Photoinduced Diffusion of Methyl Viologen across Anionic Surfactant Vesicle Bilayers

Lester Y-C. Lee,[†] James K. Hurst,*[†] Mario Politi,[‡] Kazue Kurihara,[‡] and Janos H. Fendler[‡]

Contribution from the Department of Chemistry & Biochemical Sciences, The Oregon Graduate Center, Beaverton, Oregon 97006, and Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676. *Received June 7, 1982*

Abstract: Asymmetrically organized dihexadecylphosphate (DHP) vesicles containing inorganic photosensitizers bound to the outer surface and methyl viologen dication, an electron acceptor, bound to the inner surface were prepared by chromatography on strong-acid cation-exchange resins or dextran gels. The latter method proved superior because destabilizing medium conditions arising during manipulative procedures could be avoided. Vesicle integrity was confirmed by photon correlation spectroscopy, optical spectroscopy, and ultrafiltration measurements. Continuous illumination with visible light in the presence of external electron donors gave rise to formation of reduced viologen radical; the rate and extent of reduction were markedly enhanced by the presence of hydroxylic amine buffers in the aqueous medium. Examination of vesicle suspensions after illumination by addition of the DHP membrane-impermeable reductant, sodium dithionite, revealed that extensive diffusion of MV^{2+} from the inner to outer vesicle surface had occurred. Below 30 °C passive diffusion of MV^{2+} across the bilayer does not occur at an appreciable rate, but above 30 °C in the presence of the amine buffers, transmembrane diffusion is rapid. The mechanism for viologen reduction appears to involve photoinduced transmembrane diffusion of acceptor followed by reaction with photosensitizer bound to the same vesicle surface.

Introduction

Illumination of asymmetrically organized vesicles containing bound photosensitizers has been reported to give rise to net oxidation–reduction of donor and acceptor ions separated by the bilayer membranes.[1-4] Transmembrane electron exchange between amphiphilic derivatives of ruthenium 2,2′-bipyridine ($Ru(bpy)_3^{2+/3+}$) has been proposed to account for photosensitized reduction of diheptyl viologen by EDTA in phospholipid assemblies.[1] Similarly, methyl viologen (MV^{2+}) reduction by $Ru(bpy)_3^{2+}$ electrostatically bound to the opposite surfaces of anionic dihexadecylphosphate (DHP) vesicles was thought to occur by direct transmembrane electron transfer from photoexcited ruthenium to acceptor.[2] To account for measured overall redox rates in the two systems it is necessary that electron transfer occur with apparent first-order rate constants, $k \simeq 10^5\ s^{-1}$. This requirement presents some conceptual difficulty since the electron transfer distance, presumably measured by the width of the hydrocarbon barrier, is about 40 Å. Calculations made assuming reasonable barrier heights indicate considerably lower electron tunneling rates would be expected. For example, using a mechanism[5] in which the electron is thought to "hop" to intermediate interlayer sites located at the interface between hydrocarbon chains, i.e., halfway across the barrier, we calculate $k \leq 10^2\ s^{-1}$. This mechanism has been successfully applied to electron tunneling through fatty acid monolayers and multilayers.[5] Our calculation makes use of experimentally determined barrier heights[6] for photoexcited $Ru(bpy)_3^{2+}$ (1.6 eV) and densities of interfacial states[5] for these systems; as such, it should be a good approximation for the $MV^{2+}/DHP/Ru(bpy)_3^{2+}$ vesicle.[7] Kinetic models which incorporate electron tunneling across the entire bilayer width predict even lower rates. Photoinitiated electron transfer could not be detected between $Ru(bpy)_3^{2+}$ and viologens when separated by fatty acid bilayers; electron transfer was observed over averaged distances of separation of up to only about 10 Å at the hydrophilic interface.[6]

We have sought additional characterization of the DHP assemblies to resolve the discrepancy between experimental findings and theoretical expectations. In contrast to previously reported results,[2] only trace quantities of viologen radicals were detected in the photolysis of $MV^{2+}/DHP/Ru(bpy)_3^{2+}$ by the Oregon group. Furthermore, it was noted that their vesicle preparations underwent photostimulated loss of initially encapsulated viologen. These initial observations have now been confirmed in experiments conducted independently in both laboratories. The inherent complexity of the system and its potential significance to photoredox studies in phase-separated media in general warrants, we believe, complete description of our experimental findings.

Results And Discussion

Two types of asymmetric $MV^{2+}/DHP/$sensitizer preparations were used which differ primarily in the method of removal of MV^{2+} ion from the outer vesicle surface. In type I preparations, MV^{2+} was displaced by cation exchange chromatography; in type II preparations, externally bound viologen was displaced by gel chromatography.

Steady-state illumination of freshly prepared type I preparations below 25 °C led to formation of only trace quantities of viologen radicals. Prolonged illumination of type I particles prepared using the explicit procedures previously described[2] caused buildup of methyl viologen radicals in amounts corresponding to earlier reported values,[2] although particles prepared by slightly modified methods (Experimental Section) gave considerably less reduced viologen, even after 120 min illumination under comparable experimental conditions. Conversely, exposure to the light beam for 30 s at equivalent reactant concentration levels in homogeneous solution gave extensive formation of MV^+ ions. Illumination of DHP vesicles containing both MV^{2+} and photosensitizer bound to the external surface (DHP/MV^{2+}–$Ru(bpy)_3^{2+}$)[7] also resulted in slow buildup of the viologen radicals. Similar results were obtained when 1,2,3,4-tetrakis(4-*N*-methylpyridyl)porphinatozinc(II) ($TMPyP^{4+}$) ion was substituted for $Ru(bpy)_3^{2+}$ as photosensitizer. Likewise, quenching of the ruthenium luminescence was observed in asymmetrical vesicles only after they

[†] The Oregon Graduate Center.
[‡] Clarkson College of Technology.

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(7) The notation $MV^{2+}/DHP/Ru(bpy)_3^{2+}$ is meant to represent viologen and sensitizer separated by the DHP bilayer. DHP/MV^{2+}–$Ru(bpy)_3^{2+}$ indicates sensitizer and viologen bound to the same surface.

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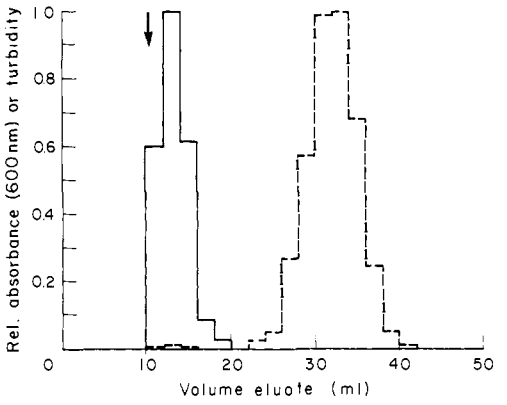

Figure 1. Sephadex G-50 chromatographic behavior of solutions containing DHP sonicated in the presence of methyl viologen. Initial conditions: [DHP] = 4.8 mM, [MV^{2+}] = 3.6 mM, in 0.05 M Tris, pH 7.8; column dimensions, 2 × 10 cm. Solid line: relative turbidity, measured with a Hach 2100A turbidimeter; dashed line: methyl viologen, measured as the MV^+ radical ion by $Na_2S_2O_4$ addition to eluate fractions. The arrow indicates the column void volume determined with blue dextran.

had been exposed to prolonged irradiation. Ruthenium luminescence quenching was readily observable in homogeneous solutions or in DHP/MV^{2+}–$Ru(bpy)_3^{2+}$ vesicles.

After illumination, a significant fraction of the originally entrapped viologen had become accessible to reduction by sodium dithionite, $Na_2S_2O_4$, which is DHP impermeable.[2] Typically, about 25% of the originally entrapped viologen is reducible after 40 min illumination.

Viologen leakage across the DHP bilayer during illumination might be associated with vesicle instability under the experimental conditions. Specifically, DHP vesicles cannot be formed in solutions containing high salt concentrations or in acidic media; polyanions such as EDTA are especially effective in preventing vesicle formation.[8] Preparation of the type I assemblies therefore necessitates subjecting the vesicle suspensions to a set of destabilizing conditions. We have developed alternative procedures that minimize these problems (type II preparations) based upon our observations[8] that hydroxylic amine buffers [tris(hydroxymethyl)aminomethane (Tris), tricine, triethanolamine (TEOA)] improve DHP vesicle longevity and, at high concentrations, partially displace bound MV^{2+} cation. Passage of sonicated solutions down amine buffer equilibrated Sephadex G-50 columns leads to clean separation of vesicles and external MV^{2+} ions when buffer concentration levels are greater than 0.01–0.05 M (Figure 1). At lower buffer concentration levels, a significant fraction of the MV^{2+} ion comigrates with the vesicles. The results suggest that labile equilibria exist between bound and free viologen, e.g., $MV^{2+} + DHP^{n-} \rightleftharpoons MV{:}DHP^{2-n}$, which are media sensitive. Retardation of the free viologen by the sieving action of the gel causes progressive equilibrium shift to the left as the sample passes down the column. Measured internal viologen concentrations in the chromatographed vesicles are equivalent to levels obtained in type I preparations.[2] Strong binding of added photosensitizers can be demonstrated by ultrafiltration experiments in which the chromophore in vesicle-containing solutions is prevented from passing through semipermeable membranes (Pellicon PSAC 04710) which exclude the vesicles, but passes freely when vesicles are absent. Binding to DHP also gives rise to diagnostic bathochromic shifts in sensitizer optical spectra.[8] This effect is illustrated for $ZnTMPyP^{4+}$ ion binding in Figure 2; optical difference spectra gave Beer's law behavior over the measured concentration range, [ZnTMPyP] = 1.6–210 μM. Autocorrelation functions obtained from quasi-elastic light scattering spectroscopy[9] are nearly exponential (relative variance, v = 0.1–0.3), indicating nearly monodisperse particle formation. Hydrodynamic radii calculated from the decay constants for vesicles containing bound cations are 400–500 Å (Table I). These sizes are smaller than reported for DHP in water (600 Å) and for DHP in buffer (Table I).

Steady-state illumination of type II preparations using either $Ru(bpy)_3^{2+}$ or $ZnTMPyP^{4+}$ as sensitizers and EDTA or TEOA as electron donors leads to substantial MV^+ buildup. Representative data are given in Figure 3, which shows that the effect is wavelength dependent, i.e., illumination of both Soret and visible metalloporphyrin bands gives more rapid formation of viologen radical than illumination of visible bands only. The reaction also shows a pronounced temperature dependence (Figure 4) with an apparent activation energy of E_a = 19.5 kcal/mol. Upon illu-

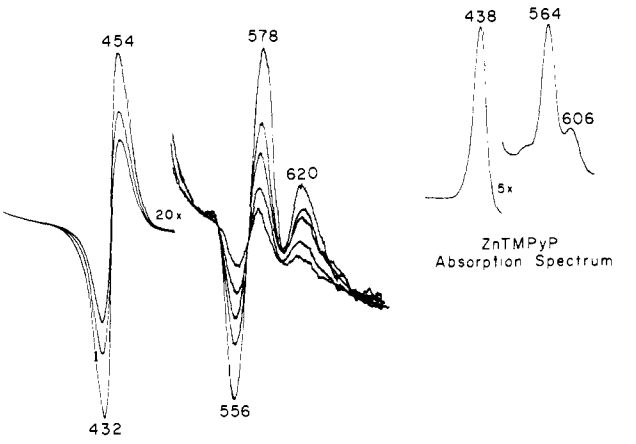

Figure 2. Optical spectra of $ZnTMPyP^{4+}$ solutions. Difference spectra with DHP/$ZnTMPyP^{4+}$ and equimolar aqueous $ZnTMPyP^{4+}$ ions in sample and reference cuvettes, respectively, are shown at the left. Medium conditions: 0.05 M TEOA, pH 7.8, 23 °C. The various traces are for differing concentrations of sensitizer; amplitudes of peak extrema follow Beer's law. The absorption spectrum of aqueous $ZnTMPyP^{4+}$ is given at the right. The numbers identify wavelengths (nm) of peak extrema.

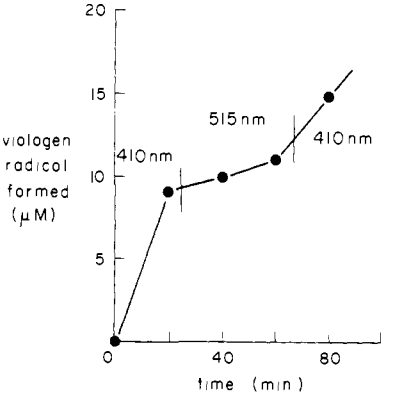

Figure 3. Viologen radical formation in type II MV^{2+}/DHP/$ZnTMPyP^{4+}$ vesicles. Initial conditions: [DHP] = 4.8 mM, [MV^{2+}] = 3.6 mM, [$ZnTMPyP^{4+}$] = 16 μM, in 0.05 M Tris, pH 7.8, at 23 °C. Optical filters with high energy cutoffs at 410 nm (Corning CS 373) or 515 nm (Corning OG 515) were used in the indicated time ranges during illumination. Viologen radical formation was determined from spectral changes at 600 nm.

Table I. Hydrodynamic Radii of DHP Vesicles from Light-Scattering Spectroscopy

vesicle[a]	medium	R_H, Å	variance[b]
DHP	0.1 M tricine, pH 7.2	638	0.21
DHP/$ZnTMPyP^{4+}$	1 M TEOA, pH 7.8	480	0.19
DHP/$ZnTMPyP^{4+}$	0.02 M Tris, pH 7.8	514	0.12
DHP/$ZnTMPyP^{4+}$-MV^{2+}	0.02 M TEOA, pH 7.8	484	0.13
MV^{2+}/DHP/$ZnTMPyP^{4+}$	0.05 M Tris, pH 7.8	400	0.18

[a] Reference 7. [b] Reference 9 and 10.

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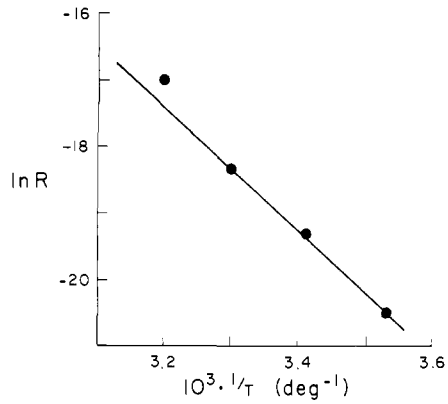

Figure 4. Temperature dependence of the initial rate of MV^+ ion formation in type II MV^{2+}/DHP/$Ru(bpy)_3^{2+}$ vesicles. Initial conditions: [DHP] = 4.8 mM, $[Ru(bpy)_3^{2+}]$ = 0.03 mM, $[MV^{2+}]$ = 3.6 mM, in 0.05 M Tris, pH 7.8, [EDTA] = 1 mM added as external donor; illuminated with filtered visible light (λ >410 nm, $I_0 \simeq 6 \times 10^{-8}$ einstein/s). Viologen radical formation was determined from spectral changes at 600 nm; initial rates (R) are given in units of Ms^{-1}.

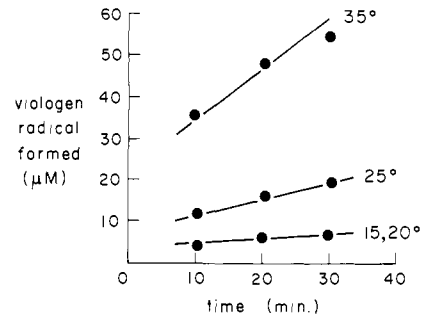

Figure 5. Temperature dependence of MV^{2+} ion diffusion across DHP vesicle bilayers. Initial conditions: [DHP] $\simeq$ 4.8 m, $[MV^{2+}] \simeq$ 3.6 mM, initial concentration within vesicles, in 0.05 M Tris, pH 7.8. The extent of a viologen leakage at the indicated times was determined by sodium dithionite addition to aliquots of the vesicle suspensions; viologen radical formation was determined from spectral changes at 600 nm. Temperatures are indicated in the figure.

mination, a major fraction of entrapped methyl viologen also become accessible to dithionite. Below 25 °C, MV^{2+} is not released by the type II vesicles in the absence of light or by illuminated vesicles that contain entrapped MV^{2+} but lack photosensitizer. At 25 °C, slow diffusion of MV^{2+} out of the vesicles is observed under these conditions, which becomes rapid above 30 °C (Figure 5). In experiments made at 15 °C, we found that MV^{2+} efflux from the vesicles ceases when the samples are removed from the light beam.

Results of laser flash photolysis of type II preparations using $Ru(bpy)_3^{2+}$ as sensitizer depended upon the number of flashes to which the samples had been exposed. No detectable buildup of MV^+ (10^{-8} M MV^+ is the limit of our detection) or quenching of ruthenium luminescence could be observed in the first 4–6 pulses. Repeated pulsing or aging of the samples resulted, however, in electron transfer. Triplet state deactivation of photoexcited vesicle-bound $ZnTMPyP^{4+}$ ion is complex, but can be described by three concurrent first-order processes spanning the microsecond–millisecond timescales. The deactivation kinetics are unaffected by incorporation of MV^{2+} within the vesicle in type II preparations, although 4-*N*-tetradecyl-4-methylbipyridinium ion ($C_{14}V^{2+}$) quenches photoexcited $ZnTMPyP^{4+}$ when bound to the same surface,[8] e.g., in DHP/$ZnTMPyP^{4+}$–$C_{14}V^{2+}$. There is, therefore, no transient-kinetic evidence for *transmembrane* redox quenching of photoexcited states using either photosensitizer.

We conclude that photoexcitation of vesicle-bound sensitizers leads to enhanced MV^{2+} ion transmembrane diffusion rates. The pronounced temperature dependence observed for thermal diffusion suggests that the mechanism involves localized heating arising from nonradiative deactivation of the photoexcited state, although the molecular details are not yet understood. The mechanism is highly dependent upon the composition of the aqueous medium, although these effects are not detectable by changes in the physical properties of the asymmetrically organized vesicles. Because these properties and the intrinsic MV^{2+} impermeability of the particles also appear to be unchanged by illumination, it is unlikely that these effects are due to photodegradative damage of the vesicle membrane. Earlier observations[2] that were taken as indicative of transmembrane electron transfer from photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} are attributable to transmembrane diffusion of MV^{2+}, followed by reaction with sensitizer bound to the same surface. The phenomenon is likely to be quite general, so that other studies involving photostimulation of bilayer separated reactants should include examination for this effect.

Experimental Section

Experiments in Beaverton. Preparation of Asymmetrical MV^{2+}/DHP/Sensitizer Vesicles. Type I. An Ultrasonic Model W 185 F Sonicator equipped with a microtip probe and operated at 70 W was used to induce vesicle formation; 50 mg of DHP (Sigma) was sonicated in 20 mL of 1.8–3.6 mM aqueous solution of methyl viologen dichloride (Aldrich) at 50 °C for 30–45 min. During sonication, 0.1 N sodium hydroxide was added dropwise to obtain clarification. The final solution pH was adjusted to 8.4. The slightly hazy solution was either filtered successively through 0.45, 0.22-μm Millipore membranes or centrifuged at 100 000g using a Beckman Model L5-65 Ultracentrifuge, then passed down a 2 × 15 cm Bio-Rad AG 50 W-X8 column in the hydrogen ion form. Vesicles were recovered in 2.0-mL fractions immediately following the column void volume. Internal methyl viologen concentrations were determined spectrophotometrically as previously described.[2] Sodium dithionite solutions used in the analysis were freshly prepared in aqueous buffer (0.05 M Tris, pH 7.8); all solutions were purged of oxygen by bubbling with argon before viologen reduction with dithionite. Sufficient EDTA (0.1 M, pH 7.8) and 0.1 M NaOH were added to the vesicle fractions (pH 2.8) to give final concentrations of 1 mM EDTA, pH 8.4. Appropriate amounts of $Ru(bpy)_3^{2+}$ or $ZnTMPyP^{4+}$ ion-containing solutions were added to give concentrations of 3×10^{-5} and 1.6×10^{-5} M, respectively. The reagents $Ru(bpy)_3(ClO_4)_2$, DHP, and methyl viologen dichloride were recrystallized before use; $ZnTMPyP^{4+}$ in aqueous solution (chloride counterion) was a gift from Dr. K. Kalyanasundaram.

Type II. DHP and methyl viologen were cosonicated in 0.05 M Tris–HCl, pH 7.8, at 50 °C for 45 min. Filtered or centrifuged vesicle solutions were passed down a 2 × 20 cm Sephadex G-50 column which had been preequilibrated with buffer. Manipulations and analysis of the chromatographed vesicles were the same as described above except that the addition of NaOH was unnecessary.

Illumination Experiments. Solutions containing type I or type II vesicles were purged of O_2 by bubbling with argon in a glass vessel for 1 h. Traces of oxygen were removed by passing the argon stream through a BASF R3-11 activated copper column before entering the vessel. The gas delivery line was made entirely of copper and glass tubing. Transfer of deoxygenated solutions was made via a special V-bore four-way stopcock to a cylindrical optical cell (1 cm pathlength) which was fitted to the purging vessel using all-glass connections. This assembly[11] allows solution transfer with minimum risk of O_2 contamination. The optical cell was immersed in a beaker-shaped glass vessel (~500 mL) through which water was circulated from a Lauda K-2/R temperature bath. The vessel was fitted with a Pyrex optical flat to allow undistorted admission of photostimulating light. During illumination, the bath temperature was maintained constant to 0.1 °C. An iron–constantan thermocouple immersed in the optical cell was used to measure temperature changes in the reaction solution during ilumination of sensitizer-bound vesicles. Under experimental conditions identical with those in the photosensitization studies, solution temperatures were found to increase only a few tenths of a degree (maximally 0.8°/h) during the illumination period. The illumination source was a Hanovia 200 W Hg–Xe compact arc lamp. Emitted light was filtered to remove high energy radiation before impinging on the sample. Generally, Corning 410-nm and 515-nm cutoff filters were used for experiments with $Ru(bpy)_3^{2+}$ and $ZnTMPyP^{4+}$ ions as photosensitizers, respectively. Incident light intensities were estimated by ferrioxalate actinometry[12] to be 6.4×10^{-8} einsteins/s for the 410-nm filtered light; calculations were based upon the assumption that $\Phi_{Fe^{2+}} \simeq 1.0$. Because the spectral envelopes of $Ru(bpy)_3^{2+}$ and ferrioxalate are

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similar under these conditions, the method gives a rough measure of the photons absorbed by sensitizer during continuous photolysis.

Individual determinations were generally repeated four times. External methyl viologen was measured immediately before and after illumination using freshly prepared dithionite solution. In instances where the viologen radical cation had accumulated as a consequence of photolysis, it was reoxidized by pulsing the solution with O_2, then repurging of residual oxygen before dithionite addition.

Instrumentation. Optical measurements were made on a Cary 16 spectrophotometer. Pulsed laser experiments of type II MV^{2+}/DHP/ZnTMPyP^{4+} vesicles were made in Michael Grätzel's laboratory at EPFL, Lausanne, Switzerland, using as excitation source a 20-ns pulse (532 nm) from a frequency doubled Nd:YAG laser. Light scattering measurements were also made at EPFL using a Chromatix KMX-6 photometer interfaced to a Langley-Ford autocorrelator.

Experiments in Potsdam. Preparation of Type II Asymmetrical MV^{2+}/DHP/$Ru(bpy)_3^{2+}$ Vesicles. A sample containing 10.5 mg of DHP (Sigma) was heated in 4.0 mL of 0.01 N Tris-HCl buffer at pH 7.6 for 5 min at 80 °C prior to sonicating for 5 min at the same temperature using the microtip of a Braunsonic sonifier set at 70 W. Methyl viologen (Aldrich, twice recrystallized from cold methanol) solution (4.6 mg in 2.0 mL of 0.01 N Tris-HCl buffer, pH 7.6) was added slowly with repeated sonication (at 70 W) to the DHP vesicles, kept at 80 °C. Total additional sonication time was 25 min. Subsequent to cooling to room temperature (in the dark) the vesicle solution was centrifuged for 20 min in a table-top centrifuge. The supernatant was passed through a prewashed and equilibrated (0.01 N Tris-HCl, pH 7.6) Sephadex G 50-80 column (21.7 × 0.7 cm) using 0.01 N Tris-HCl, pH 7.6 as the eluant; 3.5-mL fractions were collected in a fraction collector. Quantitative examination of the elution fraction profile established 99.9% recovery of MV^{2+} of which 1.8% appeared in the vesicle fraction. The vesicle fractions (fractions 5 and 6) were passed twice through a prewashed and equilibrated (with 0.01 N Tris-HCl buffer, pH 7.6) Chelex 100 (Biorad 200-400 mesh, sodium form). The vesicle fraction contained less than 1% methyl viologen outside, as determined by the $Na_2S_2O_4$ test.[2]

MV^{2+} Determinations. $Na_2S_2O_4$ stock solutions were made freshly in 0.1 N Tris-HCl buffer at pH 7.6. In typical measurements 50 μL of 4.0 × 10^{-2} M $Na_2S_2O_4$ stock solution was added to 1.0 mL of deoxygenated (purified argon bubbled) vesicle solution. Concentration of the MV^+ was determined spectrophotometrically using a Cary 118C spectrophotometer.[2] Two sets of experiments were carried out to determine MV^{2+} leakage. In the first set of experiments $Na_2S_2O_4$-induced leakage was determined in MV^{2+}/DHP vesicles. In the second set of experiments effects of photosensitized MV^{2+} leakages were determined. Irradiations were carried out in a cell thermostatted at 26 °C. The IR band of the light was removed by passage through distilled water. Five separate measurements were carried out for each set of experiments. Mean rates of MV^{2+} leakages, $\Delta Abs/\Delta t$ values, were determined to be 3 × 10^{-5} s^{-1} and 4.8 × 10^{-5} s^{-1} in the absence and in the presence of irradiation, respectively. These correspond to 2% and 3.2% MV^{2+} leakage per 5 mi. Estimated error in these measurements is 30%. Laser flash photolysis and steady-state fluorescence quenching experiments have been previously described.[2]

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; ZnTMPyP^{4+}, 40603-58-5; methyl viologen dichloride, 1910-42-5; DHP, 84065-97-4.

A Classical Dynamics Model of Plasma Desorption Mass Spectrometry Experiments

Barbara J. Garrison[†]

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received May 10, 1982*

Abstract: A classical dynamics procedure is developed to model the desorption of particles from a surface due to heavy particle bombardment. The theoretical approach is to utilize a metallic (Ni) microcrystallite with up to 8 atomic layers covered with an organic monolayer such as benzene. This ensemble of atoms is then bombarded from both the front and the back of the microcrystallite to test whether there are fundamental differences in mechanisms by which the organic molecule is ejected between the two configurations. The model calculation is performed in order to evaluate the importance of collision cascades in the desorption of large molecules using plasma desorption mass spectrometry (PDMS) where a ~100-MeV incident particle bombards a thin foil from behind. This geometry contrasts that utilized in SIMS or FAB mass spectrometry experiments where the molecular layer is bombarded directly by a 1-5-keV heavy particle. The calculated results show that most of the predicted observables for the ejected benzene molecules, including their mass spectrum and their energy and polar angle distributions, are similar. The energy distributions of the benzene molecules are Maxwell-Boltzmann-like in character even though the desorption is a consequence of a nonequilibrium energetic collision cascade. The details of the collision events that lead to desorption of particles, however, are quite different between the two calculations. These collisional differences are most apparent in the angular distributions of the ejected Ni atoms. They also indicate that molecular ejection is slightly more favorable when bombarding from behind the microcrystallite than when bombarding the sample directly, since the direction of momentum need not be reversed.

Mass spectral studies have recently become routine for experimental investigation of molecules with masses in the 1000-20000-amu range. In particular, two techniques that employ energetic beams of heavy particles to produce the molecular ion are currently being developed with considerable success. With one approach the sample is bombarded with a beam of atoms (or ions) and the ionic species that desorb from the surface are then detected with a mass spectrometer. The distinctive feature in this experiment is that the beam source and the detector are on the same side of the sample (Figure 1). This technique is called secondary ion mass spectrometry (SIMS)[1] if an ion beam is employed or fast atom bombardment mass spectrometry

[†] Alfred P. Sloan Research Fellow.

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