One-Electron Reduction of Dihexadecyl Phosphate Vesicle Bound Viologens by Dithionite Ion

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Abstract: *N*-Methyl-*N'*-alkyl-4,4'-bipyridinium (C_nMV^{2+}) ions bound to dihexadecyl phosphate vesicles are rapidly reduced to radical cations by $S_2O_4^{2-}$ in weakly alkaline solutions. For the short-chain viologens investigated (n = 1, 6, 8), the reaction obeys the rate law $d[C_nMV^+]/dt = k[C_nMV^{2+}][S_2O_4^{2-}]^{1/2}$. The measured rate constants were identical for preparations in which viologen was added to preformed vesicles and in which vesicles were formed in the presence of viologen, although in the latter systems 10–30% of the viologen was inaccessible to the reductant. For longer chain C_nMV^{2+} (n = 12, 14, 16, 18, 20), viologen radical formation was biphasic when binding was constrained to the external aqueous–vesicle interface, but it was triphasic when viologen was bound at both interfaces. Where determined, each step was first order in C_nMV^{2+} and half order in $S_2O_4^{2-}$; viologen radical yields were identical in vesicles prepared by either method. The results are interpreted to indicate the simultaneous existence of multiple binding domains for long-chain viologens within the vesicles. Possible structures and relationships to transmembrane redox pathways are briefly discussed.

The influence of interfacial partitioning and phase separation upon the dynamics of redox reactions is an area of active investigation. Dramatic kinetic effects are often seen in microheterogeneous media,[1] and mechanistic interpretation of the data can be complicated by factors not encountered in homogeneous solution. For example, apparent transmembrane redox across membrane bilayers in unilamellar vesicles or liposomes described for several asymmetrically organized systems has been variously interpreted in terms of either electron tunneling[2-4] or molecular diffusion of reactants across the hydrocarbon barrier,[5,6] although these assignments are ambiguous because insufficient information on transmembrane diffusion coefficients and intravesicular localization of reactants exists to exclude the alternative mechanism.[7] Additionally, as demonstrated in one instance,[8] photostimulated diffusion can conceivably lead to mixing of initially compartmented reactants in systems containing vesicle-bound chromophores. Interfacial reactions as well are frequently complicated by heterogeneous binding[3,9-14] or lateral phase separation[15] of reactants. Nonetheless, study of vesicular redox reactions promises rewards both with respect to conceptual developments, e.g., in stochastic modeling of complex kinetic systems and understanding long-range electron transfer, and with respect to controlling reactivity for useful purposes.

In recent studies we have focused our attention upon the structural and dynamic properties of *N*-methyl-*N'*-alkyl-4,4'-bipyridinium (C_nMV^{2+}) ions bound to unilamellar dihexadecyl phosphate (DHP) vesicles. These particles, for a variety of reasons,[7] are particularly amenable to experimentation. Indirect evidence that $C_{16}MV^{2+}$ and other long-chain analogues are capable of mediating transmembrane redox was obtained by comparing the photosensitized reduction of DHP vesicles containing viologens bound to both aqueous hydrocarbon interfaces to vesicles containing only externally bound oxidant.[16] In these experiments, the tetraanionic water-soluble porphyrin, (5,10,15,20-tetrakis-(4'-sulfonatophenyl)porphinato)zinc(II) ($ZnTPPS^{4-}$), was added to the external aqueous phase. With $Fe(CN)_6^{3-}$ occluded within the inner aqueous phase, a pronounced lag in the appearance of viologen radical cation was observed with vesicles containing both inner and outer bound viologens, but not with vesicles possessing other topographies or lacking $Fe(CN)_6^{3-}$. The nature of viologen binding was probed by examining the dynamics of oxidative quenching with laser flash spectroscopy. The kinetics are consistent with an encounter-controlled mechanism between triplet $ZnTPPS^{4-}$ ion and the vesicles, with an apparent concentration dependence upon viologen arising from the influence of extent of particle loading upon the interfacial dielectric constant.[17] Because the photoexcited sensitizer ion is the limiting reagent in these studies, the technique samples only the most reactive sites on the vesicles; in this instance, the kinetics have given no evidence of viologen surface aggregation or binding heterogeneity. Use of a chemical reductant which can be added in excess offers a means of examining all accessible viologen in the system. In this report, we present results obtained from kinetic measurements with dithionite ion that binding of the long-chain viologens ($n > 10$) is heterogeneous but that of the shorter chain analogues is not. Furthermore, circumstantial evidence suggests that only the relatively less reactive sites of the long-chain viologens are capable of supporting transmembrane redox across the bilayer membrane.

Experimental Section

Materials. Alkylviologen bromides were synthesized by a stepwise quaternization procedure[18] and converted to chloride salts by halide exchange with $AgSO_4$ and $BaCl_2$. The compounds were purified by repeated recrystallization from *n*-butanol until single spots were observed by thin-layer chromatography (stationary phase: silica gel; mobile phase:

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3:1:1 methanol:water:50% aqueous ethylammonium chloride); usually four or more recrystallizations were required to achieve this level of purity. Structures were confirmed by proton NMR spectra taken on a JEOL FX90Q spectrometer. All the purified salts were white powders after drying at 100 °C under vacuum; however, C_6MVCl_2 and C_8MVCl_2 are deliquescent, becoming syrupy liquids in less than 1 h upon standing in the atmosphere. To avoid these hydration problems, all the viologen salts were stored desiccated at −5 °C and protected from light. Stock solutions 10 mM in viologen were prepared in deionized water for routine use and stored at 5 °C. Other reagents were of highest grade commercially obtainable and used as received. Water was purified with a Corning Megapure deionization–distillation system.

Vesicle Preparation. Vesicles were prepared by ultrasonic dispersal with use of a 0.5-in. flat tip on a conventional horn energized by a Heat Systems-Ultrasonics W185 device operated at a power setting of 4.0. In a typical preparation, the tip was immersed in a suspension of 16 mM DHP in 15–25 mM Tris buffer, and two pulses of 10 min separated by a 10-min interval were applied. The resulting opalescent solution was clarified by successive filtration through 0.8, 0.45, and 0.22 μm pore size Millipore membrane filters. Vesicles to contain only externally bound viologen were prepared by 1:1 dilution of the filtered suspension with an aqueous solution of the appropriate alkylviologen with a flow apparatus equipped with a 12-jet tangential mixer; this procedure minimizes fusion of the small unilamellar particles. Vesicles to contain viologen bound at both interfaces were prepared by ultrasonication of 8 mM DHP in the presence of viologen as described above. Ultracentrifugation at 100 000 *g* for 45 min clarified the suspensions by removing multilamellar and large unilamellar vesicles, aggregates, undispersed DHP, and any remaining titanium probe particles. The supernatant was then carefully decanted and used immediately for stopped-flow kinetic studies. Vesicle suspensions were stored at 5 °C between analyses and were never allowed to age longer than 12 h.

Kinetic Analyses. The freshly prepared vesicle solution was placed in a specially designed anaerobic reservoir fitted to a stopped-flow apparatus[19] and 19 mL of buffer was placed in a second similar reservoir. These solutions were then purged with argon for 30–45 min. A few minutes before acquiring kinetic data, sodium dithionite was weighed and added to 10 mL of an anaerobic buffer system such that 1 mL diluted to 20 mL in the stopped-flow reservoir gave the desired concentration of reductant ($[S_2O_4^{2-}]$ = 0.2–2.4 mM).

All kinetic measurements were made at 23 °C with use of an observation chamber with a 1-cm optical pathlength. Voltage–time waveforms were taken at wavelengths corresponding to visible and near-UV absorption band maxima of the viologen radical cations and stored on an oscilloscope. Initial measurements were made on a Tektronix 549 instrument, for which the display was photographed and analyzed manually. More recent data acquisition was made on a Nicolet 4094A digital oscilloscope equipped with a 4568 plug-in and interfaced to a DEC PRO-350 computer. Data were analyzed by a nonlinear method of Marquardt with a program adapted from Bevington;[20] each analysis made use of 1000–2000 individual data points. Quantitative fits were obtained in all cases, as was evident from the appearance of random residuals in graphical displays. Results obtained by the two methods were identical within experimental uncertainty. Dithionite concentrations were determined spectrophotometrically at 315 nm (ϵ = 6900)[21] from solutions taken from the reservoir immediately after data acquisition. These concentration values were used to determine the reaction order with respect to dithionite.

Results

Viologen Binding to Vesicles. Previous studies using ultrafiltration, gel chromatography, and optical spectroscopic techniques have established that the C_nMV^{2+} ions bind strongly to the anionic DHP vesicles.[16] The alkylviologens possess a strong ultraviolet absorption band at 260 nm in dilute aqueous solution. Binding to DHP causes a small bathochromic shift to 262–264 nm, which is the same magnitude as caused by changing solvent to 95% ethanol or 2-propanol. The concentration dependencies follow Beer's law over the experimental range investigated, generally 10–70 μM in H_2O and 10–500 μM in DHP vesicle suspensions. Measured molar extinction coefficients of the band maxima based upon weight samples are, in H_2O, *n* (log ϵ) = 1 (4.32), 6 (4.34), 8 (4.37), 10 (4.35), 12 (4.36), 14 (4.35), 16 (4.37), 18 (4.22), 20 (4.11); and for DHP-bound C_nMV^{2+}, [DHP] = 4 mM, in 20 mM Tris, pH 8.0, *n* (log ϵ) = 6 (4.35), 8 (4.38), 10 (4.40), 12 (4.40), 14 (4.35), 16 (4.38), 18 (4.27), 20 (4.25). Spectra for vesicle-containing solutions were corrected for background scatter by referencing against vesicle suspensions of identical concentration.

Table I. Percentage of DHP-Bound $C_{16}MV^+$ Product in Its Monomeric State[a]

$[C_{16}MV^{2+}]$ (μM)	DHP/$C_{16}MV^{2+}$	% monomer[b]	A_1/A_2[c]
6	667	95	14/86
12	333	90	24/76
25	160	88	32/68
50	80	82	26/74
70	57	72	25/75
100	40	63	28/72

[a] 4 mM DHP, viologen bound to external vesicle interface, reduction by 0.2–1.5 mM $S_2O_4^{2-}$, in 20 mM Tris, pH 8.0, at 23 °C. [b] Calculated according to ref 22. [c] Relative amplitudes of k_1/k_2 pathways, eq 2.

Table II. Wavelength Dependence of Relative Contributions of Pathways for DHP-Bound $C_{16}MV^{2+}$ Reduction[a]

	A_1/A_2[b] for DHP/$C_{16}MV^{2+}$ =		
λ (nm)	400	160	80
367	14/86	12/88	26/74
395	20/80	16/84	31/69
480	15/85	7/93	
545	12/88	9/91	27/73
605	17/83	14/86	
670	17/83	12/88	

[a] 4 mM DHP, viologen bound to external vesicle surface, reduction by 0.5–1.5 mM $S_2O_4^{2-}$, in 20 mM Tris, pH 8.0, at 23 °C. [b] As defined in Table I.

Dithionite Reduction of Vesicles Containing Externally Bound C_nMV^{2+} Ions. (a) Rate Laws. Single-exponential curves for viologen radical formation were observed when DHP vesicles loaded with short-chain alkylviologens, $n < 12$, were reacted with an excess of dithionite ion. Individual vesicle preparations gave highly reproducible kinetics in replicate runs, but measured rate constants varied considerably from preparation to preparation (cf. Figure 2). This behavior is commonly found in interfacial redox reactions involving DHP vesicles,[17,22] although we can presently offer no definitive explanation. Within the scatter, the first-order rate constants exhibited half-order dependence upon $S_2O_4^{2-}$ ion concentration, which was varied from 0.025 to 1.6 mM in these experiments. The data are adequately fit by the rate law

$$d[C_nMV^+]/dt = k[C_nMV^{2+}][S_2O_4^{2-}]^{1/2} \quad (1)$$

although minor contribution from a pathway first order in $S_2O_4^{2-}$ cannot be excluded.

For longer-chain analogues, $n \geq 12$, reaction with excess $S_2O_4^{2-}$ ion was biphasic with approximately 25% of the total absorbance change corresponding to the more rapidly reacting component. A representative first-order plot, for $C_{16}MV^{2+}$–DHP reduction, is given in Figure 1. The data can be adequately fitted assuming two simultaneous first-order pathways. Both pathways exhibit half-order dependence upon $S_2O_4^{2-}$ ion concentration (Figure 2), yielding the rate law

$$d[C_nMV^+]/dt = (k_1[C_nMV^{2+}] + k_2[C_nMV^{2+}]')[S_2O_4^{2-}]^{1/2} \quad (2)$$

where the prime indicates a distinct reaction environment. For all reactions, amplitudinal changes indicate near-stoichiometric conversion of C_nMV^{2+} ion to the radical cation, based upon reported molar extinction coefficients for the methyl viologen radical ion.[23] Measured rate constants are also independent of the monitoring wavelength and amount of viologen bound per vesicle over the measured range, e.g., DHP/$C_{16}MV^{2+}$ = 40–500. Relative amplitudes (A_1, A_2) of the two pathways for the biphasic reactions are, within experimental uncertainty, also independent of the extent

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Table III. Relative Contributions of Pathways for Biphasic Reduction of C_nMV^{2+} Ions[a]

DHP/C_nMV^{2+}	% A_2[b]				
	n = 12	n = 14	n = 16	n = 18	n = 20
400	74 ± 11 (4)	73 ± 7 (2)	83 (1)	78 ± 6 (13)	72 ± 3 (6)
160	72 ± 8 (10)	76 ± 6 (6)	69 ± 5 (7)	69 ± 1 (3)	67 ± 3 (6)

[a] 4 mM DHP, viologen bound to external vesicle interface, reduction by 0.1–1.6 mM $S_2O_4^{2-}$ in 20 mM Tris, pH 8.0, 23 °C. [b] 100 $[A_2/(A_1 + A_2)]$; numbers in parentheses indicate number of data sets averaged.

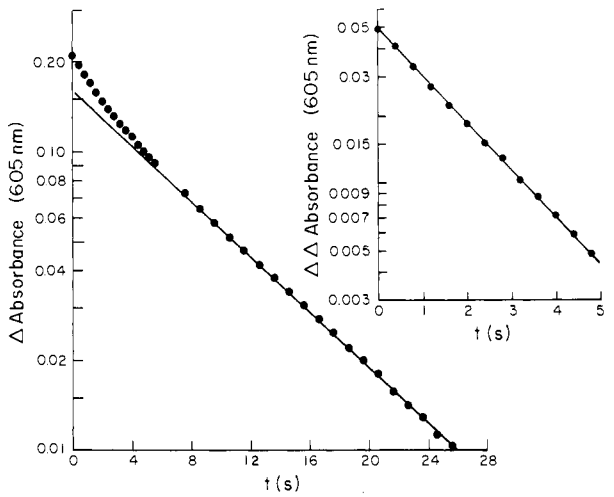

Figure 1. First-order plot of $C_{16}MV^+$ radical ion formation by reduction of $C_{16}MV^{2+}$–DHP vesicles with $S_2O_4^{2-}$. Conditions: 4 mM DHP, 25 μM $C_{16}MV^{2+}$, 0.47 mM $S_2O_4^{2-}$, 0.02 M Tris(Cl), pH 8.0, at 23 °C. The inset gives the difference between measured Δabsorbance and values extrapolated from the linear portion of the curve, also plotted as first order.

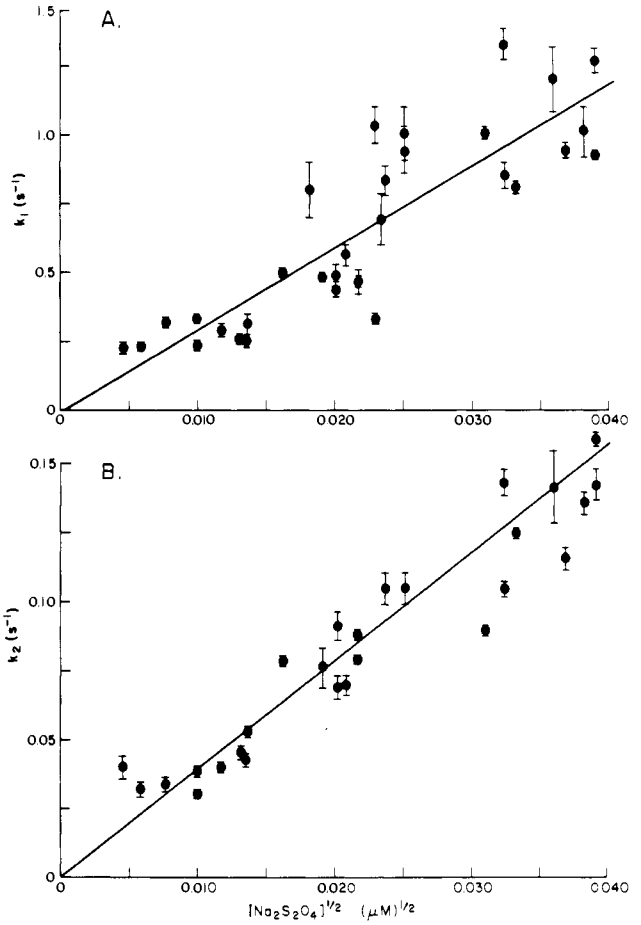

Figure 2. Concentration dependence of reduction of DHP-bound $C_{16}MV^{2+}$ by SO_2^-. Conditions: 4 mM DHP, 4–100 μM $C_{16}MV^{2+}$, in 0.015–0.025 M Tris(Cl), pH 8.0, at 23 °C. Graphs A and B give results for fast and slow components, respectively, of biphasic kinetic plots. Error limits are average deviations from the mean of four individual determinations.

of vesicle loading (Tables I–III). The most extensive data set is for DHP-bound $C_{16}MV^{2+}$, for which values averaged over all runs are DHP/$C_{16}MV^{2+}$ (% A_2) = 40 (76 ± 4), 57 (77 ± 5), 80 (72 ± 4), 160 (69 ± 5), 320 (76 ± 10), 400 (83), 500 (72 ± 13), 667 (81 ± 4), 1000 (69 ± 4). The pH dependence of $C_{16}MV^{2+}$–DHP reduction by $S_2O_4^{2-}$ ion was briefly studied. In 20 mM glycine, pH 10.0, the rate law given by eq 2 was observed, although rate constants for both fast and slow components were an order of magnitude greater than in 20 mM Tris, pH 8.0.

(b) Aggregation of DHP-Bound Viologen Radical Ion. Product spectra taken 5–15 min after completion of the kinetic runs were analyzed for the presence of multimeric forms of viologen radical by comparing visible band absorbance ratios at 535 and 605 nm.[24,25] This procedure tacitly assumes that the spectral bandshapes of DHP-bound C_nMV^+ are the same as for aqueous methyl viologen radical cation. Evidence supporting this assumption is that $\epsilon_{605}/\epsilon_{535}$ measured for monomeric $C_{16}MV^+$ formed by reduction with ascorbate in ethanol is 2.2, identical with the aqueous monomeric MV^+ value.[24] Accordingly, for the shorter chain viologens, the product was essentially completely monomeric, but for $n \geq 12$, a small amount of aggregation is suggested. Furthermore, the extent of aggregation increases with increased loading of the vesicle. Data for $C_{16}MV^{2+}$–DHP are collected in Table I. The percentage of monomer is relatively constant at approximately 90% at high DHP/$C_{16}MV^{2+}$ ratios. Consequently, in quantitative studies, DHP/C_nMV^{2+} ratios were kept above 80 to minimize interference from viologen radical association. Under these conditions, the wavelength dependence of the relative amplitudes of k_1 and k_2 components are independent of monitoring wavelength (Table II). This observation confirms that aggregation–disaggregation phenomena are not contributing significantly to the measured spectral changes.

(c) Chain-Length Dependence. Measured rate constants defined by eq 1 and 2 decrease progressively with alkyl chain length until n = 14 and then become insensitive to further elongation. This effect is presented graphically in Figure 3, where it is assumed that k_1 for the biphasic reactions correlates with k for the short-chain viologens. Parallel behavior is seen in k_1 and k_2 for the long-chain analogues. The relative contribution of each pathway to overall viologen reduction is also largely independent of alkyl chain length; relative amplitudes for the two pathways are given for two different vesicle loadings in Table III.

(d) Ionic Strength Dependence. Rate constants for $C_{16}MV^{2+}$–DHP reduction by $S_2O_4^{2-}$ ion increase with increasing buffer concentration, indicating that a net repulsive electrostatic interaction exists between the reactants. Quantitative description of this effect was attempted with use of the Debye–Hückel limiting law

$$\log \gamma_i = z_i^2 A\mu^{1/2}/(1 + aB\mu^{1/2}) \quad (3)$$

where z_i is the electrostatic charge, $\mu = {}^1/_2\sum c_i z_i^2$ is the ionic strength, a is the ionic radius, and A = 0.51 and B = 0.33 in water at 23 °C.[26] Two problems are immediately evident in application

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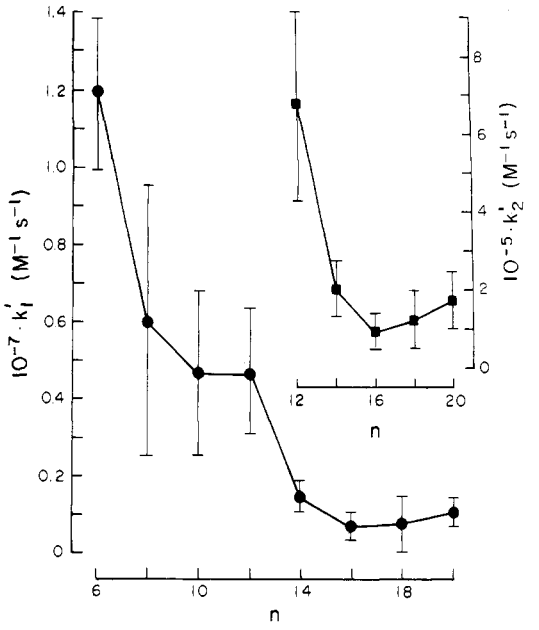

Figure 3. Second-order rate constants for SO_2^- reduction of DHP-bound C_nMV^{2+} as a function of alkyl chain length (n). Conditions: 4 mM DHP, 10–25 μM C_nMV^{2+}, in 0.015–0.025 M Tris(Cl), pH 8.0, at 23 °C. Error limits are average deviations of individual rate constants for 10–50 separate vesicle preparations from the mean values obtained by graphical fits to eq 1 or 2.

to vesicle suspensions, namely, the particle size and its charge. When prepared as described, DHP suspensions contain nearly monodisperse, unimodal, spherical vesicles comprised of ~10000 monomers and having an outer hydrodynamic radius of ~160 Å.[27] It is unreasonable to assume that the full electrostatic charge of the particle ($z_i = 10^4$) is felt in the activated complex. Minimally, the influence of ionic head groups even a few molecules removed from the reaction site is substantially diminished by the inverse distance dependence of the Coulomb potential and extensive shielding of surface charge by counterions in the diffuse double layer can be anticipated. Similarly, the effective ionic radius of the vesicle at the reaction site must be considerably less than its actual size. We have therefore adopted the procedure of assuming a normal ionic radius for the reaction center and determining empirically the contribution by the vesicles to the ionic strength by comparing rate constants for a noninteracting system in the presence and absence of vesicles. Other approaches to the problem of macromolecule–small molecule electrostatics have been explored,[28] but this one appears in the present case to provide the most straightforward, self-consistent treatment of the data.

By this analysis, measured rate constants can be expressed as

$$\log k_i = \log k_i^0 + z_A z_B \mu^{1/2}/(1 + \mu^{1/2}) \qquad (4)$$

where k_i^0 is the rate constant at zero ionicity. The contribution of 2 mM DHP vesicles to the ionic strength (μ_v) has been estimated as $\mu_v = 9$ mM by comparing $ZnTPPS^{4-}$ triplet–triplet annihilation rates[29,30] in the presence and absence of vesicles. Extrapolating to the present conditions suggests the value of $\mu_v = 20$ mM for 4 mM DHP.

The data for $C_{16}MV^{2+}$–DHP vesicles are plotted according to eq 4 in Figure 4 for both reduction pathways. Slope and y-intercept provide values for $z_A z_B$, the effective charge product at

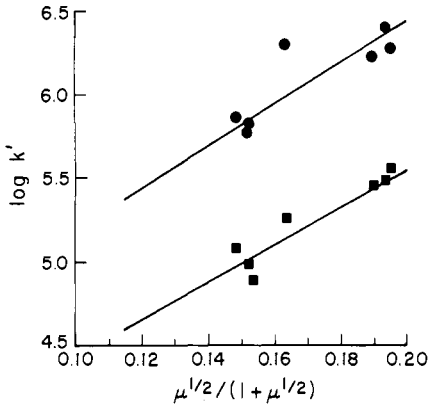

Figure 4. Ionic strength dependence of second-order rate constants for $C_{16}MV^{2+}$–DHP reduction by SO_2^-. Conditions: 4 mM DHP, 13–100 μM $C_{16}MV^{2+}$, 0.45 or 1.4 mM $S_2O_4^{2-}$, varying Tris(Cl), pH 8.0, at 23 °C. Circles: fast reaction component; squares: slow component. Each data point is the average of four kinetic runs.

the reaction site, and k_i^0, respectively. From the linear fits, $z_A z_B$ are 12.4 and 11.3 for the fast and slowly reacting components, respectively. Likewise, the limiting rate constants in pure water, expressed as bimolecular constants for SO_2^- radical ion reacting with vesicle-bound $C_{16}MV^{2+}$ as discussed below, are $k_1^{0\prime} = 9.0 \times 10^3$ M^{-1} s^{-1} and $k_2^{0\prime} = 1.9 \times 10^3$ M^{-1} s^{-1}.

Dithionite Reduction of Vesicles Containing C_nMV^{2+} Ions Bound to Both Interfaces. For the short-chain viologens (n = 6, 8), C_nMV^{2+} addition in a manner that allows access to both vesicle surfaces caused no change in dynamic behavior beyond the appearance of a slow step which was a very minor component of the overall reaction, i.e., ~5% of the total optical change at 605 nm. Measured rate constants for externally and internally/externally bound particles were identical within experimental uncertainty. For MV^{2+}–DHP (n = 1), kinetic analysis also gave single-exponential formation of MV^+, regardless of whether MV^{2+} was bound to just the external or to both interfaces. The order with respect to $S_2O_4^{2-}$ was not determined for this reaction, but pseudo-first-order rate constants averaged 6.6 and 7.8 s^{-1} in two separate determinations for only externally and internally/externally localized viologen, respectively, when $[MV^{2+}] = 50$ μM, [DHP] = 2 mM, $[S_2O_4^{2-}] = 0.5$ mM, in 0.02 M Tris(Cl), pH 8.0, at 23 °C. These values can be considered identical within the relatively wide experimental range usually encountered in these systems (cf. Figure 2). Total viologen radical formation for the vesicles containing externally bound MV^{2+} was 1.4 times greater than for the internally/externally bound MV^{2+} at identical loadings, suggesting that the internally bound viologen is inaccessible to reductant.

More complex kinetics are observed for the longer chain ($n \geq 10$) viologens when initially distributed on both surfaces. As illustrated in Figure 5 for $C_{16}MV^{2+}$–DHP, a prominent additional slow reaction step appears and the total viologen radical formation based upon absorbance changes is the same regardless of the intravesicular location of C_nMV^{2+}. For $n \geq 12$, the kinetic traces can be fitted to a three-exponential decay, the faster two of which are identical within experimental uncertainty to values determined for biphasic reduction of C_nMV^{2+}–DHP vesicles containing only externally localized viologens. The rate constant for the slowest component for reduction of $C_{16}MV^{2+}$–DHP exhibited half-order dependence upon $S_2O_4^{2-}$ concentration (Figure 6). The overall reaction was therefore adequately described by the rate law

$$d[C_{16}MV^+]/dt = (k_1[C_{16}MV^{2+}] + k_2[C_{16}MV^{2+}]' + k_3[C_{16}MV^{2+}]'')[S_2O_4^{2-}]^{1/2} \qquad (5)$$

A further complexity of these systems is that, unlike the two faster steps, the relative amplitude of the very slow step is wavelength dependent. Its contribution is relatively great in regions of the visible spectrum where the multimeric form of viologen radical cations absorbs strongly. Furthermore, the reaction product

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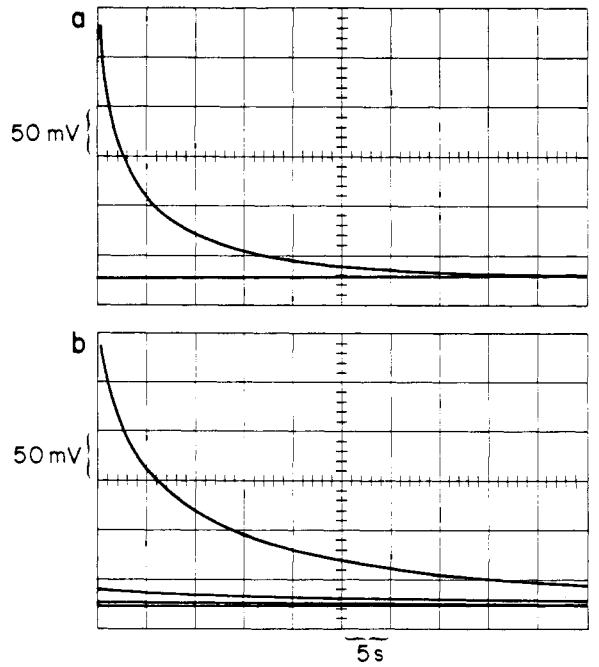

Figure 5. Kinetic traces of $C_{16}MV^+$ radical formation by reduction of $C_{16}MV^{2+}$–DHP with $S_2O_4^{2-}$. Conditions: 4 mM DHP, 50 μM $C_{16}MV^{2+}$, 1.0 mM $S_2O_4^{2-}$, in 0.02 M Tris(Cl), pH 8.0, at 23 °C; detection wavelength 600 nm. Trace a: $C_{16}MV^{2+}$ added after vesicle formation; trace b: DHP sonicated in $C_{16}MV^{2+}$-containing solution.

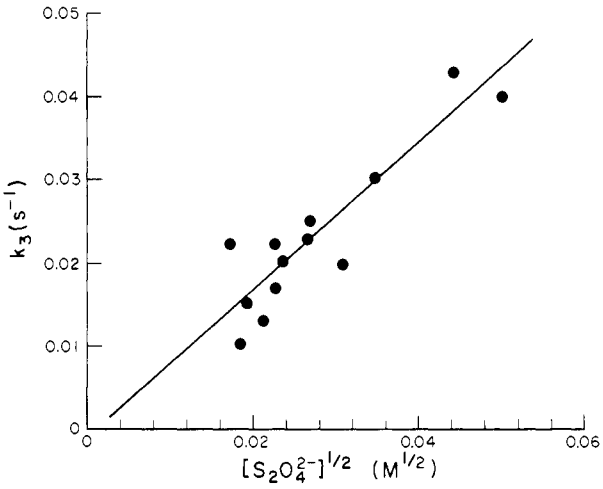

Figure 6. Dithionite dependence of k_3 pathway for $C_{16}MV^+$ formation. Conditions: 4 mM DHP, 15–50 μM $C_{16}MV^{2+}$, in 0.015–0.025 M Tris(Cl), pH 8.0 at 23 °C. Each data point is the average of 2–4 runs.

spectrum indicates a greater percentage of multimeric radical cation than is formed by vesicles containing only externally bound oxidant at comparable loadings. By rapidly and repetitively recording absorbances at 605 and 535 nm immediately following mixing, it is possible to estimate the relative amounts of monomeric and multimeric viologen present over the time course of the very slowest reaction step in $C_{16}MV^{2+}$–DHP reduction. For 31 μM $C_{16}MV^{2+}$, 4 mM DHP, 0.5 mM $S_2O_4^{2-}$ in 0.02 M Tris(Cl), the apparent percentage of monomer drops from ~80% at the earliest measurable time to 57% by the end of the reaction several minutes later. Multimer formation therefore occurs on the time scale of the slowest step.

Discussion

Mechanism of Reduction of Externally Bound C_nMV^{2+} Ions. Half-order dependence upon $S_2O_4^{2-}$ concentration, commonly observed in its reactions with organic and biological oxidants[31] including reduction of several viologens in homogeneous solution,[32] is generally interpretable in terms of the following mechanism

$$S_2O_4^{2-} \overset{K}{\rightleftharpoons} 2SO_2^-$$

$$H_2O + SO_2^- + C_nMV^{2+}\text{–DHP} \xrightarrow{k'} SO_3^{2-} + C_nMV^+\text{–DHP} + 2H^+$$

where homolytic cleavage of $S_2O_4^{2-}$ is rapid relative to the electron-transfer step. Under these conditions, the bimolecular rate constant for reduction by dithionite radical is given by $k' = k/K^{1/2}$. Values for k' reported in this paper (Figures 3 and 4) are calculated assuming $K = 1.4 \times 10^{-9}$ M;[31] for $C_{16}MV^{2+}$–DHP, $k_1' = 7 \times 10^5$ M^{-1} s^{-1}, $k_2' = 9 \times 10^4$ M^{-1} s^{-1}, and $k_3' = 2.4 \times 10^4$ M^{-1} s^{-1} in 0.02 M Tris(Cl), pH 8.0, at 23 °C.

The first-order dependence upon C_nMV^{2+} ion concentration, clearly exhibited for the short-chain viologens, is surprisingly simple. If reaction between SO_2^- and C_nMV^{2+}–DHP were encounter-controlled, one would expect the reaction to depend in the first approximation only upon the number of vesicles in solution and be relatively independent of the extent of viologen binding. In the case of $^3ZnTPPS^{4-}$ ion quenching by C_nMV^{2+}–DHP vesicles we found that the magnitudes of measured rate constants were consistent with an encounter-controlled reaction between vesicles and the photoexcited ion, yet an apparent concentration dependence arose because the effective dielectric constant at the reaction site changed upon varying the DHP/C_nMV^{2+} ratio.[17] One major difference in the two reactions is that $ZnTPPS^{4-}$ photooxidation is highly dependent upon, but SO_2^- oxidation is independent of, the extent of viologen binding by the vesicles. Also, the absolute magnitudes of the rate constants are 10- to 10^2-fold greater for the photochemical reaction, despite the reactants experiencing significantly greater charge repulsion,[17] i.e., $z_Az_B = -36$ for $^3ZnTPPS^{4-}$ and $z_Az_B = -12$ for SO_2^-. These observations indicate that the reactions with SO_2^- are not limited by diffusion to the vesicle surface.[33] Therefore, since the reaction requires collisional activation before electron transfer can occur, interfacially bound viologen will behave analogously to viologen in homogeneous solution, giving rise to simple rate behavior.

The reason for these reactivity differences may reside in thermodynamic driving forces. The standard reduction potential for $MV^{2+/+}$ is $E° = -0.44$ V,[35] and at pH 8, for two-electron reduction of SO_3^{2-} $E°' = -0.41$ V,[36] so viologen reduction may go to completion only because $S_2O_4^{2-}$ ion is supplied in large excess.[37] In contrast, oxidative quenching of $^3ZnTPPS^{4-}$ ion is exergonic by $E° = 0.31$ V.[17] The observation that the rate of $C_{16}MV^{2+}$–DHP reduction by $S_2O_4^{2-}$ ion increase with medium alkalinization is consistent with this interpretation; at pH 10, the reaction is favorable by $E° = 0.21$ V. It is unlikely that differences in the intrinsic reactivities of SO_2^- and $^3ZnTPPS^{4-}$ make a major contribution to the observed rate differences. Recent esti-

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(33) The diffusion-controlled rate constant can be estimated from $k_d = k_0 f$, where k_0 is the constant for noninteracting particle and f is an appropriate function of the interaction potential, here taken to be the Coulomb potential. From phenomenological theory,[34] we calculate[17] $k_0 = 10^{11}$ M^{-1} s^{-1}, $f = 2 \times 10^{-2}$, hence $k_d = 2 \times 10^9$ M^{-1} s^{-1}, when $D_{SO_2^-} = 0.8 \times 10^{-5}$ cm^2 s^{-1}, $r_{AB} = 165$ Å, $z_Az_B = -12$ and $\epsilon r = 100$. Even if $\epsilon r = 50$, which by other physical criteria seems unreasonably low,[17] $k_d = 2 \times 10^7$ M^{-1} s^{-1}. These values are several orders of magnitude greater than the experimentally determined rate constants extrapolated to zero ionic strength ($k_i^{0\prime}$), indicating that the reaction is not diffusion-limited.

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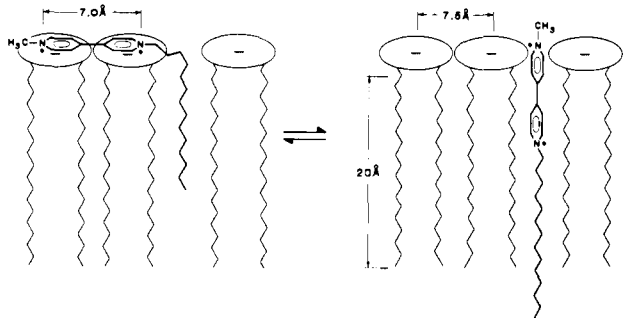

Figure 7. Hypothetical two-state model for $C_{14}MV^{2+}$ binding in the lateral plane of DHP vesicles.

mates[32,39,40] of the self-exchange rate constant for SO_2 and SO_2^- are $k = 10^7$–10^8 M^{-1} s^{-1}, which is the same order of magnitude anticipated for the $^3ZnTPPS^{4-}$,$ZnTPPS^{3-}$ pair, based upon measured values for other metalloporphyrins.[41]

The Nature of Viologen Binding. The most straightforward interpretation of the biphasic kinetics seen for the reduction of long-chain viologens by $S_2O_4^{2-}$ ion is that there exist two distinct reaction environments that are not interconvertible on the time scale of the redox reaction. Three alternative possibilities are the following: (i) that there are two types of particles in solution, (ii) that monomeric and multimeric forms exist simultaneously in otherwise similar binding environments on a single vesicle, and (iii) that two different binding environments exist within a single vesicle. Quasielastic light scattering studies on $C_{16}MV^{2+}$–DHP vesicles give no evidence for a bimodal distribution of particles;[27] by this technique, ≥5% of a minority fraction could be detected. Chromatography on Sephacryl-500 and -1000 gels also gives elution profiles containing a single peak whose size, determined by calibration with spherical latex standards, corresponds to that determined by light scattering. Finally, the absence of biphasic kinetics for C_nMV^{2+}–DHP vesicles when $n < 12$ is consistent with the existence of only a single type of particle. The strongest evidence against biphasic kinetics arising from monomer—multimer equilibria on the vesicle is that the relative proportion of reaction by the two pathways is unchanged when the amount of bound viologen is varied over the range investigated, corresponding to DHP/C_nMV^{2+} ratios of 40–1000. This conclusion is supported by the optical spectra of the product radical anions, which show negligible aggregation at low levels of viologen binding when binding is limited to the external surface. These observations also tend to exclude the possibility that viologen micelles coexist with vesicle-bound material since spectra for long-chain alkylviologen radical ions in aqueous dispersions are those of the multimeric form.[24,25] The analytical concentration of C_nMV^{2+} used in these experiments is far below their reported critical micelle concentrations,[42] so the possibility of micellarization in these systems is remote.

By inference, then, we conclude that the biphasic kinetics are a manifestation of two types of binding domains existing within the vesicles. An attractive model (Figure 7) is that the sites may entail either of two binding geometries—interfacial association or incorporation of the viologen within the bilayer structure—which, by virtue of having differing accessibilities to external reductants, possess distinct kinetic behavior. The forces for interfacial binding would be primarily electrostatic, while hydrophobic interactions of the alkyl chains would contribute significantly to stabilization of the intercalated form. Inasmuch as the latter forces increase with chain elongation, the model provides an explanation, at least qualitatively, for the appearance of biphasic kinetics only after the chain length exceeds a critical distance. Surface binding may occur with the viologen oriented parallel to the plane of the vesicle surface. Surface tension measurements at the air/water interface indicate that the limiting molecular area of DHP head groups is very nearly that predicted by space-filling models[43] such that average O^- to O^- separation distances in the membrane plane are about 5.3 and 7.6 Å along the major axes. The viologen N–N′ separation distance is 7.0 Å,[44] so simultaneous ion-pairing to two neighboring DHP phosphate head groups can occur with minimal disruption of the bilayer structure. Similarly, it has been shown that single-chain amphiphiles possessing bulky aromatic spacer groups near their polar head groups cause relatively minor perturbation when incorporated into the bilayer structures of a variety of synthetic vesicles, whereas surfactants with other structural features introduce considerable instability upon binding.[45] The alkylviologens used in these studies can be considered in the former class, and they should therefore readily adopt an intercalated geometry. Indirect evidence supporting these concepts is obtained from determination of vesicle sizes by quasielastic light scattering.[27] The hydrodynamic diameters appear to increase upon binding of $C_{16}MV^{2+}$, consistent with intercalation into the bilayer structure, but are unchanged with addition of C_6MV^{2+} ion. Other researchers have also recently suggested two-site binding to account for chemical and photophysical reactivities of vesicle-bound compounds.[3,9-14] Most notably, Whitten and co-workers have recently interpreted the behavior of alkylstilbene derivatives in DHP and dipalmitoyllecithin in terms of simultaneous interfacial and "inclusion" sites that are very similar to the types proposed here.[9]

The origin of decreasing rate constants for viologen reduction that accompanies chain elongation when $n \leq 14$ (Figure 3) is uncertain. One possibility is that the viologen is pulled progressively into the bilayer interface by the increased hydrophobic interactions attending addition of ethylene units to the chain. Although one might anticipate that variations in the position of viologen within the bilayer would be reflected in changing electrostatic forces at the reaction site, this is apparently not so since the ionic strength dependencies for surface and "embedded" pathways are nearly identical, comprising a repulsive potential equivalent to 11–12 monomer units.

Binding at Both Interfaces and Transmembrane Redox. The kinetics of reduction of short-chain viologens by $S_2O_4^{2-}$ and $Co(CN)_5^{3-}$[22] suggest that interaction with DHP vesicles is limited to surface adsorption. Particularly for MV^{2+} and C_6MV^{2+}, a significant fraction of the viologen is protected from $S_2O_4^{2-}$ reduction when cosonicated with DHP during vesicle formation. This stoichiometry can be explained by assuming that the viologen in this instance distributes on inner and outer vesicle surfaces and that transmembrane redox does not occur, so that the inner bound viologen is isolated from exogenous reductants. This interpretation is consistent with calculations which show that electron tunneling probabilities are prohibitively low for electron exchange between reactants that are surface-bound to membrane bilayers.[4,6] Likewise, one infers that transmembrane diffusion of the surface-bound viologens is extremely slow in these systems.

For the longer-chain viologens ($n \geq 10$), no difference is seen in the radical ion product yields whether C_nMV^{2+} is present during vesicle formation or added subsequently. Assuming that these viologens also distribute between both interfaces during sonication, this result implies that internally localized C_nMV^{2+} is accessible to reduction by exogenous $S_2O_4^{2-}$. It is also consistent with the indirect evidence cited in the introduction that DHP-bound $C_{16}MV^{2+}$ can mediate transmembrane reduction of $Fe(CN)_6^{3-}$ by $^3ZnTPPS^{4-}$.[16] It is tempting, therefore, to ascribe the additional slow kinetic step observed with cosonicated preparations to transmembrane redox between externally localized C_nMV^+ and internally localized C_nMV^{2+}. This simple interpretation is not

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supported by the rate law, however. For rate-limiting transmembrane redox, viologen reduction will be independent of $S_2O_4^{2-}$, yet k_3 shows half-order dependence upon reductant concentration (Figure 6).

It is also evident from product spectra that the k_3 pathway is associated with formation of multimeric viologen radical, as opposed to the predominantly monomeric ions formed by k_1 and k_2 pathways. This reaction involves viologen reduction, i.e., is not merely monomer–multimer equilibration, because absorbance increases are observed over the entire spectral range, including regions where the monomer is more strongly absorbing than multimers,[25] and because simple aggregation–disaggregation equilibration also cannot account for the reaction dependence upon $S_2O_4^{2-}$ concentration.

The intracellular location and structural character of these multimers are presently unknown. One intriguing possibility is that they are organized in a fashion that allows both access by reagents in the external aqueous phase and rapid transmembrane redox, comparable to recently proposed liposome-bound cytochrome c_3[46] and metalloporphyrin[47] dimers, which are described as membrane-traversing electron channels. Aggregation might arise as a consequence of differences in surfactant packing forces on the convex and concave vesicular surfaces; asymmetric binding of tris(2,2′-bipyridine)ruthenium(II) to inner and outer DHP surfaces has recently been proposed based upon optical spectroscopic and equilibrium distribution data.[48] In part to resolve these issues, we are currently characterizing the viologen binding environments by a variety of physical techniques.

Concluding Comments. These studies illustrate the exquisite sensitivity of reaction dynamics in probing environments of vesicle-bound reagents. Even though considerable care was taken to eliminate complications that might arise from microcompartmentation, particle heterogeneity, or surface aggregation of reactants, the kinetics reveals a diversity of viologen binding that is dependent upon subtle structural factors and topographic organization of the particles. Characterization of the molecular organization comprising the kinetically distinct sites may be crucial to understanding transmembrane redox, since the data suggest that this process may occur from only one of the several distinguishable binding domains.

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Partial Valence Trapping in a Trinuclear Mixed-Valence Iron(III,III,II) Cluster: Vibrational Spectra of $[Fe_3O(OOCCH_3)_6L_3]$ and Related Mixed-Metal Complexes[1]

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Abstract: Infrared spectra (800–130 cm^{-1}) of the mixed-metal and mixed-valence complexes $[Fe^{III}_2M^{II}O(OOCCH_3)_6L_3]$ (M = Mn, Fe, Co, Ni; L = H_2O, pyridine), and Raman spectra of the aquo-adducts, are reported and assigned by using a variety of isotopic substitutions. It is concluded that in the mixed-valence complexes (M = Fe) the oxidation states are partially localized on the vibrational time scale.

Mixed-valence materials are important for understanding the dynamics of electron-transfer processes,[2] and for this purpose the family of metal complexes of the general formula $[M_3O(OOCR)_6L_3]$ (see Figure 1) is proving to be particularly interesting. The best-known complexes are those containing the $Fe^{III}_2Fe^{II}$ cluster,[3-10] but the range has been extended to include $V^{III}_2V^{II}$,[11] $Cr^{III}_2Cr^{II}$,[12] $Mn^{III}_2Mn^{II}$,[13,14] $Ru^{III}_2Ru^{II}$,[15] $Ir^{IV}_2Ir^{III}$,[16] and, in the case of ruthenium[17] and iridium[18] clusters, several other combinations of oxidation states obtained by electrolytic oxidation and reduction.

With all these compounds, a key question is whether the metal ion triangle is exactly equilateral, with all other corresponding metal–ligand bonds equal (D_{3h} symmetry), or whether one metal

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