

Photophysical Deactivation Dynamics of Excited Porphyrin Molecules Adsorbed onto Dihexadecyl Phosphate Vesicles

Rafail F. Khairutdinov* and James K. Hurst

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

Received: December 10, 1998

Deactivation of triplet-excited *meso*-tetra(*N*-methyl-4-pyridyl)porphine on the surface of dihexadecyl phosphate vesicles was measured by pulsed-laser transient spectrophotometry. Both unimolecular and triplet–triplet annihilation pathways were identified from the concentration dependence of the decay profiles. The data were analyzed using the Monte Carlo method to obtain a surface diffusion coefficient for the adsorbed porphyrin of $D \approx 8 \times 10^{-9} \text{ cm}^2/\text{s}$ at ambient temperatures. The diffusion coefficient underwent a discontinuous change at the major phase-transition temperature of the vesicles, exhibiting an Arrhenius activation energy of $E_a = 31 \text{ kJ/mol}$ below 62°C and 7.9 kJ/mol above 62°C . Comparisons of Monte Carlo simulations to approximate kinetic equations for diffusion-controlled bimolecular reactions confined to spherical surfaces indicate that the latter can be used to estimate diffusion coefficients for reactions on particles that are the dimensions of small unilamellar vesicles.

Introduction

Considerable attention has been given to understanding how membranes can be used to control chemical and photochemical oxidation–reduction reactions. These studies are related in part to endeavors to create artificial photosynthetic systems of photoconversion and photostorage, as well as molecular electronic devices and related advanced materials.¹ A critical issue in the proper design of these assemblies is the dynamics of energy and electron transfer reactions of membrane-localized redox components, which are dependent at least in part upon the surface diffusion rates of bound components. Nevertheless, no quantitative data are available in the literature for surface diffusion at membrane interfaces. Strictly speaking, diffusion coefficients can be determined only from experiments where the motions of individual molecules are monitored. Indirect methods to obtain diffusional information are to study simple bimolecular processes that require close approach of the reactants, including spin exchange,^{2,3} excimer formation,⁴ fluorescence quenching,⁵ or triplet–triplet energy transfer.^{6,7} However, kinetic analyses of reactions on the surfaces of mesoscopic structures are complicated by the finiteness of the reaction space, which may obviate the use of ordinary equations of chemical kinetics that treat the reaction environment as an infinite surface populated with constant average densities of reactant molecules. In these cases, relatively sophisticated stochastic or Monte Carlo calculations are required for accurate dynamical analyses of reactions,^{8–13} and the extent to which simpler approximate methods might be valid has not been extensively explored for particles with the dimensions of small vesicles (i.e., with radii $\approx 10 \text{ nm}$).

In this paper, we present a laser flash photolysis study with Monte Carlo analyses of the triplet–triplet annihilation reactions of *meso*-tetra(*N*-methyl-4-pyridyl)porphine cations ($\text{H}_2\text{TMPyP}^{4+}$) on the anionic surfaces of dihexadecyl phosphate (DHP) small unilamellar vesicles. The porphyrin diffusion coefficient is

evaluated using both conventional kinetic equations and Monte Carlo techniques. These data are used to test the applicability of simple approximate dynamical models of reactions in restricted geometries^{9–14} to bimolecular reactions on the surfaces of small unilamellar vesicles.

Experimental Section

Materials. *meso*-Tetra(*N*-methyl-4-pyridyl) porphine tetra-chloride was obtained from Porphyrin Products Inc. Dihexadecyl phosphate small unilamellar vesicles with an average radius of 12.5 nm were prepared by sonication and characterized essentially as described elsewhere.^{15–17} Typical DHP concentrations in the vesicle suspensions were 4.5 mg/mL , which corresponds to a vesicle concentration of approximately $2 \mu\text{M}$.¹⁷ $\text{H}_2\text{TMPyP}^{4+}$ was subsequently added to the vesicles suspensions as required to give concentrations ranging from 1 to $42 \mu\text{M}$. The extent of $\text{H}_2\text{TMPyP}^{4+}$ binding to the DHP vesicles was determined by membrane ultrafiltration¹⁵ to be approximately 95% for these loadings; accordingly, the average number of porphyrin molecules on the surface of each vesicle varied from 0.5 to 20 over the dopant range analyzed. All experiments were done in 20 mM Tris chloride, $\text{pH } 8.0$, which was prepared with water purified using a MilliQ system. Solutions were deoxygenated by bubbling with argon immediately prior to their use in kinetic studies.

Laser Pulse Photolysis. Absorption spectra and decay kinetics of photoinduced intermediates were measured by laser flash photolysis; the general methods and instrumentation have been previously described.^{15,16} Excitation was accomplished using the second harmonic (532 nm) from a Continuum Surelite III Nd:YAG laser; pulse half widths were $\sim 4 \text{ ns}$ for outputs adjusted to 10 – 200 mJ/pulse . For temperature-dependence measurements (280 – 368 K), samples were thermostated to an accuracy of $\pm 1^\circ\text{C}$; otherwise, experiments were performed at ambient temperature ($\sim 296 \text{ K}$). The average number of excited triplet molecules generated was evaluated from the initial change in absorbance at 470 nm following flash excitation, assuming that $\epsilon_{470} = 2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.^{18,21}

* Correspondence should be addressed to this author. E-mail: rafail@wsunix.wsu.edu. Fax: (509) 335-8867.

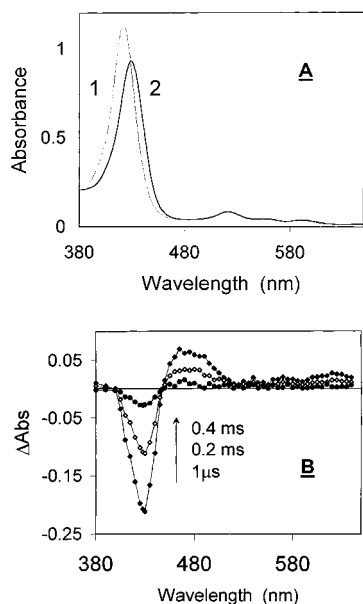


Figure 1. (A) Absorption spectra of 5 μM $\text{H}_2\text{TMPyP}^{4+}$ in water (1) and in a 2 μM aqueous suspension of DHP vesicles (2). (B) Transient absorption spectra of 5 μM $\text{H}_2\text{TMPyP}^{4+}$ in a 2 μM aqueous suspension of DHP vesicles at different times following laser flash excitation. $E = 30$ mJ/pulse.

Results and Discussion

Dynamical Behavior. Absorption spectra of $\text{H}_2\text{TMPyP}^{4+}$ in aqueous buffer and DHP vesicle suspensions are compared in Figure 1, panel A; adsorption to the vesicle is accompanied by a bathochromic shift of both Soret and visible absorption bands. Similar effects were previously reported for ZnTMPyP^{4+} binding to DHP vesicles and were attributed to the reduced medium polarity at the membrane interface.¹⁹ In the present case, the Soret maximum of DHP-bound $\text{H}_2\text{TMPyP}^{4+}$ was at 430 nm, which can be compared to maxima at 424 nm in H_2O and 426 nm in 2-propanol, consistent with localization of the porphyrin within the headgroup region of the vesicle.²⁰

The difference absorption spectra taken in the microsecond time domain following photoexcitation of suspensions of DHP vesicle-bound $\text{H}_2\text{TMPyP}^{4+}$ are displayed in Figure 1, panel B. Overall, the spectral band shape is very similar to the ($^3\text{H}_2\text{TMPyP}^{4+} - \text{H}_2\text{TMPyP}^{4+}$) difference absorption spectrum observed in homogeneous solution,²¹ except that the isosbestic points appear at slightly different wavelengths (450, 510, and 535 nm). Consequently, the spectral changes observed following flash excitation of the DHP-bound porphyrin can be attributed to formation of $^3\text{H}_2\text{TMPyP}^{4+}$ on the vesicle surface. The amplitudinal change, hence, the porphyrin triplet yield, was proportional to the intensity of the laser pulse at energies below 100 mJ/pulse and decreased at higher laser energies, consistent with partial saturation of the excited state.

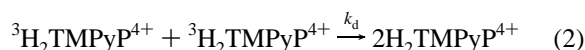
Porphyrins and other molecules can associate on vesicle surfaces at sufficiently high dopant concentrations, apparently forming aggregates that give complex dynamical response in photoinitiated reactions. To minimize interferences that might arise from these sources, the amount of bound porphyrin was restricted to relatively low dopant levels; in these systems, none of the complicating effects previously reported for DHP vesicles containing bound ZnTMPyP^{4+} were evident.¹⁹

At excitation levels such that, on average, there was less than one initially excited porphyrin per vesicle, the decay of $^3\text{H}_2\text{TMPyP}^{4+}$ followed simple first-order kinetics with a characteristic time (τ_0) of 350 ± 30 μs (eq 1).



A typical kinetic curve, for which 0.8 porphyrins/vesicle were photoexcited, is given as the upper trace in Figure 2. Under these first-order conditions, τ_0 was independent of both the detection wavelength and the average number of porphyrins per vesicle (n) over the range $n = 0.5$ –20. This independence of surface concentration indicates that quenching by ground-state porphyrins is negligible. The measured characteristic time is somewhat larger than the lifetime of $\tau_0 = 165$ –175 μs reported for $^3\text{H}_2\text{TMPyP}^{4+}$ in aqueous solution.^{21,22}

At excitation levels where on average more than one $^3\text{H}_2\text{TMPyP}^{4+}$ was initially present on each vesicle, the decay kinetics became nonexponential and the apparent triplet lifetime decreased with increasing surface concentration of the photoexcited ion (Figure 2, lower traces). These features suggest participation of a concurrent bimolecular deactivation pathway under these conditions, i.e.,



Porphyrin triplet–triplet annihilation (reaction 2) is commonly observed at high levels of laser excitation in both homogeneous solutions and nonhomogeneous environments;^{7,23} in the present case, accumulation on the vesicle surface apparently provides a local concentration of photoexcited ions that is sufficiently high to promote the bimolecular reaction. Photoexcitation and deactivation by reactions 1 and 2 appeared to be fully reversible, since no changes were detected in the transient absorption spectrum, in the intermediate decay rates, or in the ground-state absorption spectra of the porphyrin after exposure to more than 100 laser flashes.

In homogeneous solutions, T–T annihilation takes place by collisional deactivation following diffusional approach of the photoexcited molecules. The reaction kinetics follows a simple rate equation corresponding to mixed first- and second-order decay.²³ This treatment may become unsuitable when bimolecular reactions are confined to a finite surface^{10,24} and in these instances should be replaced by more adequate treatments based on stochastic or Monte Carlo methods.^{8–10} In the present case, we use the Monte Carlo approach, which has been shown to successfully describe exciton annihilation²⁵ and deactivation of excited porphyrins on layered MoS_2 semiconductor nanoparticles.⁷ These analyses have afforded estimates of both the T–T annihilation rate constant and porphyrin diffusion coefficient on the nanoparticle surface.

Monte Carlo Analyses. Before presenting our computational results, it may be instructive to consider the diffusional model on which the calculations are based. At the molecular level, the membrane surface consists of anionic and neutral phosphate headgroups, which are assumed through electrostatic and polar interactions to form discrete binding sites for the porphyrin cations. Thus, the potential energy hypersurface representing the adsorbate–membrane interaction consists of a regular two-dimensional array of minima (binding sites) separated by potential barriers. At low surface coverage, the adsorbed porphyrins occupy only a small fraction of these minima and therefore should be able to move (jump) from one site to another. If the residence time at a particular site is long relative to the vibrational time associated with the jump, the porphyrin will lose all memory of its directional origin and a new jump direction will be independent of the previous one. In this case, the movement of the porphyrin can be described as a stochastic two-dimensional random walk whose mean square displacement

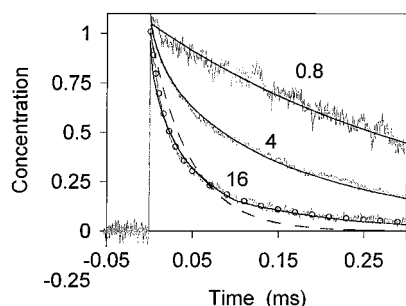


Figure 2. Decay at 23 °C of $^3\text{H}_2\text{TMPyP}^{4+}$ bound to DHP vesicles monitored at 470 nm. The numbers over the individual curves indicate the average number of $^3\text{H}_2\text{TMPyP}^{4+}$ ions formed per vesicle in the excitation pulse. The smooth solid curve at $n = 0.8$ is the best fit by exponential decay kinetics, for which $\tau_0 = 350 \mu\text{s}$; the smooth curves at $n = 4$ and 16 are results of Monte Carlo fittings using the parameters $\tau = 3.5 \times 10^{-4} \text{ s}$, $\nu = 10^{13} \text{ s}^{-1}$, $\lambda_D = 0.1 \text{ nm}$, and (for $n = 4$) $\tau_D = 1 \times 10^{-9} \text{ s}$, $a \approx 0.09 \text{ nm}$ or (for $n = 16$) $\tau_D = 2 \times 10^{-9} \text{ s}$, $a \approx 0.08 \text{ nm}$. The circles show the best fit of the decay kinetics to eq 5, for which $\alpha D' = 8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, and the dashed line is the best fit by an exponential equation, for which the mean reaction time (τ_{av}) equals $4.7 \times 10^{-5} \text{ s}$.

$\overline{r^2}$ is proportional to the time of observation,²⁶ i.e., $\overline{r^2} = 4Dt$. The proportionality constant (D), which is identified as the porphyrin diffusion coefficient, is related to the energy difference (E_a) between the binding site minimum and the saddle point between two adjacent minima by the equation

$$D = \frac{1}{4} \lambda_D^0 (\tau_D^0)^{-1} e^{-E_a/(kT)} \quad (3)$$

where λ_D^0 is the jump length and $(\tau_D^0)^{-1}$ is the effective attempt frequency of an adsorbed porphyrin, and the coefficient $1/4$ reflects the two-dimensional character of the diffusion.²⁶ The temperature dependence of the diffusion coefficient therefore provides valuable information on the binding site energetics.

The Monte Carlo calculations were made using a previously described model.¹⁶ Briefly, the vesicles were taken to be spheres with radii (R_s) of 12.5 nm and $\text{H}_2\text{TMPyP}^{4+}$ ions were modeled as circles with radii (r_m) of 0.5 nm. The initial state was prepared by randomly distributing the porphyrins on the surface of the spheres and randomly selecting some of them to be triplet-excited. Monte Carlo moves were then made at time intervals (τ) within the range $\tau = 0 - \tau_D$ such that every porphyrin ion was permitted to shift randomly in any direction for a distance (λ) within the range $\lambda = 0 - \lambda_D$ along the spherical surface. Each excited porphyrin molecule underwent unimolecular decay with a lifetime of 350 μs , and all pairs of triplet molecules were permitted to undergo annihilation at each Monte Carlo move with the probability per unit time (w) given by^{27–29}

$$w = \nu \exp(-2(r - d)/a) \quad (4)$$

where ν is a frequency factor, a is the parameter that describes the decrease of annihilation rate with distance r between interacting molecules, and $d = 1 \text{ nm}$ is the sum of the reactant radii. Parameters ν and a in eq 4 define a critical interaction distance, $R_c = d + (a/2)\ln(\nu\tau)$, such that triplet–triplet annihilation occurs with a probability approaching unity within the time interval τ when the distance between two excited molecules is $r < R_c$, whereas the probability of annihilation is negligible for pairs with $r > R_c$. Both the total number of porphyrins and the fractional excitation per sphere were randomly changed from one trial to another such that their values averaged over all trials were fixed and equal to the correspond-

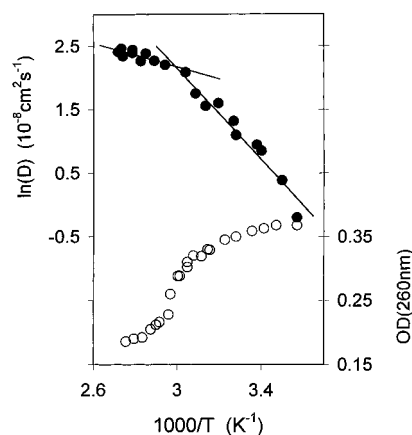


Figure 3. Temperature dependence of the lateral diffusion coefficient for $^3\text{H}_2\text{TMPyP}^{4+}$ on the DHP vesicle surface (solid circles) and the apparent absorbance at 260 nm of DHP vesicles (open circles). The lines are the data fits according to eq 3, for which $E_a = 7.9 \pm 2.3 \text{ kJ/mol}$ at $T \geq 62 \text{ °C}$ and $E_a = 31 \pm 2.2 \text{ kJ/mol}$ at $T \leq 62 \text{ °C}$.

ing average numbers in the system. For each experimental decay profile, the number of trials performed exceeded 50 000. The calculated decay curves were obtained by averaging the results from all trials.

Different sets of the variables ν , a , τ_D , and λ_D gave acceptable fits to experimental data. To decrease the number of fitting parameters, we fixed the critical distance of triplet–triplet annihilation at $R_c(\tau_D) = d + (a/2)\ln(\nu\tau_D) = 1.4 \text{ nm}$,³⁰ a value that only slightly exceeds the sum of porphyrin radii, and fixed the elementary shift length to a value corresponding to an appropriate molecular dimension, i.e., $\lambda_D = 0.1 \text{ nm}$. With these assumptions, good fits to the experimental data were obtained with different sets of ν and a subject to the constraint given by the equation $R_c(\tau_D) = \text{constant}$. The corresponding value for τ_D that gave the best fit to the experimental data was insensitive to the individual value assumed for ν (10^{10} – 10^{15} s^{-1}) and thus could be uniquely determined from the kinetic profiles. Typical data fits, made assuming that $\nu = 10^{13} \text{ s}^{-1}$,^{28,30} are shown as the smooth curves in Figure 2; best-fit solutions are obtained with $\tau_D = 1 \times 10^{-9} \text{ s}$ and $a \approx 0.09 \text{ nm}$ for an average of four initially excited porphyrins/vesicle, and $\tau_D = 2 \times 10^{-9} \text{ s}$ and $a \approx 0.08 \text{ nm}$ for an average of 16 initially excited porphyrins/vesicle. The optimal value determined for τ_D was insensitive to the critical distance of triplet–triplet annihilation, varying from $\sim 7 \times 10^{-10}$ to $1.3 \times 10^{-9} \text{ s}$ for $n = 4$ and from $\sim 1.6 \times 10^{-9}$ to $2.5 \times 10^{-9} \text{ s}$ for $n = 16$ when $R_c(\tau_D)$ was changed from 1 to 1.8 nm. Thus, the average value of τ_D for triplet–triplet annihilation of excited porphyrin molecules on the surface of DHP vesicles is $\tau_D \approx 1.5 \times 10^{-9} \text{ s}$.

For an isotropic two-dimensional vesicle surface, the diffusion coefficient D can be written as $D = (1/4)\lambda^2/\bar{\tau}$, where $(\lambda^2)^{1/2}$ and $\bar{\tau}$ are the average jump length and the average time between two contiguous jumps, respectively.^{4,26,31,32} Assuming that $(\lambda^2)^{1/2} = \lambda_D/2$ and $\bar{\tau} = \tau_D/2$, we estimate the diffusion coefficient of $\text{H}_2\text{TMPyP}^{4+}$ molecules on the surface of DHP vesicles to be $D = 8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

The magnitude of D at other temperatures was calculated using the same parameters as at 296 K, i.e., $\nu = 10^{13} \text{ s}^{-1}$, $a = 0.09 \text{ nm}$, and $\lambda_D = 0.1 \text{ nm}$. The temperature dependence obeys eq 3, with the exception that there is an apparent discontinuity in the $\ln D$ vs T^{-1} plot at $\sim 62 \text{ °C}$. In this region, the turbidity of the medium also underwent a large change (Figure 3, open circles) indicative of a major phase transition in the membrane bilayer.^{33–35} This behavior is consistent with earlier studies by

differential scanning calorimetry, which showed a complex thermogram exhibiting several endothermic bands in the region between 45 and 65 °C for undoped DHP small unilamellar vesicles formed by sonication in Tris-HCl, pH 8.0.¹⁷ Raman spectroscopy of the hydrocarbon C-H stretching modes has indicated that this behavior is associated with increasing chain disorder at the higher temperatures, most likely associated with a gel-to-liquid crystalline type transition; in both phases, however, the side chains remained relatively ordered compared to typical phospholipid vesicles.¹⁷ The discontinuity in the temperature dependence of D can therefore be attributed to a change in the porphyrin binding energy accompanying the abrupt changes in the surfactant fluidity and packing density attending the major phase transition of the membrane. Discontinuities of this type are often observed in kinetic processes on surfactant membranes.^{36–38} The activation energies for diffusion evaluated from the temperature dependence are $E_a = 31 \pm 2.2$ kJ/mol at $T < T_c$ and $E_a = 7.9 \pm 2.3$ kJ/mol at $T > T_c$ (Figure 3).

Diffusion of lipophilic probes inside bilayer membranes has been extensively studied.^{39–41} For planar lipid membranes and vesicles in their liquid-crystalline phases, diffusion coefficients generally range between 10^{-8} and 5×10^{-7} cm² s⁻¹. The diffusion coefficient of ³H₂TMPyP⁴⁺ on the surface of DHP vesicles falls in this range, which is much smaller than the typical value for molecular diffusion in water ($D \approx 10^{-5}$ cm² s⁻¹). This observation suggests that the porphyrin binding site may penetrate somewhat the aqueous–organic interface rather than just involve surface electrostatic attractions. This model is consistent with the relatively large bathochromic shift in the porphyrin optical bands that accompanies binding, which suggests that the chromophore may be located in the region containing the phosphate ester bonds.^{20,42} Further, the diffusion coefficient is of the same order of magnitude as measured for lateral diffusion of amphiphilic surfactants in bilayer films,⁴³ suggesting that motions of the porphyrin and DHP monomeric units are correlated. In this case, the larger D and lower E_a values measured above the phase transition would reflect the increased fluidity of the surfactant monomers associated with the porphyrin.

Comparison to Simpler Approximate Methods. Monte Carlo analysis of the kinetics of triplet–triplet annihilation on the surface of vesicles involves laborious calculations. Alternative, simpler procedures based on the treatment of decay by approximate analytical equations can at least be contemplated.^{11–13} Two somewhat different models are evaluated below by comparing predicted results to a family of curves generated by Monte Carlo calculations with the same parameters used to fit the ³H₂TMPyP⁴⁺ experimental decay profiles on DHP vesicles. One, a diffusion model for bimolecular reactions on the surface of a sphere, gives a rate law in terms of a Legendre series that must be evaluated numerically. Calculations have shown, however, that a single exponential is often a good approximation except at short times.^{11–13} The mean reaction time, τ_{av} , is related to the radii, R_s and r_m , by the either of the equations¹²

$$\tau_{av} = \frac{R_s^2}{0.68D'} \left(\frac{R_s}{2r_m} \right)^{0.613}$$

or¹³

$$\tau_{av} = \frac{(R_s + r_m)^2}{D'} \left[\frac{2}{1 - (r_m/(R_s + r_m))^2} \ln \frac{R_s + r_m}{r_m} - 1 \right]$$

where D' is the sum of the diffusion coefficients of the reacting species. The single-exponential approximation to the kinetics of ³H₂TMPyP⁴⁺ annihilation displayed in Figure 2 by the dashed line gives a best-fit value for τ_{av} of 4.7×10^{-5} s. Using this value, with $R_s = 12.5$ nm and $r_m = 0.5$ nm, we obtain $D = D'/2 \approx 5.5 \times 10^{-9}$ cm² s⁻¹ from the first equation and $D \approx 6 \times 10^{-9}$ cm² s⁻¹ from the second equation; these are fairly close to the value estimated from the Monte Carlo analyses, i.e., $D = 8 \times 10^{-9}$ cm² s⁻¹.

Another approach is to use a decay law appropriate for a large two-dimensional system. As developed in the Appendix, the decay kinetics of excited triplet molecules on an infinite isotropic surface can be expressed by eq 5:

$$\frac{C}{C_0} \approx \frac{e^{-t/\tau_0}}{1 + \alpha\pi D'\tau_0 C_0 - \alpha\pi D'\tau_0 C_0 e^{-t/\tau_0}} \quad (5)$$

where C_0 is the initial concentration of excited molecules per unit area, τ_0 is their intrinsic lifetime, and α is a constant. In general, eq 5 fits the decay kinetics of ³H₂TPyP⁴⁺ on DHP vesicle surfaces better than a simple exponential decay equation. An example is given in Figure 2, where the best fit achievable by eq 5 (circles) is compared to an exponential fit (dashed line) for a reaction in which the initial number of excited molecules/vesicle is 16. The corresponding value of $\alpha D'$ is 8×10^{-9} cm² s⁻¹. Using typical values of α for diffusion-controlled reactions on the surface of vesicles, $0.2 < \alpha < 0.7$ (see Appendix), one obtains 6×10^{-9} cm² s⁻¹ $< D < 2 \times 10^{-8}$ cm² s⁻¹. This interval brackets the value of $D = 8 \times 10^{-9}$ cm² s⁻¹ obtained from the Monte Carlo analysis.

Conclusions

Triplet–triplet annihilation is an important decay pathway on DHP small unilamellar vesicles when each vesicle contains more than a single ³H₂TPyP⁴⁺ ion. The surface diffusion coefficient ($D = 8 \times 10^{-9}$ cm² s⁻¹) obtained from Monte Carlo analyses of this reaction is similar to lateral diffusion coefficients of lipophilic probe molecules that are located within bilayer membranes and amphiphilic surfactant molecules that are intercalated within the bilayer leaflet structure. The temperature dependence of D reveals a breaking point at the major phase-transition temperature. These observations suggest that lateral movement of the porphyrin is constrained by strongly associated DHP surfactant monomers. Approximate treatments of T–T annihilation kinetics based on simple exponential or mixed first- and second-order kinetic equations also gave reasonable values for D , suggesting that these methods can be used to estimate diffusion coefficients of reactants on spherical surfaces whose dimensions are equal to or greater than those of small unilamellar vesicles.

Acknowledgment. Funding for this research was provided by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Grant DE-FG03-99ER14943.

Appendix

Diffusion-limited bimolecular reactions, $A + A \rightarrow B$, on infinite surfaces can be approximated by the rate law⁴⁴

$$\frac{dC}{dt} \approx -\alpha\pi D'C^2 \quad (A1)$$

where C is the concentration of reactant A per unit area and α

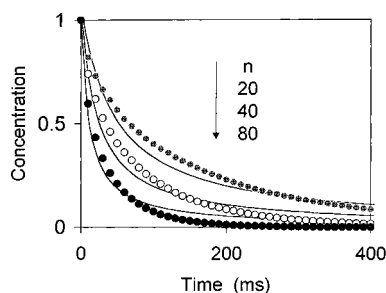


Figure 4. Decay curves for triplet-triplet annihilation generated by Monte Carlo calculations (points) and the best fit of these data by eq 5 (curves) for different average number of excited molecules per sphere (n). Parameters used for the Monte Carlo calculations were $r_m = 5 \text{ \AA}$, $R_s = 12.5 \text{ nm}$, $\tau_o = 350 \text{ }\mu\text{s}$, $\nu = 10^{13} \text{ s}^{-1}$, $a = 0.1 \text{ nm}$, $\lambda_d = 0.1 \text{ nm}$, and $\tau_d = 2 \times 10^{-9} \text{ s}$. The best fit to the Monte Carlo curves by eq 5 corresponded to $\alpha D' = 5.4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, $\tau_o = 350 \text{ }\mu\text{s}$.

is a slowly decreasing function of time that can often be replaced by a mean value within the range 0.3–0.6.^{24,44} If molecules A also disappear via unimolecular decay with a lifetime given by τ_o , then the overall decay is given by eq A2:

$$\frac{dC}{dt} \approx -\alpha\pi D' C^2 - \frac{1}{\tau_o} \quad (\text{A2})$$

Integration assuming α is constant gives eq 5.

The general applicability of eq 5 was tested by fitting it to kinetic decay profiles that were generated by Monte Carlo calculations. These comparisons were made using a relatively wide range of calculational parameters, specifically, with $R_s = 10\text{--}20 \text{ nm}$, $r_m = 0.3\text{--}0.7 \text{ nm}$, $\tau = 10^{-4}\text{--}10^{-2} \text{ s}$, $a = 0.08\text{--}0.12 \text{ nm}$, $\lambda_d = 0.1 \text{ nm}$, $\nu = 10^{10}\text{--}10^{15} \text{ s}^{-1}$, $\tau_D = 10^{-7}\text{--}10^{-10} \text{ s}$, and the initial fraction of excited molecules equal to 4×10^{-4} to 1×10^{-1} . Under all these conditions, reasonably good fits to the computed decay curves could be found for eq 5. The values of α required to match the diffusion coefficients for the Monte Carlo simulations ranged from 0.2 to 0.7, with the higher values being required when the initial fraction of excited molecules was relatively large. This same trend was reported earlier for other bimolecular reactions on an "infinite" surface.⁴⁴ The interval of α required to fit the simulations is also very similar to the interval for bimolecular reactions on an infinite surface, i.e., $\alpha = 0.3\text{--}0.6$.²⁴

An illustrative example of the use of these results is given in Figure 4, where a series of decay curves obtained by Monte Carlo calculations (points) for triplet-triplet annihilation for several average number of excited molecules is plotted against best fit values (curves) obtained using eq 5. The best "experimental" fit corresponds to $\alpha D' = 5.4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Using $0.2 < \alpha < 0.7$, we obtain $4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} < D < 1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. This interval of D brackets the diffusion coefficient ($D = 6 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) estimated from the Monte Carlo calculations for these particular computational parameters (Figure 4).

References and Notes

- (1) For leading references see, for example, the following. Lei, Y.; Hurst, J. K. *Langmuir*, in press. Steinberg-Yfrach, G. S.; Rigaud, J.-L.; Durantini, E. N.; Moore, A. L.; Gust, D.; Moore, T. A. *Nature* **1998**, 392, 479. Willner, I. *Acc. Chem. Res.* **1997**, 30, 347. Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; Wiley-VCH: Weinheim, 1995. Whitten, D. G. *Acc. Chem. Res.* **1993**, 26, 502. Mirkin, C. A.; Ratner, M. A. *Annu. Rev. Phys. Chem.* **1992**, 43, 719. Drain, C. M.; Mauzerall, D. C. *Biophys. J.* **1992**, 63, 1556. Hurst, J. K. In *Kinetics and Catalysis in*

- Microheterogeneous Solutions*; Gratzel, M., Kalyanasundaram, K., Eds.; Surfactant Science Series, 38; Marcel Dekker: New York, 1991; p 183. Lyman, S. V.; Parmon, V. N.; Zamaraev, K. I. In *Photoinduced Electron Transfer III*; Mattay, J., Ed.; Topics in Current Chemistry 159; Springer-Verlag: Berlin, 1991; p 1. Shinkai, S. In *Cation Binding by Macrocycles: Complexation of Cationic Species by Crown Ethers*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker: New York, 1990; Chapter 9.
- (2) Molin, Yu. N.; Salikhov, K. M.; Zamaraev, K. I. *Spin Exchange: Principles and Application in Chemistry and Biology*; Springer-Verlag: Berlin, 1980.
- (3) Galla, H.-G.; Sackmann, E. *Biochim. Biophys. Acta* **1975**, 401, 509.
- (4) Sackmann, E. *Z. Phys. Chem. Neue Folge* **1976**, 101, 391.
- (5) Stryer, L.; Thomas, D. D.; Meares, C. F. *Annu. Rev. Biophys. Bioeng.* **1982**, 11, 203.
- (6) Agranovich, V. M.; Galanin, M. D. *Electronic Excitation Energy Transfer in Condensed Matter*; North-Holland: Amsterdam, 1982.
- (7) Khairutdinov, R. F.; Levin, P. P.; Costa, S. M. B. *Langmuir* **1996**, 12, 714.
- (8) McQuarrie, D. A.; Jachimowski, C. J.; Russell, M. E. *J. Chem. Phys.* **1964**, 40, 2914.
- (9) Freeman, G. R. *Kinetics of Non Homogeneous Processes*; Wiley: New York, 1987.
- (10) Khairutdinov, R. F.; Serpone, N. *Prog. React. Kinet.* **1996**, 21, 1.
- (11) Hatlee, M. D.; Kozak, J. J.; Rothenberg, G.; Infelta, P. P.; Gratzel, M. *J. Phys. Chem.* **1980**, 84, 1508.
- (12) Van der Auweraer, M.; Dederen, J. C.; Gelade, E.; De Schryver, F. C. *J. Chem. Phys.* **1981**, 74, 1140.
- (13) Sano, H.; Tachiya, M. *J. Chem. Phys.* **1981**, 75, 2870.
- (14) Klafter, J.; Drake, J. M. *Molecular Dynamics in Restricted Geometries*; Wiley: New York, 1989.
- (15) Lyman, S. V.; Khairutdinov, R. F.; Soldatenkova, V. A.; Hurst, J. K. *J. Phys. Chem.* **1998**, 102, 2811.
- (16) Khairutdinov, R. F.; Hurst, J. K. *J. Phys. Chem.* **1998**, 102, 6663.
- (17) Humphry-Baker, R.; Thompson, D. H.; Lei, Y.; Hope, M. J.; Hurst, J. K. *Langmuir* **1991**, 7, 2592.
- (18) Lachish, U.; Infelta, P. P.; Gratzel, M. *Chem. Phys. Lett.* **1979**, 62, 317.
- (19) Hurst, J. K.; Lee, L. Y. C.; Gratzel, M. *J. Am. Chem. Soc.* **1983**, 105, 7048.
- (20) Mazeres, S.; Schram, V.; Tocanne, J.; Lopez, A. *Biophys. J.* **1996**, 71, 327.
- (21) Kalyanasundaram, K.; Neumann-Spallart, M. *J. Phys. Chem.* **1982**, 86, 5163.
- (22) Bonnett, R.; Ridge, R. J.; Land, E. J.; Sinclair, R. S.; Tait, D.; Truscott, T. G. *J. Chem. Soc., Faraday Trans. 1* **1982**, 78, 127.
- (23) Ballard, S. G.; Mauzerall, D. C. *J. Chem. Phys.* **1980**, 20, 933.
- (24) Gosele, U. *Prog. React. Kinet.* **1984**, 13, 63.
- (25) Scheidler, M.; Cleve, B.; Bassler, H.; Thomas, P. *Chem. Phys. Lett.* **1994**, 225, 431.
- (26) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, 15, 1.
- (27) Jortner, J.; Choi, S.; Katz, J. L.; Rice, S. A. *Phys. Rev. Lett.* **1963**, 11, 323.
- (28) Khairutdinov, R. F.; Zamaraev, K. I.; Zhdanov, V. P. *Electron Tunneling in Chemistry*; Elsevier: Amsterdam, 1989.
- (29) Although eq 4 was used in all Monte Carlo calculations reported in ref 16, the corresponding equation cited in that paper was in error. Specifically, the coefficient 2 in the exponential term was placed in the denominator rather than in the numerator.
- (30) Likhtenshtein, G. I. *Biophysical Labeling Methods in Molecular Biology*; Cambridge University Press: New York, 1993; p 305.
- (31) Smoluchowski, M. V. *Ann. Phys. (Leipzig)* **1915**, 48, 1103.
- (32) Einstein, A. *The Collected Papers*; Princeton University Press: Princeton, 1989; Vol. 2.
- (33) Carmona-Ribeiro, A. M. *J. Colloid. Interface Sci.* **1990**, 139, 343.
- (34) Yi, P. N.; MacDonald, R. C. *Chem. Phys. Lipids* **1973**, 11, 114.
- (35) Peterson, N. O.; Chan, S. I. *Biochim. Biophys. Acta* **1978**, 509, 111.
- (36) Lee, A. G. *Biochim. Biophys. Acta* **1977**, 472, 237.
- (37) Suddaby, B. R.; Brown, P. E.; Russell, J. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1985**, 107, 5609.
- (38) Seki, T.; Ichimura, K. *J. Colloid Interface Sci.* **1989**, 129, 353.
- (39) Vaz, W. L. C.; Derzko, Z. I.; Jacobson, K. A. *Cell Surf. Rev.* **1982**, 8, 83.
- (40) Wade, C. G. *Struct. Prop. Cell Membr.* **1985**, 1, 51.
- (41) Tocanne, J.-F.; Dupou-Cezanne, L.; Lopez, A. *Prog. Lipid. Res.* **1994**, 33, 203.
- (42) Khairutdinov, R. F.; Giertz, K.; Hurst, J. K.; Voloshina, E. N.; Voloshin, N. A.; Minkin, V. I. *J. Am. Chem. Soc.* **1998**, 120, 12707.
- (43) Majda, M. In *Kinetics and Catalysis in Microheterogeneous Solutions*; Gratzel, M., Kalyanasundaram, K., Eds.; Surfactant Science Series 38; Marcel Dekker: New York, 1991; p 227.
- (44) Gosele, U.; Huntley, F. A. *Phys. Lett.* **1975**, 55A, 291.