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Reaction Control of Photoinduced Electron Transfer in Porphyrin-Viologen Linked System by the Use of External Magnetic Fields

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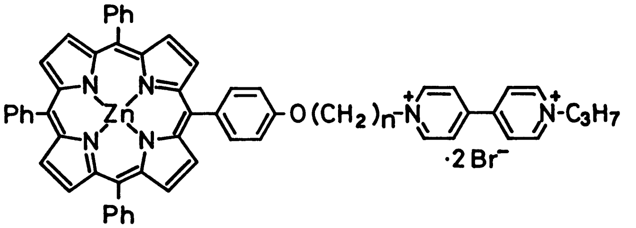
Effects of external magnetic fields on electron transfer reactions in porphyrin-viologen linked systems ($ZnPC_nV$) were investigated by laser photolysis. Rates of reverse electron transfer in the photogenerated intramolecular ion radical pair, as originated from quenching of porphyrin triplet by viologen, were remarkably suppressed (by a factor of ten for n=8) at above 0.1 T. The lifetime of the charge separated state could be correspondingly extended by the use of external magnetic fields, which perturb electron spin relaxation process.

External magnetic field effects on a chemical reaction provide a unique method for reaction control, as revealed by extensive studies on radical reactions.[2)] As to electron transfer reactions several papers have also been published.[3-7)] However, most of them were devoted to the study of the reaction product yields of ion radical pairs. Now, we found that external magnetic fields are extremely useful to control intramolecular electron transfer rates in porphyrin-viologen linked system under various microenvironment as discussed in this paper.

Porphyrin-viologen linked compounds (abbreviated to $ZnPC_nV$; n=4, 6, and 8) were prepared according to the previous paper.[8)] The laser photolysis experiments were carried out either with 20 µM (1 M= 1 mol dm^{-3}) $ZnPC_nV$ dissolved in aqueous acetonitrile (50% v/v), or with that (10 µM) incorporated in dihexadecyltrimethylammonium chloride (2C16NC) bilayer dispersion in water. The sample solution in a quartz cell with 3.5 cm optical path length was placed in the gap of an electromagnet (0 T to 1.0 T) with 8 cm polepieces, and was irradiated with a laser beam (XeF excimer laser; λ = 351 nm, pulse width 15 ns).

On laser excitation of $ZnPC_nV$ in the aq. acetonitrile solutions, photogenerated ion radical pairs ($ZnP^{\ddagger}$-$V^{\ddagger}$ as resulted from intramolecular electron transfer reaction) with an absorption maximum at around 640 nm were observed as previously described.[8)] The decay profile of the absorption at 640 nm for $ZnPC_8V$ is shown in Fig. 1. The decay profiles could be resolved into a very fast decay and a slow decay, which were



ZnPCnV (n=4,6,8)

attributed to reverse electron transfer in an intramolecular ion radical pair ($ZnP^{+\cdot}\text{-}V^{+\cdot}$) and that via intermolecular process ($ZnP^{+\cdot}\text{-}V^{2+}$ and $ZnP\text{-}V^{+\cdot}$), respectively, in the absence of a magnetic field (0 T).[8] In the presence of a magnetic field of 0.5 T, both the absorbance and the lifetime of the fast decay component appreciably increased, and the absorption due to the slow decay components also increased as shown in Fig. 1. The above-described facts may be explained by the following scheme (path 1 for the fast decay, and path 2 for the slow decay):

$$\begin{tikzcd}
ZnP\text{-}V^{2+} \arrow[r, "h\nu"] & \overset{3}{\overline{ZnP^{+\cdot}\text{-}V^{+\cdot}}} \arrow[r, "k_{isc}"] \arrow[d, "k_2"', "ZnP\text{-}V^{2+}"] & \overset{1}{\overline{ZnP^{+\cdot}\text{-}V^{+\cdot}}} \arrow[r, "k_{b1}"] & ZnP\text{-}V^{2+} \quad \text{(path 1)} \\
& ZnP^{+\cdot}\text{-}V^{2+\cdot} + ZnP\text{-}V^{+\cdot} \arrow[rr, "k_{b2}"] & & 2\cdot\ ZnP\text{-}V^{2+} \quad \text{(path 2)}
\end{tikzcd} \qquad (1)$$

In short, the fast decay of the triplet ion radical pair via intersystem crossing process competes with the electron transfer to another molecule of $ZnPC_nV$ in the ground state, which leads to the formation of slow decay components ($ZnP^{+\cdot}\text{-}V^{2+}$ and $ZnP\text{-}V^{+\cdot}$). Since the fast decay follows the first-order reaction kinetics, it is suggested that the intersystem crossing is the rate-determining step ($k_{isc} < k_{b1}$). It should also be noted that k_{isc} is the major component of the observed rate constant (k_1^{obsd}) of the fast decay under the present experimental condition.

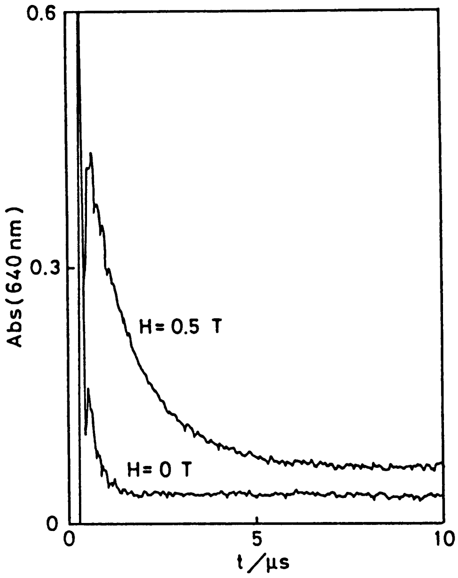


Fig. 1. Decay profiles of transient absorption on the laser photolysis of $ZnPC_8V$ in aq. acetonitrile at zero field and 0.5 T.

The k_1^{obsd}-value for $ZnPC_8V$ in aq. acetonitrile rapidly decreased with the magnetic field strength, and reached an asymptotic value ($k_{1,as}^{obsd} = 8.5 \times 10^5\ s^{-1}$) at above 0.5 T as shown in Fig. 2(c). Similar magnetic field effects were also observed with the k_1^{obsd}-values for $ZnPC_4V$ and $ZnPC_6V$ in the aq. acetonitrile solutions (Figs. 2(a) and (b)). The asymptotic values ($k_{1,as}^{obsd}$) for k_1^{obsd} at above 0.5 T are nearly the same between the three cases: $k_{1,as}^{obsd} = 6.7 \times 10^5$ (n=4), 7.0×10^5 (n=6), and $8.5 \times 10^5\ s^{-1}$ (n=8). The k_1^{obsd}-value at zero magnetic field, on the other hand, considerably increases with n. Consequently, the difference in k_1^{obsd} values between 0 T and high magnetic field (>0.3 T) increase with the number of methylene chains (n) in the linked system.

Because the rate of intermolecular electron transfer (k_2) could not be affected by the magnetic field, the decrease of k_1^{obsd}-value should be ascribed to the variation in k_{isc}. In other words, the effects of external magnetic fields on the k_1^{obsd}-value are explained as due to the perturbation of electron spin relaxation process in the intramolecular ion radical pair. From this point of view, the small but discernible difference in the $k_{1,as}^{obsd}$-values may be taken to indicate the effect of methylene chain length on the electron spin relaxation mechanism.

In the case of 2C16NC bilayer system, the intramolecular ion radical pair

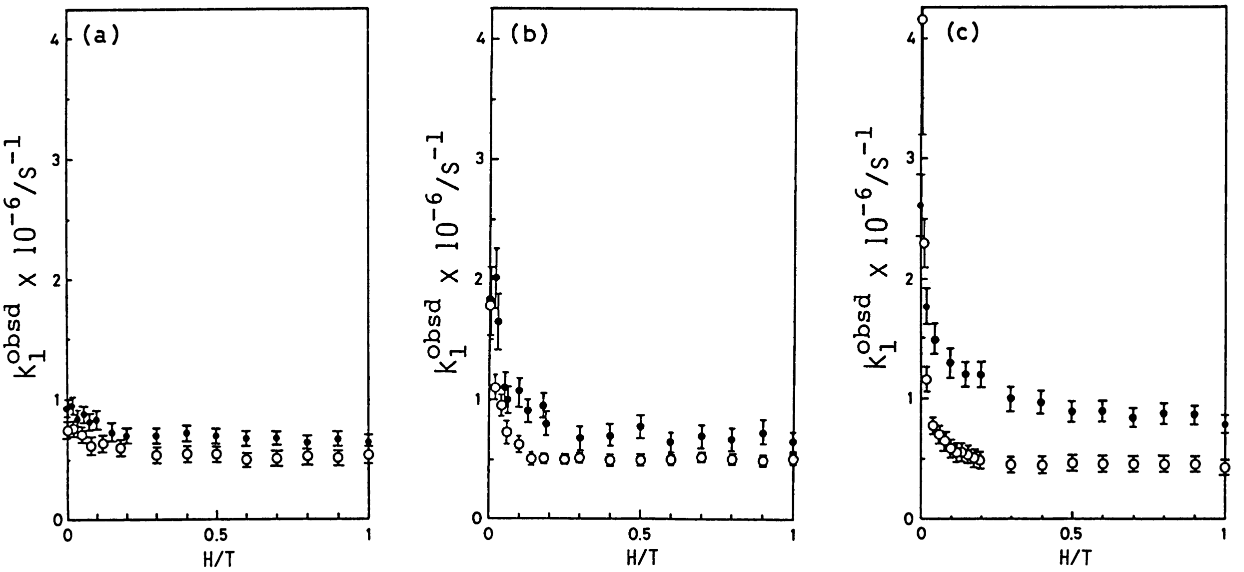


Fig. 2. The effect of magnetic fields on the rate of reverse electron transfer (k_1^{obsd}) in the photogenerated ion radical pairs of porphyrin-viologen linked system in aq. acetonitrile (●) and 2C16NC bilayer (○) systems: (a) $ZnPC_4V$, (b) $ZnPC_6V$, and (c) $ZnPC_8V$.

generated from $ZnPC_8V$ decayed too fast to afford an accurate rate constant in the absence of the magnetic field. In the presence of magnetic fields above 0.2 T, however, the decay curves were clearly observed in μs region, and k_1^{obsd} reached asymptotic value. The $k_{1,as}^{obsd}$-value (4.5×10^5 s^{-1}) is appreciably less than that in aq. acetonitrile system (Fig. 2(c)). In this system, no absorption due to the ionic species was detected in the time domain 20 μs after laser pulsing. Thus, the contribution of path 2 in Eq. 1 is concluded to be negligible and k_1^{obsd} becomes essentially the same to k_{isc} in the bilayer system. Similar phenomena were also observed with $ZnPC_4V$ and $ZnPC_6V$ in the bilayer systems (Figs. 2(a) and (b)). The $k_{1,as}^{obsd}$-values for the three systems are hardly different each other: $k_{1,as}^{obsd} = 5.2 \times 10^5$ (n=4), 5.0×10^5 (n=6), and 4.5×10^5 s^{-1} (n=8).

The above-described phenomena are typical magnetic field effects which are essentially explained by the electron spin relaxation process, as described by Hayashi and Nagakura,[9)] in the following manner. Since none of singlet linked ion radical pair has been so far reported to survive beyond 1 μs, the most plausible process for generating the long-living intramolecular ion radical pair is oxidative quenching of porphyrin triplet by the linked viologen as suggested in the previous paper.[8)] Thus, the electron spin of the photogenerated ion radical pair under discussion is assigned to triplet state (T_{+1}, T_0, and T_{-1}). Intersystem crossing to the corresponding singlet state (S) of the ion radical pair is required for the reverse electron transfer to take place. At a high magnetic field, the triplet sublevels are split by the Zeeman effect and the transition from the shifted sublevels (T_{+1} and T_{-1}) to S becomes less efficient than at the zero magnetic field. Since the intersystem crossing is the rate-determining step, the k_1^{obsd}-value decreases with magnetic field as observed in Fig. 2. The asymptotic value for the reverse electron transfer may be determined by the rate of electron spin flipping from the shifted sublevels (T_{+1} and T_{-1}) to T_0 or S. The k_1^{obsd}-values are curiously affected by the spacer methylene chain length (n). In 2C16NC bilayer system, the k_1^{obsd}-value clearly increases with n in the vicinity of zero field (<0.02T). Since the contribution of path 2 is negligible in this system, the observed facts indicate that the intersystem crossing rate increases with n for the three linked compounds. Considering the size of molecule, we can suggest that the singlet-triplet separation of the ion radical pair may not be negligible for $ZnP^{\dagger}C_4V^{\dagger}$. The intersystem crossing rate will be consequently reduced in comparison with the case with larger n values, where the spin pairs are separated further and the singlet-triplet separation will be diminished.[7)]

Major difference between aq. acetonitrile and 2C16NC bilayer systems comes from two factors: (1) contribution of path 2 and (2) conformational flexibility of the spacer methylene chains in the linked system. Both of the two factors, which are negligible in the bilayer, play important roles in less viscous microenvironment such as aq. acetonitrile. The observed microenvironmental effects on the $k_{1,as}^{obsd}$-values for $ZnPC_4V$ and $ZnPC_6V$ in Fig. 2 are mainly explained by the contribution of path 2 as estimated from the experimental conditions. In the case of $ZnPC_8V$, the conformational flexibility should also be taken into consideration in order to explain the large difference in the k_1^{obsd} values between aq. acetonitrile and 2C16NC bilayer systems. Due to the increased flexibility of the longer methylene chain, $ZnP^{\dagger}C_8V^{\dagger}$ may have more chances of assuming specific conformations, which favor the intersystem crossing of the ion radical pair than otherwise.

In conclusion, external magnetic fields were found to control electron transfer rates in the photogenerated ion radical pairs in porphyrin-viologen linked systems. These informations will be extremely useful for molecular design of photoreaction centers of artificial photosynthesis.

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