This can be verified by the observation that the components of the 2-′H signal (peak z) exhibit a line width of ~500 Hz. Since dipolar relaxation[31,41] varies as r^{-6}, the nearest heme resonances at ~16 Å can be broadened at maximum 0.1 Hz by a Ru(III) compared to the 500 Hz for 2′-H (at 4 Å).

Since the primarily iron-centered dipolar relaxation is modulated[31,42] by the iron electron spin relaxation time, T_{1e}, the broader 2-′H lines and shorter proton T_1s dictate that T_{1e} must be longer in the presence of the a_5Ru chromophores. Apparently there is some minor interaction between the iron and ruthenium centers. The effect seems to depend on the spin state of the iron (i.e., less for high spin than low spin) as well as the oxidation state, suggesting that some form of electron exchange between centers may be involved for which the rate naturally depends on the detailed redox properties of the two types of metal centers.

Conclusions

Detailed comparisons of the hyperfine-shifted region of the ^1H NMR spectra of metaquo, methydroxy, metcyano, metazide, and deoxy myoglobin reveal that the protein conformation near the heme cavity in $[a_5Ru]_3Mb$ is essentially unchanged from that of the native protein. For the most sensitive probe, the high-spin/low-spin equilibrium, we estimate a *difference* of only 24 cal between $metMbN_3$ and $[a_5Ru]_3metMbN_3$ in the low-spin, high-spin separation; the Ru-labeled protein is suggested to exhibit a very slightly weaker axial ligand field.

The 2′-H signal for the Ru(III)-coordinated histidyl imidazole is readily detected and integrated and provides a very rapid and quantitative index of the average degree of reaction between protein and the a_5Ru^{III} chromophore. Such ^1H NMR integration should prove useful in a variety of proteins. The only consistently detectable influence of the appended Ru chromophores is in the form of increased line widths (and decreased T_1s) which must reflect interaction between the metals rather than direct interaction between heme protons and the a_5Ru chromophore.

Proton NMR studies of the influence of these a_5Ru chromophores on dynamic properties of these proteins are in progress.

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Registry No. $[a_5RuImH]Cl_3$ ($a = NH_3$), 51982-73-1; ImH, 288-32-4.

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Application of Multielectron Charge Relays in Chemical and Photochemical Debromination Processes. The Role of Induced Disproportionation of *N*,*N*′-Dioctyl-4,4′-bipyridinium Radical Cation in Two-Phase Systems[1]

Ruben Maidan,[2a] Zafrir Goren,[2a] James Y. Becker,[2b] and Itamar Willner*[2a]

Contribution from the Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel, and the Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva 84120, Israel. *Received February 27, 1984*

Abstract: Photochemical and chemical reduction of *N*,*N*′-dioctyl-4,4′-bipyridinium (C_8V^{2+}, **1**) to the corresponding radical cation $C_8V^{+\cdot}$ (**2**) leads to an induced disproportionation of $C_8V^{+\cdot}$ in a water–organic two-phase system. This process yields the two-electron reduction product *N*,*N*′-dioctyl-4,4′(1*H*,1*H*′)-bipyridylidene (C_8V, **3**). The induced disproportionation reaction is a result of opposite solubility properties of the disproportionation products in the two phases. The two-electron reduction product C_8V (**3**) mediates the debromination of 1,2- and 1,1-dibromo substrates.

A variety of reducing fixation processes in nature involve multielectron transfer reactions, i.e., N_2 or CO_2 fixation. Yet, the initial photoinduced electron-transfer reactions are single-electron-transfer processes. Therefore, the mode of conversion of one-electron-transfer product to multielectron charge relays seems to be of basic interest. In the past few years substantial efforts have been directed toward the design of artificial photosensitized electron-transfer cycles capable of mimicking photosynthesis.[3-5] In particular, the photoinduced decomposition of water to hydrogen and oxygen has been the subject to many reports.[6-9] The photosensitized reduction of protons to hydrogen has been accomplished in the presence of colloidal platinum using 4,4′- or 2,2′-bipyridinium radicals[6,7] (paraquats or diquats) or $Rh(bpy)_2^{2+}$ as mediators[8] for H_2 evolution. In these systems the Pt colloid provides an interface for the utilization of the single-electron-transfer products in the generation of two hydrogen radicals that combine at the solid interface. Further developments of photosensitized electron-transfer reactions in the reduction of abundant materials such as N_2 or CO_2 might involve multielectron relays formed via single-electron-transfer reactions.

One possible mode for the transformation of a single-electron-transfer product to the corresponding doubly reduced species is its disproportionation process (eq 1). This disproportionation

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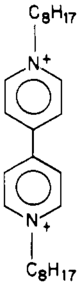
$$2A^{+}\cdot \rightleftarrows A^{2+} + A \qquad (1)$$

equilibrium is controlled by the reduction potentials of the species involved, $E_1(A^{+2}/A^{+}\cdot)$ and $E_2(A^{+}\cdot/A)$. Usually, $E_2(A^{+}\cdot/A) < E_1(A^{2+}/A^{+}\cdot)$ and consequently the comproportionation equilibrium lies overwhelmingly toward the one-electron reduction product $A^{+}\cdot$. Nevertheless, this consideration is valid in a single-phase system and might be rather altered when the components are introduced into a two-phase system. A balance of the hydrophilic–hydrophobic properties of the disproportionation products might persist where $A^{+}\cdot$ and A are mainly soluble in the organic phase, while A^{2+} is mainly solubilized in an aqueous medium. Under these conditions disproportionation of $A^{+}\cdot$ in the organic phase is accompanied by extraction of A^{2+} into the aqueous phase and consequently A is accumulated in the organic phase. Thus, by proper design of the hydrophilic–hydrophobic solubility properties of the comproportionation components, their equilibrium might be shifted toward the doubly reduced product in a heterogeneous two-phase system, a situation that is not favored in a homogeneous phase.

Here we wish to report on the induced disproportionation of the one-electron reduction product of *N,N'*-dioctyl-4,4'-bipyridinium (C_8V^{2+}, **1**) in organic–aqueous two-phase systems.[1]



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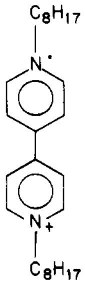

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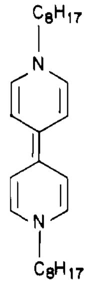

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The single-electron-transfer product $C_8V^{+}\cdot$ (**2**) is formed by chemical and photochemical means. Subsequently, it undergoes an induced comproportionation process in the two-phase system into the doubly reduced form *N,N'*-dioctyl-4,4'(1*H*,1*H'*)-bipyridylidene (C_8V, **3**). This doubly reduced product is utilized in dehalogenation of 1,2-dibromo and 1,1-dibromo substrates.

Experimental Section

Absorption spectra were recorded with a Uvikon-820 (Kontron) spectrophotometer equipped with a ψ-80 (Kontron) computer. Cyclic voltammetry experiments were performed with Princeton Applied Research (PAR) instruments: A potentiostat Model 173 and Universal Programmer Model 175. *N,N'*-Dioctyl-4,4'-bipyridinium dibromide (**1**, $C_8V^{2+}\cdot 2Br^-$) was prepared by refluxing 4,4'-bipyridine with 7-fold excess of octyl bromide in dimethylformamide under nitrogen for 8 h. The precipitate formed upon heating was filtered and washed several times with acetone (mp >300 °C. Elementary anal. Calcd for $C_{26}H_{42}N_2Br_2$: 57.57% C, 7.80% H, 5.17% N. Found: 57.86% C, 7.62% H, 5.30% N). $Ru(bpy)_3^{2+}$ and 1,2-dibromostilbenes were prepared by literature procedures.

Determination of Disproportionation Constants (K_d) in Two-Phase Systems. The partition coefficients of C_8V^{2+} between water and the respective organic phase were determined spectroscopically. To an aqueous solution (0.5 mL) of C_8V^{2+} (1×10^{-4} M) was added 2.5 mL of the respective organic phase. After the two-phase system was stirred, the layers were separated and their precise volumes were determined. The absorbance of C_8V^{2+} at λ = 257 nm (ε 20 700 M^{-1} cm^{-1}) in the water phase was recorded. Partition coefficients (K_p) are expressed as

$$K_p = \frac{[C_8V^{2+}]_w}{[C_8V^{2+}]_o}$$

where $[C_8V^{2+}]_w$ and $[C_8V^{2+}]_o$ are the concentrations of C_8V^{2+} in the water and organic phase respectively.

Disproportionation constants (K_d) were estimated by the determination of the $[C_8V^{+}\cdot]$ and $[C_8V]$ concentrations in the different organic phases in the presence of an aqueous phase. A two-phase system composed of an organic layer (2.5 mL) and an aqueous solution (0.5 mL, pH 8.5) that includes $Ru(bpy)_3^{2+}$ (1×10^{-4} M), $(NH_4)_3EDTA$ (1×10^{-1} M), and C_8V^{2+} (2.3×10^{-4} M) was illuminated with a halogen–quartz 1000-W lamp (through a Kodak 2C filter, λ > 400 nm). The spectra of the organic phase were recorded in the region 340–700 nm, at time intervals of illumination, and stored in the spectrophotometer computer system (for example, Figure 1). The spectra of the organic phase at early stages of illumination are a composite of the two components $C_8V^{+}\cdot$ and C_8V (C_8V^{2+} does not absorb between 340 and 700 nm). From the absorbance at λ = 602 nm (ε 13 800 M^{-1} cm^{-1}) the concentration of $C_8V^{+}\cdot$ in the organic phase was estimated (C_8V does not absorb at λ = 602 nm). The absorption spectrum of $C_8V^{+}\cdot$ in a homogeneous phase was subtracted at the concentration ratio as determined at λ = 602 nm from the recorded composite spectra of the two species. The subtracted spectrum gives the clean absorbance of C_8V in the organic phase (see, for example, Figure 1b). The concentration of C_8V was estimated at λ = 395 nm (ε 45 000 M^{-1} cm^{-1}).[10,11] The total amount of all forms of C_8V (C_8V^{2+}, $C_8V^{+}\cdot$, C_8V) (C_8V_T) for every illuminated system is given by eq 2 and 3. Since

$$C_8V_T = C_8V_w{}^{2+} + C_8V_o{}^{2+} + C_8V^{+}\cdot_w + C_8V^{+}\cdot_0 + C_8V_w + C_8V_o \qquad (2)$$

$$C_8V_T = [C_8V^{2+}]_wV_w + [C_8V^{2+}]_oV_o + [C_8V^{+}]_oV_o + [C_8V]_oV_o \qquad (3)$$

$$[C_8V^{2+}]_o = \frac{C_8V_T - [C_8V^{+}]_oV_o - [C_8V]V_o}{V_o + K_pV_w} \qquad (4)$$

no $C_8V^{+}\cdot$ and C_8V could be detected spectroscopically in the aqueous phase, the two terms $C_8V^{+}\cdot_w$ and C_8V_w are negligible. From the partition coefficient of C_8V^{2+}, its concentration in the organic phase was determined by eq 4, where V_o and V_w are the volumes of the organic and water phase, respectively.

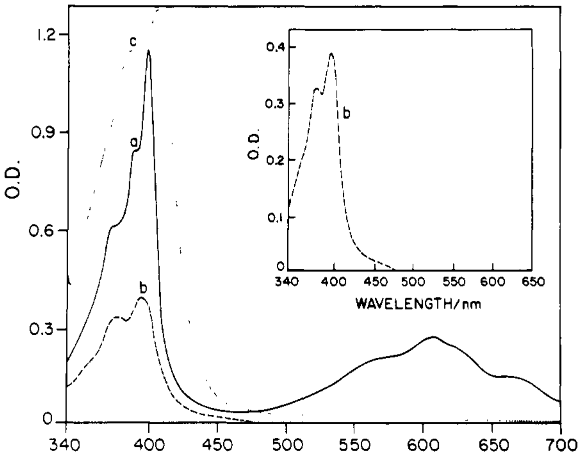

Figure 1. Absorption spectra of disproportionation products of $C_8V^{+}\cdot$: (a) Composite spectrum of $C_8V^{+}\cdot$ and C_8V in ethyl acetate; (b) spectrum of C_8V in ethyl acetate, after subtraction of the $C_8V^{+}\cdot$ spectrum; (c) spectrum in toluene.

Chemical Debromination of 1,2-Dibromo-1,2-diarylethanes. The system is composed of an organic ethyl acetate phase (100 mL) that includes *meso*-1,2-dibromostilbene (**4**) (0.5 g, 1.5 mmol) and an aqueous solution (50 mL) of sodium dithionite (1 g, 5.7 mmol). The two-phase system is stirred under nitrogen and *N,N'*-dioctyl-4,4'-bipyridinium dibromide (**1**) (54 mg, 0.1 mmol) is added to the deaerated solution. The immediate formation of the blue radical cation $C_8V^{+}\cdot$ was observed in the aqueous phase without stirring. Upon stirring the radical is extracted into the organic phase. Stirring was continued for 3 h. After evaporation of the organic phase *trans*-stilbene (**5**), mp 122 °C, was isolated (yield, 90%). It was identified by comparison to an authentic sample (TLC, ^1H NMR). Elementary anal. calcd for $C_{14}H_{12}$: 93.28% C, 6.72% H. Found: 93.22% C, 6.77% H.

Using the similar procedure the following *meso*-1,2-dibromodiarylethanes **6–9** were debrominated to the respective *trans*-stilbene derivatives **10–13**: *meso*-1,2-dibromo-1-(4-methoxyphenyl)-2-phenylethane (**6**), *meso*-1,2-dibromo-1-(4-chlorophenyl)-2-phenylethane (**7**), *meso*-1,2-dibromo-1-(4-pyridyl)-2-phenylethane (**8**), *meso*-1,2-dibromo-1-(2-pyridyl)-2-phenylethane (**9**). Debromination of *d,l*-1,2-dibromostilbene (**14**) under similar conditions afforded trace amounts of *trans*-stilbene (**5**) (Table I).

Debromination of *meso*-1,2-dibromostilbene (**4**) was similarly accomplished in a two-phase system composed of an organic ethylacetate phase

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Table I. Chemical Debromination of 1,2-Dibromo-1,2-diarylethanes in a Two-Phase System[a]

substrate	product	yield,[b] %		anal. of products		
				% C	% H	% N
4	**5**	90	calcd	93.28	6.72	
			found	93.22	6.77	
6	**10**	90	calcd	85.68	6.71	
			found	85.55	6.92	
7	**11**	92	calcd	78.32	5.16	
			found	78.21	5.24	
8	**12**	88	calcd	74.26	5.27	1.9
			found	74.32	5.17	2.2
9	**13**	90	calcd	74.26	5.27	1.9
			found	74.22	5.31	2.1
14	**5**	trace[c]				

[a] In these experiments $Na_2S_2O_4$ is used as reducing agent in the aqueous phase (for experimental details see text). [b] Reaction time for all substrates, 3 h. [c] For this system reaction time was 24 h.

(100 mL) that included **4** (0.5 g, 1.5 mmol) and an aqueous solution of glucose (0.7 g, 3.8 mmol).[12] Stirring the two-phase system under nitrogen (2 h, 50 °C) afforded after workup *trans*-stilbene (**5**), 70% yield.

Debromination of Benzal Bromide (15). The two-phase system is composed of ethyl acetate (100 mL) that includes benzal bromide (**15**) (2.5 g, 10 mmol) and an aqueous sodium dithionite solution (9 g, 50 mmol). The system was stirred under nitrogen and *N,N'*-dioctyl-4,4'-bipyridinium dibromide (C_8V^{2+}, **1**) (108 mg, 0.2 mmol) was added. The blue color of $C_8V^{+\cdot}$ is observed in the organic phase that turns to red after about $^1/_2$ h. Stirring was continued for 48 h and C_8V^{2+} (216 mg, 0.4 mmol) was added portionwise to the reaction mixture during this time. Evaporation of the organic phase affords a red oily product that was separated by PLC (silica gel plates, cyclohexane as eluant). Three components were isolated: The first band (R_f 0.52) corresponds to benzal bromide (**15**), the second band (R_f 0.35) corresponds to *trans*-stilbene (**5**), and the third band (R_f 0.24) was identified as *d,l*-1,2-dibromostilbene (**14**), mp 112–113 °C (lit.[13] mp 114 °C). The ^1H NMR of **14**, δ 7.15 (s, 10 H) and 5.45 (s, 2 H), is in accordance with the reported data.[14]

Photochemical Debromination of *meso*-1,2-Dibromostilbene (4). The system is composed of an organic ethyl acetate solution (100 mL) that includes **4** (0.5 g, 1.5 mmol) and an aqueous solution (pH 8.5, 50 mL) that includes ruthenium tris(bipyridine) dichloride, $Ru(bpy)_3^{2+}$ (10 mg, 0.01 mmol), $(NH_4)_3EDTA$ (1 g, 2 mmol), and C_8v^{2+} (54 mg, 0.1 mmol). The system was flushed with argon and sealed. The two-phase system was illuminated with stirring with a 1000-W halogen-quartz lamp through a Kodak 2C filter (λ > 400 nm). After a few minutes of illumination the blue color of $C_8V^{+\cdot}$ was observed in the organic phase. Illumination was continued for 3 h. Evaporation of the organic phase afforded after recrystallization (30% toluene in ethanol) *trans*-stilbene (**5**) (70% yield). No formation of $C_8V^{+\cdot}$ or *trans*-stilbene (**5**) was observed in the dark.

Results and Discussion

Induced Diproportionation of C_8V^{2+} in Two-Phase Systems. Dioctyl-4,4'-bipyridinium (**1**) undergoes in water two consecutive reduction processes to the respective radical cation $C_8V^{+\cdot}$ (**2**) (E_1° = −0.47 V vs. NHE) and the doubly reduced product **3** (C_8V) (E_2° = −0.90 V, vs. NHE) (eq 5). From the respective reduction potentials, the comproportionation constant of the one-electron reductant C_8V^+ in water is estimated to be $K_d = 5 \times 10^{-8}$ (eq 6 and 7).

$$C_8V^{2+} \xrightarrow{e^-} C_8V^{+\cdot} \xrightarrow{e^-} C_8V \qquad (5)$$

$$2C_8V^{+\cdot} \overset{K_d}{\rightleftarrows} C_8V^{2+} + C_8V;\ K_d = \frac{[C_8V][C_8V^{2+}]}{[C_8V^{+\cdot}]^2} \qquad (6)$$

$$K_d = 10^x \quad \left(x = -\frac{nF\Delta E^\circ}{RT}\right); \quad \Delta E^\circ = E_1^\circ - E_2^\circ \qquad (7)$$

The oxidized form C_8V^{2+} is soluble in an aqueous media and almost insoluble in organic phases such as ether, toluene, or ethyl acetate. C_8V^{2+} can be photoreduced in an aqueous medium to the blue radical cation $C_8V^{+\cdot}$ in the presence of a photosensitizer, i.e., ruthenium(II) tris(bipyridine) ($Ru(bpy)_3^{2+}$) and an electron donor, such as $(NH_4)_3EDTA$. Illumination of stirred two-phase systems composed of an organic phase and an aqueous phase that includes C_8V^{2+}, the photosensitizer, and $(NH_4)_3EDTA$ results in the spectral changes displayed in Figure 1.

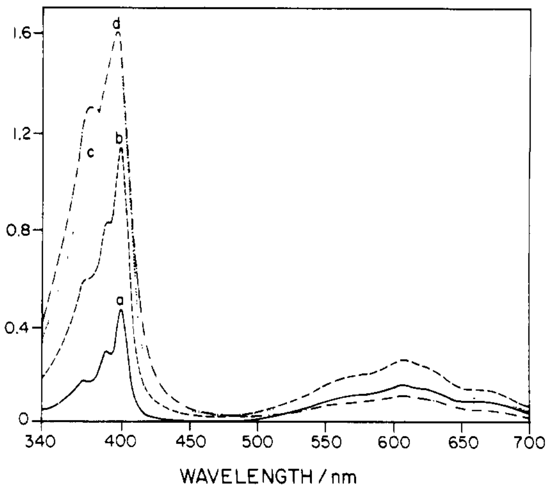

Figure 2. Absorption spectra of disproportionation products in ethyl acetate at time intervals of illumination: (a) 5 min, (b) 10 min, (c) 20 min, (d) 75 min.

No radical cation $C_8V^{+\cdot}$ could be observed in the aqueous phases, while the blue color of $C_8V^{+\cdot}$ is observed in the organic phases of ethyl acetate or ether. With toluene as organic phase, the organic layer turned yellowish and no color of $C_8V^{+\cdot}$ is observed (Figure 1c). The spectrum of the entity formed in the toluene solution λ_{max} = 400 nm is identical with the spectrum reported for *N,N'*-dialkyl-4,4'(1*H*,1*H'*)bipyridylidenes.[10,11] Thus, in a toluene–water two-phase system the observed product is C_8V rather than the one-electron-transfer photoproduct $C_8V^{+\cdot}$. Careful examination of the spectrum of the photoproducts formed in the ethyl acetate solution of the two-phase system (Figure 1a, b) confirms that the spectum is composed of the two absorbing species, $C_8V^{+\cdot}$ and C_8V. The spectrum of $C_8V^{+\cdot}$ in homogeneous ethyl acetate is composed of two absorption bands at λ = 400 nm (ε 42 000 M^{-1} cm^{-1}) and λ = 602 nm (ε 13 800 M^{-1} cm^{-1})(ratio of intensities 3.04). The absorbance ratio of the two bands in the ethyl acetate solution of the two-phase system (Figure 1a) is OD 400/OD 602 = 4.88. This suggests the presence of an additional species absorbing in the region of 400 nm. Assuming that at λ = 602 nm only $C_8V^{+\cdot}$ is absorbing, the spectrum of $C_8V^{+\cdot}$ was substracted from the composite spectrum displayed in Figure 1a. The subtracted spectrum is shown in Figure 1b. It is identical with that of C_8V produced by electrochemical means[11] (λ = 394 nm, ε 45 000 M^{-1} cm^{-1}). This analysis demonstrates that in a two-phase system the photoreduction of C_8V^{2+} leads to the formation of the doubly reduced species in the organic phase. The spectral changes in the ethyl acetate solution at time intervals of illumination of the two-phase system are displayed in Figure 2. It can be seen that at initial stages of illumination, the two reduction products $C_8V^{+\cdot}$ and C_8V are concomitantly present, while after prolonged illumination times the only observable species is C_8V. This suggests that in the two-phase system, a cyclic process is operative, whereby $C_8V^{+\cdot}$ is pumped into the doubly reduced species C_8V.

These results are attributed to an induced disproportionation process of $C_8V^{+\cdot}$ in the two-phase system. Due to the lipophilic character of $C_8V^{+\cdot}$, it is extracted from the aqueous phase into the organic phase. Disproportionation of $C_8V^{+\cdot}$ forms two products, C_8V^{2+} and C_8V, that exhibit opposite solubility properties. Consequently, the comproportionation equilibrium of $C_8V^{+\cdot}$ is shifted toward the two-electron reduction product C_8V, and a continuous pumping mechanism for formation of C_8V is operative upon continuous illumination. The quantitative spectral analysis

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Table II. Disproportionation Constants (K_d) of $C_8V^{+\cdot}$ in Different Organic Phases[a]

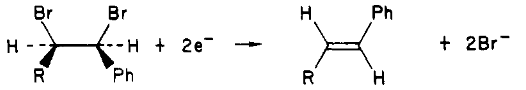
solvent	K_d
ethyl acetate	3×10^{-1}
ether	1.5
toluene	>10[b]

[a] Calculated from eq 6 using the partition coefficients (K_p) for C_8V^{2+} in the different two-phase systems (see text). [b] Lower limit for disproportionation constant. No $C_8V^{+\cdot}$ could be observed in the toluene layer. An absorbance of OD = 0.01 was taken as limit for detection at λ = 602 nm.

of $C_8V^{+\cdot}$ and C_8V in the organic phase allowed us to determine the disproportionation equilibrium constants of $C_8V^{+\cdot}$ (K_d) in different organic phases in the presence of an aqueous phase. These comproportionation constants are summarized in Table II. It is evident that, while in a homogeneous phase $K_d = 5 \times 10^{-8}$, it is increased by a factor of 10^7–10^9 in organic–water two-phase systems where the two-electron-reduction product C_8V is the predominating product.

Debromination Reactions in Two-Phase Systems. Phase-transfer catalysis has found significantly synthetic applications in recent years.[15,16] Among the many reactions that have been examined are reduction[17] and oxidation[18] processes of organic substrates. In these reactions the oxidizing reagent, i.e., MnO_4^- or $HCr_2O_7^-$, is transferred to the organic phase by means of a hydrophobic tetraalkylammonium salt. An amphiphilic electron acceptor such as *N*,*N'*-dioctyl-4,4'-bipyridinium (C_8V^{2+}, **1**) might be used as an electron carrier between two phases since the reduced form $C_8V^{+\cdot}$ (**2**) is extracted into the organic phase.[19] Consequently, reduction of substrates in the organic phase by $C_8V^{+\cdot}$ or its disproportionation product C_8V might occur, and therefore the redox couple $C_8V^{2+}/C_8V^{+\cdot}$ can be regarded as a potential electron phase-transfer catalyst.

This idea led us to examine the debromination of *meso*-1,2-dibromostilbene (**4**) in a two-phase system composed of ethyl acetate and an aqueous solution of sodium dithionite ($Na_2S_2O_4$). Introduction of a catalytic amount of C_8V^{2+} into the deaerated system results in the blue color of $C_8V^{+\cdot}$ (in the water phase). Upon stirring of the two-phase system the radical is extracted into the organic phase and the reduction of **4** to trans-stilbene (**5**) proceeds quantitatively. No reduction of the dibromide **4** occurs when C_8V^{2+} is excluded from the system. This implies that C_8V^{2+} mediates the debromination process, and since the molar ratio of C_8V^{2+} to the dibromide is 1:15, it is clear that the active reductant in the debromination of **4** is recycled in the process. In a similar way, a variety of substituted *meso*-1,2-dibromo-1,2-diarylethanes (**6–9**) afford in quantitative yields (>90%) the corresponding *trans*-stilbenes (**10–13**). The net reaction in these debromination processes (eq 8) corresponds to the two-electron reduction of the 1,2-dibromodiarylethanes to the respective diarylethylenes.


(8)

4, R=Ph
6, R=4-MePh
7, R=4-ClPh
8, R=4-Py
9, R=2-Py

5, R=Ph
10, R=4-MeOPh
11, R=4-ClPh
12, R=4-Py
13, R=2-Py

The mediated reduction of the dibromides was also accomplished when glucose was substituted for dithionite as the reducing agent in the aqueous phase.[12] Under these conditions glucose is oxidized by C_8V^{2+}, and the resulting $C_8V^{+\cdot}$ is extracted into the organic phase where debromination occurs.

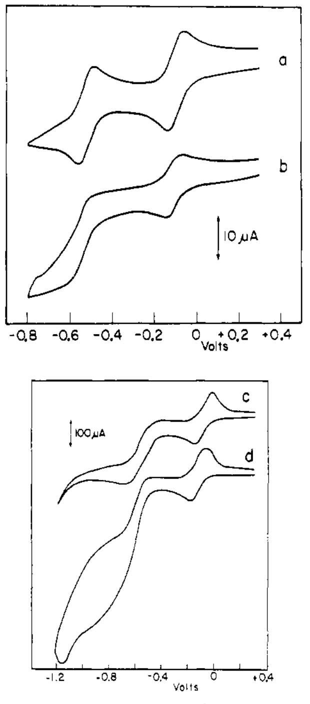


Figure 3. Cyclic voltammogram of C_8V^{2+} (**1**) 5×10^{-3} M in CH_3CN with 0.1 M tetrabutylammonium tetrafluoroborate. Sweep rate, 0.1 V/s. Reference electrode, Ag wire (0.39 V vs. NHE). (a) Without added *meso*-1,2-dibromostilbene (**4**), Pt working electrode; (b) with **4**, 5×10^{-3} M, Pt working electrode; (c) with **4**,5×10^{-3} M, GC working electrode; (d) with **4**, 2.5×10^{-2} M, GC working electrode.

In order to elucidate the nature of the active species being involved in the reduction of the dibromides, we have examined the reduction of C_8V^{2+} by means of cyclic voltammetry and the effect of added dibromostilbene on its reduction products (Figure 3). The cyclic voltammogram of C_8V^{2+} shows two reversible one-electron reduction waves at $E_{1/2}{}^1 = -0.47$ V and $E_{1/2}{}^2 = -0.90$ V (vs. NHE) corresponding to the formation of the radical cation $C_8V^{+\cdot}$ and C_8V (eq 5) (Figure 3a). Addition of dibromostilbene to C_8V^{2+} does not affect the reversibility of the first reduction wave, while the second reduction wave is strongly affected by the added substrate (Figure 3b,c,d). It can be seen that the reoxidation wave of C_8V is depleted while a strong cathodic current is observed at the reduction potential where C_8V is produced. This cathodic current is independent of the working electrodes employed (Pt or glassy carbon). These results point to a rapid chemical consumption of C_8V in the presence of dibromostilbene. The chemical reaction results in a high local concentration of $C_8V^{+\cdot}$ near the electrode, and, consequently, the cathodic current for C_8V formation is increased. These results demonstrate that the active species in the debromination processes discussed previously is the two-electron reductant C_8V rather than $C_8V^{+\cdot}$. Similarly, we have produced electrochemically C_8V in acetonitrile at a constant potential of −1.0 V (vs. NHE). Addition of an equivalent amount of 1,2-dibromostilbene to the electrochemically produced C_8V afforded *trans*-stilbene in 50% yield. Thus, the electrochemical studies allow us to conclude that the doubly reduced species C_8V is the active reducing agent in the debromination reactions of the 1,2-dibromoarylethanes.

The reduction potentials of sodium dithionite in the neutral aqueous solutions used in our studies ($E° = -0.386$ V)[20a] as well as that of glucose ($E° = -0.362$ V)[20b] (vs. NHE) are only adequate for generating the one-electron reduction product $C_8V^{+\cdot}$ (**2**). Yet, we have provided evidence that in an organic–water two-phase system $C_8V^{+\cdot}$ undergoes an induced disproportionation to C_8V^{2+}

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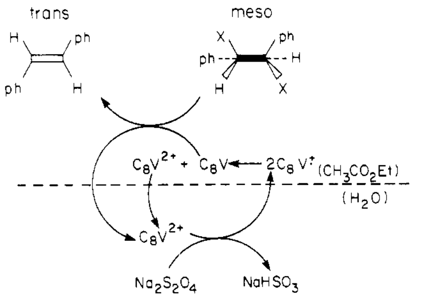
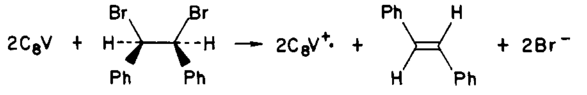
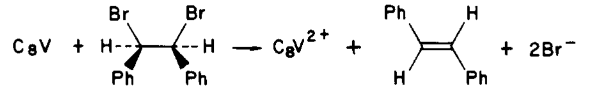


Figure 4. Cyclic chemical debromination of *meso*-1,2-dibromostilbene (**4**) in a two-phase system.

and C_8V due to reextraction of C_8V^{2+} into the aqueous phase. As a result, the doubly reduced species C_8V, being the active species in the debromination reaction, is formed (Figure 4). The debromination process of the 1,2-dibromides by C_8V might proceed via one of the two alternative routes outlined in eq 9 and 10. The first mechanism involves one-electron-transfer reaction of C_8V (as a concerted or consecutive process), while the second route suggests a concerted two-electron-transfer mechanism.[21] At this point we cannot distinguish between the two alternative routes. Nevertheless, product analysis of debromination reactions of other substrates (vide infra) supports the former route as the operative mechanism.

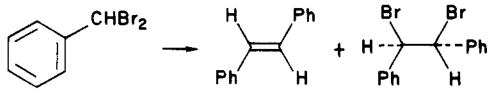


(9)



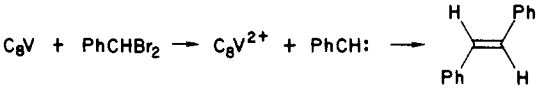
(10)

The similar debromination process has been examined with 1,1-dibromo substrate, i.e., benzal bromide (**15**). In the cyclic voltammogram, addition of benzal bromide (**15**) depletes the reoxidation wave of C_8V while the wave of $C_8V^{+\cdot}$ is unaffected. This suggests that also with 1,1-dibromo substrates the active species in debromination is C_8V. The chemical debromination of **15** in an ethyl acetate–water two-phase system, with sodium dithionite ($Na_2S_2O_4$) as the reducing agent, yields a mixture of *trans*-stilbene (**5**) and *d,l*-1,2-dibromostilbene (**14**) (eq 11). The product, *trans*-stilbene (**5**) can originate from two alternative routes (eq 12 and 13). The first route involves a concerted two-electron reduction to yield phenylcarbene, which is known[22] to dimerize to *trans*-stilbene. The second route involves a one-electron reduction process of benzal bromide by C_8V to form bromobenzyl radical. This radical can then dimerize to form 1,2-dibromostilbenes that undergo further debromination by C_8V to *trans*-stilbene as described previously. Phenylcarbene (PhCH:) in addition to its dimerization to stilbenes undergoes addition reaction to olefinic substrates such as cyclohexene.[22] When cyclohexene was added to the organic phase of the reaction mixture, no addition products of phenylcarbene to cyclohexene could be isolated. Yet, all reaction products can be attributed to the second route, which includes a one-electron-transer process followed by dimerization and 1,2-vicinal debromination. We therefore conclude that the reduction of benzal bromide by C_8V proceeds via a one-electron-transfer process (eq 13) rather than a concerted two-electron-transfer mechanism. Nevertheless, it seems peculiar that only *d,l*-1,2-dibromostilbene (**14**) is found in the reaction products, and no meso isomer **4** is obtained. We therefore examined the effect of added *d,l*-1,2-dibromostilbene on the reduction products of C_8V^{2+} by means of cyclic voltammetry. We find that at a scanning rate of 0.05 V/s none of the reduction waves of C_8V^{2+} is affected by added **14**. Yet, at a slower scanning rate (0.005 V/s) the oxidation wave of C_8V is depleted, implying that a chemical reaction of C_8V with **14** occurs. It should, however, be noted that the meso isomer **4** affects the reversibility of C_8V already at the faster scanning rate (0.05 V/s). These results demonstrate that debromination of **14** is substantially slower as compared to that of the meso isomer **4**. Similarly, we find that the chemical debromination of **14** in the two-phase system is very inefficient. Using sodium dithionite as the reducing agent, only traces of *trans*-stilbene (**5**) are obtained, under the similar conditions where debromination of **4** proceeds quantitatively. Thus, we conclude that the success in isolating **14** from the debromination reaction mixture of **15** is due to the stability of **14** against the debromination process.



(11)

15 **5** **14**



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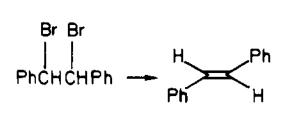

(13)

The entire scheme leading to the cyclic debromination of the dibromides is displayed in Figure 4. $C_8V^{+\cdot}$ is formed in the aqueous phase and extracted into the organic phase due to its hydrophilic character. In the organic phase $C_8V^{+\cdot}$ undergoes an induced disproportionation process to C_8V since the complementary oxidized component, C_8V^{2+}, is reextracted into the aqueous phase. Consequently, the active species capable of reducing the dibromides is produced. We should note, however, that the success in reducing the dibromides by the reductants dithionite and glucose is due to induced disproportionation of $C_8V^{+\cdot}$ in the two-phase system whereby C_8V is formed. This suggests, as indeed observed (vide infra), that a similar comproportionation process is unfavored in a homogeneous phase with the same reductants.

Photochemical Debromination of 1,2-Dibromostilbene. 4,4′-Bipyridinium salts (viologens) have been widely explored as electron acceptors and electron carriers in photosensitized electron-transfer reactions.[6,7,23] Presently, such photoinduced electron-transfer reactions are extensively studied in particular as a means of solar energy conversion and storage.[3-5] For example, the photoinduced production of 4,4′-bipyridinium radical cations with visible light is well-known.[23] In these systems, coordination compounds such as ruthenium(II) tris(bipyridine), $Ru(bpy)_3{}^{2+}$, or zinc porphyrins are used as sensitizers and triethanolamine, ethylenediaminetetraacetic acid (EDTA), or cysteine are introduced as electron donors. Thus, we have substituted the reductant in the aqueous phase by a photosystem composed of $Ru(bpy)_3{}^{2+}$ and the electron donor $(NH_4)_3EDTA$. Illumination ($\lambda > 400$ nm) of an ethyl acetate acetate–water two-phase system that includes the sensitizer $Ru(bpy)_3{}^{2+}$, $(NH_4)_3EDTA$ as electron donor, and C_8V^{2+} as electron acceptor in the aqueous phase and *meso*-1,2-dibromostilbene (**4**) in the organic phase affords quantitatively *trans*-stilbene (**5**). No formation of **5** is detected in the dark. Since the molar ratio of C_8V^{2+} to the dibromide is 1:15, the electron acceptor is recycled during the quantitative formation of **5**. Furthermore, when the dibromide is excluded from the two-phase system and C_8V^{2+} is illuminated in the presence of the photosystem

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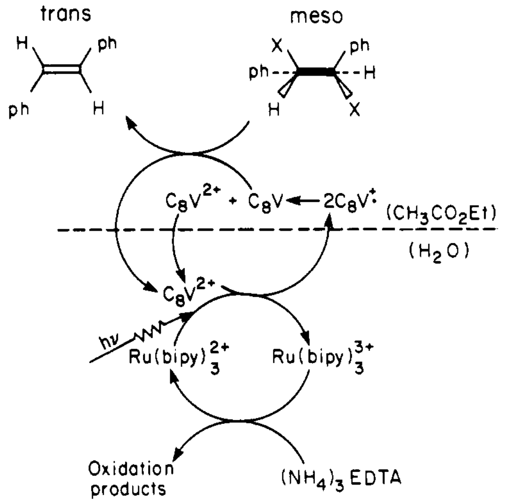

Figure 5. Photosensitized debromination of *meso*-1,2-dibromostilbene (**4**) in a two-phase system.

the doubly reduced species C_8V is formed in the organic phase (Figure 2). This is a result of the induced disproportionation of $C_8V^{+\cdot}$ as described previously. Addition of 1,2-dibromostilbene to the ethyl acetate solution that contains the photoproduced C_8V yields *trans*-stilbene and the blue radical cation $C_8V^{+\cdot}$. All of these results demonstrate the photosynthetic formation of stilbene via oxidation of $(NH_4)_3$EDTA by dibromostilbene in a cyclic process mediated by C_8V^{2+} (Figure 5). In this cycle, quenching of the excited $Ru(bpy)_3^{2+}$ by C_8V^{2+} ($k_q = 1.1 \times 10^8\ M^{-1}\ s^{-1}$)[24] results in the photoproducts $Ru(bpy)_3^{3+}$ and $C_8V^{+\cdot}$. The oxidized photosensitizer $Ru(bpy)_3^{3+}$ oxidizes $(NH_4)_3$EDTA and the sensitizer is recycled. The reduced photoproduct $C_8V^{+\cdot}$ is extracted into the organic phase where it undergoes disproportionation to C_8V. The subsequent debromination of 1,2-dibromostilbene recycles the mediating electron acceptor C_8V^{2+}.

Our previous discussion implies that such debromination processes should be unfavorable in a homogeneous solution that includes $C_8V^{+\cdot}$. This conclusion is based on the unfavored comproportionation of $C_8V^{+\cdot}$ in a homogeneous phase ($K_d = 5 \times 10^{-8}$). Indeed illumination of an acetonitrile solution that includes $Ru(bpy)_3^{2+}$ as sensitizer, C_8V^{2+} as electron acceptor, triethanolamine as electron donor, and 1,2-dibromostilbene does not result in the formation of stilbene, despite the effective formation of $C_8V^{+\cdot}$. These results emphasize the importance of an organized two-phase media in driving a photosensitized single-electron-transfer product to a doubly reduced charge relay that is utilized in the chemical route.

Conclusions

We have demonstrated that a single-electron-transfer product can undergo an induced disproportionation process to the two-electron reduction product. The advantages of such transformation seem obvious: (i) The reduced form has a lower reduction potential than the one-electron reductant and can be utilized in versatile reduction processes. (ii) The comproportionation process establishes a charge relay of two reduction equivalents. Consequently, multielectron reduction reactions being mediated by such relays seem conceivable.

In nature multielectron-transfer processes are common, i.e., CO_2 or N_2 fixation, while the initial process are single-electron-transfer reactions. Since these reactions proceed in natural cellular media that include hydrophilic and hydrophobic microenvironments, similar mechanisms of induced disproportionation might lead to the multielectron charge relays.

Further developments of this system seem feasible. Introduction of coordination complexes into the organic phase might offer an active site that utilizes the multielectron relay in reduction processes. Also, design of amphiphilic dimeric electron acceptor can serve as four-electron charge delay relay via a similar disproportionation mechanism. These subjects are currently being examined in our laboratory.

Registry No. **1**·2Br, 36437-30-6; **2**, 87922-26-7; **3**, 87922-27-8; **4**, 13440-24-9; **6**, 24533-06-0; **7**, 91606-58-5; **8**, 87922-25-6; **9**, 87922-24-5; **15**, 618-31-5.

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Surface Photochemistry: Semiconductor Photoinduced Dimerization of Phenyl Vinyl Ether[1]

Anthony M. Draper, Mohammad Ilyas, Paul de Mayo,* and V. Ramamurthy[2]

Contribution from the Photochemistry Unit, Department of Chemistry,
University of Western Ontario, London, Ontario, Canada N6A 5B7. *Received March 8, 1984*

Abstract: The dimerization of phenyl vinyl ether at an illuminated semiconductor surface has been demonstrated, and that reaction induced on ZnO was studied in detail. The involvement of surface-related processes has been shown to affect both the rate and stereochemistry of the system. Langmuir–Hinshelwood treatment has been found to be applicable for kinetic analysis. The effect of various quenchers has been described in terms of competitive adsorption with or without interference with electron-transfer processes on the surface. A reaction scheme involving the simultaneous formation of dimer both in the adsorbed state and in solution has been suggested, the former being the more important.

One of the most active areas of current photochemical research is the light-induced generation of fuels, and among these the use of semiconductors has been prominent. The use of semiconductors for other photochemical objectives has been far less and consists, essentially, of oxidative or reductive operations.[3] Among the very few examples outside these main categories are the reports of the CdS powder photocatalyzed retrocycloaddition of **1** to give **2**,[4]

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(1) Publication No. 327 from the Photochemistry Unit, University of Western Ontario.

(2) On leave from the Indian Institute of Science, Bangalore.

(3) For an important and lucid review of semiconductors in organic photochemistry, see: Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314.

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