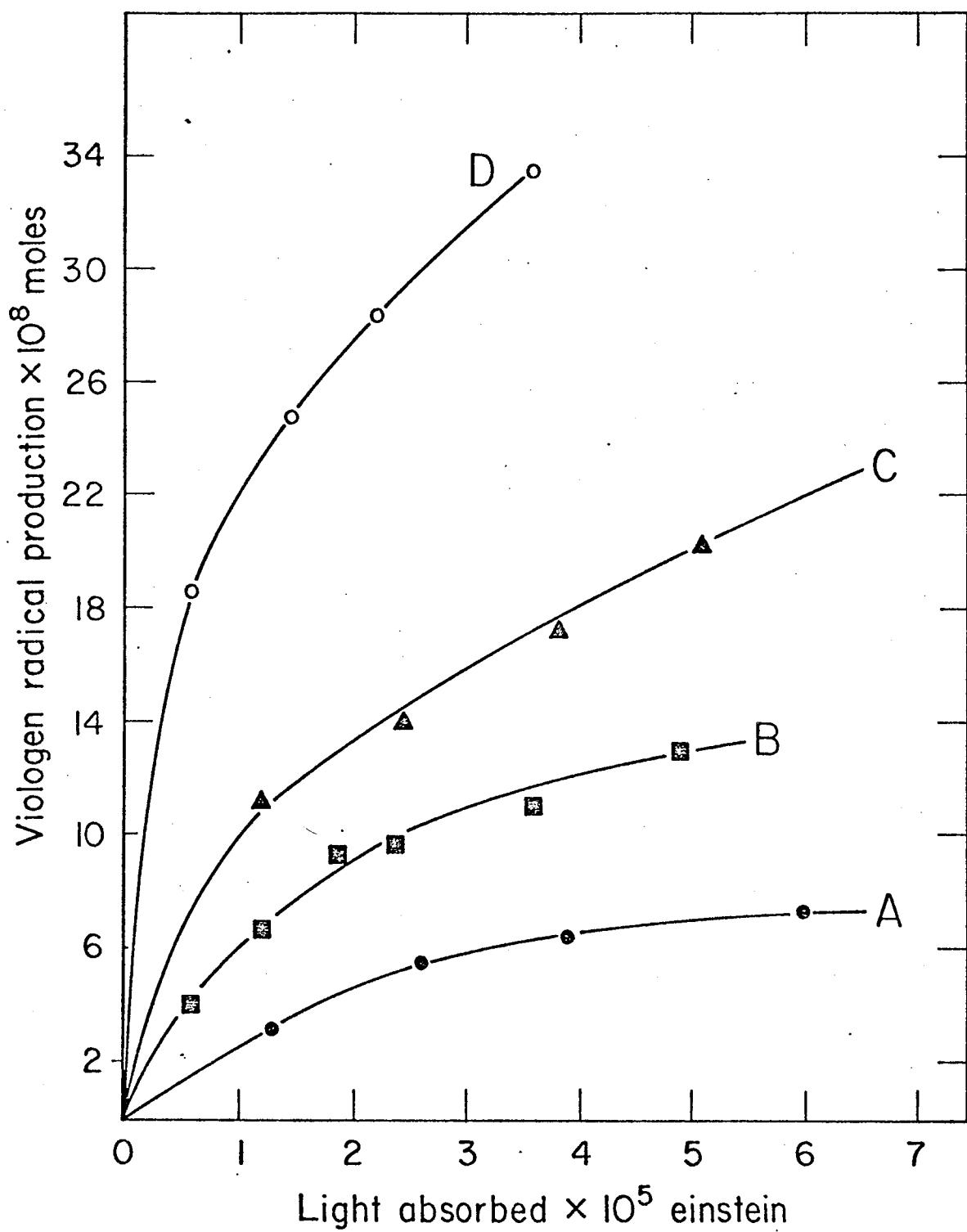
Figure 6
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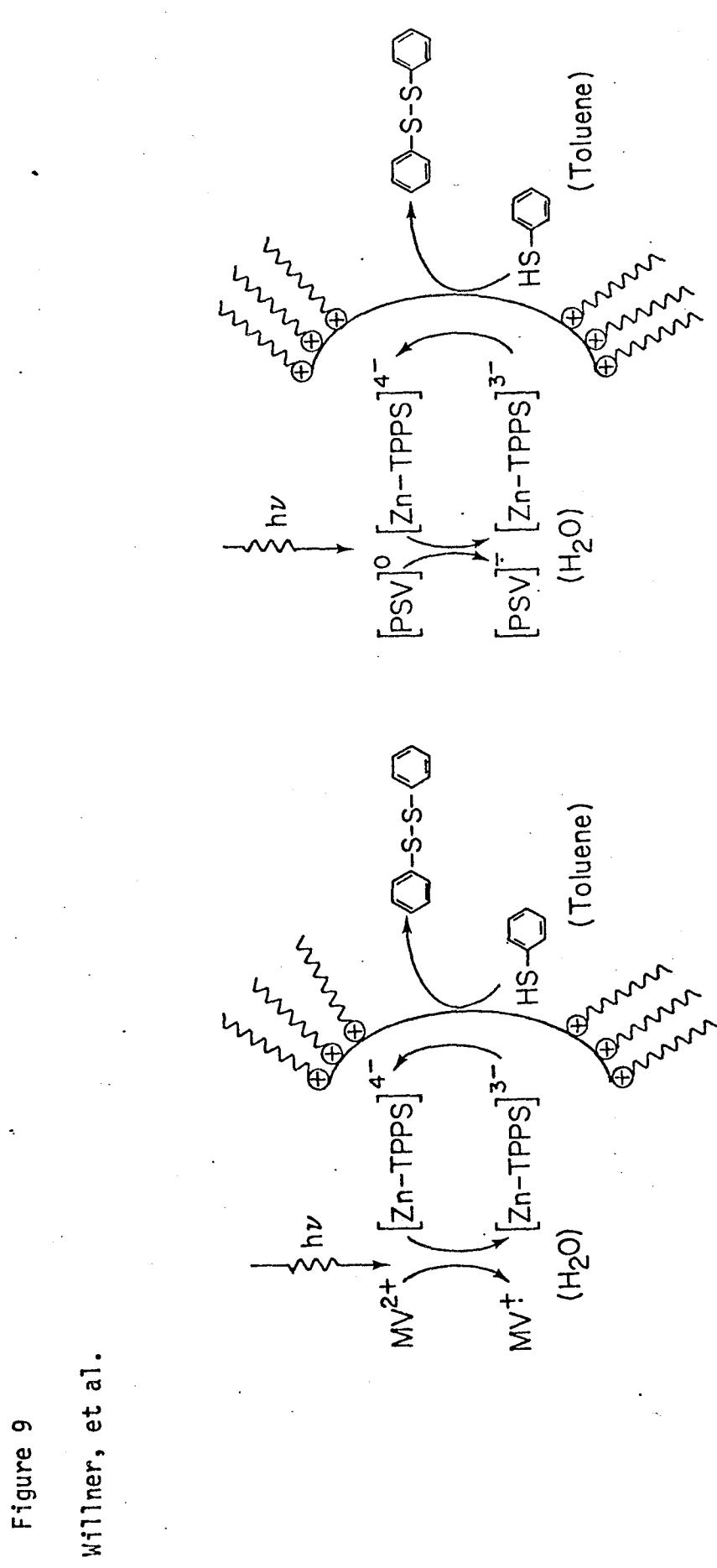
Figure 7

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Figure 8



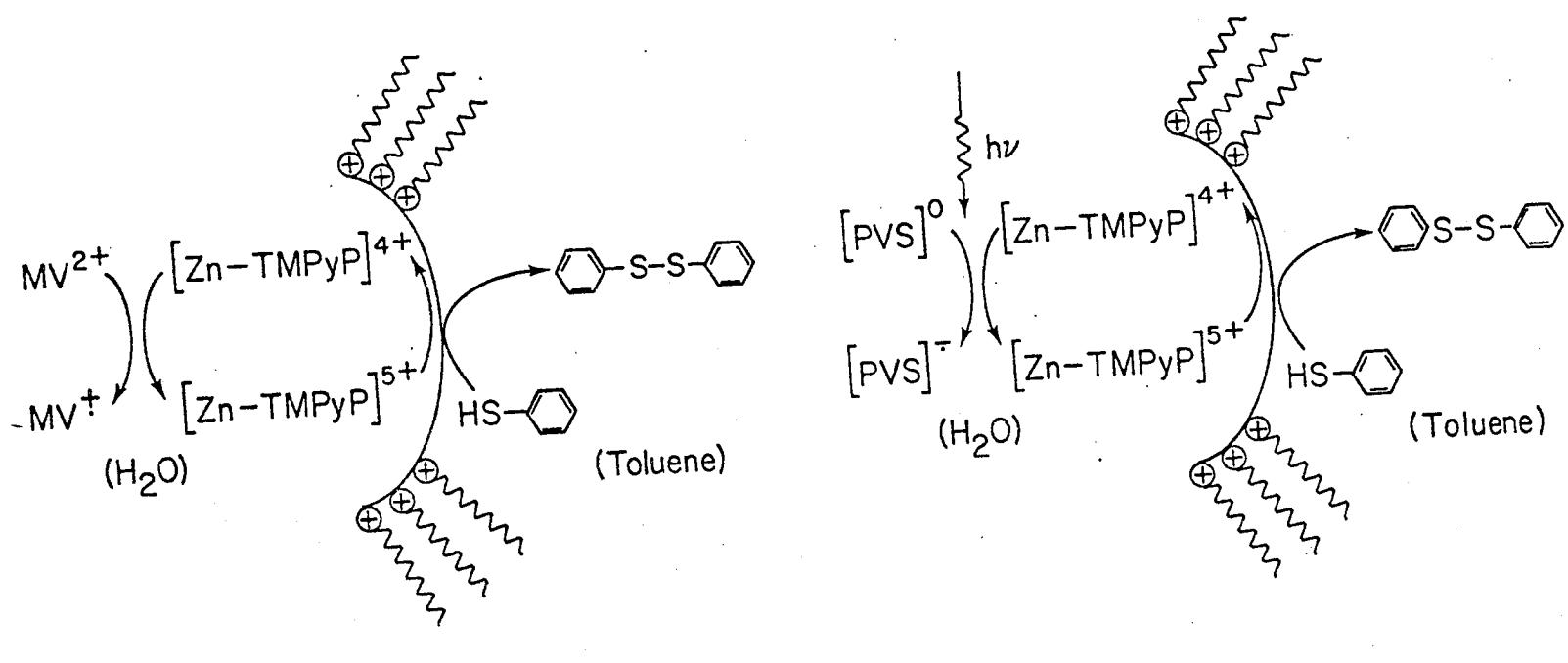


Figure 10

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