

TRANSFORMATION OF SINGLE-ELECTRON TRANSFER PHOTOPRODUCTS INTO MULTIELECTRON CHARGE RELAYS: THE FUNCTIONS OF WATER-OIL TWO-PHASE SYSTEMS AND ENZYME CATALYSIS[†]

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Summary

Water-in-oil microemulsions provide an organized environment that effectively controls photosensitized electron transfer processes. Effective charge separation and stabilization of the intermediate photoproducts against back electron transfer processes are achieved by means of hydrophobic and hydrophilic interactions of the photoproducts with the water-oil phases.

Water-oil two-phase systems also provide a means for induced disproportionation of a photogenerated one-electron transfer product to the corresponding two-electron charge relay. This induced disproportionation can be achieved by design of opposite solubility properties of the comproportionation products in the two phases. The two-electron charge relay mediates the reduction of *meso*-1,2-dibromostilbene to *trans*-stilbene.

An alternative route for generating multielectron charge relays involves the enzyme-catalysed production of dihydronicotinamide adenine dinucleotide phosphate (NADPH) using the 4,4'-bipyridinium radical cation as an electron carrier. NADPH is subsequently utilized in the reduction of 2-butanone to (–)-2-butanol in the presence of the enzyme alcohol dehydrogenase.

1. Introduction

Mimicking photosynthesis by means of artificial systems seems to be a promising route for chemical synthesis as well as for solar energy conversion and storage [1, 2]. One possible cycle that has been extensively examined in recent years [3, 4] is displayed in Fig. 1. It involves a light absorbent S that

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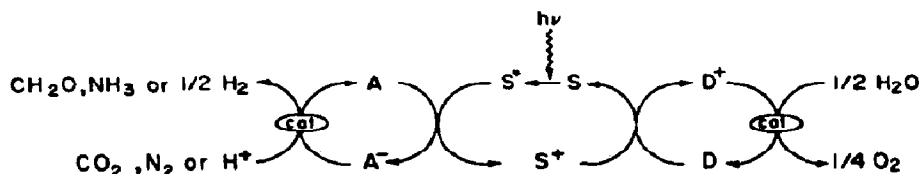


Fig. 1. Scheme for conversion of light energy to chemical potential using a photosensitized electron transfer cycle.

on excitation induces transfer of an electron to an electron acceptor A, leading to the photoproducts S^+ and A^- . Subsequent oxidation of an electron donor D recycles the sensitizer and results in the conversion of light energy to chemical potential, stored in the products A^- and D^+ :



The photoproducts A^- and D^+ can then be utilized in chemical routes, e.g. the reduced photoproduct A^- can be used for the reduction of water to hydrogen, fixation of CO_2 or nitrogen to organic fuels or ammonia and reduction of organic substrates. The oxidized photoproduct D^+ might be utilized in oxidation processes such as evolution of oxygen from water or oxidation of organic compounds, i.e. epoxidation of olefins. Thus, a variety of coupled photochemical-chemical processes might be envisaged that drive photosynthetic or photocatalytic reactions, converting abundant materials to fuels or useful chemicals:



The design of such artificial photosynthetic systems suffers from some basic limitations.

(a) The recombination of the photoproducts A^- and S^+ or D^+ is a thermodynamically favoured process. These degradative pathways prevent effective utilization of the photoproducts in chemical routes.

(b) The processes outlined in eqns. (2) - (4) are multielectron transfer reactions, whereas the photochemical reactions are single-electron transformations. Thus, the design of catalysts acting as charge relays is crucial for the accomplishment of subsequent chemical fixation processes.

Significant progress in the development of such artificial photosynthetic systems, particularly aimed at the photolysis of water, has been reported in recent years [3, 4]. Several approaches to resolve the problems involved in controlling the photoinduced electron transfer process as well as the develop-

ment of catalysts for multielectron fixation processes will be discussed in this paper.

2. Control of charge separation by means of water-in-oil microemulsions

The photosensitized electron transfer process involves two successive steps:



In the primary event an encounter cage complex of the photoproducts is formed. This can either recombine to yield the original reactants or dissociate into separated photoproducts. The separated photoproducts can then recombine by a diffusional back electron transfer reaction to form the original reactants. Two conceptional approaches might be used as a means of assisting the separation of the encounter cage complex and the stabilization of the separated photoproducts against the degradative recombination processes. One approach involves the use of electrostatic interactions between a charged interface and photoproducts that exhibit properly designed electric properties [5]. A variety of charged interfaces such as micelles [6, 7], polyelectrolytes [8] and colloids [9 - 11] have been used to assist the separation of the components of the primary encounter cage complex as well as to stabilize the photoproducts against the back electron transfer reactions. A second approach for controlling the electron transfer process involves the use of water-oil two-phase systems, where hydrophobic and hydrophilic interactions of the photoproducts with the microenvironments affect the charge separation [12]. This approach is exemplified in Fig. 2 in which a water-in-oil microemulsion is used as the two-phase system. The photoreactants are solubilized in the aqueous microdroplets, while the reduced photoproduct is designed to exhibit hydrophobic character. The photoinduced electron transfer process occurring in the aqueous media results in the extraction of the reduced photoproduct A^+ from the water phase into the oil medium and consequently charge separation might be assisted.

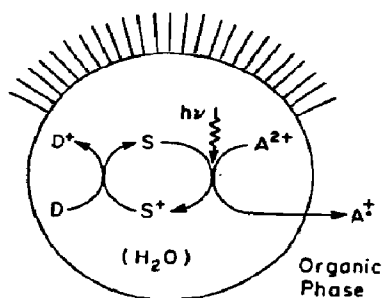
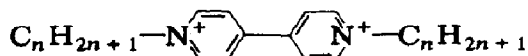


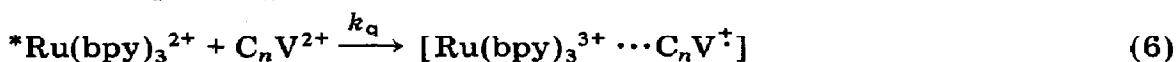
Fig. 2. Charge separation and retardation of back electron transfer reactions by means of hydrophobic and hydrophilic interactions in water-in-oil microemulsions.

To test the feasibility of controlling photosensitized electron transfer reactions in multiphase systems, we have examined the photoreduction of a series of *N,N'*-dialkyl-4,4'-bipyridinium salts C_nV^{2+} 1 (where $n = 1 - 18$)



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with ruthenium(II) tris-bipyridine ($Ru(bpy)_3^{2+}$) as a sensitizer and triammonium ethylenediaminetetraacetic acid ($(NH_4)_3(edta)$) as an electron donor in a water-in-oil microemulsion [12]. The microemulsion systems consisted of 1.5 vol.% water in toluene stabilized by dodecylammonium propionate (9×10^{-2} M) and included the sensitizer $Ru(bpy)_3^{2+}$ (2×10^{-5} M), the electron acceptor C_nV^{2+} (1×10^{-4} M) and $(NH_4)_3(edta)$ as the electron donor (6×10^{-4} M). Under steady state illumination ($\lambda > 400$ nm) the quantum yield for C_nV^+ formation strongly depends on the alkyl chain length of the electron acceptor (Fig. 3). It improves as the hydrophobicity of C_nV^+ is increased, and reaches an optimal value for $n = 8 - 18$. To account for the differences in the quantum yields of C_nV^+ production, the different steps involved in the photosensitized electron transfer reaction have been examined: (a) the quenching effectiveness of $*Ru(bpy)_3^{2+}$ by the different electron acceptors C_nV^{2+}



(b) the quantum yield for the dissociation of the encounter cage complex

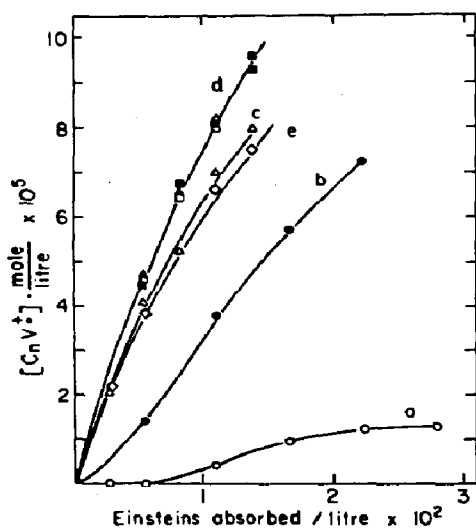
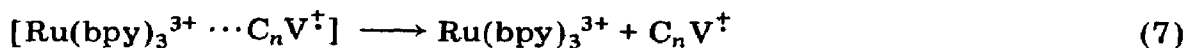
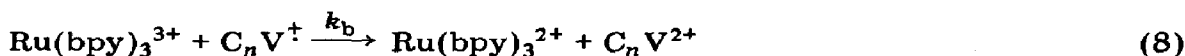


Fig. 3. Quantum yields for C_nV^+ formation in the water-in-oil microemulsion ($[C_nV^{2+}] = 1.0 \times 10^{-4}$ M; $[Ru(bpy)_3^{2+}] = 2 \times 10^{-5}$ M; $[(NH_4)_3(edta)] = 6.0 \times 10^{-4}$ M): curve a, $n = 4$; curve b, $n = 6$; curve c, $n = 8$; curve d, $n = 10, 12$ and 14 ; curve e, $n = 18$.



and (c) the diffusional recombination rate of the separated photoproducts



Using laser flash photolysis, the fluorescence quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by C_nV^{2+} in the water-in-toluene microemulsion has been examined. It is found that the electron transfer quenching process of the excited species $^*\text{Ru}(\text{bpy})_3^{2+}$ by the different electron acceptors is of similar effectiveness. On the assumption that all the components are localized in the aqueous microdroplets of the microemulsion [12] a value of $k_q = (1.1 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is estimated. These results imply that the differences in the quantum yield for $\text{C}_n\text{V}^{\ddagger}$ formation under steady state illumination are not affected by the primary electron transfer quenching process. Nevertheless, substantial differences in the charge separation yields (eqn. (7)) and in the recombination rate constants for the separated photoproducts (eqn. (8)) have been observed with the different electron acceptors. The values for the quantum yield for dissociation of the encounter cage complex and the bimolecular recombination rate constants for the intermediate separated photoproducts are summarized in Table 1. It is evident that, while C_1V^{2+} does not lead to any separated photoproducts, the yield of separated $\text{C}_4\text{V}^{\ddagger}$ is very low and its recombination rate is fast. In turn, the amphiphilic N,N' -dialkyl-4,4'-bipyridinium salts C_8V^{2+} - $\text{C}_{18}\text{V}^{2+}$ reveal an effective charge separation yield ($\phi_{\text{sep}} = (4 - 5.4) \times 10^{-2}$) as well as a retardation in the diffusional recombination rates of the photoredox products. The recombination rates of the long-chain reduction products $\text{C}_8\text{V}^{\ddagger}$ - $\text{C}_{18}\text{V}^{\ddagger}$ are about fiftyfold retarded compared with the back electron transfer reaction of $\text{C}_4\text{V}^{\ddagger}$.

We thus conclude that a water-in-oil microemulsion medium provides an effective microenvironment for controlling photosensitized electron transfer processes by proper design of the hydrophobic-hydrophilic properties

TABLE 1

Charge separation yields and recombination rates in the photosensitized reduction of a series of N,N' -dialkyl-4,4'-bipyridinium salts in water-in-toluene microemulsions [12]

C_nV^{2+}	1	4	6	8	14	18
$\phi_{\text{sep}} \times 10^3$	0	6	36	40	50	54
$k_b^a (\times 10^9 \text{ s}^{-1} \text{ mol}^{-1})$	—	26	8	0.7	0.33	1.2
$\phi_{\text{ss}} \times 10^3^b$	10^{-5}	0.8	2.5	7.5	8.1	7.2

ss, steady state.

^aDetermined by monitoring the disappearance of $\text{C}_n\text{V}^{\ddagger}$ at $\lambda = 602 \text{ nm}$ ($\epsilon = 12\,500 \text{ M}^{-1} \text{ cm}^{-1}$).

^bLight intensity, $7.56 \times 10^{-3} \text{ einsteins l}^{-1} \text{ min}^{-1}$.

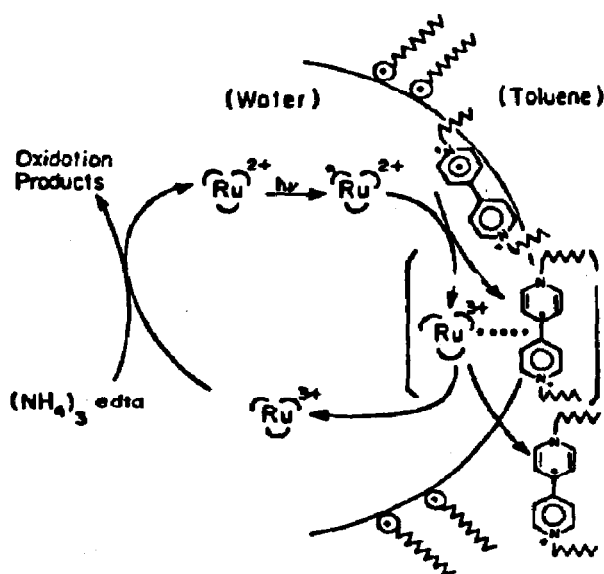


Fig. 4. Functions of a water-in-oil microemulsion in the charge separation of the amphiphilic photoproduct C_nV^{\dagger} and its stabilization against back reactions.

of the electron transfer products. The functions of the water-in-oil microemulsion in the charge separation and stabilization of the photoproducts against the degradative back electron transfer reactions are schematically presented in Fig. 4. With an amphiphilic electron acceptor, photoinduced electron transfer results in a hydrophobic encounter cage complex that is associated with the water-oil interface of the microemulsion. Extraction of the hydrophobic component C_nV^{\dagger} ($n \geq 8$) from the interface into the organic phase assists the charge separation and stabilizes the photoproducts against the back electron transfer reactions by means of the two phases.

3. Formation of multielectron charge relays in two-phase systems

Transformation of single-electron transfer products into multielectron charge relays is a basic requirement for accomplishing complex fixation reaction processes (eqns. (3) and (4)). A possible way to achieve such transformations is the disproportionation of a single-electron transfer product to the corresponding doubly reduced species:



The comproportionation equilibrium constant K_d is determined by the reduction potentials of the two species involved in the process:

$$K_d = \frac{[A][A^{2+}]}{[A^{\dagger}]^2} \quad K_d = 10^{-nF \Delta E^{\circ} / RT} \quad (10)$$

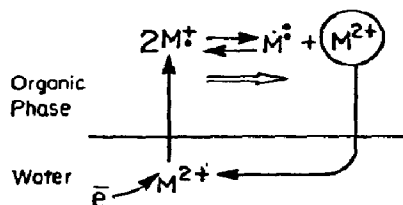


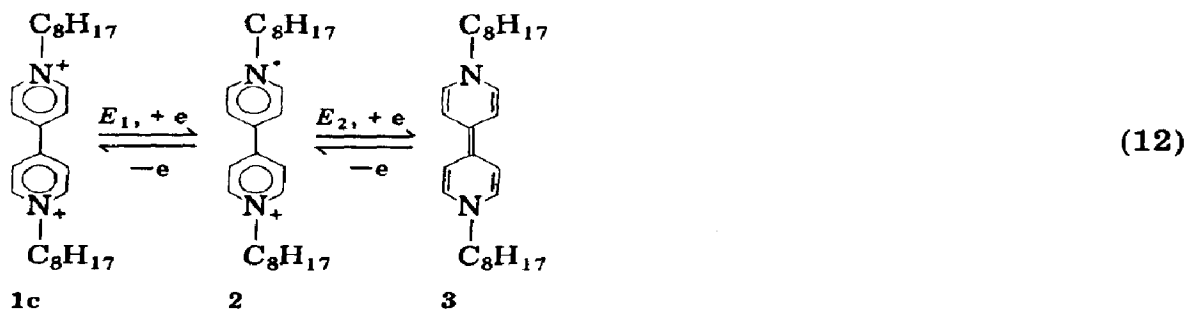
Fig. 5. Proposed induced disproportionation of a single-electron transfer product in a water-oil two-phase system.

Where $\Delta E^\circ = E_1^\circ - E_2^\circ$. Usually, $E_2 < E_1$ and consequently the disproportionation equilibrium lies overwhelmingly towards the single-electron transfer product. However, this situation is valid in a homogeneous phase only, and might be rather altered in a two-phase system (Fig. 5). Let us assume that the electron acceptor exhibits a designed hydrophilic-hydrophobic balance, where the oxidized form A^{2+} is soluble in an aqueous medium, while the monoreduced product A^\cdot is hydrophobic in nature and is extracted from the aqueous solution into organic phases. Under such conditions, disproportionation of A^\cdot in the organic phase is accompanied by re-extraction of A^{2+} to the aqueous phase. Consequently, a two-phase system and the proper design of hydrophilic-hydrophobic balance of the disproportionation products provide an organized environment for inducing disproportionation of a single-electron transfer product to the doubly reduced charge relay. It is also evident from this cycle that continuous reduction of A^{2+} (e.g. on illumination) will ultimately form the doubly reduced species A that functions as an electron sink.

We have found [13] that the electron acceptor, *N,N'*-dioctyl-4,4'-bipyridinium C_8V^{2+} **1c** and its reduction products meet the correct hydrophobic-hydrophilic balance to induce disproportionation of C_8V^\cdot **2** to *N,N'*-dioctyl-4,4'-bipyridinylidene **3** in (organic solvent)-water two-phase systems:



The electron acceptor **1c** undergoes two successive one-electron reduction processes to the *N,N'*-dioctyl-4,4'-bipyridinium radical cation C_8V^\cdot **2** and the *N,N'*-dioctyl-4,4'-bipyridinylidene C_8V **3**:



($E_1 = -0.47$ V and $E_2 = -0.90$ V measured with respect to a normal hydrogen electrode (NHE).) Thus, the comproportionation constant K_d for C_8V^{\ddagger} in a homogeneous aqueous phase is 5.3×10^{-8} , and the disproportionation equilibrium of C_8V^{\ddagger} in a homogeneous aqueous phase lies overwhelmingly towards the single-electron reduction product. The electron acceptor C_8V^{2+} is soluble in water and insoluble in organic media such as toluene or ethyl acetate. In turn, the one-electron reduction product C_8V^{\ddagger} is hydrophobic in nature and extracted into organic phases from aqueous environments. The consequence of the opposite solubility properties of C_8V^{2+} and its reduction products in the organized two-phase system on the disproportionation of C_8V^{\ddagger} is shown in Fig. 5. The electron acceptor C_8V^{2+} is photoreduced by using $Ru(bpy)_3^{2+}$ as the sensitizer and $(NH_4)_3(edta)$ as the electron donor. The photoproduct C_8V^{\ddagger} is extracted from the aqueous phase to the organic phase and the results are displayed in Fig. 6. After a short illumination time of the aqueous phase, the absorption spectrum of the photoproduct in the organic phase resembles that of C_8V^{\ddagger} (Fig. 6, curve a). However, when the absorption spectrum of C_8V^{\ddagger} in a homogeneous phase, where disproportionation is negligible, is subtracted from the experimental absorption spectrum of the photoproducts present in the organic phase (Fig. 6, curve c), an absorption pattern of a second component present in the organic phase and absorbing at $\lambda = 400$ nm is observed (Fig. 6, curve b). This absorption band is identical with that of C_8V 3 that is produced electrochemically [14].

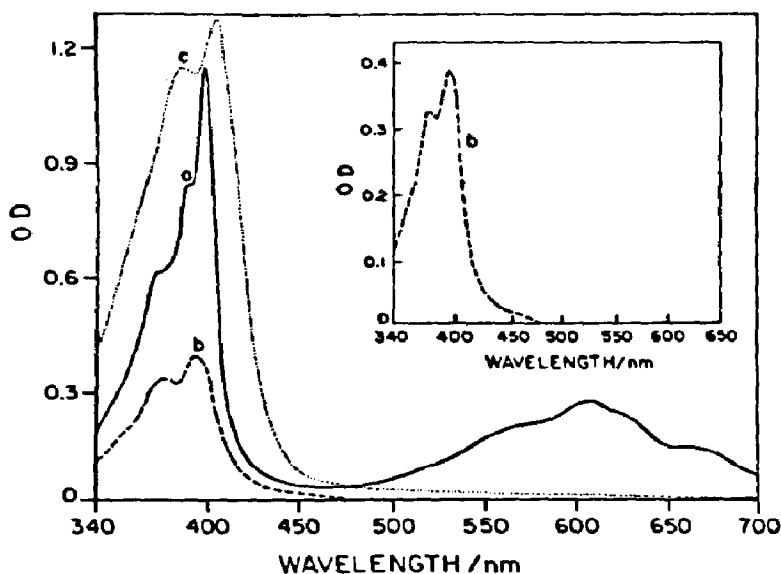
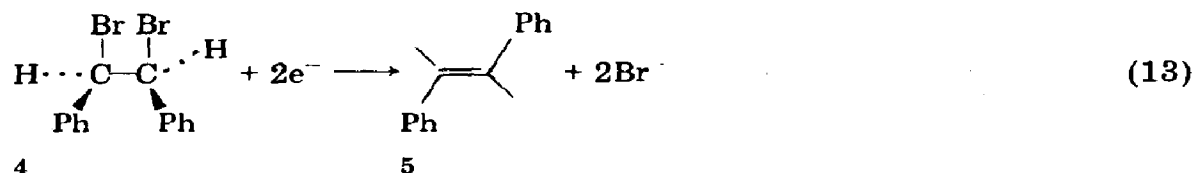


Fig. 6. Absorption spectra of the components in the organic phase obtained after photo-reduction of C_8V^{2+} in the aqueous phase: curve a, composite spectrum of C_8V^{\ddagger} and C_8V in ethyl acetate after 15 min of illumination; curve b, spectrum of C_8V in ethyl acetate after 15 min of illumination and subtraction of the C_8V^{\ddagger} spectrum; curve c, spectrum of photoproducts in the organic phase after 75 min of illumination (spectrum corresponds to C_8V only).

Thus it is evident that in the two-phase system the doubly reduced photoproduct C_8V is formed in conjunction with the photosensitized one-electron transfer process [13,15]. In addition, prolonged illumination results in the accumulation of the doubly reduced product C_8V in the organic phase, at the expense of the single-electron transfer product $C_8V^{\dot{+}}$ (Fig. 6, curve c). These results are consistent with the previously discussed induced disproportionation mechanism outlined in Fig. 5. As a result of the opposite solubility properties of the disproportionation products in the two phases, C_8V^{2+} is re-extracted from the organic phase into the aqueous phase and the doubly reduced comproportionation product C_8V accumulates in the organic phase. Quantitative spectroscopic estimation of $C_8V^{\dot{+}}$ and C_8V in the organic phase allowed us to estimate the comproportionation constants of $C_8V^{\dot{+}}$ in various (organic solvent)-water two-phase systems [15]. For example, in ethyl acetate and dimethyl ether we have estimated K_d values of $3 \times 10^{-1} M^{-1}$ and $1.5 M^{-1}$ respectively for the disproportionation equilibrium constant of $C_8V^{\dot{+}}$. These values are about $10^7 - 10^8$ times higher than the comproportionation constant of the similar process in a homogeneous aqueous medium.

We thus conclude that a single-electron transfer photoproduct is transformed into a doubly reduced charge relay in two-phase systems. The primary processes in the natural photosynthetic apparatus involve single-electron transfer reactions and proceed in hydrophobic-hydrophilic cellular microenvironments. Thus we suggest similar induced disproportionation mechanisms as possible routes for the formation of multielectron charge relays, effective in nature in the fixation of CO_2 or nitrogen.

The subsequent chemical utilization of the two-electron charge relay has also been accomplished [15]. The electrochemical reduction of C_8V^{2+} 1c by means of cyclic voltammetry shows two reversible one-electron reduction waves at $E_1 = -0.47$ V (NHE) and $E_2 = -0.90$ V (NHE), corresponding to the formation of $C_8V^{\dot{+}}$ and C_8V respectively (eqn. (12)). Addition of *meso*-1,2-dibromostilbene 4 does not affect the reversibility of the first reduction wave, while the re-oxidation wave of C_8V is depleted on addition of 4. This implies that a chemical reaction of 4 with C_8V occurs. Introduction of *meso*-1,2-dibromostilbene 4 into the organic phase of an (ethyl acetate)-water two-phase system that includes $Ru(bpy)_3^{2+}$ as the sensitizer, C_8V^{2+} as the electron acceptor and $(NH_4)_3(edta)$ as the electron donor in the aqueous phase results on illumination in the quantitative formation of *trans*-stilbene 5 in the organic phase:



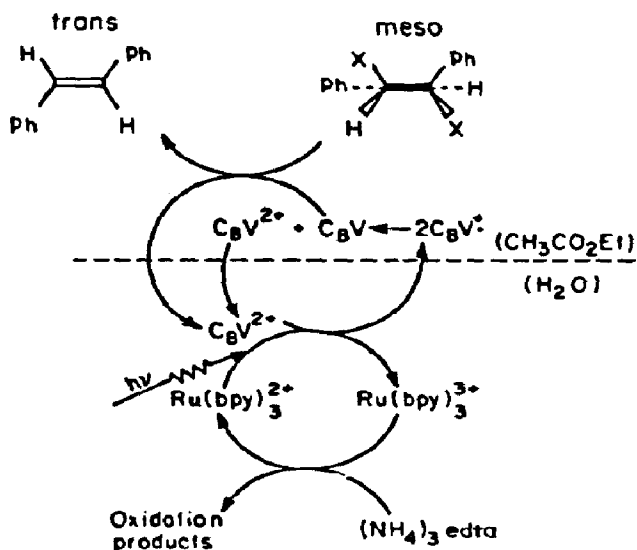


Fig. 7. Photosensitized debromination of *meso*-1,2-dibromostilbene 4 to *trans*-stilbene 5 in a water-(organic solvent) two-phase system.

The electrochemical studies reveal that the active species in debromination is the two-electron reduction product C₈V. However, the primary photochemical process is a single-electron transfer reaction that yields C₈V[†]. In view of our previous discussion, we suggest the cycle presented in Fig. 7 as the mechanistic route for debromination of 4. In this cycle photoreduction of C₈V²⁺ in the aqueous solution is accompanied by extraction of C₈V[†] from the aqueous phase into the organic phase. Induced disproportionation of C₈V[†] yields the doubly reduced species C₈V which is the active reductant in the debromination process. The discussion suggests that a similar process should be prevented in a homogeneous phase since the formation of C₈V is not favoured. Indeed, illumination of 4 and the previously described photo-system in a homogeneous acetonitrile solution does not lead to the formation of *trans*-stilbene 5, despite the effective formation of C₈V[†].

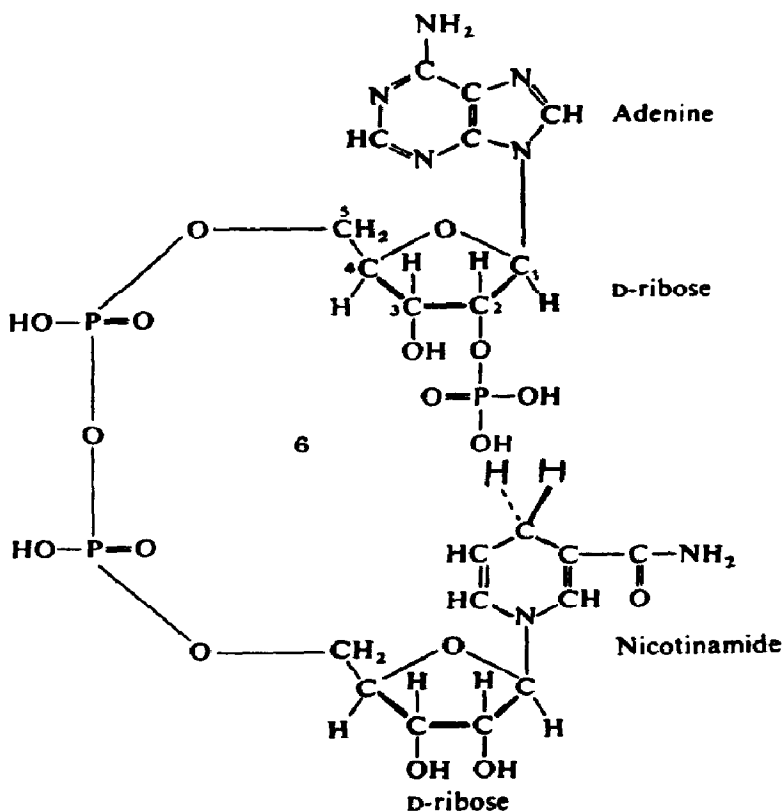
4. Dihyronicotinamide adenine dinucleotide phosphate as a multielectron charge relay

For chemical utilization of the electron transfer photoproducts inclusion of catalysts seems to be essential. These catalysts might function as charge storage sites for the complex multielectron complex fixation processes and/or might participate in the activation of the substrates towards chemical reactions. In the natural photosynthetic system enzymes function as catalytic sites for complex fixation processes. We might envisage two alternative approaches in developing catalysts for the chemical utilization of the photoinduced electron transfer products.

(i) One possibility involves the development of synthetic catalysts mimicking the functions of enzymes with respect to charge storage and substrate activation capabilities.

(ii) The second approach might involve the introduction of natural enzymes into artificial chemical systems (provided that the enzymes are stable in this artificial environment).

In nature, dihydronicotinamide adenine dinucleotide (NADH) and dihydronicotinamide adenine dinucleotide phosphate (NADPH) 6 participate as reducing cofactors in a variety of enzymatic reduction processes:



Thus, the development of photochemical NADH and NADPH regeneration cycles is anticipated to allow a variety of multielectron reduction processes by inclusion of substrate-specific NAD(P)H-dependent enzymes [16].

Several chemical routes have been developed for the regeneration of NADH and NADPH [17, 18]. We have developed [19] a photochemical system for regeneration of NADPH. Illumination of a system ($\lambda > 400$ nm) composed of the sensitizer $\text{Ru}(\text{bpy})_3^{2+}$, $(\text{NH}_4)_3(\text{edta})$, the electron acceptors N,N' -dimethyl-4,4'-bipyridinium dichloride (methyl viologen MV^{2+}) and NADP^+ and the enzyme ferredoxin reductase (FDR) leads to the quantitative formation of NADPH 6. Addition of 2-butanone and the second enzyme, alcohol dehydrogenase ALDH (from the bacteria *T. Brockii*) [20], yields

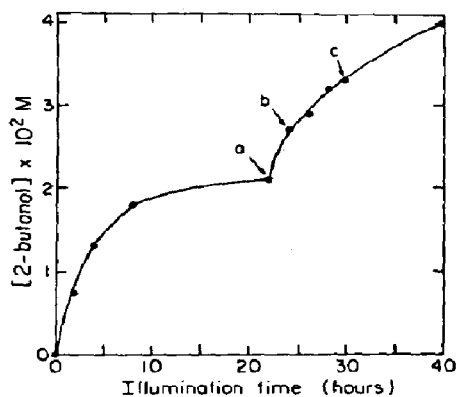
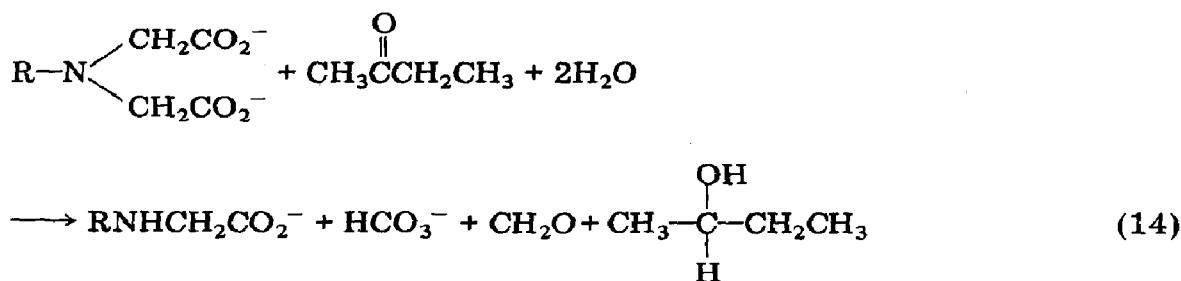


Fig. 8. Rate of (-)-2-butanol production at different illumination time intervals (initial $(\text{NH}_4)_3(\text{edta})$ concentration, $2 \times 10^{-2} \text{ M}$): point a, addition of $2 \times 10^{-2} \text{ M}$ $(\text{NH}_4)_3(\text{edta})$; points b, c, addition of $1.7 \times 10^{-2} \text{ M}$ $(\text{NH}_4)_3(\text{edta})$.

(-)-2-butanol and NADP^+ . Continuous illumination of a system that includes all these components results in the accumulation of (-)-2-butanol at the expense of the sacrificial electron donor $(\text{NH}_4)_3(\text{edta})$ (Fig. 8). It can be seen that the rate of (-)-2-butanol formation levels off as illumination is continued. This is a result of the consumption of the electron donor. Renewal of the $(\text{NH}_4)_3(\text{edta})$ concentration to its original value results in the initial rate of reduction which can be further maintained by constant addition of the electron donor to the system. The net reaction accomplished in this cycle is the reduction of 2-butanone by $(\text{NH}_4)_3(\text{edta})$:



This process is endoergic by about 33 kcal per mole of edta consumed. The process of 2-butanone reduction involves two enzyme-catalysed subcycles (Fig. 9). The primary cycle represents the photoregeneration of NADPH. In this part the photogenerated 4,4'-bipyridinium radical cation MV^+ mediates the production of NADPH using the enzyme FDR as the catalyst. The subsequent cycle describes the chemical utilization of NADPH in the fixation of the keto substrate to an alcohol, using ALDH as the enzyme catalyst.

A major aspect to be considered in such enzyme-catalysed photochemical systems is the stability of the enzymes in the artificial chemical environments. Table 2 summarizes the turnover numbers TN for the different

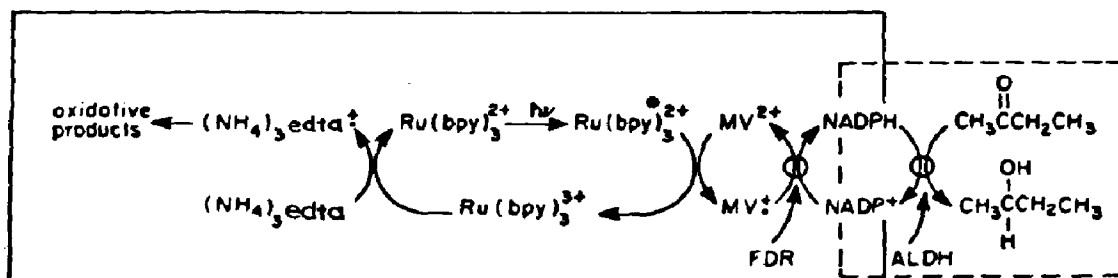


Fig. 9. Photoreduction of 2-butanone using an NADPH regeneration cycle and two coupled enzymes.

TABLE 2

Turnover numbers of the components involved in the photosensitized reduction of 2-butanone^a

Component	Ru(bpy) ₃ ²⁺	MV ²⁺	FDR ^b	NADP ⁺	ALDH ^c
TN	530	40	24000	40	6000

^aNo loss of system activity could be detected after determination of these turnover numbers.

^bFormula weight, about 40 000 (see ref. 21).

^cFormula weight, about 40 000 (see ref. 20).

enzymes and cofactors involved in the reduction of 2-butanone. It is evident that the enzymes exhibit high stability towards denaturation and that the rate of product formation is unaffected even after prolonged illumination times. The stability of the system and the optical purity of the product (–)-2-butanol (100%) demonstrate an effective method for production of optically active alcohols. Certainly, such photosensitized fixation cycles based on the regeneration of NAD(P)H might be generalized. By proper substitution of the secondary NAD(P)H-dependent enzyme, reduction of various other substrates is conceivable. Some of these possibilities, e.g. production of amino acids and CO₂ fixation, are now being examined in our laboratory.

5. Conclusions

Water–oil two-phase systems provide an organized environment for controlling photosensitized electron transfer processes. With amphiphilic electron acceptors, charge separation of the primary encounter cage complex of photoproducts can be assisted by means of the two phases. Similarly, the separated photoproducts are stabilized against diffusional back electron transfer reactions using opposite solubility properties of the photoproducts in the two phases.

Induced disproportionation of a photogenerated single-electron transfer product to the doubly reduced charge relay can be accomplished in a water-oil two-phase system. To accomplish such induced disproportionation processes, proper design of opposite solubility properties of the comproportionation products in two phases must be met. The two-electron reduction product exhibits amplified reduction properties as well as relay properties capable of transferring two electrons in a concerted fashion. It is conceivable that introduction of proper catalysts into the organic phase could utilize the two-electron reduction product in complex fixation processes, *i.e.* nitrogen and CO₂ fixation.

An alternative route for generating multielectron charge relays in a homogeneous aqueous phase involves the use of enzymes as catalysts for the formation of NADPH (a two-electron reducing agent) via primary photo-induced single-electron transfer processes. This hydride-equivalent charge relay can be subsequently utilized by the introduction of NADPH-dependent enzymes and proper substrates.

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