Transmembrane Electron Transfer Mediated by a Viologen: A Mechanism Involving Diffusion of Doubly Reduced Viologen Formed by Disproportionation of Viologen Radical

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A stopped-flow study of electron transfer (ET) through vesicle membranes composed of egg lecithin (phosphatidyl choline) was made. Cetylmethylviologen (*N*-methyl-*N*'-hexadecyl-4,4'-bipyridine, CMV) acted as transmembrane redox mediator by transferring electrons from dithionite in the bulk aqueous phase to CMV^{2+} or ferricyanide in the vesicle interior. Transmembrane ET was observed when viologen was bound only to the outer interface and the overall reaction was second order in viologen radical on the outside ($[CMV^+]_{out}$). Both facts exclude electron tunneling/self-exchange as mechanism. A mechanism is proposed where the rate-determining step is the disproportionation of two viologen radicals initially formed at the outer interface of the vesicle ($2CMV^+ = CMV^0 + CMV^{2+}$). CMV^0 diffuses rapidly through the membrane and is re-oxidized in the vesicle interior. A brief study of $Ru(bpy)_3^{2+}$-sensitized, photoinduced transmembrane ET was made, giving further evidence for transmembrane viologen migration. Preliminary results from pulse-radiolytically induced transmembrane ET support the observation that the reaction is second order in $[CMV^+]_{out}$.

Introduction

Electron transfer through vesicle membranes has been studied for more than a decade.[1-3] The main ambition has been to obtain model systems both for artificial photosynthesis as a whole and for studies of the elementary process of electron transfer. The transmembrane electron transfer is the crucial step in a reaction chain leading to separated photoproducts, since it offers an opportunity to increase the ratio of the foreward/backward reaction rates.

The viologens (*N*,*N*'-dialkyl-4,4'-bipyridine) are known to exist in three redox states: the water soluble, air-stable oxidized C_nV^{2+} (n = number of carbon atoms in each alkyl chain), the less water soluble, reduced radical C_nV^+, and the water insoluble, doubly reduced C_nV^0. They exhibit a chemistry where different dimerizations complicate interpretations of experimental results.[4] Nevertheless, they have often been used as redox mediators in microheterogeneous media[1-3] due to the reversibility of the oxidation/reduction and the stability and strong absorption of the radical, C_nV^+. The difference in hydrophilicity between the redox states has been used to stabilize charge separation, and, with use of different alkyl chains,[5-9] sometimes with charged groups,[10,11] a fine tuning of solubility properties to fit a particular system is possible.

The mechanism behind the transmembrane electron transfer is still a matter of controversy. In systems where viologen acts as transmembrane redox mediator, diffusion of C_nV^+,[7,8,11-13] electron tunneling/self-exchange between C_nV^+ and C_nV^{2+} on opposite sides of the membrane,[9,14] and a combination of those two[15a,16,17] have been proposed. One great problem in determining the mechanism is that the predicted kinetic behavior and rate dependences often are the same for the different mechanisms, as are the amounts and distribution of the products.[18]

We have studied transmembrane electron transfer mediated by cetylmethylviologen (*N*-methyl-*N*'-hexadecyl-4,4'-bipyridine, abbreviated CMV), an asymmetrically alkylated bipyridine, in small, unilamellar vesicles of egg lecithin by stopped-flow and steady-state photolysis techniques. CMV^{2+} binds to the vesicle membranes, where it is sited with its alkyl tail buried in the membrane and its viologen group at the interface, directly accessible to water soluble reductants, as for example dithionite. We present evidence excluding the possibility of electron tunneling/self-exchange and instead propose a mechanism where the doubly reduced CMV^0—formed in a disproportionation reaction between two viologen radicals (CMV^+)—diffuses through the membrane. This mechanism might well be general for viologens in heterogeneous media and not only in lecithin vesicles.[33]

Experimental Section

Materials. Methylviologen dichloride ($MVCl_2$, Sigma), tris(bipyridine)ruthenium dichloride ($Ru(bpy)_3Cl_2$, Ventron), egg lecithin (first grade, Lipid Products, Nutfield, England), and sodium dithionite (Merck), as well as all other chemicals, were of the highest commercially available purity and were used as received.

N-Methyl-*N*'-hexadecyl-4,4'-bipyridinium dichloride (CMV) was synthesized by a modification of the procedure described for *N*-methyl-*N*'-dodecyl-4,4'-bipyridinium dichloride.[19]

***N*-Methyl-4,4'-bipyridinium Iodide.** A 4.5-g (32-mmol) sample of methyl iodide was added to 4.95 g (32 mmol) of 4,4'-bipyridine in 250 mL of benzene. The reaction mixture became turbid and yellow after 20 min. It was stirred at room temperature for 4–5 days. The precipitate was filtered off, air-dried by suction, and placed in a soxhlet extractor. Unreacted 4,4'-bipyridine was removed by extraction with toluene (250 mL, 3 h), and the remaining *N*-methyl-4,4'-bipyridine was dried in vacuo; yield, 3.7 g, 38% (typical). TLC: $R_f \approx 0.29$. ^1H NMR (D_2O as solvent and internal standard at 4.75 ppm vs TMS): δ 8.83 (2 H, H2 and H6, d, J = 6.6 Hz), 8.69 (2 H, H2' and H6', d, J = 5.7 Hz), 8.30 (2 H, H3 and H5, d, J = 6.5 Hz), 7.83 (2 H, H3' and H5', d, J = 5.0 Hz), 4.36 (3 H, Me–N, s).

***N*-Methyl-4,4'-bipyridinium Chloride.** A 4.22-g (≈14-mmol) sample of *N*-methyl-4,4'-bipyridinium iodide was placed in a Soxhlet extractor. Extraction with acetonitrile (250 mL, 3 h) transferred *N*-methyl-4,4'-bipyridinium iodide into the acetonitrile solution, and any dialkylated product (*N*,*N*'-dimethyl-4,4'-bipyridinium diiodide) was retained in the Soxhlet filter (0.66 g). The acetonitrile was evaporated, and the resulting 3.56 g (11.9 mmol) of *N*-methyl-4,4'-bipyridinium iodide were dissolved in 50 mL of deionized water and passed through 50 mL of Dowex 1-X8 (20–50 mesh, ≈70 meq) anion exchange resin, which was further eluted with deionized water. Three fractions of about 40 mL each were collected, and the water was removed under reduced pressure until 5 mL remained (removal to dryness led to a green discoloration of the product). The rest of the water was removed by azeotropic distillation with benzene in a Dean-Starke setup, and the yield of off-white crystals (mp 135–7 °C) was 2.36 g (11.4

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mmol, 96%). TLC: $R_f \approx 0.29$. ^{1}H NMR (D_2O as solvent and internal standard at 4.75 ppm vs TMS): δ 8.83 (2 H, H2 and H6, d, J = 6.6 Hz), 8.69 (2 H, H2′ and H6′, d, J = 6.1 Hz), 8.32 (2 H, H3 and H5, d, J = 6.5 Hz), 7.83 (2 H, H3′ and H5′, d, J = 6.2 Hz), 4.36 (3 H, Me–N, s).

N-Methyl-N′-hexadecyl-4,4′-bipyridinium Dihalide. A 2.66-g (12.8-mmol) sample of *N*-methyl-4,4′-bipyridinium chloride and 6.11 g (20 mmol) of hexadecyl bromide were dissolved in 250 mL of acetonitrile and kept under reflux. After 30 h the product formed (≈1.6 g) was allowed to precipitate and was filtered off. Since TLC indicated unreacted starting material in the reaction solution, 3 mL of hexadecyl bromide was added four times during the following 6 days. The conversion was followed by TLC, and the reaction was stopped after 7 days. The precipitate was washed with acetonitrile and then recrystallized from 1-butanol. The yield of yellow crystals was 3.38 g (≈6.1 mmol, 47%). TLC: $R_f \approx 0.07$.

N-Methyl-N′-hexadecyl-4,4′-bipyridinium Dichloride (CMV). A 3.38-g (6.1-mmol) sample of *N*-methyl-*N*′-hexadecyl-4,4′-bipyridinium dihalide (calculated for dibromide) was dissolved in 100 mL of deionized water and passed through 65 mL of Dowex 1-X8 (20–50 mesh, ≈90 meq) anion exchange resin, which was further eluted with 200 mL of deionized water. Removal of the water under reduced pressure afforded 2.73 g (5.86 mmol, 96%) of white crystals, dec above 270 °C. Halide analysis indicated 97% chloride in the product. The mass spectrum contained peaks at m/z 396.3 (corresponding to $C_{27}H_{44}N_2$), at m/z 381.2 (loss of methyl group), and at m/z 171.1 (loss of hexadecyl group). ^{1}H NMR ($CDCl_3$ and di(methyl-d_3) sulfoxide (DMSO-d_6) (1:1 by volume) as solvent, with DMSO-d_6 as internal standard at 2.5 ppm vs TMS): δ 9.47 (2 H, H2 and H6, d, J = 6.5 Hz), 9.37 (2 H, H2′ and H6′, d, J = 6.4 Hz), 8.86 (2 H, d, J = 6.5 Hz), 8.83 (2 H, d, J = 6.5 Hz), 4.72 (2 H, N′CH_2CH$_2$, t, J = 5 Hz), 4.50 (3 H, N′CH_3, s), 1.95 (2 H, N′CH$_2$CH_2–, m), 1.2 (≈26 H, –(CH_2)$_{13}$–), 0.82 (3 H, –CH_3, t, J = 6.7 Hz).

Experimental Techniques. Stopped-flow experiments were made on a Hi-Tech SF-51 apparatus working anaerobically, using supplied lamp, monochromator, and photomultiplier. Solutions were bubbled with nitrogen for 20 min and transferred with gas-tight syringes to the reservoir of the stopped flow through a rubber septum. Stray light from the monochromator prevented accurate determination of absorbance, but for the small changes in absorbance occurring in this study ($\Delta A < 0.1$) the Lambert–Beer law was followed. Slower absorbance changes and absorption spectra were recorded on a Varian CARY 2400 spectrophotometer.

An eximer laser (Lambda Physik EMG 100, XeF yielding λ = 351 nm) was used for determining emission lifetimes of Ru(bpy)$_3^{2+}$.

All experiments were performed at 20 °C.

Preparative and Analytical Equipment. Proton NMR spectra were run on Bruker AM 400 and AC-F250 spectrometers. Melting point measurements were made on a Büchi SMP-20 (uncorrected). Mass spectra were obtained by direct inlet on a Finnigan MAT 4500-series GC/MS. TLC was performed on Merck aluminum oxide 60 F_{254} neutral (Type E), eluted with ethyl acetate/methanol/50% aqueous acetic acid (15:5:2 parts by volume). Ion exchange chromatography was performed on Dowex 1-X8 anion exchange resin. Halide analysis was performed by Centrala Analyslaboratoriet, Kemikum, Uppsala University.

Fitting of Experimental Curves. The curves from the fast reduction were fitted to one exponent with a good result (Figure 1). Curves from the transmembrane reaction step were fitted to a second-order rate equation (see Results and Discussion) and gave excellent to fair residuals (Figure 2). The residuals were worse for the faster reactions, so for comparable results for curves with a different quality of the fits, the fit was always made over the first 75 ± 3% of the amplitude starting after a time delay equal to 3 ± 1% of the fitted part of the curve (see arrows in Figure 2).

Redox and Spectral Properties of Viologen, Dithionite, and Ferricyanide. Absorption spectra for MV^{2+} and MV^+ were recorded early,[20] but the accuracy of the extinction coefficient for

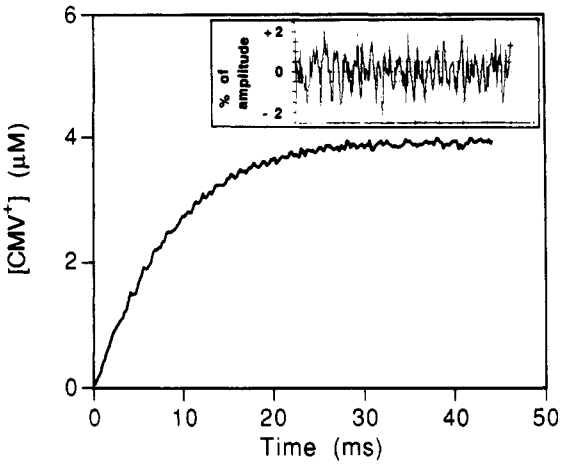

Figure 1. Typical kinetic curve for the fast reduction of CMV^{2+}_{out} (k_f). The residual for a single-exponential fit is shown. Conditions: $[CMV^{2+}]_{out}$ = 4.0 μM, $[S_2O_4^{2-}]$ = 6.0 mM.

MV^+ has been questioned.[21,22] When the viologens do not aggregate, the spectra are independent of the length of the alkyl chains. We have used the values $\epsilon_{602} = 1.3 \times 10^4$, $\epsilon_{396} = 4.0 \times 10^3$, and $\epsilon_{420} = 2.6 \times 10^3$ M^{-1} cm^{-1} (this study) for C_nV^+, $\epsilon_{260} = 2.0 \times 10^4$ M^{-1} cm^{-1} for C_nV^{2+} and $\epsilon_{420} = 1.0 \times 10^3$ for ferricyanide. An absorption spectrum for MV^0 has been recorded[21] showing substantial overlap with the near UV absorption of MV^+ but no absorption in the visible region. MV^0 can in principle be detected by comparing the absorbances at 602 and 396 nm.

The redox potentials for the C_nV^+/C_nV^{2+} and C_nV^0/C_nV^+ redox couples have been determined for different lengths of the alkyl chain and in different solvents[4] and are in water generally taken as –0.45 V and –0.70 to –0.90 V vs NHE, respectively. There is large scatter in the value for the C_nV^0/C_nV^+ couple since even for dimethylviologen the uncharged form is water insoluble. More relevant in vesicular media are potentials determined for membrane-bound viologens (–0.33 and –0.77 V vs NHE respectively for cetylmethylviologen in phospholipid membranes,[23] –0.29 and –0.63 V vs NHE respectively for octadecyl ethylviologen in planar lecithin bilayers[24]). It seems that care still must be taken when the values for the potentials are used, since for example the identity of electrolytes present strongly affects both potentials.[4]

Dithionite, $S_2O_4^{2-}$, is capable of reducing viologens according to

$$SO_2^- + C_nV^{2+} + H_2O \rightarrow HSO_3^- + C_nV^+ + H^+ \quad (1)$$

That SO_2^-, formed after dissociation of $S_2O_4^{2-}$, is to be considered as the active reductant has been shown.[25] The redox potential of the SO_2^-/HSO_3^- redox couple has been thoroughly studied[26] and was found to become less negative as the pH decreases or $[S_2O_4^{2-}]$ increases. A theoretical value for 1×10^{-8} M dithionite at pH = 8.0 was given as –0.78 V vs NHE, but at the concentrations used in this study the potential is less negative (E(midpoint) = –0.6 V vs NHE for $[S_2O_4^{2-}]$ = 6 mM, pH = 8[26]) and can only accomplish the first reduction step of the viologen (eq 1, see Results and Discussion).

Ferricyanide, $Fe(CN)_6^{3-}$, can be reduced to ferrocyanide, $Fe(CN)_6^{4-}$, by C_nV^+, C_nV^0, or dithionite.

Preparation of Vesicles. Egg lecithin in chloroform was added to a glass tube. The chloroform was evaporated with a stream of nitrogen gas followed by the tube being kept under low pressure (50 mmHg) overnight. A 5-mL aliquot of buffer solution (50 mM phosphate/HCl, pH = 8.0) was added. After 1–2 h of sonication (MSE Scientific Instruments Soniprep 150) on an ice bath, a slightly turbid solution of small, unilamellar vesicles, 200–300 Å in diameter, was obtained.[27] If the vesicles were to contain any substance in the inner water pool, or CMV^{2+} bound to both interfaces, this was added before the lecithin was sonicated. The bulk solution was replaced by gel exclusion chromatography (Sephadex G-50 fine). KCl was added to the external buffer used in chromatography to compensate osmotically for the occluded

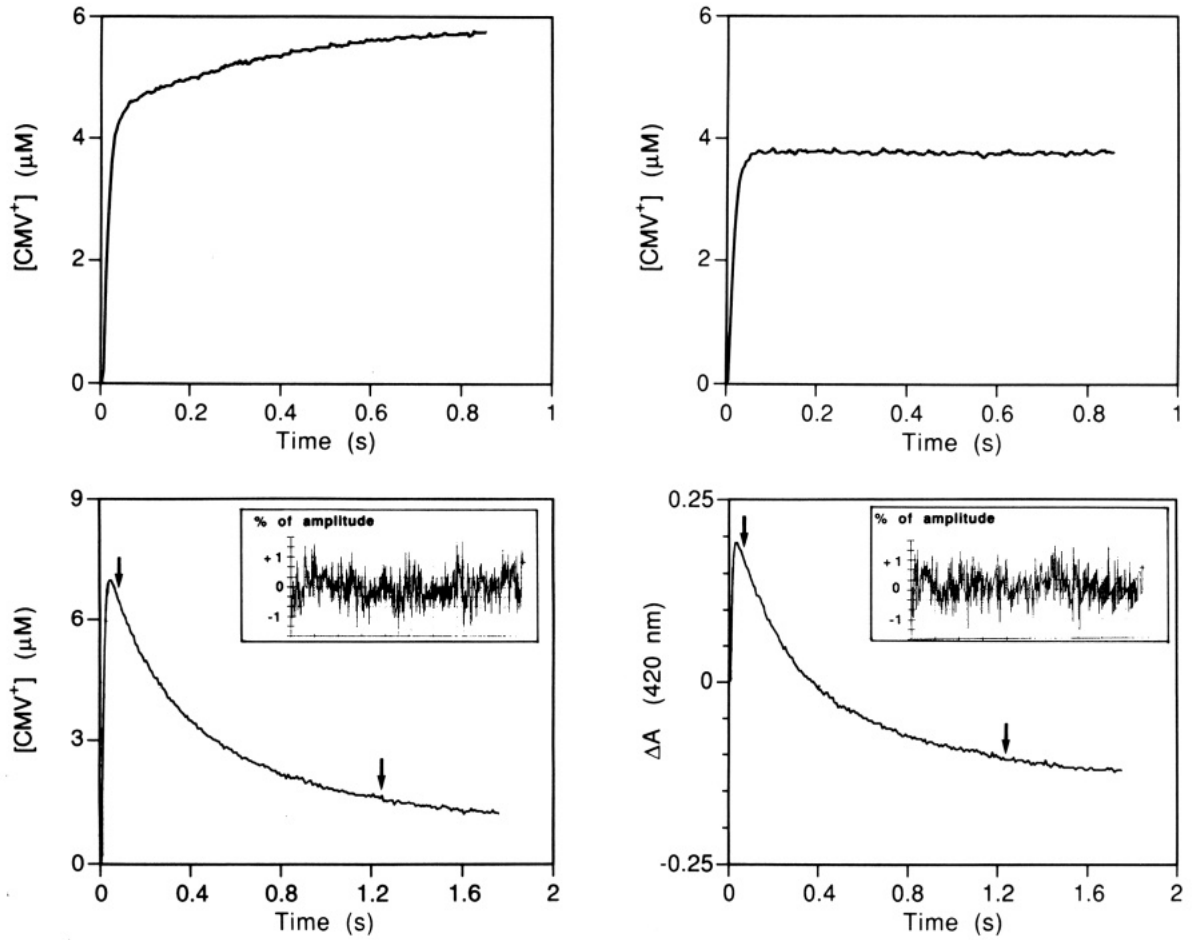

Figure 2. (a, top left) Typical kinetic curve for solutions of type I, showing biphasic reduction of viologen. The amplitude of the slow phase is half of the amplitude of the fast phase, as seen by comparison of a and b. Conditions: $[CMV^{2+}]_{out}$ = 3.8 μM, $[CMV^{2+}]_{in}$ = 1.9 μM, $[CMV^{2+}]_{out}$/[lipid] = 1.0×10^{-2}, $[S_2O_4^{2-}]$ = 6.0 mM. (b, top right) Typical kinetic curve for solutions of type II, showing no sign of further reduction of viologen after the initial fast reduction phase. Conditions: As in a, but no $[CMV^{2+}]_{in}$ present. (c, bottom left) Typical kinetic curve for solutions of type IV (identical with curves for type III) showing a decrease in reduced viologen after the initial fast reduction phase. The residual from a second-order fit is shown. The arrows indicate the part of the curve over which the fit was made. Conditions: $[CMV^{2+}]_{out}$ = 7.0 μM, $[CMV^{2+}]_{out}$/[lipid] = 9.1×10^{-3}, $[Fe(CN)_6^{3-}]$ = 50 μM, $[S_2O_4^{2-}]$ = 6.0 mM. (d, bottom right) Kinetic curve recorded at 420 nm for the same solution as in c, showing concomitant loss of CMV^+ and $Fe(CN)_6^{3-}$. Conditions: As in c.

species. Vesicle integrity was maintained even when membrane impermeable $Fe(CN)_6^{3-}$ was distributed asymmetrically. In experiments with CMV^{2+} bound only to the outer interface, this substance was added after the vesicles were sonicated but before chromatographic separation. Concentrations of occluded substances were determined by recording an absorbance spectrum with a pure vesicle solution as reference. Also, for viologens, the concentration was determined by destroying the vesicles by adding sufficient Triton X-100 and then measuring the absorbance of the radical CMV^+ at 602 nm after addition of an excess of dithionite.

To check the efficiency of the chromatographic separation, vesicles with only dimethylviologen (MV^{2+}) or ferricyanide in the interior were prepared. The absorbances at 602 and 420 nm respectively after addition of an excess of dithionite was observed by stopped flow and on a spectrophotometer. The pseudo-first-order rate constant for reduction of ferricyanide by 6 mM of dithionite in homogeneous solution (50 mM phosphate buffer) had been determined as 1×10^{-3} s^{-1} (this work). In the solution with ferricyanide in the interior of the vesicles, no detectable decrease in the concentration in ferricyanide on such a time scale was observed. In the solution with MV^{2+} inside the vesicles, a minor reduction corresponding to less than 2×10^{-7} M MV^{2+} on the outside was observed. A very slow reduction was observed in both types of vesicles, due to transmembrane diffusion of dithionite. This diffusion was observed in all types of vesicles, but did not interfere on the time scale of the other processes.

Types of Solutions Used in This Study. All solutions used in stopped-flow experiments contained 50 mM of phosphate buffer (pH = 8.0), 7–15 μM CMV^{2+}, and 1–3 mM lecithin, depending on the viologen/lecithin ratio. For experiments with dithionite-induced reduction, four types of vesicle solutions were prepared. Types I and III contained CMV^{2+} bound to both interfaces of the vesicles. Types II and IV contained CMV^{2+} bound to only the outer interface. Types III and IV also contained ferricyanide (added as $K_3Fe(CN)_6$) in the inner water pool of the vesicles, and KCl was added to the outer water phase. The amount of ferricyanide was always greater than twice the amount of viologen; i.e. the local concentration was 50–150 mM giving a total concentration around 50 μM. All concentrations in this section are given for the prepared solutions before mixing in the stopped-flow apparatus; i.e. they are twice the concentrations in the actual experiments.

Dithionite solutions were prepared by adding an appropriate amount of dithionite to degassed buffer (50 mM phosphate, pH = 8). If the desired concentration was very small, a stepwise dilution in degassed buffer was used in the preparation. All dithionite solutions were used within 2 h.

For experiments with light-induced reduction tris(bipyridine)ruthenium ($Ru(bpy)_3^{2+}$) was used as sensitizer. Vesicles of type V formed of 4.5 mM lecithin contained 0.018 M $Ru(bpy)_3^{2+}$ and 0.15 M EDTA in the inner water pools, corresponding to total concentrations of 9 and 70 μM, respectively, and 77 μM CMV^{2+} was bound to both interfaces. $K_3Fe(CN)_6$ (1.0 mM) was added to the outer water phase.

Viologen Binding to the Vesicles. Vesicle solutions with CMV^{2+} bound to both interfaces (type I) and only to the outer interface (type II) were prepared. During the chromatographic separation,

fractions of the eluted solution were collected. The absorbance at 320 nm was taken as a measure of the relative vesicle concentration for the different fractions. The concentration of viologen in each fraction was determined by measuring the absorbance at 602 nm after destruction of the vesicles with Triton X-100 and reduction by dithionite. The elution profiles were identical for vesicles and viologen, for vesicles of both types I and II, and no viologen could be detected in the solution eluted after the vesicles (data not shown). The total amount of eluted viologen in the vesicle fractions was in good agreement (±10%) with the amount that was added initially. It was thus concluded that CMV^{2+} binds completely to the vesicles.

Results and Discussion

Kinetic Behavior. A stopped-flow apparatus was used to follow the dithionite-induced change of absorbance at 602 nm with time for vesicle solutions of types I–IV (Figures 1 and 2). After the samples were mixed, a rapid increase in absorbance was observed for solutions of all types, as all viologens bound to the outer side of the vesicle membrane were reduced according to eq 1. The reduction was pseudo-first order, since dithionite was in great excess, and the curves were fitted to a single-exponential model with a good result (Figure 1).

Solutions of type I exhibited a biphasic increase in absorbance; i.e. a reduction on a longer time scale was observed after the initial one. The slower phase was fitted to a second-order rate equation (see Experimental Section). The amplitude of the faster phase was twice that of the slower (Figure 2a,b). In vesicles of type II only the fast phase was present. This shows that there are, in vesicles of type I, viologens that are less accessible to reduction from the bulk phase than those initially reduced. They could either be bound to the interface of the inner side of the vesicle membrane, where they are reduced in an indirect process, or located at sites on the outer interface, where the viologen head-group is more deeply buried in the membrane and where they are reduced directly by dithionite. Binding heterogeneity of the latter type has been considered in dihexadecyl phosphate (DHP) vesicles before.[9,28] The results from vesicle solutions of types III and IV show, however, that the slow phase originates from reduction of viologen bound to the inner side of the membrane (see below). There is no sign of the other type of binding heterogeneity. The ratio of the amplitudes of the fast and slow phase is consistent with a statistical distribution of viologens over the two sides of the vesicle membrane since the area of the inner side is about $^1/_3$ of the total interfacial area of the vesicle. The absence of the slower reduction phase in vesicles of type II shows that CMV^{2+} does not "flip-flop" or diffuse through the membrane during the time of preparation and experiments (<4 h).

Solutions of types III and IV showed no difference in behavior upon reduction: the rapid initial reduction was followed by a slower decrease in absorbance at 602 nm until all reduced viologen formed initially was consumed (Figure 2c,d). The decreasing phase was fitted to a second-order rate equation (see Experimental Section). The rate constant was the same as for the slow phase in solutions of type I when viologen/lecithin ratios were identical. The decrease in absorbance at 420 nm as ferricyanide was reduced gave curves that could be fitted to the same equation as the slow phase at 602 nm. The rate constants were the same for the two wavelengths in all experiments. The slower phase was therefore attributed to a transmembrane redox process where, in vesicles of type I, viologens bound to the inner membrane interface were reduced and, in vesicles of types III and IV, ferricyanide in the inner aqueous phase was reduced by viologens initially on the outer side by a mechanism explained below.

Viologen Migration. Absorption spectra showed that, in vesicles of types III and IV, no reduced viologen was present at the end of the reaction—in spite of the fact that dithionite was in great excess—so long as the initial amount of entrapped ferricyanide was more than twice the amount of viologen. This has earlier been noticed for the same system with dihexadecylviologen (CCV^{2+}) by Khramov et al.[15a] who suggested that all viologen diffused as radical (CCV^{+}) to the inside where it was oxidized by the ferricyanide and was thus membrane impermeable and inaccessible to dithionite. They also showed that when Triton X-100 was added to destroy the vesicles, viologen radical was formed immediately. This was confirmed in our laboratory.

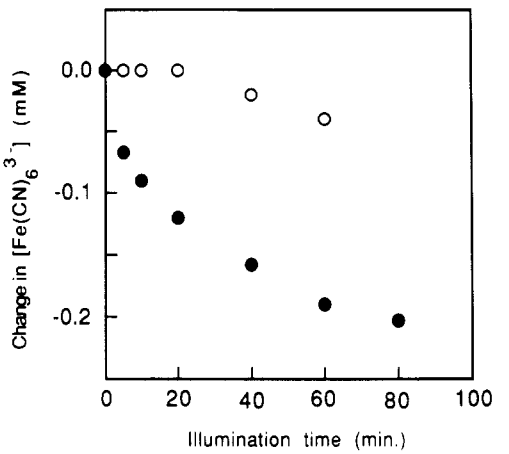

Figure 3. Decrease in $[Fe(CN)_6^{3-}]$ upon illumination for a solution of type V. Conditions: see Experimental Section; (●) CMV^{2+} added; (○) no CMV^{2+} added.

After complete reduction of vesicles of type I or II, an absorption spectrum from pure radical monomer was obtained.[20,21] Other researchers[9,17] have reported formation of radical dimers in the transmembrane reduction process in vesicles composed of dihexadecyl phosphate. There was no sign of CMV^0 in the spectrum.

Evidence for viologen migration was also obtained from preliminary measurements of $Ru(bpy)_3^{2+}$ emission in vesicles of type V. The lifetime for the $Ru(bpy)_3^{2+}$ emission in the vesicles was 0.30 μs due to quenching by viologen. After 5 min of exposure to filtered light from a xenon lamp (λ > 400 nm), the emission lifetime had increased to 0.42 μs. Differential absorption spectra showed no sign of viologen radical or oxidized ruthenium complex, but ferricyanide in the bulk phase had been reduced (Figure 3). Since quenching of ruthenium emission is more efficient by 0.1 mM $Fe(CN)_6^{3-}$ ($k_q = 6.5 \times 10^9\ M^{-1}\ s^{-1}$ [29]) than by the CMV^{2+} in these vesicles, this shows that the emitting $Ru(bpy)_3^{2+}$ was still located inside the vesicles but the CMV^{2+} had moved from the inner interface. Since the oxidized viologens reside at the interfaces, it must have moved to the outer interface of the vesicles. Continued illumination did not increase the lifetime of the emission, but ferricyanide was further reduced. The experiment was repeated with a solution of the same type, but lacking viologen giving a lifetime of 0.42 μs for the ruthenium emission. No reduction of the ferricyanide during the first 20 min of illumination was observed. No conclusion about the stoichiometry in the reduction of ferricyanide by viologen can be drawn from this experiment since the lifetime of $Ru(bpy)_3^{2+}$ emission indicates that all viologen had migrated to the outside after 5 min, while reduction of ferricyanide continued to be faster in vesicles with viologen rather than in vesicles without viologen for at least 20 min. The reason for the prolonged reduction of ferricyanide in vesicles with viologen is not clear at this stage, since it seems that all viologen has moved to the outside. The experiment shows anyhow that viologen migrates in a far from reversible manner during transmembrane redox even in this system. Note, though, that the time scale is much longer than in the stopped-flow experiments.

Rate Dependences. To elucidate the mechanism behind the transmembrane redox process, a study of the dependence of the transmembrane reaction rate on the viologen/lecithin ratio was made for vesicles of type IV (Figure 4). A linear relationship was found, partially in accordance with earlier results,[15a,b] indicating that the transmembrane redox reaction must include a rate-limiting step which is second order in viologen. This was earlier taken as evidence for tunneling/self-exchange between viologen radical at the outer interface ($C_nV^{+}_{out}$) and oxidized viologen at the inner interface ($C_nV^{2+}_{in}$).[15a] In our study the same result was obtained with vesicles where viologen was bound only

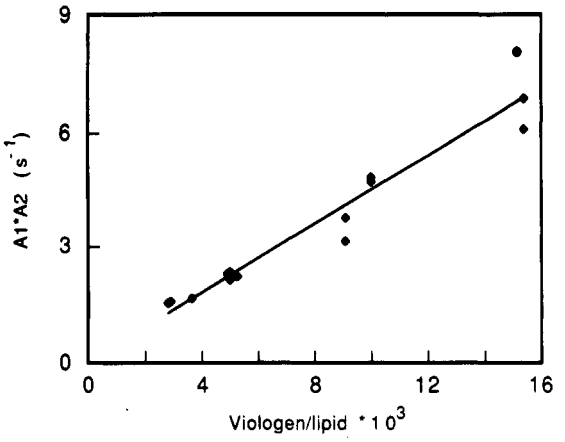

Figure 4. Rate of transmembrane redox for solutions of type IV versus the ratio $[CMV^{2+}]_{out}/[lipid]$. A1 and A2 are the amplitude and the second-order rate constant, respectively, for the fitted curves (i.e. $(A1)(A2) = t_{1/2}^{-1}$). Each point is an average of four to eight individual determinations for the same vesicle preparation. Standard deviation (SD, not shown) was less than twice the size of the points. The line is a least-squares linear fit to the points. Conditions: see Experimental Section; $[S_2O_4^{2-}] = 6.0$ mM.

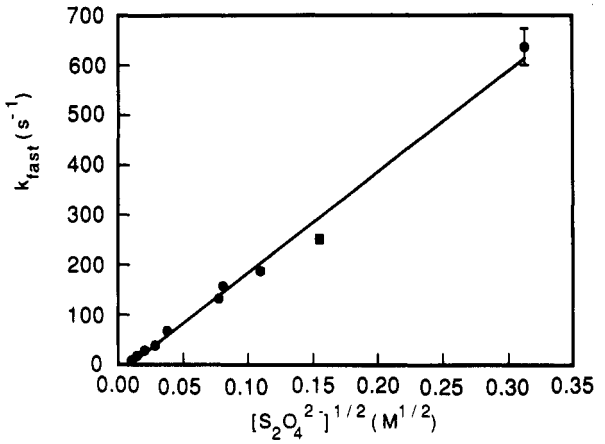

Figure 5. Rate of the initial fast reduction of CMV^{2+}_{out} versus $[S_2O_4^{2-}]^{1/2}$. Each point is an average of four to six individual determinations for the same vesicle solution. The error bars show ±SD, although this is only visible for some points. The line is a least-squares linear fit to the points. The line does not go exactly through the origin, reflecting the fact that the actual concentration of dithionite is slightly lower than calculated (see text). Conditions: $[CMV^{2+}]_{out}/[lipid] = 5.0 \times 10^{-3}$.

to the outside (type IV), thus ruling out this mechanism. Electron tunneling between membrane-bound CMV^{+}_{out} and ferricyanide in the inner water pools of the vesicles is impossible on a reasonable time scale due to long transfer distance and mismatch of electronic energy levels. The rate of reduction of external viologen in the rapid step was independent of the viologen/lecithin ratio.

The rate of the fast reduction step (k_f) was found to be proportional to the square root of the concentration of dithionite in accordance with eq 1 (Figure 5). The transmembrane reaction rate in vesicles of type IV was found to be independent of the concentration of dithionite until the latter reached low enough values (Figure 6), when it decreased steadily. It was noted, however, that the decrease in rate was accompanied by a decrease in amplitude of the absorbance versus time curves for the initial reduction, due to that the residual concentration of oxygen in the solution becomes more important at low concentration of dithionite. The oxygen in the vesicle solution and in the degassed buffer used for preparation of the dithionite solution oxidized dithionite, thus decreasing the SO_2^-/HSO_3^- ratio. The reductive power of the dithionite was therefore lowered, and the viologen could only be partially reduced. Dithionite was in excess, however, so as viologens were transported to the vesicle interior, all viologens initially on the outer side could eventually be reduced, but at a lower rate than if there was a complete reduction of external

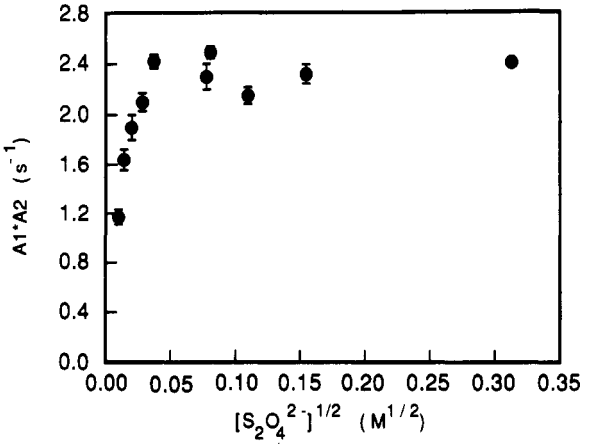

Figure 6. Rate of transmembrane redox for solutions of type IV versus $[S_2O_4^{2-}]^{1/2}$. A1 and A2 as in Figure 4. Each point is an average of four to six individual determinations. The error bars show ± SD. Conditions: $[CMV^{2+}]_{out}/[lipid] = 5.0 \times 10^{-3}$.

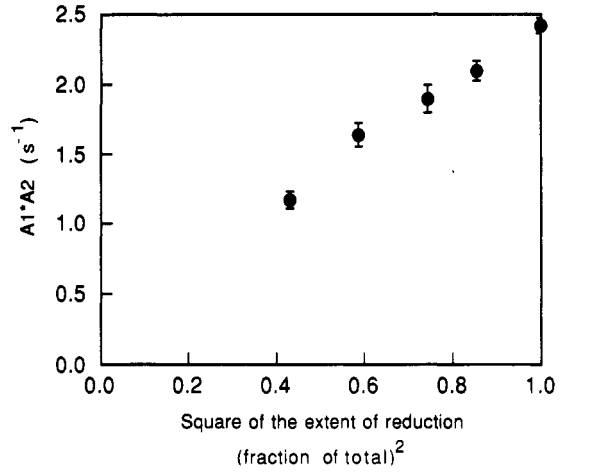

Figure 7. Rate of transmembrane redox versus the square of the extent of reduction for the points at the lowest $[S_2O_4^{2-}]$ in Figure 6 (see text). Conditions: See Figure 6.

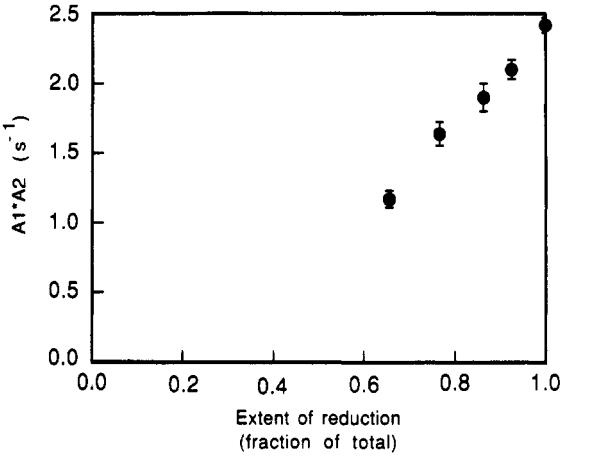

Figure 8. Same situation as in Figure 7, but plotted versus the extent of reduction.

viologen. A plot of the rate of transmembrane reduction versus the square of the extent of reduced external viologen (calculated from the amplitude of the curves from the fast reduction) gives an almost linear dependence (Figure 7). The slight curvature suggests some small systematic deviation ("real", or obtained in the fitting process) from a straight line going through the origin, indicating a proportional relationship. A plot made versus the extent of reduced external viologen also gives an almost straight line (Figure 8), since the range is rather narrow. In this case, however, a line through the points crosses the x-axis far from the origin, showing that the relationship is far from proportional. This

is consistent with a reaction being second order in $[CMV^+]_{out}$. The rate (M s^{-1}) of a normal second-order reaction (eq 2) is

$$-d[A]/dt = k[A]^2 \quad (2)$$

proportional to the square of the concentration of reactant making $1/t_{1/2}$ proportional to [A], but in this case the pre-equilibrium (eq 1) with dithionite in excess eventually makes all $CMV^{2+}{}_{out}$ reactant ($CMV^+{}_{out}$). The amount of reactant that has to be consumed in the reaction is therefore the same, irrespective of the extent of reduction, making $1/t_{1/2}$ (=(A1)(A2) in Figures 6–8) proportional to the square of the extent of reduction (i.e. the concentration of CMV^+ formed initially). This last rate dependence is an evidence against the electron tunneling/self-exchange mechanisms, since they are only first order in $[CMV^+]_{out}$ and first order in $[CMV^{2+}]_{in}$. This was a way to discriminate between mechanisms including electron tunneling/self-exchange on one hand and mechanisms being second-order in $[CMV^+]_{out}$ on the other, a way that is not possible when all outer viologens are reduced initially. The second-order dependence on $[CMV^+]_{out}$ is also consistent with the shape of the experimental curves.

Preliminary results from pulse-radiolytic measurements on vesicles of type IV also show that the transmembrane redox rate is second order in $[CMV^+]_{out}$. The pulse generates radicals that act as reducing agents before they recombine with each other. The $CMV^{2+}{}_{out}$ is very rapidly ($<10^{-4}$ s) reduced to CMV^+, but after that there is no further reduction of viologen. This means that CMV^{2+} formed in the disproportionation is not re-reduced but stays on the outer interface of the vesicle. The rate of transmembrane redox should exhibit the same dependence on the $[CMV^+]$ formed initially ($[CMV^+]^0$) as a normal second-order reaction, i.e. $1/t_{1/2}$ should be proportional to $[CMV^+]^0$. The pulse was varied to give different $[CMV^+]^0$ (i.e. different extents of reduction), and the disappearance of CMV^+ was followed as in the stopped-flow measurements. The kinetic curves were fitted to a second-order rate equation, and a good proportional relationship between $[CMV^+]$ formed initially and the rate ($1/t_{1/2}$) was obtained (a full account for the pulse-radiolytic measurements will be published separately[30]). The pulses were kept at a level where no CMV^0 was produced in the initial reduction.

The transmembrane reaction rate in the stopped-flow experiments was independent of the internal concentration of ferricyanide.

Stoichiometry. In the stopped-flow experiments on vesicles of types III and IV, it was also noticed that the curves recorded at 420 nm exhibited a fast increase in absorbance, the kinetics of which was identical with the rapid phase observed at 602 nm. An accurate extinction coefficient for the viologen radical at 420 nm was determined as 2600 ± 100 M^{-1} cm^{-1} by comparison of the absorption at 602 and 420 nm in the same spectrum for pure CMV^+. This is more than twice as much as the extinction coefficient for ferricyanide at the same wavelength. Ferricyanide contributes to almost half of the total absorbance change at 420 nm due to the stoichiometry of the reaction (see below), and the correspondence between kinetics at 420 and 602 nm is excellent. This is therefore good support for the assumption that viologen radicals and ferricyanide are consumed in the same reaction step. The shape of the curves recorded at 420 nm provided an opportunity to determine the stoichiometry in the reaction between CMV^+ and $Fe(CN)_6^{3-}$ when stray light in the monochromators of the stopped-flow apparatus made accurate comparisons between measured absorbances at different wavelengths impossible (see Experimental Section). It was found (see Figure 2d) that the relative amplitudes of the fast increase/slow decrease in absorbance at 420 nm was 1:1.7 (estimated error ±10%). This shows that two ferricyanides are reduced for every viologen initially reduced ($\epsilon_{CMV^+}:\epsilon_{CMV^+} + 2\epsilon_{Fe(CN)_6^{3-}} = 1:1.77$), as also found by absorption spectra for vesicle solutions recorded immediately after dithionite addition, i.e. after the transmembrane reaction was completed but before dithionite had diffused through the membrane (data not shown). The stoichiometry implies that each viologen on the outer side must be reduced twice before being trapped as CMV^{2+} inside the vesicle, as earlier found by Khramov et al.[15a]

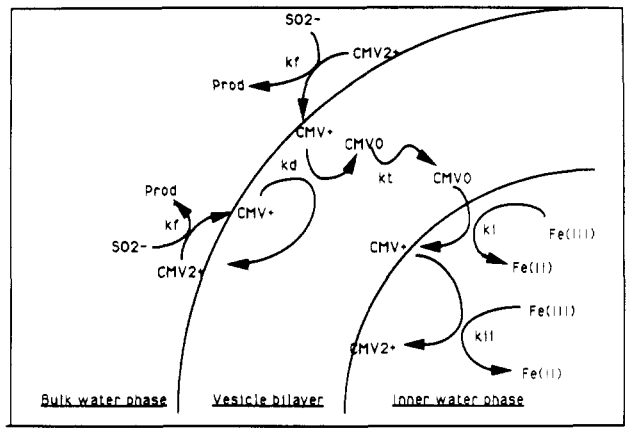

Figure 9. Reaction scheme for the proposed mechanism (solutions of type IV).

Mechanism. We propose a mechanism in which the disproportionation

$$2CMV^+ = CMV^0 + CMV^{2+} \quad (3)$$

is the rate-determining step (k_d, Figure 9) and is followed by a rapid transmembrane diffusion (k_t) of the doubly reduced CMV^0. In vesicles of type I, CMV^0 then reduces internal CMV^{2+} in a conproportionation reaction. In vesicles of types III and IV, CMV^0 reduces 2 equiv of ferricyanide, which is in excess, in a direct reaction with the ferricyanide. The reduction of ferricyanide in two steps (k_i and k_{ii}) is rapid compared to the disproportionation, and the overall rate is therefore, as observed, independent of the internal concentration of ferricyanide within the range used in this study (50–150 mM). The CMV^{2+} formed in the disproportionation is rapidly re-reduced by external dithionite, which is always in excess, making the viologens participate in two disproportionation reactions on the average before diffusing through the membrane. Since dithionite and ferricyanide are in excess (types III and IV), all viologen initially on the outside will be located in the vesicle interior at the end of the reaction. There is never any detectable amount of CMV^0 present in the system.

The proposed mechanism is consistent both with the linear dependence of the transmembrane rate on the viologen/lecithin ratio at full reduction of $CMV^{2+}{}_{out}$ (Figure 4) and the quadratic dependence on the extent of reduction of $CMV^{2+}{}_{out}$ at lower concentrations of dithionite (Figure 7). It is consistent with the stoichiometry of the reduction of ferricyanide by viologen radical, as well as with the fact that transmembrane redox is observed even though viologen is bound only to the outer interface of the vesicle. It is also consistent with the shape of the experimental curves.

The disproportionation reaction (eq 2) is well-known in homogeneous solution, and the equilibrium is shifted far to the left,[4,31] even if exact values are difficult to determine since the redox potentials are uncertain. In a heterogeneous medium, the disproportionation should be more favorable, even if the redox potentials as determined by Cotton et al.[23] give a value of 2.5×10^{-6} for the disproportionation constant, which is roughly equal to the value for methylviologen in a homogeneous water phase. This is probably incorrect since the vesicular media offer considerable increase in stabilization and spatial separation of the different redox forms.

It is interesting that, in vesicles of type IV, the back-reaction (conproportionation) seems to be negligible once a disproportionation couple has separated, since no dependence of the transmembrane reaction rate on concentration of dithionite was observed. Even at the lowest concentrations of dithionite—when only partial reduction of outer viologen was obtained and there was a substantial surface concentration of CMV^{2+}—no decrease in the transmembrane rate due to back-reaction was observed. This can be explained by the large differences in hydrophilicity between the redox forms. CMV^{2+} is water soluble in substantial amounts and is likely to be bound to the vesicle membrane with the viologen head-group relatively well-exposed to the water. The reduced radical form (C_nV^+) is water soluble in large amounts

only if the alkyl chains are short. The doubly reduced C_nV^0 is water insoluble for all lengths of the alkyl chains. CMV^0 is probably dissolved in the hydrophobic core of the membrane, which is why the rate of transmembrane diffusion must be increased considerably compared to the more oxidized forms. The CMV^{2+} and CMV^0 are thus residing in different environments, and the rate of CMV^0 transmembrane diffusion and subsequent reaction in the vesicle interior is probably rapid compared to the back-reaction (conproportionation) on the outside (rate constant k_{-d}); i.e. $k_i k_t/(k_i + k_t) \gg k_{-d}$, which is why encounters between those species rarely occur. The fate of a separated disproportionation couple (dc) in vesicles of type IV is determined by eq 4, where n_{e^-} is the number of electrons transferred through the membrane,

$$n_{e^-}/n_{dc} = 2\{k_i k_t/(k_i + k_t) + k_f\}/\{k_i k_t/(k_i + k_t) + k_f + k_{-d}\} \quad (4)$$

n_{dc} is the number of separated disproportionation couples formed, and the rate constants are first or pseudo-first order ones as defined in Figure 9. If either the CMV^{2+} or the CMV^0 in a dc reacts in a consecutive reaction step before they recombine, two electrons are transferred through the membrane. It can be seen that if k_i, k_t, and k_f are large compared to k_{-d}, the transmembrane redox rate (as n_{e^-} per time unit) is equal to twice the rate of dc formation (each CMV^0 transfers two electrons). If $k_i k_t/(k_i + k_t) \gg k_f$, the rate is also independent of the concentration of dithionite, as was observed (Figure 6).

In vesicles of type I, where transmembrane redox proceeds through a conproportionation between CMV^0_{in} and CMV^{2+}_{in} yielding CMV^+_{in} as a result, a more complicated behavior is predicted. The rate of reaction is determined by the relative concentrations of CMV^{2+}_{in} and CMV^{2+}_{out}, the latter which only exists momentarily after a disproportionation reaction and disappears either through reduction by dithionite or through conproportionation. At full reduction of viologen on the outside much more CMV^{2+}_{in} than CMV^{2+}_{out} is available, driving the reaction forward ($k_{-d}[CMV^{2+}]_{in} \gg k_{-d}[CMV^{2+}]_{out}$). As the reaction proceeds the amount of CMV^{2+}_{in} decreases, which is why the probability for back-reaction (conproportionation on the outside) increases until the reaction stops when all, or nearly all, CMV^{2+}_{in} has been reduced. The amount of CMV^+_{out} has then been reduced to half of its initial value. A theoretical analysis of the overall reaction rate for vesicles of type I results in very complicated expressions, making predictions of the rate dependences difficult. In the beginning of the transmembrane redox, when $[CMV^{2+}]_{in}$ is high, the reaction should behave as second order in $[CMV^+]_{out}$, but competing terms complicates later behavior. The fact that the first 80% (of the amplitude) of the curves can be fitted to a second-order rate equation does not prove that the reaction is of pure second order. The complexity of the transmembrane redox for vesicles of type I and the fact that electron tunneling/self-exchange automatically could be excluded were the reasons why vesicles of type IV were chosen for detailed studies.

Direct reduction of a minor fraction of CMV^{2+} to CMV^0 by dithionite cannot be responsible for the production of CMV^0 since the rate of transmembrane redox would then be pseudo-first order in $[CMV^+]_{out}$ and first order in $[S_2O_4^{2-}]^{1/2}$, which is far from the observed behavior. The fact that detectable amounts of doubly reduced viologens by direct reduction with dithionite has been observed in other vesicular systems[32] must be viewed considering the influence of temperature, pH, type of viologen, and type of surfactant used for vesicle formation on the redox potentials for the viologen and the dithionite (for example, $\Delta E/\Delta pH = -0.118$ V for the dithionite potential[26]). A reviewer suggested that dithionite could reduce a viologen radical dimer ($(CMV)_2^{2+}$) to CMV^+ and CMV^0, if the redox potential was more favorable than for reduction of CMV^+. In that case there would be a second-order dependence on $[CMV^+]_{out}$, consistent with our results, but the reaction would also be first order in $[S_2O_4^{2-}]^{1/2}$.

Transmembrane diffusion of CMV^+ on the time scale of reaction can not be excluded but can for stoichiometric reasons only contribute to a minor part of the overall reaction. A minor diffusion of CMV^+ could, though, explain why some deviation from a second-order behavior is observed (see Experimental Section). This path would contribute to a greater part of the overall reaction as the reaction proceeds since it is only first order in $[CMV^+]_{out}$, and deviations from second-order behavior at the end of the reaction would follow. The deviation should in this case be greater for a lower viologen/lipid ratio, the opposite to what is observed.

The proposed mechanism has an advantage over mechanisms involving a major contribution from electron tunneling/self-exchange or diffusion of charged species (C_nV^+, $(C_nV)_2^{2+}$, or $(C_nV)_2^+$) in that no charge compensating flow of ions through the membrane is necessary to neutralize the electrostatic potential that otherwise would build up and terminate the reaction before it had gone to completion. Such proposed charge compensating ions are not always identified, and if they are, it is still uncertain which is the rate-determining process. It is therefore easy to end up in a patchwork of different rate-limiting steps for different circumstances where sometimes diffusion of unidentified ions and sometimes diffusion of or electron transfer between viologens determine the rate of transmembrane reduction.[2]

Recently an article appeared[2] where the author mentioned the mechanism proposed in this work as one of four possible in a system with MV^{2+} in DHP vesicles but rejected it after only brief consideration since he found no dependence of the transmembrane rate on the concentration of dithionite. The author had earlier published results[9] where he found such a dependence for CMV^{2+} in DHP vesicles for the examined range of concentrations ($[S_2O_4^{2-}] = 2.5 \times 10^{-4}$ to 2.5×10^{-3} M).

The mechanism was proposed earlier[33] in microemulsions where the oil phase constitutes a major part of the total volume. The oil phase in our system constitutes less than one part in 10^4 of the total volume. It seems likely that this mechanism is generally at work when viologens are reduced in heterogeneous media and should therefore be considered also in vesicular systems where the vesicles are formed of amphiphiles other than phospholipids.

This is yet another example of how microheterogenous media and the varying hydrophilicity of redox compounds can promote a reaction that leads to spatially separated redox products, which is the goal in artificial photosynthesis. Further work has been initiated, where the viologen mediated transmembrane redox is studied by laser flash photolysis and pulse radiolysis techniques. Comparisons are also made with monoalkylated bipyridines (*N*-alkyl-4,4′-bipyridine).

Conclusions

The transmembrane electron transfer (TMET) in this system can not be explained by mechanisms involving electron tunneling/self-exchange. This was based on the following observations.

(1) The same TMET is observed for vesicles of types III and IV even though the latter lack viologen on the inside.

(2) The observed rate of TMET is second order in $[CMV^+]_{out}$ (not first order in $[CMV^+]_{out}$ and $[CMV^{2+}]_{in}$, respectively, as expected for electron tunneling/self-exchange).

Simple transmembrane diffusion of CMV^+ can also be ruled out as mechanism for TMET since (1) the observed rate of TMET is second order in $[CMV^+]_{out}$ (not first order in $[CMV^+]_{out}$, as expected for diffusion of CMV^+) and (2) the stoichiometry shows that two ferricyanides are reduced for each viologen diffusing through the membrane.

The mechanism we propose is consistent with the observations above, as well as with the following ones.

(1) The rate of TMET in vesicles of type IV is independent of the concentration of dithionite over a wide range (Figure 6).

(2) All viologen in vesicles of type III and IV migrates to the vesicle interior upon reduction by an excess of dithionite.

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Registry No. CMV, 75805-30-0; CH_3I, 74-88-4; NaS_2O_4, 7775-14-6; $Ru(bpy)_3Cl_2$, 14323-06-9; $K_2Fe(CN)_6$, 13746-66-2; 4,4'-bipyridine, 553-26-4; *N*-methyl-4,4'-bipyridinium iodide, 38873-01-7; *N*-methyl-4,4'-bipyridinium chloride, 4397-88-0; *N*-methyl-*N'*-hexadecyl-4,4'-bipyridinium dibromide, 79957-89-4; hexadecyl bromide, 112-82-3.

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Zeolite-Entrapped $Ru(bpy)_3^{2+}$: Intermolecular Structural and Dynamic Effects

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This study examines the spectral properties of $Ru(bpy)_3^{2+}$ synthesized within zeolite Y cages. Major spectral perturbations, including a red shift of the metal-to-ligand charge-transfer band by ~40 nm, shifts in bipyridine ring breathing modes, and emission and lifetime quenching, are observed. It is proposed that these changes are brought about by the highly polar nature of the intracrystalline space that promotes interactions of coordinated bipyridine ligands through the 7-Å cage openings. Emission quenching of neighboring $Ru(bpy)_3^{2+}$ occurs by the Perrin mechanism with a sphere of action radius of 13 Å. At high excitation energies, evidence for triplet–triplet quenching is also found to occur. Overall, this study shows that the ordered arrangement of supercages within a zeolite crystal makes it possible to examine the spectroscopic properties of $Ru(bpy)_3^{2+}$ as a function of controlled contact with neighboring $Ru(bpy)_3^{2+}$ molecules.

Introduction

The photochemistry and photophysics of tris(bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$ have attracted considerable attention over the past two decades.[1] Much of this interest stems from its possible role as a photosensitizer in the conversion of solar to other useful forms of energy.[2] This role is made possible by the particular distribution of the energy levels of this molecule.[3] Absorption of visible photons leads to a charge-transfer transition from the metal to the ligand (^{1}MLCT). The energy is then transferred with unit efficiency to a ^{3}MLCT by intersystem crossing. The light energy is stored in this state for hundreds of nanoseconds and can be used in chemical reactions. Also, close to the triplet excited state are manifolds of d–d and ligand-field states. Much work has focused on understanding the nature of these states by spectroscopic examination of crystals,[4] influence of solvents,[5] substituents on ligands,[6] and the metal center.[7] Another direction of study has dealt with the energetics of this molecule on a variety of supports, including micelles, silica, clays, semiconductors, and other surfaces.[8] Of obvious interest has been the influence of the microheterogeneous systems on the photochemistry of $Ru(bpy)_3^{2+}$.

Zeolites provide an attractive medium for encapsulation of metals, semiconductors, and organic and organometallic complexes.[9] Both the steric and electrostatic effects can influence the structure and reactivity of the enclosed species. In the case of $Ru(bpy)_3^{2+}$–zeolite Y, this is particularly so, since the ~12-Å $Ru(bpy)_3^{2+}$ molecules are held securely in the zeolite Y ~13-Å supercages and cannot escape through the ~7-Å ring openings. Previous work in this area has dealt with synthesis and spectroscopic studies.[10,11] In particular, it was found that dehydration of the zeolite cages had a profound effect on the excited-state structure and decay of $Ru(bpy)_3^{2+}$.[11b] Also, photoelectron transfer from zeolite-entrapped $Ru(bpy)_3^{2+}$ to methylviologen in neighboring cages has been examined.[11a] In addition, photoelectron transfer from $Ru(bpy)_3^{2+}$ in solution to acceptors in zeolite cages has also been reported.[12]

In this study, we have used zeolite Y as a host in which the occupancy of the supercages by $Ru(bpy)_3^{2+}$ is altered over a wide

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