Photoredox Reactions in Water-in-Oil Microemulsions. The Functions of Amphiphilic Viologens in Charge Separation and Electron Transfer across a Water-Oil Boundary

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The photosensitized reduction of the series of dialkyl-4,4'-bipyridinium salts, $C_n V^{24}$, is examined in water-in-oil microemulsions, by using $Ru(bpy)_3^{2+}$ as sensitizer and $(NH_4)_3EDTA$ as electron donor. With the amphiphilic electron acceptors (n = 8-18) the water-in-oil microemulsion media affect the charge separation of the initial encounter cage complex, $[Ru(bpy)_2^{3+}\cdots C_n V^+]$, and stabilize the photoproducts, $C_n V^+$ and $Ru(bpy)_3^{3+}$, against the recombination process. Consequently, enhanced quantum yields for $C_n V^+$ formation are observed under continuous illumination.

Photosensitized electron-transfer reactions in organized environments are currently of interest as a means of solar energy conversion and storage.¹⁻³ Different molecular organizates including micelles,^{4,5} colloids^{6,7} and polyelectrolytes⁸ were used as interfacial barriers that control the photoredox reactions, i.e., electron-transfer quenching and recombination of the intermediate photoproducts. In the presence of these charged interfaces, electrostatic repulsions and attractions of the charged photoproducts and the interference are operative in controlling the electron-transfer processes. A different conceptional approach for the retardation of the recombination reaction of the photoredox products has been recently introduced by Gratzel using lipophilic electron acceptors.⁹ In these systems proper design of a delicate hydrophobic-hydrophilic balance of the electron acceptors in their oxidized and reduced forms allowed the stabilization of the photoproducts against the degradative recombination reaction in micellar systems. Namely, the hydrophobic reduced acceptor was extracted into the micellar core and separated from the oxidized photoproduct being solubilized in the continuous aqueous phase. This system suggests that organization of photoredox reactions in an oil-water two-phase system might be a general approach for controlling photoinduced electron-transfer reactions.

Microemulsions (oil-in-water and water-in-oil) offer hydrophilic-hydrophobic two-phase systems.¹⁰ Owing to the high surface area of the one-phase microdroplets in the continuous second phase, efficient separation of an amphiphilic product across the two-phase boundary is anticipated. Although the detailed physical structural characteristics of water-in-oil microemulsions are still a matter of controversy,¹⁰ the aqueous-phase microenvironment allows the concentration of the photoactive reactants, and the subsequent extraction of a hydrophobic product into the

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Here we wish to report on the photosensitized reduction of a series of dialkyl-4,4'-bipyridinium salts, $C_n V^{2+}$ (1), in water-in-oil



microemulsions composed of toluene as the continuous organic phase. The sensitizer in these systems is tris(bipyridine)ruthenium dichloride, Ru(bpy)₃²⁺, and ethylenediaminetetraacetic acid, EDTA, is used as an ultimate sacrificial electron donor. We emphasize the functions of the hydrophobic oil-water boundary in assisting charge separation of the initial "encounter cage complex" of the photoproducts and provide evidence for the stabilization of the separated photoproducts of amphiphilic character against degradative back-electron-transfer processes.

Experimental Section

N, N'-Dialkyl-4,4'-bipyridinium dibromides were prepared by refluxing 4,4'-bipyridine with excess of the corresponding alkyl bromide in dimethylformamide for 8 h under nitrogen. The precipitate formed upon heating was filtered and washed several times with acetone. All bipyridinium salts gave satisfactory elementary analysis. Dodecylammonium propionate was prepared by dropping propionic acid into an equimolar amount of dodecylamine in benzene. After the mixture was refluxed for 3 h, the solvent was evaporated. The resulting oil crystallized upon cooling and was washed with 100 mL of petroleum ether.

Absorption spectra were recorded with a Uvikon-820 (Kontron) spectrophotometer. Flash photolysis experiments were performed with a DL200 (Molectron) dye laser pumped by a UV-IU (Molectron) nitrogen laser. Flashes were recorded on a Biomation 8100 and pulse collection was performed by a Nicolet 1170.

For continuous-illumination experiments a water-in-oil microemulsion composed of $Ru(bpy)_3^{2+}$ (2 × 10⁻⁵ M), dialkylviologen, $C_n V^{2+}$ (1 × 10⁻⁴ M) as electron acceptor, triammonium ethylenediaminetetraacetic acid, $(NH_4)_3EDTA$ (6 × 10⁻⁴ M) as

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Figure 1. Quantum yield for $C_n V^+$ production in the water-in-oil microemulsion: (a) n = 4; (b) n = 6; (c) n = 8; (d) n = 10, 12, and 14; (e) n = 18. In all experiments $[C_n V^{2+}] = 1.0 \times 10^{-4} \text{ M}$, $[\text{Ru(bpy)}_3^{2+}]$ = 2.0×10^{-5} M, and [(NH₄)₃EDTA] = 6.0×10^{-4} M.

electron donor, and dodecylammonium propionate (9 \times 10⁻² M) as a surfactant was prepared (all are bulk concentrations). The microemulsion consisted of 1.5% water (v/v) in toluene. The microemulsions were prepared by adding all the components to the toluene and stirring the composition by Vortex till the solution became clear. Samples (3 mL) were transferred to a $1 \times 1 \text{ cm}$ glass cuvette equipped with a valve and a serum stopper. The system was deaerated by repeated evacuation followed by free oxygen-argon flushings. The cuvette was immersed in a water bath with a 5×5 cm glass window. Illuminations were performed with a 1000-W halogen-quartz lamp. The light was filtered through a 400-nm cutoff fitter (Kodak 2C). Light intensities were determined by actinometry¹⁵ (photon flux 7.56×10^{-3} einstein L^{-1} min⁻¹). The progress of the reactions was followed spectroscopically at time intervals of illumination at $\lambda = 602$ nm ($\epsilon =$ $1.25 \times 10^4 \,\mathrm{M^{-1} \, cm^{-1}}$ for $\mathrm{C}_n \mathrm{V}^+$.). Fluorescence quenching studies were made on the same system without the $(NH_4)_3EDTA$ and with various concentrations of dialkylviologen ((0-10) \times 10⁻³ M in water-phase concentration). The decrease in the lifetime of *Ru(bpy)₃²⁺ upon addition of quencher was followed at $\lambda = 600$ nm. Charge separation and recombination rates were examined by following the initial absorption intensity and the decay of $C_n V^+$. at $\lambda = 602$ nm.

Results and Discussion

Steady-State Illumination. Illumination of the investigated systems, water-in-oil microemulsions that include $Ru(bpy)_3^{2+}$ as sensitizer, (NH₄)₃EDTA as electron donor, and the different dialkyl-4,4'-bipyridinium salts, $C_n V^{2+}$, resulted in the formation of the corresponding dialkyl-4,4'-bipyridinium radical cation, $C_n V^+$. The quantum yield of $C_n V^+$ production is displayed in Figure 1. It is evident that no viologen radical is formed for n= 1 under the conditions employed in our study. With butyl-viologen (n = 4) the formation of C₄V⁺ proceeds inefficiently $(\phi = 8 \times 10^{-4})$. Increasing the chain length of the dialkylviologens

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Figure 2. Plot of k_{obsd} against quencher $(C_n V^{2+})$ concentrations.

TABLE I: Charge Separation Yields and Recombination Rates in the Photosensitized Reduction of C_nV²⁺

$n (C_n V^{2+})$	1	4	6	8	14	18	
$\phi_{separation}^{a}$	0	0.006	0.036	0.040	0.050	0.054	
10 ⁹ $k_{b}^{,b}$ s ⁻¹ mol ⁻¹	c	26	8	0.7	0.33	1.2	
10 ³ $\phi_{steady state}^{d}$	<10 ⁻⁵	0.8	2.5	7.5	8.1	7.2	

^a Light intensity of laser pulse was determined by actinometry of the system Ru(bpy)₃²⁺, MV²⁺, pH 7; $\phi = 0.35$ (ref 16). ^b Determined by following the disappearance of $C_n V^+$ at $\lambda = 602$ nm ($\epsilon = 12500$ M⁻¹ cm⁻¹). No charge separation of C_1V^+ is observed in the water-in-oil microemulsion. ^dLight intensity 7.56 × 10⁻³ einsteins L⁻¹ min⁻¹.

(n = 6-14) improves the quantum yields for $C_n V^+$. formation, and no significant difference in the quantum yield for n = 8-14is observed ($\phi_{av} = 7.8 \times 10^{-3}$). With the octadecylviologen (n = 18) a minor decrease in the quantum yield for the radical $C_{18}V^+$. production is noticed ($\phi = 7.2 \times 10^{-3}$). To account for the difference in the quantum yields for C_nV^+ . formation, the different steps involved in the photosensitized electron-transfer reaction (Scheme I) have been examined: (a) the quenching process of Scheme I

*Ru(bpy)₃²⁺ + C_nV²⁺
$$\xrightarrow{k_q}$$
 [Ru(bpy)₃³⁺...C_nV⁺.] (1)

$$[\operatorname{Ru}(\operatorname{bpy})_{3}^{3+}\cdots C_{n}V^{+}\cdot] \to \operatorname{Ru}(\operatorname{bpy})_{3}^{3+} + C_{n}V^{+}\cdot \qquad (2)$$

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{3+} + \operatorname{C}_{n} \operatorname{V}^{+} \xrightarrow{\kappa_{b}} \operatorname{Ru}(\operatorname{bpy})_{3}^{2+} + \operatorname{C}_{n} \operatorname{V}^{2+}$$
(3)

*Ru(bpy)₃²⁺ by $C_n V^{2+}$ (eq 1), (b) the quantum yield of the dissociation of the initial encounter cage complex of photoproducts (eq 2), and (c) the recombination rates of the intermediary separated photoproducts (eq 3).

Quenching and Charge Separation. The fluorescence quenching of the $*Ru(bpy)_3^{2+}$ by $C_n V^{2+}$ in the water-in-toluene microemulsions has been examined. The observed quenching rate constants of the excited species by the different $C_n V^{2+}$ electron acceptors are displayed in Figure 2. It can be seen that similar Stern-Volmer plots are obtained for the different quenchers. This implies a similar effectiveness in the quenching of the excited species by the different $C_n V^{2+}$ electron acceptors. Assuming that all the components of the system, i.e., $Ru(bpy)_3^{2+}$ and C_nV^{2+} , are localized in the aqueous microdroplet environment of the microemulsion (vide infra), a value of $k_q = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is estimated.

Substantial differences in charge separation (eq 2) and recombination rates (eq 3) have been observed with the different acceptors. The quantum yields for the dissociation of the initial encounter cage complex of photoproducts and the bimolecular recombination rate constants of the intermediate separated photoproducts, $\operatorname{Ru}(\operatorname{bpy})_3^{3+}$ and $\operatorname{C}_n V^+$, are summarized in Table I. It is evident that while $\operatorname{C}_1 V^{2+}$ does not lead to any separated photoproducts, the yield of separated C_4V^+ is very low. Thus, despite the effective quenching of the excited species by $C_1 \hat{V}^{2+} - C_4 V^{2+}$, the yield of separated photoproducts is extremely inefficient. This is attributed to a rapid geminate recombination of the electron-transfer products in the initial "encounter cage structure". With C_6V^{2+} as electron acceptor the cage complex already dissociates to photoredox products, yet relatively ineffi-

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Figure 3. Transient decay of $C_n V^+$ followed at $\lambda = 602$ nm: (a) for $C_8 V^+$ in water-in-oil microemulsion; (b) for $C_4 V^+$ in water-in-oil microemulsion; (c) for $C_1 V^+$ in a homogeneous aqueous phase.

ciently ($\phi_{\text{separation}} = 6 \times 10^{-3}$). In turn the amphiphilic dialkyl-4,4'-bipyridinium salts, $C_8 V^{2+} - C_{18} V^{2+}$, reveal an effective charge separation of the photoredox products ($\phi = 4 \times 10^{-2} - 5.4 \times 10^{-2}$) as compared to the short-chain electron acceptors. Thus, the properties of charge separation of the initial cage complex of the photoredox products, $[Ru(bpy)_3^{3+}\cdots C_nV^{2+}]$, are in accordance with the quantum yields of C_nV^{+} formation under steady-state illumination. No $C_1 V^+$ is formed under steady-state illumination since no charge separation occurs, and the yield of $C_4V^{\textbf{+}}\textbf{\cdot}$ is very poor owing to the inefficient charge separation of C_4V^+ . The enhanced yield for the formation of C_8V^+ - $C_{18}V^+$ relative to the quantum yield of C_6V^+ is attributed to the differences in the effectiveness of charge separation in the respective cage structures.

The recombination rates of the separated photorpducts (eq 3) have been determined by following the decay of $C_n V^+$ at 602 nm ($\epsilon = 12500 \text{ M}^{-1} \text{ cm}^{-1}$). The bimolecular rate constants for the back-electron-transfer reaction are summarized in Table I. The decay curve of C₈V⁺ is displayed in Figure 3 and compared to the decay curve of $C_4 V^+$ in toluene-in-water microemulsion and C_1V^+ (methylviologen radical) in a homogeneous aqueous phase. In a homogeneous aqueous phase, methylviologen radical recombines with the oxidized product, $Ru(bpy)_3^{3+}$, with a diffusion-controlled rate constant,²² i.e., $k_b = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, for the recombination of C_1V^+ and $Ru(bpy)_3^{3+}$. In the water-in-toluene microemulsion the recombination rate depends on the alkyl chain length of the electron acceptor. The back-electron-transfer reaction of C_1V^+ could not be verified since no charge separation occurs. C_4V^+ back-reacts with Ru(bpy)₃³⁺ in the water-in-oil microemulsion with a recombination rate constant of 2.6×10^{10} mol⁻¹ s⁻¹. This value is enhanced as compared to the back-electrontransfer of dialkyl-4,4'-bipyridinium radicals with Ru(bpy)₃³⁺ in homogeneous aqueous solutions ($\sim 5 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$).¹

The long-chain reduction photoproducts C_8V^+ - $C_{18}V^+$ · recombine with a similar bimolecular rate constant (5 × 10⁸ M⁻¹ s⁻¹). This recombination rate constant is ca. 50-fold retarded as compared to the back-electron-transfer reaction of C4V+. in the similar

microemulsion and 20-fold retarded as compared to C_1V^+ in a homogeneous aqueous phase.¹⁸ Thus, the water-in-oil microemulsion stabilizes the photoproducts C_8V^+ . $-C_{18}V^+$. against the degradative back-electron-transfer reaction. The electron acceptor C_6V^{2+} exhibits intermediate behavior in respect of the backelectron-transfer reaction $(k_b = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$. While the recombination rate constant of $C_6 V^+$. with Ru(bpy)₃³⁺ is retarded as compared to those of $C_1 V^+ \cdot - C_4 V^+$, its back-reaction is enhanced relative to $C_8 V^+ \cdot - C_{18} V^+$.

Hydrophobic Interactions in the Photochemical Reactions. This analysis reveals a consistent behavior in the photosensitized reduction of the series of $C_n V^{2+}$ by $Ru(bpy)_3^{2+}$ in the water-in-oil microemulsion: (a) The quenching of $*Ru(bpy)_3^{2+}$ by the C_nV^{2+} electron acceptors is of similar effectiveness. (b) The charge separation yield of $C_n V^+$ from the initial encounter cage complex is enhanced as *n* increases. For n = 8-18 charge separation is of similar efficiency. (c) As n increases, the intermediate photoproducts are further stabilized against the recombination process (for C_1V^+ , $-C_8V^+$). The long-chain reduction products, C_8V^+ . $-C_{16}V^+$, are stabilized to a similar extent against the backelectron-transfer reaction, though we can notice that the C₁₈V⁺. already recombines more efficiently.

To account for this behavior of the $C_n V^{2+}$ series in the photosensitized reduction reactions in the water-in-oil microemulsions, we refer to three microenvironments present in these media; the water microdroplets, the detergent oil-water boundary, and the continuous organic oil phase. We suggest that the sensitizer is solubilized in the aqueous phase, while the electron acceptor, $C_n V^{2+}$, is either solubilized in the aqueous phase or localized at the oil-water boundary, depending on the length of the alkyl chain (n). Several observations indicate that the sensitizer, $Ru(bpy)_3^{2+}$, is indeed solubilized in the aqueous phase: (a) The absorption spectrum of $Ru(bpy)_3^{2+}$ strongly depends on the polarity of its environment.¹⁹ The absorption spectrum of $Ru(bpy)_3^{2+}$ in the toluene-water microemulsion is similar to that of $Ru(bpy)_3^{2+}$ in water. (b) The excited-state lifetime of the excited $Ru(bpy)_3^{2+}$ is similarly affected by the polarity of the microenvironment.²⁰ For example, while the lifetime of $Ru(bpy)_3^{2+}$ in water is $\tau = 0.58$ μ s, its lifetime is lengthened to $\tau = 0.80 \ \mu$ s when associated with an oil micellar core.²⁰ The lifetime Ru(bpy)₃²⁺ in the water-intoluene microemulsion is $\tau = 0.59 \,\mu s$, similar to the value obtained in pure water. (c) The recently reported method for the determination of the aqueous environment of an excited species using

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the solvent isotope effect²⁰ has been applied to the water-in-toluene microemulsion. By this method the excited-state lifetime of Ru(bpy)_3^{2+} is determined in H₂O and D₂O, and compared to its lifetime in H₂O-in-toluene and D₂O-in-toluene microemulsions. The lifetimes of *Ru(bpy)_3²⁺ in H₂O and D₂O are $\tau_{\text{H}_2\text{O}} = 0.58 \,\mu\text{s}$ and $\tau_{\text{D}_2\text{O}} = 0.94 \,\mu\text{s}$ in accordance with literature data. In the microemulsions, $\tau_{\text{H}_2\text{O}} = 0.59 \,\mu\text{s}$ and $\tau_{\text{D}_2\text{O}} = 0.87 \,\mu\text{s}$. From these data the *F* value (eq 4) is equal to 0.83 (where $\tau_{\text{H}(\text{S})}$ and $\tau_{\text{D}(\text{S})}$ are

$$F = [\tau_{H(m)}^{-1} - \tau_{D(m)}^{-1}] / [\tau_{H(s)}^{-1} - \tau_{D(s)}^{-1}]$$
(4)

the lifetimes of *Ru(bpy)₃²⁺ in surfactant-free media with pure H₂O or D₂O, respectively, as solvent; $\tau_{H(m)}$ and $\tau_{D(m)}$ are the lifetimes of $*Ru(bpy)_3^{2+}$ in the microemulsion containing H₂O or D_2O , respectively). The high F value implies that the Ru- $(bpy)_3^{2+}$ is essentially in an aqueous microenvironment. For comparison, F = 0.1-0.3 for sensitizers that are associated with the hydrophobic micellar core and only partially exposed to an aqueous environment.²⁰ (d) The energy-transfer quenching rate constant of $*Ru(bpy)_3^{2+}$ by anthracene has been examined in the water-in-toluene microemulsions. While in a homogeneous toluene--ethanol 1:1 mixture the quenching rate constant is $k_q = 2.2$ $\times 10^9$ M⁻¹ s⁻¹, very ineffective quenching of toluene-solubilized anthracene is observed in the microemulsion ($k_q = 3.1 \times 10^7 \text{ M}^{-1}$ s⁻¹). With respect to the location of the electron acceptor, $C_n V^{2+}$, we assume that $C_1 V^{2+} - C_4 V^{2+}$ are solubilized in the aqueous microdroplets, $C_{10} V^{2+} - C_{18} V^{2+}$ are concentrated at the oil-water "detergent-rich" interface, while $C_6 V^{2+} - C_8 V^{2+}$ might be equilibrated between the aqueous phase and the oil-water interface. These assumptions are based on the solubility properties of the different $C_n V^{2+}$ electron acceptors in the different phases. While $C_1V^{2+}-C_4V^{2+}$ are soluble only in water, $C_{10}V^{2+}-C_{18}V^{2+}$ are soluble in neither water nor toluene. In the presence of the detergent in the water-in-toluene microemulsion $C_{10}V^{2+}-C_{18}V^{2+}$ are completely solubilized, and thus their concentration at the water-oil boundary is conceivable. For $C_6V^{2+}-C_8V^{2+}$, we believe that an intermediate behavior exists where a distribution in both of the microenvironments occurs.21,25

The reduced photoproducts $C_n V^+$ show interesting solubility properties in organic phase vs. water. While the short-chain radicals $C_1 V^+ - C_4 V^+$ are only soluble in water and are not extracted into organic phases, $C_8 V^+ - C_{18} V^+$ are extracted from an aqueous phase into polar organic phases such as ethyl acetate, anisole, and 1,2-dichloroethane. The effectiveness of the extraction process is affected by the chain length of the radical cation and $C_8 V^+ - C_{18} V^+$ are quantitatively partitioned in the organic layers.²¹ Thus, the short-chain reduced electron acceptors are solubilized in the water droplets while the amphiphilic photoproducts $C_8 V^+ - C_{18} V^+$ are extracted into the polar oil-water boundary.

These observations allow us to rationalize the events involved in the photoinduced reduction of $C_n V^+$ in the water-in-toluene microemulsions. The similar quenching rate constant of *Ru-(bpy)₃²⁺ by the entire series of $C_n V^{2+}$ is easily interpreted in terms of the structural properties of the aqueous microdroplets in the water-in-toluene microemulsion. The size of the aqueous droplets of some water-in-oil microemulsions has been estimated to be 20-30 Å (in diameter).^{10b} As mentioned earlier, the lifetime of *Ru(bpy)₃²⁺ in the water-in-oil microemulsion is $\tau = 0.59 \ \mu s$. The mean diffusive movement \vec{d} of the excited species is given by eq 5, where D is the diffusion constant and τ is the excited-state

$$\bar{d}^2 = 2D\tau \tag{5}$$

lifetime. Assuming²² a diffusion constant of $D = 2.5 \times 10^{-5}$ cm² s⁻¹ we get $\bar{d} = 5.4 \times 10^{-6}$ cm. This means that in a 20-Å droplet the *Ru(bpy)₃²⁺ "touches" the interface more than 25 times during its lifetime. Thus, under these conditions the quenching rate of *Ru(bpy)₃²⁺ by C_nV²⁺ is independent of the location of the electron acceptor (at the interface or water droplets), since the excited species can diffuse across the droplets toward the interface



Figure 4. Schematic function of the water-in-oil microemulsion in charge separation and retardation of back electron transfer.

several times during its lifetime. Yet, the charge separation and retardation in the recombination rates, observed with $C_8V^{2+}-C_{18}V^{2+}$ is attributed to the function of the oil-water interface in extraction of the amphiphilic photoproducts C_8V^+ . $-C_{18}V^+$ (Figure 4). The initially formed encounter cage complex is associated with the interface owing to the hydrophobic character of the reduced acceptor countercomponent. Extraction of $C_8V^{\textbf{+}} {\boldsymbol{\cdot}} {\boldsymbol{-}} C_{18}V^{\textbf{+}} {\boldsymbol{\cdot}}$ into the detergent-rich oil-water boundary assists charge separation and stabilizes the photoproducts against the recombination process. With $C_1V^{2+}-C_4V^{2+}$ all of the components are localized in the "water pools" and no mechanism for charge separation exists. The intermediary properties that C_6V^{2+} exhibits are a result of a limited lipophilic character. This leads to an equilibrium distribution of C_6V^+ in the water phase and interface boundary. Consequently, the effects on charge separation and recombination rates are limited. It should be noted that electrostatic effects of the positively charged reversed micelles on charge separation can be excluded. Addition of 0.5 M NaCl to the aqueous microdroplets does not affect the charge separation and recombination rates of the photoproducts. This excludes the possibility that an electric field cooperates in controlling the electron-transfer reaction since the interfacial electrical surface potential sharply declines at this salt concentration.²³ The lack of electrostatic interactions operative in the charge separation is in accordance with the low surface potential of microemulsion interfaces.12

The effective charge separation and stabilization of the photoproducts against the degradative back-electron-transfer reactions observed with the $C_8V^{2+}-C_{18}V^{2+}$ electron acceptors allow the subsequent oxidation of (NH₄)₃EDTA with Ru(bpy)₃³⁺ (eq 6).²⁴

$$Ru(bpy)_{3}^{3+} + (NH_{4})_{3}EDTA \longrightarrow Ru(bpy)_{3}^{2+} + (NH_{4})_{3}EDTA^{\frac{1}{2}}$$

decomposition products (6)

Our results are closely related to those reported by Gratzel using the amphiphilic electron acceptor $MeC_{16}V^{2+}$ in CTAB micellar media.⁹ There, the amphiphilic photoproduct $MeC_{16}V^{+}$ formed in the aqueous phase extracted into the hydrophobic micellar core leading to the stabilization of the photoproducts against the recombination reactions. Yet, in Gratzel's system no effect of the micelles on the charge separation of the encounter cage complex could be detected. This is probably due to the fact that the encounter cage complex is positively charged and repelled by the positively charged micellar interface.

Conclusions

We have demonstrated pathways to assist charge separation and stabilize the photoproducts of electron-transfer reactions by means of a water-in-oil microemulsion. In the present study we

⁽²⁵⁾ A referee informed us that evidence for the location of $C_n V^{2+}$ in microemulsions has been examined. CF.: Mackay R. A.; et al. J. Disp. Sic., in press. This work seems to be in essential agreement with our hypothesis.

have used water-in-toluene microemulsions. The extraction properties of $C_n V^+$, where n = 8-18, into the continuous phase of toluene are poor. Other organic solvents such as ethyl acetate or anisole appear to extract effectively these radical ions. Recently,²¹ we have demonstrated that C_8V^+ undergoes an induced disproportionation reaction (eq 7) in a two-phase system of

$$2C_8V^+ \rightleftharpoons C_8V: + C_8V^{2+} \tag{7}$$

water-ethyl acetate and have utilized the two-electron reductant, C_8V^+ , in reduction of dibromostilbenes. This disproportionation equilibrium is unfavored in a homogeneous phase. It is forced toward the two-electron reductant, C_8V : due to the opposite solubility properties of C_8V^{2+} and C_8V : in the water-ethyl acetate phases. Thus, application of a water-in-oil microemulsion media

for the production of two-electron reductants via single-electron-transfer reactions, followed by an induced disproportionation, seems feasible. Consequently, the utilization of the doubly reduced product in the fixation of substrates being solubilized in the organic phase is conceivable. Such experiments utilizing this principle in the fixation of valuable products, i.e., reduction of ketones and CO_2 reduction, are now under way in our laboratory.

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Registry No. C1V2+, 3240-78-6; C4V2+, 32449-18-6; C6V2+, 6198-51-2; C_8V^{2+} , 36437-30-6; $C_{14}V^{2+}$, 33243-09-3; $C_{18}V^{2+}$, 90179-58-1; (NH₄)₃EDTA, 15934-01-7; Ru(bpy)₃²⁺, 15158-62-0.

Pressure and Temperature Dependence of the Reaction $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

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The kinetics of the reaction $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ (1) were studied with flash photolysis/visible absorption by monitoring the disappearance of NO₃ under pseudo-first-order conditions over the temperature range 236-358 K and pressure range 20-700 torr of helium and nitrogen. Reaction 1 was found to be in the falloff region between second- and third-order kinetics in this range. Falloff parameters were obtained by fitting the experimental data to the falloff equation of Troe and co-workers. When one uses a published temperature-dependent broadening factor (F_c) , the data are described by $k_0(N_2) = 4.5 \times 10^{-30}$ cm⁶ molecule⁻² s⁻¹ and $k_{\infty} = 1.65 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K with T dependencies of $T^{-3.4}$ and $T^{-0.4}$ for k_0 and k_{∞} , respectively. This expression was used in conjunction with recent measurements of the rate constant for N_2O_5 thermal decomposition to obtain an improved measurement $\Delta H_f^{\circ}(298)$ for NO₃, which was determined to be 17.3 ± 0.7 kcal mol⁻¹. From these data the recommended equilibrium constant expression is $K_{eq} = k_1/k_{-1} = 2.31 \times 10^{-8} \exp(11350/T)$ $(atm^{-1}).$

Introduction

The nitrate radical, NO₃, is an important member of the NO_x family in both the troposphere and lower stratosphere. Although its daytime concentration is limited to a few parts per trillion (ppt) due to rapid photolysis in the visible, nighttime concentration measurements have been reported at levels up to several hundred parts per trillion in both the urban and nonurban troposphere.¹⁻⁴

More significantly, the NO₃ lifetime has been observed to be considerably shorter^{1,4-6} than that expected on the basis of the simple scheme in which NO_3 is formed by the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

and removed via the equilibrium

$$NO_2 + NO_3 (+M) \rightleftharpoons N_2O_5 (+M)$$
 (1,-1)

This discrepancy can result from three sources: (1) incorrect rate or equilibrium constant data for reaction 1; (2) additional NO₃ loss processes such as reactions with aldehydes, alkenes, and aromatics; (3) additional losses for N_2O_5 , possibly via the reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{2}$$

which may be either homogeneous⁷ or heterogeneous.³⁻⁵ Errors in the equilibrium constant result only in changes in the partitioning of species in the NO_x family with little effect on the overall NO_x budget. On the other hand, if the short lifetime arises from the rapid loss of either NO_3 or N_2O_5 by other processes, then these losses may constitute a removal mechanism for NO_x which is more important that those already known, such as the formation of HNO_3 via the OH + NO_2 + M recombination. The discrepancy

in the NO₃ lifetime would then reflect a fundamental uncertainty in the atmospheric loss rate of NO_x .^{2,7}

A first step in the resolution of this question, then, is the establishment of accurate kinetic data for reaction 1. In previous evaluations of the rate constant for reaction 1,^{8,9} rate data for the N2O5 decomposition step have been combined with thermodynamic estimations of the equilibrium constant to obtain k_1 . The accuracy of this method has been limited by uncertainties in the thermochemistry of NO₃, and in the kinetic data for reaction -1. As a result, previous estimates of k_1 in the low-pressure limit span a factor of 3 ((1.4–3.7) × 10^{-30} cm⁶ molecule⁻² s⁻¹) and a factor of 7 in the high-pressure limit ((6.8–50) $\times 10^{-13}$ cm³ molecule⁻¹ s^{-1}). In a more recent study over a limited pressure range at 298 K, Fowles et al.¹⁰ derived values for k_1 and k_{-1} from a comparison

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