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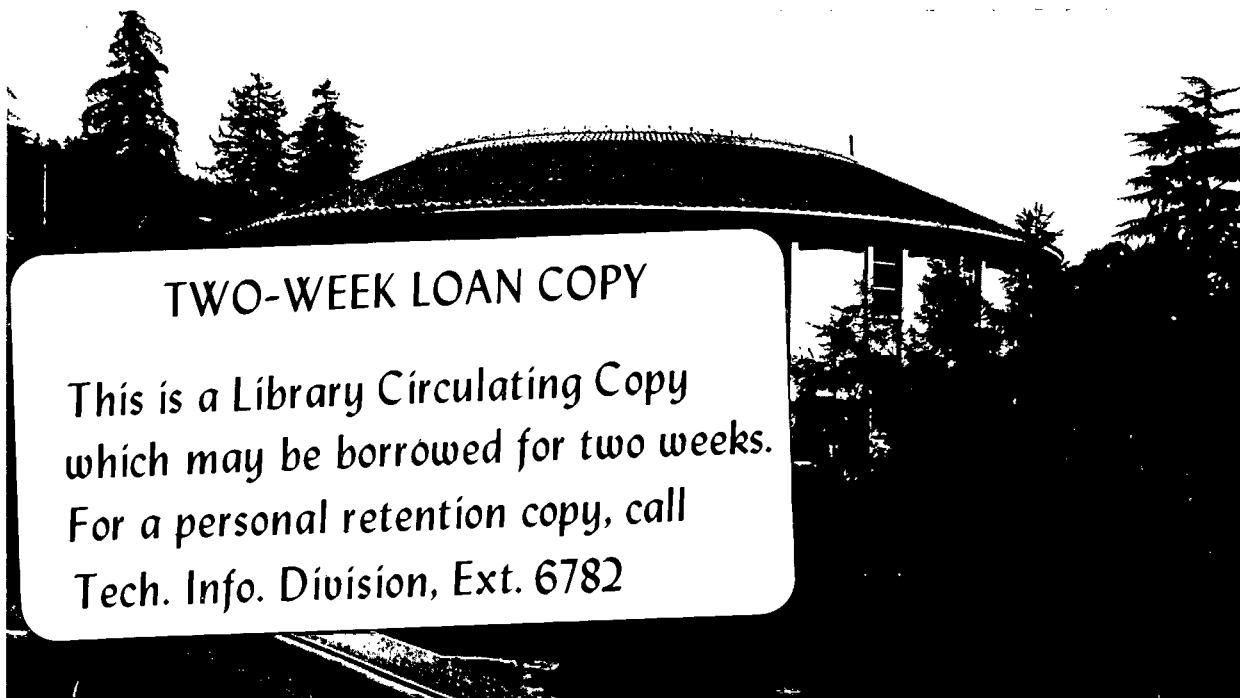
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BOUNDARY: A MODEL FOR REDOX REACTION SEPARATION

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Itamar Willner, William E. Ford, John W. Otvos, and Melvin Calvin

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**PHOTOINDUCED ELECTRON TRANSFER ACROSS
A WATER-OIL BOUNDARY:**

A MODEL FOR REDOX REACTION SEPARATION

by

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Photoinduced Electron Transfer Across a Water-Oil Boundary:

A Model for Redox Reaction Separation

The creation of artificial solar energy conversion and storage systems that mimic the photosynthetic pathway has evoked great interest in recent years.¹ One approach to the photolysis of water involves the mediation of a sensitizer in the generation of reduced and oxidized species that are the active components in the decomposition of water.^{2,3} However, homogeneous (aqueous) solutions of these components suffer from the basic limitation that the reducing and oxidizing agents can react with each other and thus no net reaction can be observed. Several kinds of synthetic "photosynthetic membranes" have been suggested as a means of separating the two redox units and overcoming these fundamental difficulties.³ Recently, photosensitized electron transfer across vesicle walls has been demonstrated and suggested as a means for generating oxidizing and reducing agents in separate water compartments.⁴

We wish to report a photochemical electron transfer across the interface of a water-in-toluene microemulsion, and to propose this system as a model for the separation of oxidized and reduced species. It is well known that surfactant molecules aggregate to reversed micelles in organic solvents.⁵ Reversed micelles entrap water to form "water pools" in a continuous oil phase. The proposed general model for the compartmentalization of two water phases and its utilization in the photolysis of water is represented in Figure 1. The model system involves the generation of an oxidized donor (D_1^+) and a reduced acceptor (A_2^-) in the water droplets of two separate half cells \wedge using the two sensitizers S_1 and S_2 respectively. The complementary redox

agents of these process (A_1^- and D_2^+) are confined to the organic phase and thus back reactions are inhibited. The two half cells are bridged by electron and proton carriers to regenerate the active components of the system. Thus, all the components, except water, are recycled.

In principle, the electron transfer process of one half cell can be divided into two distinct parts: (a) from the water to the interphase, (b) from the interphase into the continuous organic solution. Electron transfer from the water phase to the interphase was investigated in a microemulsion in which the "water pools" included ethylenediamine-N,N,N',N'-tetracetate (EDTA) as donor and tris(2,2'-bipyridine)ruthenium(II) ($Ru(bipy)_3^{2+}$) as photosensitizer. The acceptor, 1,1'-dihexadecyl-4,4'-bipyridinium chloride (HV^{2+}), is expected to be located at the interphase boundary as a result of its amphiphilic structure. The microemulsion was prepared by adding 0.15 ml of 0.3 M ammonium EDTA solution (pH = 8.5) and 21 μ l of 10^{-2} M $[Ru(bipy)_3]Cl_2$ solution to 2.9 ml of toluene containing 220 mg of dodecylammonium propionate as surfactant (0.3 M with respect to the surfactant). The mixture was vortex stirred to clarity. Into the resulting solution 2 mg of HV^{2+} were dissolved by vortex stirring. The microemulsion solution was transferred into a cuvette of 1 cm pathlength, and an inert atmosphere in the cell was generated by evacuation followed by nitrogen bubbling through the solution for 15 minutes. The contents of the sealed cuvette were stirred while being illuminated with blue light (incident photon flux $\sim 10^{-16} \times 10^{-7}$ einstein \cdot s $^{-1}$). The formation of HV^+ was followed spectroscopically.⁶ After 4 minutes of illumination 75% of the parent HV^{2+} had been reduced ($\phi_{max} = 1.3 \pm .4\%$). Introducing air into the cuvette reoxidized HV^+ to HV^{2+} and revealed that no change in the original $Ru(bipy)_3^{2+}$ concentration occurred.

Furthermore, the fact that the mole ratio $HV^{2+}:Ru(bipy)_3^{2+}$ was 13:1 emphasizes that the photosensitizer acted as a catalyst and was recycled during the HV^{\dagger} formation. These results are rationalized by the electron transfer from the excited $Ru(bipy)_3^{2+}$ to the interphase located acceptor HV^{2+} . The resulting $Ru(bipy)_3^{3+}$ is reduced by EDTA and thus the photosensitizer is recycled (Figure 2). Therefore, electron transfer from a donor in the water phase to an acceptor in the interphase has been demonstrated.

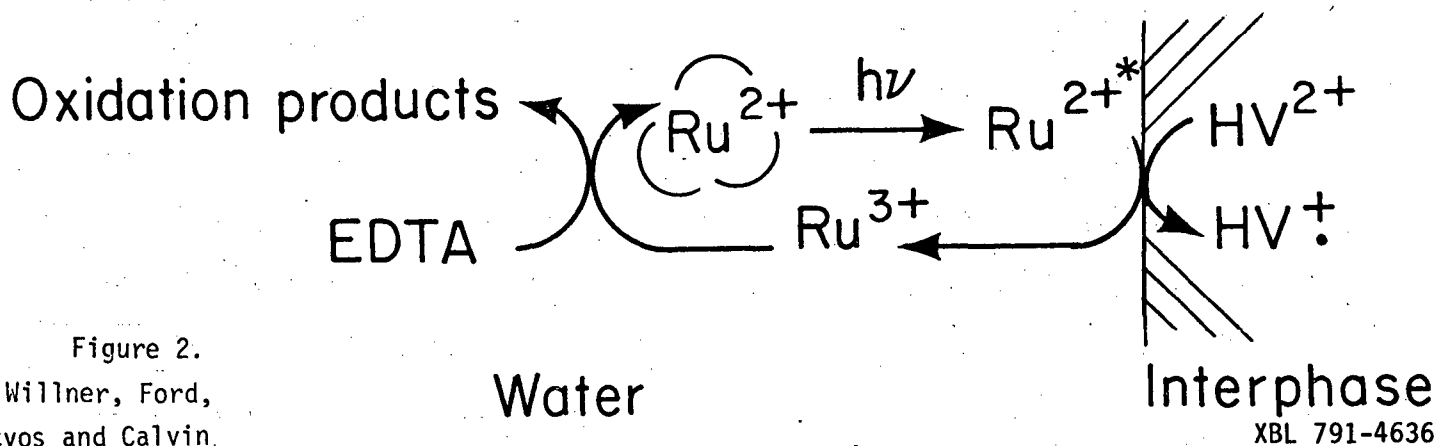


Figure 2.
Willner, Ford,
Otvos and Calvin.

However, in order to simulate the general scheme proposed in Figure 1, electron transfer into the continuous organic phase is required. An acceptor that is originally located in the interphase, while its reduced form is extracted from this region, into the bulk organic phase, seems to be desirable for this purpose. Furthermore, coupling of this acceptor with a second acceptor present in the continuous organic phase should regenerate the acceptor at the interface. Benzylnicotinamide (BNA^{\dagger}) seems to fulfill these requirements, as it is expected to concentrate at the interface, while its reduced form should migrate into the bulk organic solution.⁷ Hence, we have investigated the photosensitized reduction of the dye, 4-dimethyl-aminoazobenzene (Dye) present in the continuous organic phase, mediated by

BNA^+ at the interface and $\text{Ru}(\text{bipy})_3^{2+}$ in the water droplets. As in the previous experiment, EDTA was used as donor. The microemulsion system was prepared as follows. Into 2.9 ml of a 5×10^{-5} M solution of 4-dimethylaminoazobenzene in toluene were dissolved 230 mg of dodecylammonium propionate and 3.7 mg of BNA^+ (4.8×10^{-3} M). To the toluene solution were added 0.1 ml of ammonium EDTA solution (0.3 M, pH=8.5) and 3 μl of $\text{Ru}(\text{bipy})_3^{2+}$ solution (10^{-2} M). The resulting microemulsion solution was illuminated under an inert atmosphere with blue light. The progress of the electron transfer process was followed by the disappearance of the dye absorption at $\lambda = 402$ nm ($\epsilon = 22000 \text{ M}^{-1} \text{ cm}^{-1}$). The change in the dye concentration as a function of illumination time is represented in Figure 3. After 4 minutes of illumination, 80% of the dye had been reduced ($\phi_{\text{max}} = 0.13 \pm .04\%$). The reduced dye product (DyeH_2) was identified as the corresponding hydrazo derivative. Upon the introduction of I_2 or H_2O_2 , the reduction product DyeH_2 could be reoxidized to the diazo-dye.⁸ At the end of the dye photoreduction, the $\text{Ru}(\text{bipy})_3^{2+}$ concentration appeared to be unchanged. The experimental mole ratio of Dye: $\text{Ru}(\text{bipy})_3^{2+}$ (5:1), indicates the photocatalytic activity of the ruthenium complex. Furthermore, in control experiments excluding any of $\text{Ru}(\text{bipy})_3^{2+}$, EDTA, or BNA^+ , no reduction of the dye could be observed upon illumination. Hence, all the components of the system are crucial in the reduction process. The fact that BNA^+ is required in the process emphasizes that it serves as a mediating agent in photoreduction of the dye.

as shown in Figure 4.

These results are rationalized by a cyclic redox mechanism. The electron transfer from photoexcited $\text{Ru}(\text{bipy})_3^{2+}$ to BNA^+ is followed by the reduction of the dye dissolved in the continuous organic phase. The photosensitizer is in turn regenerated by the oxidation of EDTA. The thermodynamic balance

of the net reaction, reduction of the Dye by EDTA to the corresponding hydrazo derivative, is uphill in free energy ($\Delta G^\circ \sim 37$ kcal/mole of EDTA consumed).⁹ Thus, the process represents a net storage of energy.

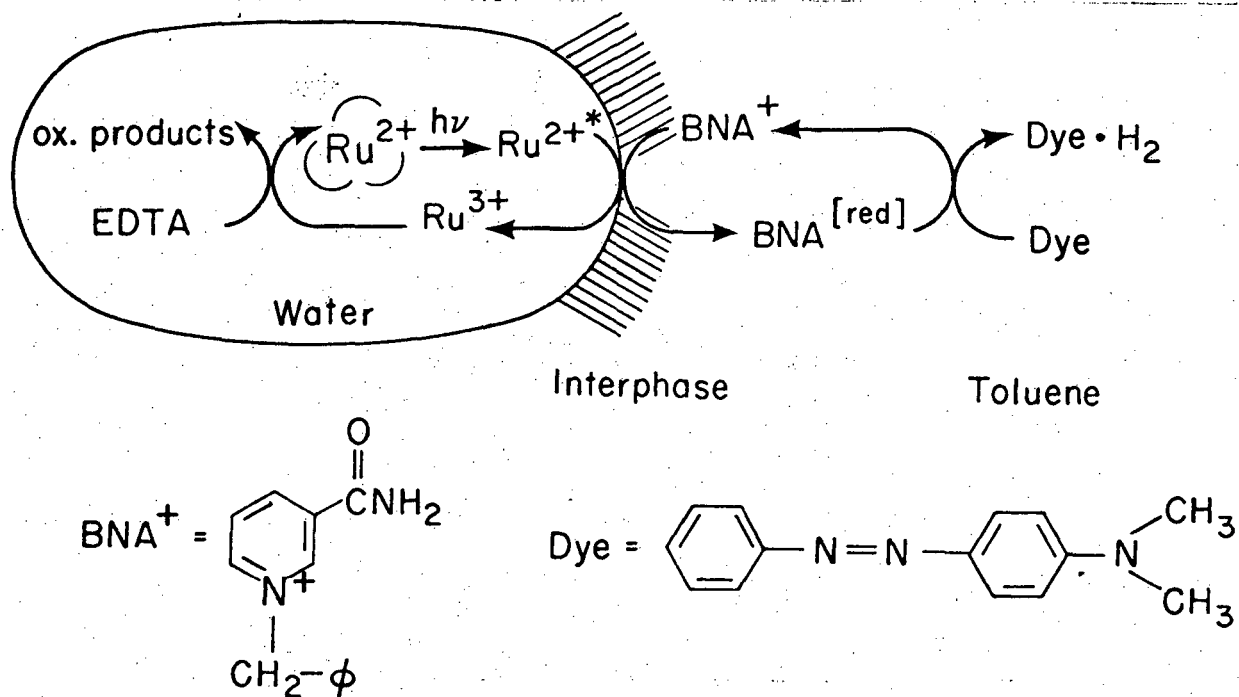


Figure 4. Willner, Ford, Otvos and Calvin

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In view of these results, a photosensitized uphill redox reaction across the interface of water-oil has been carried out. The compartmentalization of the redox reaction may serve as a key solution in the photolysis of water. Further steps, involving reversible acceptor/donor couples separated by this interface, as well as the introduction of adequate agents for the oxidation and reduction of water, are under current investigation.

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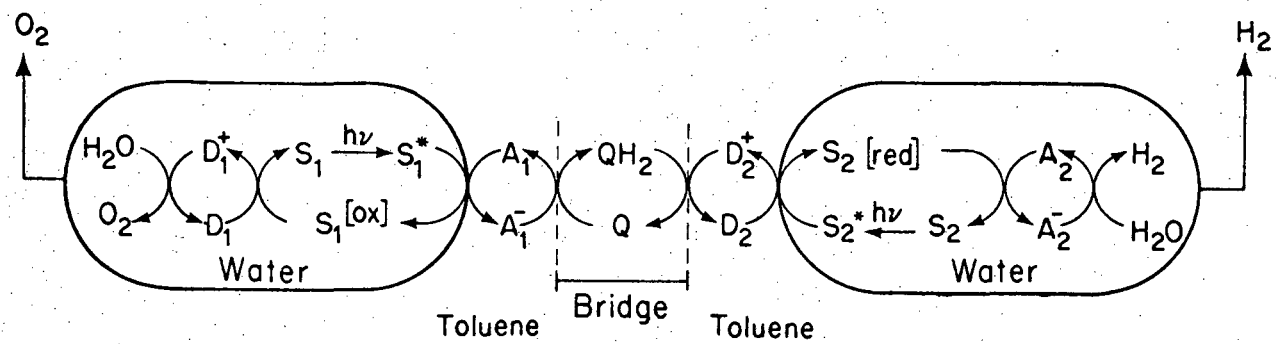
Figure Legends

Figure 1. General scheme for water photolysis.

Figure 2. Electron transfer from the aqueous phase to an acceptor in the interphase.

Figure 3. The reduction of 4-dimethylaminoazobenzene as a function of illumination time.

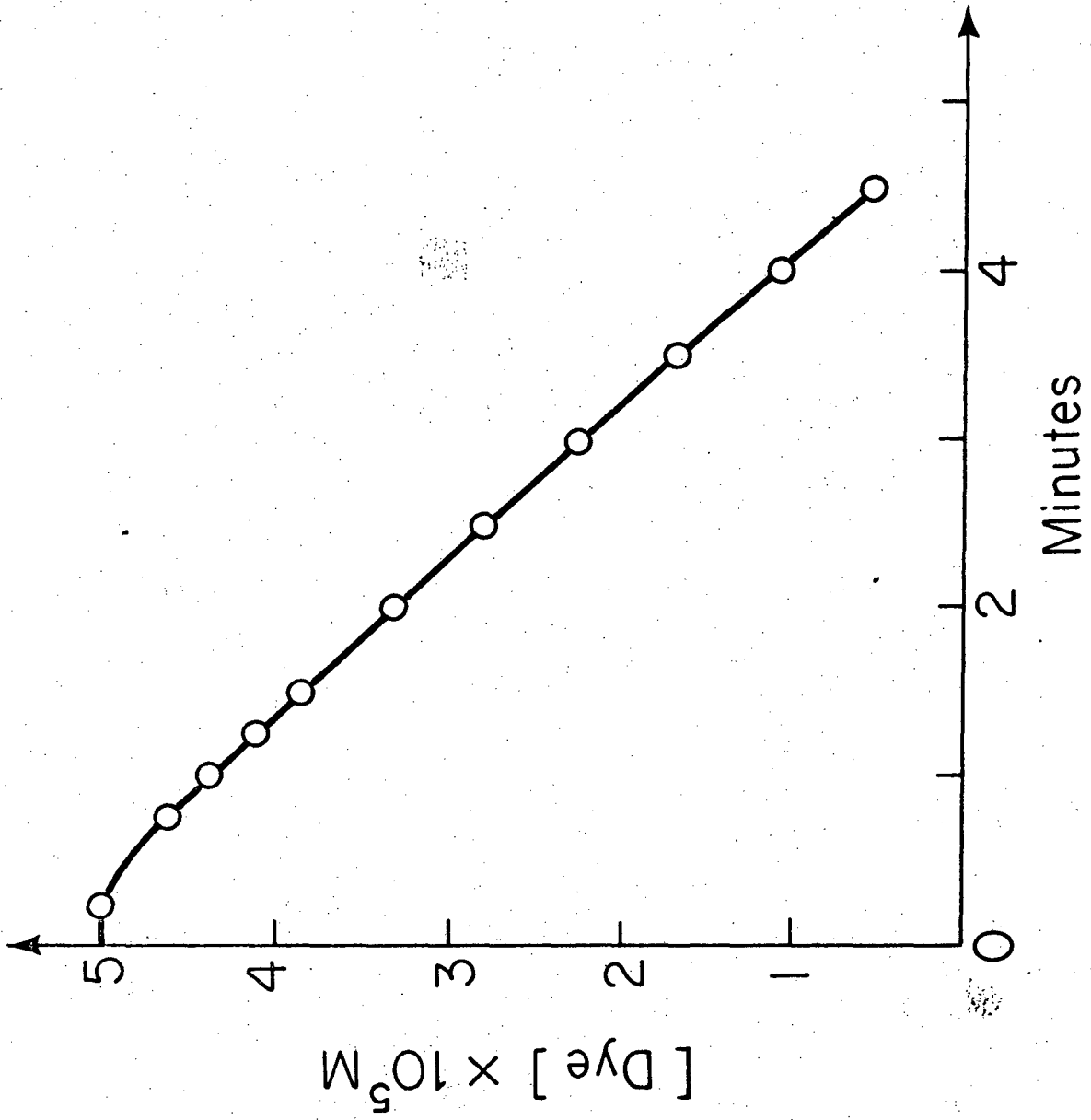
Figure 4. Cyclic mechanism for electron transfer across the interface.



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Figure 1. Willner, Ford, Otvos and Calvin

Figure 3. Willner, Ford, Otvos and Calvin



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