DISTRIBUTED KINETICS OF DECAY OF THE PHOTOVOLTAGE AT THE LIPID BILAYER-WATER INTERFACE

T. M. LIU AND D. MAUZERALL
The Rockefeller University, New York, New York 10021

ABSTRACT The decay kinetics of the photovoltage formed on pulsed illumination of a chlorophyll *a*- (chl *a*-) containing lecithin-bilayer adjacent to a ferricyanide solution on one side show characteristics of a system with distributed rate constants, i.e., the decay approaches linearity in log of time. The kinetics can be explained by a distribution of the chl cation over a few angstroms depth in the interfacial region of the bilayer and a rate constant exponentially dependent on distance as expected from tunneling theory. Addition of the donor ferrocyanide both increases the average rate and sharpens the distribution. There is a competitive inhibition by ferricyanide of the reaction of pigment cation with ferrocyanide. Removal of oxygen increases the rate of decay when an acceptor, methyl viologen or anthraquinone-2-sulfonate, forms oxygen-sensitive radicals. The cation charge does not cross the bilayer on a time scale of <0.01 s. These data define a reaction localized precisely in the finite interfacial region of the lipid bilayer-water interface.

INTRODUCTION

Many studies have been made of light-induced photo voltages and photo currents across a pigmented lipid bilayer (Tien, 1982; Hong, 1976). However, in very few cases have the kinetics been reduced to molecular terms. One example is the observation of fast transient photovoltages in bilayers containing erythrosin, which are attributed to de- and re-protonation of the triplet state of the dye (Varnadore et al., 1982). An early study on the MgOEP–bilayer-ferricyanide system showed the decay kinetics could be explained by an apparent second-order reaction of the lipophilic pigment cation formed in the photoreaction with added aqueous ferrocyanide (Hong and Mauzerall, 1974). We have now made a more thorough study of the chlorophyll *a* (chl *a*) bilayer-ferricyanide system. The kinetics show characteristics of a system with distributed rate constants. A distribution of the chl a cation over only a few angstroms distance and electron tunneling can explain these kinetics. We confirm the direct reaction between pigment cation and ferrocyanide. Inhibition by ferricyanide of the decay is observed. The voltage decay is accelerated in the absence of oxygen when the reduced acceptor is a reactive free radical such as the methyl viologen monocation. These data define more closely a reaction localized precisely in the interesting interfacial region of the lipid bilayer-water interface.

T. M. Liu is presently at the Institute of Chemistry, Academia Sinica, Bejing, China.

EXPERIMENTAL

The experimental details, including the deoxygenation procedure, are as given before (Ilani et al., 1985). The bilayers were brush formed from a mixture of 0.5% (5.5 mM) chl *a*, 3% egg lecithin, and 0.8% cholesterol in n-decane. The aqueous solution contained 0.1 M NaCl and 1 mM phosphate, pH 6.8, with acceptor and donor as specified. Illumination was by a flashlamp-pumped dye laser at 590 nm (Rhodamine 6G), full width at half maximum (FWHM) 0.3 μs. For most of the experiments a conical light pipe made of high refractive index glass (1.693) was used to guide the light to the center of the lipid bilayer. This made it easier to illuminate only or chiefly the bilayer and not the thick annulus, in comparison with our usual purely optical focusing arrangement. It also homogenized the beam intensity. However, some light was lost because of the difficulty in keeping below the critical angle at the glass-water interface. The capacitance of the membrane was determined to ensure a true bilayer (6–7 nF) before measurement. The membrane resistance with added donors and acceptors was $\sim 10^8\Omega$. A high impedance ($10^{10}\Omega$) amplifier (Tektronix 3A7; Tektronix, Inc., Beaverton, OR) was used to obtain the true membrane voltage over an extended time range, 1 μs to 1 s. The total instrument response time was just under 1 μs. Because of the extended time range of the decay, the data were collected using three or more time scales of the digitizer, e.g., 0.2, 1, and 5 μs per channel with 2,000 channels being recorded.

RESULTS

Decay of Photovoltage as a Function of Ferricyanide and Ferrocyanide Concentration

The decay of the photovoltage of chl *a*-containing lipid bilayers is somewhat complex. Typical data are presented in Fig. 1, which show the enormous time span covered by the decay. The data were collected using three or more time scales of the digitizer, e.g., 0.2, 1, and 5 μs per

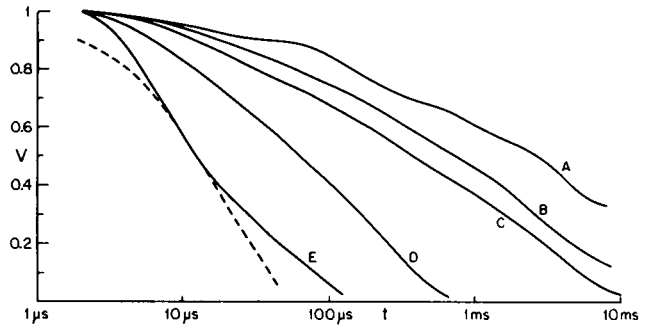

FIGURE 1 The normalized photovoltage is plotted vs. time on a log scale as a function of ferri-ferrocyanide concentration. The lines are as follows, *right* to *left*: *A*, Fe^{3+} 0.5 mM; *B*, Fe^{3+} 2 mM; *C*, Fe^{3+} 10 mM; *D*, Fe^{3+} 10 mM, Fe^{2+} 0.2 mM; *E*, Fe^{3+} 10 mM, Fe^{2+} 1 mM. The dashed line is a single exponential decay.

channels with 2,000 channels recorded. It is also seen that the shape of the voltage decay curve changes drastically, from nearly linear vs. log t at low ferricyanide concentration to approaching a single exponential when both ferricyanide and ferrocyanide are at high concentration. The curves that are almost linear in log t are characteristic of processes with distributed rate constants, i.e., having a wide distribution of rate constants or rate constants that are themselves a function of time. Because of these complexities we will first give a general argument as to the form of the kinetics, then analyze the cases of added donor and of acceptor only.

General Kinetics. Based on our previous studies (Hong and Mauzerall, 1976; Ilani and Mauzerall, 1981) and on what will be presented below, the following equations describe the decay of the photovoltage in the bilayer

$$V = \Sigma \frac{e}{C_i} P_i^+ \text{ and } \dot{P}_i^+ = -k_i A_i^- P_i^+. \quad (1)$$

The electronic charge is e and C_i is the chemical capacitance (Hong and Mauzerall, 1974) that converts charge in the membrane (P^+) to observed voltage, V. We assume that P^+ has been formed during the laser flash, which is short compared with the present time scale. P_i^+ is a specific pigment cation in the lipid bilayer at the acceptor side of the interface and A_i^- is the corresponding aqueous donor species.

The concentration terms can be variously interpreted. If A_i^- formed in conjunction with P_i^+ is taken to be an interfacial concentration, similar to P_i^+ but free to diffuse only along the interface, then the voltage decay would be second order. If A_i^- escapes to the bulk solution, then the decay will be pseudo-first order since the bulk solution contains an infinite amount of A^- (if only as an impurity) when compared with the amount of photogenerated A_i^-. If the P_i^+ and A_i^- react exclusively with one another, the kinetics will be strictly first order. The large effect of added A^- (ferrocyanide) shows that mixing with the A_i^- occurs rapidly, i.e., on the time scale of diffusion over the unstirred layer. Under some conditions, second-order plots ($1/V$ vs. t) are quite linear. A distribution of rate constants k_i can, however, show very similar behavior. The possibility of rapid interfacial diffusion with second-order recombination at low outside concentration of A^- was ruled out by varying the laser pulse energy and thus $P_i^+ A_i^-$. We found that the halftime of a fraction of the voltage decay over a defined time range is a convenient representation of the kinetics (see below). Fig. 2 shows that a plot of the fast halftime over a 50-fold change in pulse energy is a constant, and the slow halftime changes by only a factor of 1.5. The observed V_{max}, i.e., V at infinite acceptor concentration, showed some saturation, increasing by 7–9-fold over the 50-fold range of pulse energy, depending on the illumination system, lens or light pipe. The minimal change of decay time over an eightfold change of initial $P_i^+ A_i^-$ rules out any significant second-order recombination. Thus, the intriguing possibility of two-dimensional interfacial diffusion of negative donor ions captured by the field of clusters of the pigment cations can be ruled out.

According to simple tunneling theory (De Vault, 1984;

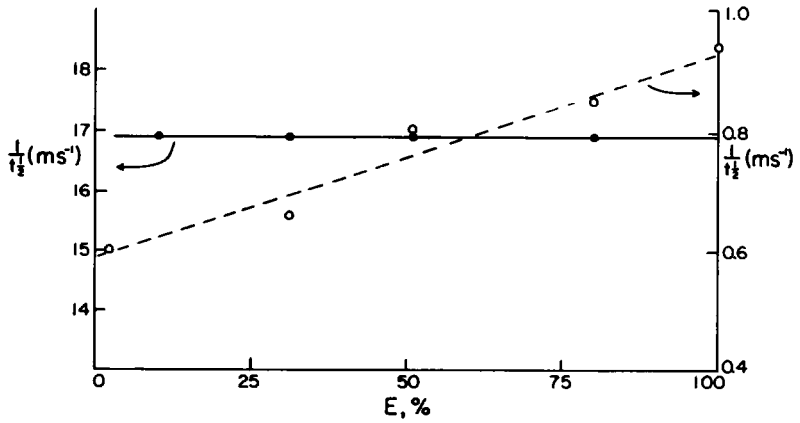

FIGURE 2 The reciprocal of the half time on two recorder scales, 0 to 400 μs *left* (●) and 0.2 to 20 ms *right* (○), is plotted vs. the percent of full energy in the flash. Note the expanded vertical scales.

Miller, 1972; Mauzerall, 1976) the rate constant for electron transfer will decrease exponentially with distance, r, for $r > 1/\alpha$, where α is the space parameter for tunneling. Thus the k_1 of Eq. 1 will be given by

$$k(r) = \gamma \exp(-\alpha r), \tag{2}$$

where r is the edge to edge distance between pigment and acceptor as defined by Mauzerall (1976) and γ is a frequency factor related to the energy of the bound electron. The problem can be treated in one dimension because of the symmetry in the plane of the membrane and the freedom of the reduced acceptor, A^-, to move at the aqueous interface (see above). Thus A^- can be assumed to be at the closest position opposite to the pigment cation, P^+. Combining Eqs. 1 and 2, and assuming P^+ is immobile, the amount of P^+ remaining at a given r, P_r, after time t will be

$$P_r^+ = P_{r_o}^+ e^{-A^- tk(r)} \tag{3}$$

and thus the total amount of P^+ in the membrane after time t will be

$$P^+ = P_o^+ \int_{r_o}^{r_d} e^{-A^- \gamma t e^{-\alpha r}} dr, \tag{4}$$

where r_o and r_d are the minimum and maximum distances between P^+ and A^-. The integral is readily computed and the results for the case of a uniform initial distribution of P^+ between r_o and r_d are shown in Fig. 3. The shape of the curves are determined by $\alpha(r_d - r_o)$ and the time scale by $A^- \gamma \exp(-\alpha r_o)$. The latter is simply the value of the rate constant when $r = r_o$ and the decay then becomes exponential in time. The curves have a close generic resemblance to the data in Fig. 1, the shape changing from exponential to linear in log time over the similar two to three orders of magnitude of time scale. Moreover, the parameters that fit the data are quite reasonable. Curve D of Fig. 1 is fit with $\alpha(r_d - r_o) = 5$ and $A^- \gamma \exp(-\alpha r_o) = 10^5 M^{-1} s^{-1}$. Since α, the reciprocal tunneling length, is estimated to be 1–2 $Å^{-1}$ (Hopfield, 1974; Mauzerall, 1976, 1978; Strauch et al., 1983), $(r_d - r_o)$ is 2.5–5 Å. Thus the distribution of distances can be quite narrow and yet explain the very broad distribution of rate constants. This agrees with the expectation that the porphyrin cation is held in a rather narrow energetic well in the polar region of the bilayer. Both energy calculations (Brasseur et al., 1984) and site selection spectroscopy (Funfschilling and Walz, 1983) place the ring of chl *a* in the polar region of the bilayer. The variable A^- measures the probability that a donor species is at the closest distance to P^+, and should be proportional to the added donor concentration since no saturation is observed (see below). Assuming no binding or repulsion, A^- is 2×10^{-4}M, and $\gamma \exp(-\alpha r_o)$ is $5 \times 10^8 s^{-1}$. The frequency parameter, γ, can be as high as $10^{14} s^{-1}$ for unimpeded tunneling. Then αr_o is 13 and r_o is 6.5–13 Å. This is an upper limit, since other factors, such as bond and solvent reorganization energies, may also slow the electron transfer process, i.e., reduce γ. However, γ would have to be reduced by $>10^5$ to bring r_o to zero. The $\alpha(r_d - r_o)$ parameter increases to 10 as the donor concentration is lowered. A possible cause is the movement of P^+ with time. The distribution distance may increase to 5–10 Å on the millisecond time scale. A second possibility is that shorter distances are less probable (membrane structural fluctuations?) and require a high concentration of A^- to be observed. These possibilities and the small effect of increasing observable voltage with increasing depth of P^+ in the membrane will be discussed in a later publication. It is interesting that calculated solutions of analogues of Eq. 4 with a distance distribution in three dimensions, i.e., with both A^- and P^+ fixed, do not fit the data. Thus the one-dimensional distribution is required by the data.

The constant distribution of P^+ was chosen for clarity, but any reasonable distribution will give similar decay curves and may be useful to fine-tune the fit to data. In fact as time progresses the initially sharp gradient at r_o changes to a steady state S-shaped gradient that is a function of $\alpha(r_d - r_o)$. This gradient moves distancewise into the

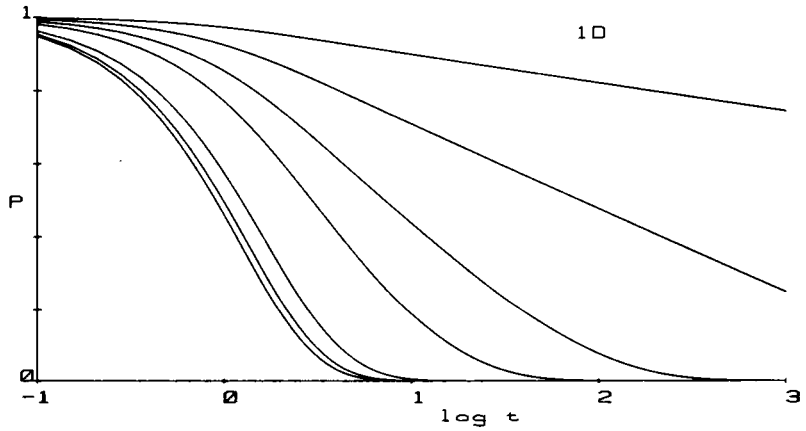

FIGURE 3 Calculated P^+ as a function of time by integration of Eq. 4. The curves were calculated with $A^- \gamma \exp(-\alpha r_o) = 10^5$ and values of $\alpha(r_d - r_o) = 0.3, 0.5, 1, 3, 5, 10$, and 30 from *left* to *right*.

square distribution as an exponentially decreasing function of time. An extreme assumption is that of a rigid distribution: the gradient remains sharp and the initial square distribution simply becomes narrower with time. This allows one to replace r by the concentration of P^+ in Eq. 2 and integrate directly. This is the approach of Miller (1972, see also Huddelston and Miller, 1982) as applied to the decay of radicals in organic glasses. Our calculations show that the extreme rigid distribution model underestimates ($r_d - r_o$) by about a factor of two when r_d is of the order of r_o.

Voltage Decay in the Presence of Added Ferrocyanide. We shall first analyze experiments with added donor, ferrocyanide. A variety of curve-fitting procedures, graphical and by computer, convinced us that division into slow and fast rate constants on a given partial time scale was an adequate representation. Since the distribution of k_i was found to be homogeneous in A^-, this is allowable. The rate constant obtained from the fastest time scale is plotted vs. concentration of added ferrocyanide, for three concentrations of ferricyanide, in Fig. 4. The rate constant is accurately linear in ferrocyanide but the apparent second-order constant calculated from the slope, is inversely related to the ferricyanide concentration (Fig. 5). A reasonable interpretation is that these highly charged negative ions compete for a site at the interface close to P^+. The resulting equation, assuming these ionic species exchange rapidly and thus are at equilibrium, is

$$-\dot{P}_i^+ = k_i (P^+A^-)_i = \frac{k_i K_{A^-} [A^-][P_i^+]}{K_{A^-}[A^-] + K_A[A] + 1}, \qquad (5)$$

where

$$K_A = \frac{[P^+ A^-]_i}{[P_i^+][A^-]}; \quad K_A = \frac{[P^+ A]_i}{[P_i^+][A]}.$$

Here we distinguish between the bulk aqueous concentration of the acceptor as $[A]$ and donor as $[A^-]$ and the interfacial concentration at the reactive site, $[P_i^+]$, as $[P^+A]_i$ and $[P^+ A^-]_i$. Since the concentrations of A and A^- are ~1 mM, the encounter time will be $\sim 10^{-7}$ s and thus assumption of equilibrium is justified on the relevant time scale, $>10^{-6}$ s.

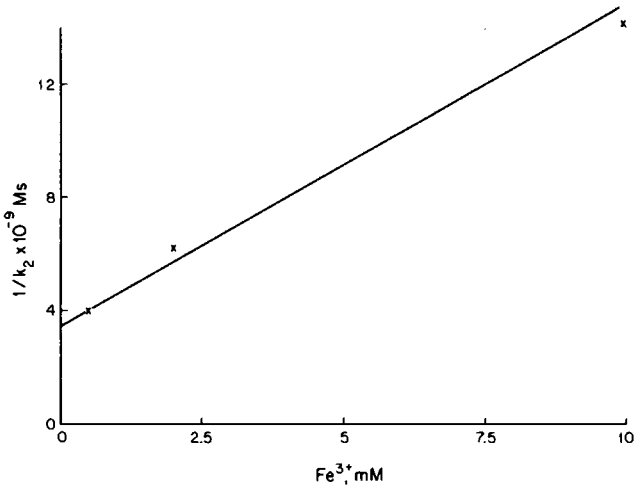

FIGURE 5 The reciprocal of the slope of the lines in Fig. 4, k_2, is plotted vs. the concentration of ferricyanide.

The good linearity of the pseudo–first-order rate constant vs. A^- (Fig. 4) shows that the $K_{A^-}[A^-]$ term in the denominator of Eq. 5 is negligible. Thus a plot of the reciprocal of the slope of the lines of Fig. 4 vs. concentration of ferricyanide (A) should be linear (Eq. 6) as is shown in Fig. 5. The intercept and

$$1/\text{slope (Fig. 4)} = \frac{K_A[A]}{k_i K_{A^-}} + \frac{1}{k_i K_{A^-}} \qquad (6)$$

slope give the apparent second-order rate constant $k_i K_{A^-}$ as 3×10^8 $M^{-1}s^{-1}$, and K_A as 0.3 mM^{-1}. The former value is close to the maximum rate at r_o obtained by fitting the

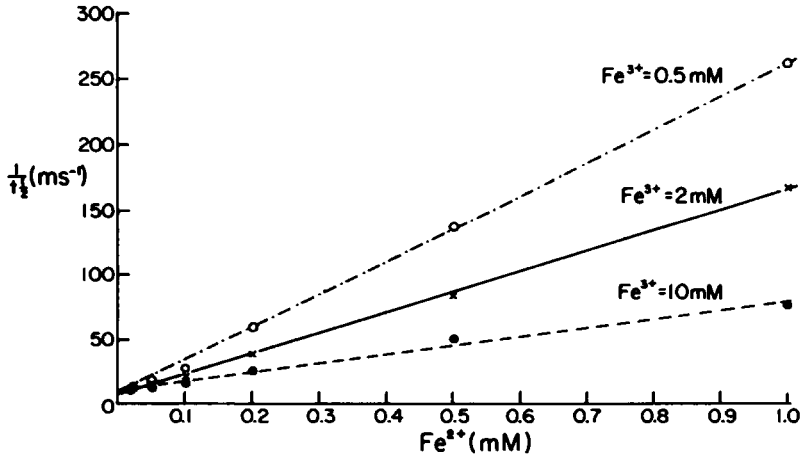

FIGURE 4 The reciprocal of the half time of the voltage decay on the time scale 0 to 400 μs is plotted vs. ferrocyanide concentration as a function of ferricyanide concentration.

decay curve with the P^+ distribution and tunneling model (see above). It is also similar to that measured some time ago with MgOEP (Hong and Mauzerall, 1976). The value of K_A is some four times smaller than the saturation constant for the initial photoreaction with ferricyanide, 1.2 mM^{-1} (Ilani and Mauzerall, 1981). It is clear that the effect of the pigment positive charge on the binding of ferricyanide is not large. This is consistent with a quite finite, if not large, separation of the reactants across the interface. The same conclusion is obtained if one assumes the charged choline head groups screen, and thus separate, the pigment cation and acceptor anion. If other negative ions in the solution (Cl^-, HPO_4^{-2}) also compete for the site close to P^+, the rate constant $k_i K_{A^-}$ will be smaller than quoted and K_A larger.

Similar conclusions can be drawn from the slower rate constant of decay, the rate constants being an order of magnitude smaller. Note that this is a proof of the homogeneity expressed in Eq. 1. Although the constants of the equation are distributed, the dependence on P^+ on A^- is homogeneous. Thus though the kinetics shown in Fig. 1 appear complex, they are capable of resolution, and even of simple fits (Figs. 4 and 5), as long as one is careful to analyze the data consistently and with due regards for scale.

Voltage Decay in the Absence of Added Ferrocyanide. Enlarged plots of data such as shown in Fig. 4 show a finite rate when extrapolated to zero-added ferrocyanide concentration. One can calculate an equivalent ferrocyanide concentration of 0.05 mM when the ferricyanide concentration is 10 mM. If the kinetics strictly followed Eq. 4, then the observed decay would simply be the curve of Fig. 1 *E* moved to the right by a factor of 20. The actual curve (Fig. 1 *C*) is much broader. A possible explanation is that the distribution depth, i.e., $(r_d - r_o)$ of Eq. 4, increases with time, possibly with a scale of $\sim 10^{-4}$ s. Added donor competes with this movement, rendering the kinetics relatively simple at donor concentrations where the decay half life is $<10^{-4}$ s. A second possibility is that the short distances are improbable configurations, which arise by fluctuations in the membrane structure, and are observed only at high concentrations of A^-. The fact that the fraction of slow component (defined as that component unreacted in 400 μs) decreases from >40% to 0 as the donor concentration is increased (Table I) can support either hypothesis.

TABLE I
FRACTION OF PHOTOVOLTAGE REMAINING AFTER 400 μs AS A FUNCTION OF FERRI AND FERROCYANIDE CONCENTRATION

Fe^{2+} *mM*	Fe^{3+} *mM*		
	0.5	2	10
0	0.44	0.43	0.40
0.02	0.18	0.32	—
0.05	0	0.20	0.24
0.1	0	—	0.16
0.2	0	0.01	0.07
0.5	0	0	0.02
1	0	0	0

Oxygen Effect on Kinetics

Methyl Viologen (MV) and Anthraquinone Sulfonate (AQS) Acceptors. The photoreaction forms the porphyrin cation and acceptor radical. Since both semiquinone and viologen radicals react rapidly with O_2, the photovoltage decay in the presence of air must be caused in part by O_2^- and in part by adventitious donors. Thus removal of O_2 is expected to lead to a more rapid voltage decay because of the greater probability of reaction of pigment cation with reactive semiquinone and viologen radicals. This is just what is observed (Figs. 6 and 7). The half-life of the photovoltage formed in the presence of MV decreased 20 times (1 ms to 60 μs) on deoxygenating the solution (Fig. 6). Moreover, the decays are largely independent of added concentration of MV (data not shown). As expected (Ilani and Mauzerall, 1981) the symmetrical dication does not bind to the interface and no acceptor inhibition, as seen with ferri-ferrocyanide (see above), is observed. Since the effect of O_2 removal is so large, the inference is that the MV radical monocation is held in the polar region of the bilayer. There is evidence that this monocation can move across the membrane (Lee et al., 1983).

A similar increase in rate of decay of photovoltage (half-time 1 to 0.1 ms) is seen with dilute (0.1 mM) AQS as acceptor (Fig. 7, curve *A*). However, at 1 mM concentration of AQS, the rates with and without O_2 are more similar (Fig. 7, curve *B*). This is readily explained as inhibition by the strongly bound AQS (Ilani and Mauzerall, 1981). The half-times are in fact very slow: 2 ms (with O_2) and 1 ms (no O_2). This small difference in rates may be caused by the unavoidably differing adventitious donors (i.e., impurities) in the aerobic and anaerobic solutions. We note that for both MV and AQS, the initial rates in the first few microseconds are similar in the presence of absence of O_2. This may be the time it takes O_2 to scavenge the radicals from the interfacial region, with a rate constant of $\sim 10^9 M^{-1}s^{-1}$.

Ferricyanide Acceptor. Since neither product of the photoreaction, porphyrin cation and ferrocyanide, react rapidly with O_2 we expect the decay to be unaffected by its removal. This inertness was the basis of our choice of this system in our first quantitative study of lipid bilayers (Hong and Mauzerall, 1974). The surprising stability of the free radical porphyrin cation (Fuhrhop and Mauzerall, 1968) may be related to its high redox potential. The decay

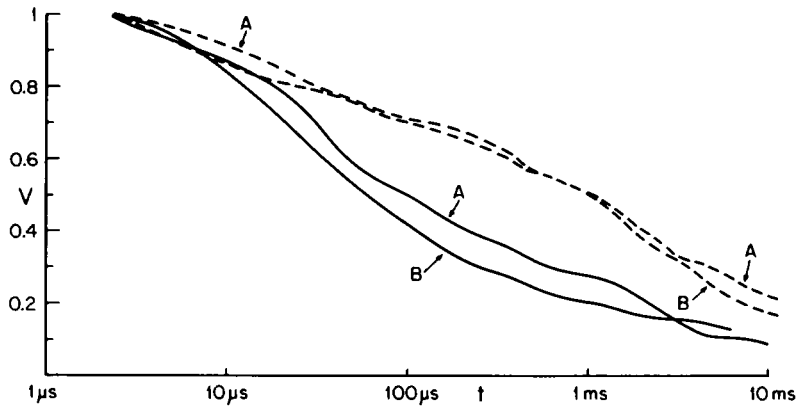

FIGURE 6 The normalized photovoltage is plotted as a function of time on a log scale. Conditions: *A*, 5 mM MV; *B*, 60 mM MV; dashed line, with O_2; solid line, without O_2.

of the photovoltage in the chl *a* bilayer-ferricyanide-ferrocyanide system deoxygenated with glucose-glucose oxidase was found to be somewhat slowed relative to that in air, the effect increasing with increasing concentration of ferrocyanide (data not shown). This effect is assigned to the reoxidation of the added ferrocyanide by the H_2O_2 generated in the glucose-glucose oxidase deoxygenation. This hypothesis is supported by the observation that catalase removed most of this effect. The residue may be caused by inhibition of catalase in the presence of ferrocyanide. It was also shown that the reaction of ferrocyanide and H_2O_2 is fast enough to cause the apparent loss of ferrocyanide. Thus the apparent slowing of the photovoltage decay in the absence of O_2 is caused by an artefact of the deoxygenation technique.

CONCLUSION

The drawn out decay of the photovoltage formed across a lipid bilayer containing chl *a* has the characterization of a distributed system. The highly nonexponential decay is explained by a rate constant that exponentially decreases with distance between pigment cation and reduced acceptor, and by a distribution of such distances in the membrane interface system. The exponential dependence on distance of the rate constant is consistent with electron tunneling between pigment cation and reduced acceptor. The shape of the observed voltage decay is shown to depend only on α, the tunneling parameter and on $(r_d - r_o)$, the distance distribution. Since α is $1 - 2$ Å^{-1}, one has an objective means of determining distances with less than angstrom resolution. In collaboration with Professor Tsuchida's group, we will attempt to calibrate the system by determining α with "choline-porphyrins" (Matsushita et al., 1983) held in the membrane at a known distance from the interface. The absolute time scale of the decay provides information on the minimum separation (r_o) between pigment cation and reduced acceptor. Details of the process such as shape of the distance distribution, possible movement of the pigment cation and donor, and increase of observable voltage with distance of cation into the membrane will be dealt with in continuing work.

The use of acceptors that produce reactive free radicals following electron transfer results in the expected observation of an inhibitory effect of O_2 on the decay of the photovoltage. The rapid reaction of these radicals with O_2 leads to the slower reaction of P^+ with O_2^- or even slower reactions with adventitious impurities as O_2^- disproportion-

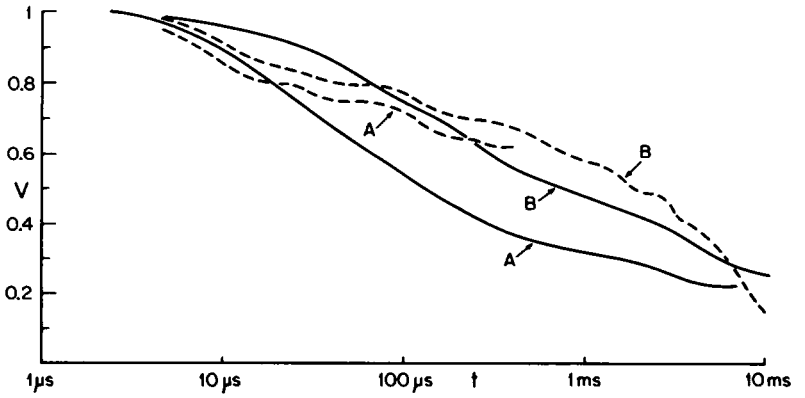

FIGURE 7 The normalized photovoltage is plotted as a function of time on a log scale. Conditions: *A*, 0.1 mM AQS; *B*, 1 mM AQS; dashed line, with O_2; solid line, without O_2.

ates. In these cases O_2 acts as a facilitator for the interfacial charge transfer.

The striking inhibitory effect of similarly charged ions on the voltage decay suggests that this may be an important effect in biological interfacial charge transfer. In these reactions the soluble protein component (e.g., cytochrome *c*) will usually not change its overall charge on reaction. Thus similar inhibition by the product molecule is to be expected. The resulting kinetics will be similar to those shown in Figs. 6 and 7. Analysis of rate constants without taking into account this product inhibition will lead to erroneous conclusions.

The research was supported by the National Institutes of Health, grant GM 25693-05.

Received for publication 10 January 1985.

REFERENCES

Brasseur, R., J. de Meutter, and J. M. Ruysschaert. 1984. Mode of insertion of chlorophyll a in a lipid bilayer. A conformational approach. *Biochim. Biophys. Acta.* 764:295–300.

De Vault, D. 1984. Quantum Mechanical Tunnelling in Biological Systems. Cambridge University Press. Second ed. 207 pp.

Fuhrhop, J., and D. Mauzerall. 1969. The one-electron oxidation of magnesium octaethyl porphyrin. *J. Am. Chem. Soc.* 90:2875.

Funfschilling, J., and D. Walz. 1983. Site selection spectroscopy of chlorophyll b in membranes of lecithin vesicles and in other solvents. *Photochem. Photobiol.* 38:389–393.

Hong, F. T. 1976. Charge transfer across pigmented bilayer lipid membrane and its interfaces. *Photochem. Photobiol.* 24:155–189.

Hong, F. T., and D. Mauzerall. 1974. Interfacial photoreactions and chemical capacitance in lipid bilayers. *Proc. Natl. Acad. Sci. USA.* 71:1564–1568.

Hong, F. T., and D. Mauzerall. 1976. Tunable voltage clamp method. Application of photoelectric effects in pigmented bilayer lipid membranes. *J. Electrochem. Soc.* 123:1317–1324.

Hopfield, J. J. 1974. Electron transfer between biological molecules by thermally activated tunneling. *Proc. Natl. Acad. Sci. USA.* 71:3640–3644.

Huddleston, R. K., and J. R. Miller. 1982. Determination of electron-transfer rate constants from data on tunneling to randomly distributed acceptors in a rigid medium. *J. Phys. Chem.* 86:200–203.

Ilani, A., T. M. Liu, and D. Mauzerall. 1985. The effect of oxygen on the amplitude of photodriven electron transfer across the lipid bilayer-water interface. *Biophys. J.* 47:679–684.

Ilani, A., and D. Mauzerall. 1981. The potential span of photoredox reactions of porphyrins and chlorophyll at the lipid bilayer-water interface. *Biophys. J.* 35:79–92.

Lee, L. Y-C., J. K. Hurst, M. Politi, K. Kurihara, and J. H. Fendler. 1983. Photoinduced diffusion of methyl viologen across anionic surfactant vesicle bilayers. *J. Am. Chem. Soc.* 105:370–373.

Matsushita, Y., E. Hasegawa, K. Eshima, and E. Tsuchida. 1983. Synthesis of amphilic porphinato iron complexes having phosphorylcholine groups. *Chem. Lett.* 1387–1390.

Mauzerall, D. 1976. Electron-transfer reactions and photoexcited porphyrins in chlorophyll-proteins reaction centers and photosynthetic membranes. *Brookhaven Symp. Biol.* 28:64–73.

Mauzerall, D. 1978. Electron transfer photoreaction of porphyrins. *In* The Porphyrins. D. Dolphin, editor. Academic Press, Inc., New York. 5:29–52.

Miller, J. R. 1972. Scavenging kinetics of electrons produced by irradiation of organic glasses; experimental evidence for long range tunnelling. *J. Chem. Phys.* 56:5173–5183.

Strauch, S., G. McLendon, M. McGuire, and T. Guarr. 1983. Distance dependence of photoinduced electron transfer; time-resolved electron transfer emission quenching in rigid solution. *J. Phys. Chem.* 87:3579–3581.

Tien, H. T. 1982. Photoeffects in pigmented bilayer lipid membranes. *In* Transport in Biomembranes; Model Systems and Reconstitution. R. Antolini, A. Gliozzi, and A. Gorio, editors. Raven Publishers, New York. 57–74.

Varnadore, W. E., Jr., R. T. Arrieta, J. R. Duchek, and J. S. Huebner. 1982. Erythrosin and pH gradient induced photo-voltages in bilayer membranes. *J. Membr. Biol.* 65:147–153.