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ESR and ENDOR Study of the Photooxidation of Magnesium and Zinc Tetrakis(4-sulfonatophenyl)porphyrins

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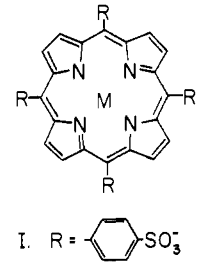
Abstract: An ESR and ENDOR study has been made of the photoinduced electron transfer from magnesium and zinc tetrakis(4-sulfonatophenyl)porphyrins (Mg- and ZnTPPS) to $K_3Fe(CN)_6$ in a H_2O–Me_2SO glass. ESR signals from the porphyrin photoexcited triplet state and π-cation radical were used to monitor the yield of the photooxidation reaction and the kinetics of growth and decay of the redox ions. At low temperture, electron-transfer products are formed very slowly. However, a slight softening of the glassy matrix causes a dramatic increase in the rate of the establishment of a photostationary equilibrium between reactants and redox ion products. In a soft glass, virtual quantitative photooxidation of the porphyrin can be attained within seconds. The electron-transfer reaction is completely reversible. A comparison of the rigid matrix ENDOR spectra from chemically oxidized ZnTPP (or MgTPP) and the photochemically generated doublet radical confirms that the doublet radical ESR signal is due to the π-cation radical of Zn(or Mg)TPPS. ENDOR spectra provide evidence that under the conditions of the experiments, molecular motion is restricted severely. It is concluded that free radicals are formed as a result of long-range electron transfer. The viscosity effect is attributed to the fact that during the excited-state lifetime of the donor molecules, donor–acceptor pairs can attain a configuration favoring electron transfer. Solvent reorganization around the solvent-separated redox pairs stabilizes the electron-transfer products. Kinetic data show that the back reaction takes place before the redox ions have a chance to diffuse apart. The results show that efficient production of photoinduced electron-transfer products is possible under conditions that preclude rapid separation of ion pairs.

In the photoinduced charge separation reaction

$$D + A \rightleftharpoons D^+ + A^-$$

a fraction of incident light is converted into chemical energy. The application of the reaction for the efficient conversion and storage of solar energy requires a system of donor and acceptor molecules which optimizes the forward reaction and minimizes the energy wasting back electron transfer. Over the past decade, research has been concerned with the identification of suitable donor and acceptor molecules as well as environmental factors that affect the efficiency of photoredox reactions. In particular, photoinduced electron-transfer reactions involving metallotetraphenylporphyrins (MTPP) and various electron acceptors in fluid as well as solid solution have been studied with the aid of optical spectroscopy and ESR.[1-12] Numerous optical studies have focused on water-soluble tetraphenylporphyrins.[13-21] This is because the photophysical and photochemical properties of these molecules make them suitable for use as photocatalysts in photoinduced water splitting reactions. In several papers dealing with optical studies of electron transfer involving water-soluble porphyrins, the formation of relatively long-lived free-radical products has been reported.[13-17,21] Even so, ESR appears not to have been used so far in studies of these systems.

This paper is concerned with the ESR and ENDOR study of the photoinduced electron-transfer reaction between magnesium (or zinc) tetrakis(4-sulfonatophenyl)porphyrin (MgTPPS, ZnTPPS, I) and $K_3Fe(CN)_6$ in glassy matrices. The ESR signal of the photooxidized porphyrins is used to probe the factors that affect the electron-transfer reaction and the kinetics of formation and decay of the redox ions. The ESR signal from the photoexcited triplet state of the porphyrins is used to monitor the extent of photooxidation. Hyperfine structure resolved in the ENDOR spectra serves to identify the free-radical products of the electron-transfer reaction.



Earlier investigations of the photooxidation of porphyrins in solid solution have shown that the yield of redox ion products is very low.[4-6,10-12] On the other hand, in fluid solution the lifetime of the electron-transfer products generally is too short for ESR detectable quantities to be generated. In the case of the systems considered here, it is found that the photostationary free-radical concentration increases dramatically upon cooling. Virtual *quantitative electron transfer can be attained readily.* The reasons for this matrix effect are considered in this paper.

Experimental Section

Free base tetrakis(4-sulfonatophenyl)porphyrin was obtained from Strem Chemicals. The preparation of the metalloporphyrins followed published procedures.[22] Samples used for magnetic resonance mea-

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(1) Quinlan, K. P. *J. Phys. Chem.* **1968**, *72*, 1797.

(2) Shakhverdov, P. A. *Doklady Akad. Nauk S.S.S.R.* **1967**, *174*, 1141.

(3) Shakhverdov, P. A. *Opt. Spektrosk.* **1971**, *30*, 42.

(4) Bobrovskii, A. P.; Kholmogorov, V. E. *Opt. Spectrosc.* (*Engl. Transl.*) **1971**, *30*, 17.

(5) Siderov, A. N. *Biophysics* (*Engl. Transl.*) **1974**, *19*, 44.

(6) Umrikhin, V. A.; Gribova, Z. P. *Biophysics* (*Engl. Transl.*) **1974**, *19*, 651.

(7) Shiozawa, M.; Yamamoto, H.; Fujita, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2177.

(8) Harriman, A.; Porter, G.; Searle, N. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1515.

(9) Loach, P. A.; Runquist, J. A.; Kong, J. L. Y.; Dannhauser, T. J.; Spears, K. G. In *Electrochemical and Spectrochemical Studies of Biological Redox Components*; Kadish, K. M., Ed.; ACS Symposium Series 201; American Chemical Society: Washington, DC, 1982; pp 515–561.

(10) McIntosh, A. R.; Siemiarczuk, A.; Bolton, J. R.; Stillman, M. J.; Ho, T.-F.; Weedon, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 7215.

(11) Siemiarczuk, A.; McIntosh, A. R.; Ho, T.-F.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224.

(12) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1985**, *24*, 2440.

(13) McLendon, G.; Miller, D. S. *J. Chem. Soc., Chem. Commun.* **1980**, 533.

(14) Nahor, G. S.; Rabani, J.; Grieser, F. *J. Phys. Chem.* **1981**, *85*, 697.

(15) Schmehl, R. H.; Whitten, D. G. *J. Phys. Chem.* **1981**, *85*, 3473.

(16) Rougee, M.; Ebessen, T.; Ghetti, F.; Bensasson, R. V. *J. Phys. Chem.* **1982**, *86*, 4404.

(17) Brugger, P.-A.; Grätzel, M.; Guarr, T.; McLendon, G. *J. Phys. Chem.* **1982**, *86*, 944.

(18) Richoux, M.-C.; Harriman, A. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1873.

(19) Okura, I.; Kusunoki, S.; Aono, S. *Inorg. Chem.* **1983**, *22*, 3828.

(20) Okura, I.; Kusunoki, S.; Aono, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1184.

(21) Nahor, G. S.; Rabani, J. *J. Phys. Chem.* **1985**, *89*, 2468.

(22) Adler, A. D.; Longo, F. R.; Varadi, V. *Inorg. Synth.* **1976**, *16*, 213.

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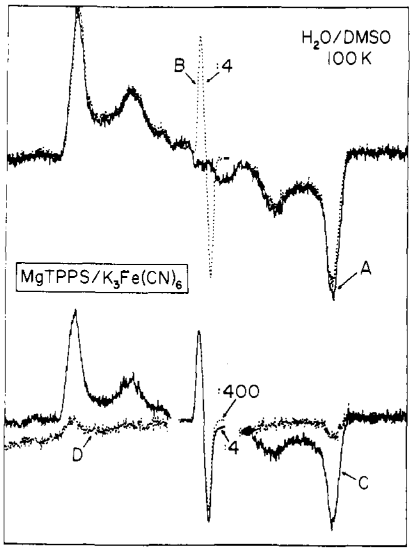

Figure 1. ESR of MgTPPS ($\approx 10^{-3}$ M) in H_2O–Me_2SO at 100 K, excitation with argon laser (514.5 nm, 0.8 W). Field range, 100 mT; field modulation, 4 mT at 100 kHz; microwave power, 1 mW. Top, no acceptor; bottom, with $K_3Fe(CN)_6$ ($\approx 10^{-2}$ M). Solid line spectra (A, C), no excitation during cooling; dotted line spectra (B, D), excitation during cooling. Center peaks were recorded with reduced amplification; the reduction factors are given in the figure.

surements were prepared in an all-glass apparatus on a high vacuum line and were sealed off after degassing by several freeze–pump–thaw cycles. Typically the porphyrin concentration ranged from 5×10^{-4} to 10^{-3} M and the ferricyanide concentration from 0 to 10^{-2} M. A water–dimethyl sulfoxide (1:1 v/v) mixture was used as solvent. This solvent combination was chosen because it gives a glass upon cooling. ESR spectra were recorded with a VARIAN E9 X-band spectrometer with standard variable-temperature accessory. Temperatures were monitored directly above the sample with a Cu–constantan thermocouple. A Mn^{2+}–SrO sample served as an internal magnetic field and spin concentration standard. For the photoexcitation, a Spectra Physics argon ion laser (514.5 nm, 0.1–1 W) was used. ENDOR spectra were recorded by using a home-built accessory described previously.[23,24] The ESR/ENDOR instrument is interfaced to a Nicolet 1180E minicomputer which is used for data acquisition and analysis. In the kinetic studies, the light was square-wave modulated with a variable-frequency chopper. A photodiode provided the trigger signal used to synchronize data acquisition with the light on–off period.

Results

Figure 1 shows low-temperature (100 K) ESR spectra from MgTPPS in H_2O–Me_2SO in the absence and presence of $K_3Fe(CN)_6$ recorded while the sample was being irradiated. Figure 1A gives the ESR spectrum from MgTPPS alone frozen in the dark. It displays the characteristic rigid matrix ESR signal of the photoexcited triplet.[25] If the sample is irradiated while it is being cooled from room temperature to 100 K, which takes about 3–4 min, a doublet radical signal is observed as well in the center of the spectrum (Figure 1B). This is attributed to photooxidation of the porphyrin. From the absence of a reduction in the triplet signal amplitude, it can be inferred that only a minor fraction of the MgTPPS is involved in the photooxidation reaction. Upon addition of the acceptor ($\approx 10^{-2}$ M) and cooling to 100 K in the dark, the photoinduced ESR spectrum consists of a triplet and doublet radical signal (Figure 1C). The triplet signal amplitude is about 25% less than that observed in the absence of ferricyanide. It is clear that this loss cannot be attributed to doublet radical formation because a conversion from triplet to doublet would have generated a much stronger signal in the center of the spectrum. Apparently the triplet quenching at 100 K is not associated with a buildup of redox products. By constrast, Figure 1D illustrates that a practically complete conversion to redox products can be attained by irradiation of the sample during cooling. That the photooxidation reaction has progressed almost to completion under those conditions is evident from three observations. First, the triplet signal intensity is reduced strongly. Second, the doublet radical signal is a factor of 100 more intense than that obtained by cooling followed by irradiation for 10 min or more (cf. Figure 1C). Third, the fluorescence emitted by the sample, which is intense under the conditions employed to record the spectra displayed in Figure 1A–C, is barely observable. By raising the temperature 60–70 deg and blocking the light beam, the sample can be restored to its original state in a matter of seconds. That the photochemical reaction is fully reversible is evident from the fact that a sample in a 1-mm-i.d. ESR tube displayed no degradation after many hours of irradiation and numerous quantitative photooxidation cycles.

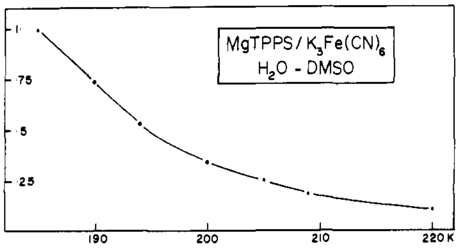

Figure 2. Photostationary doublet radical signal amplitude (in arbitrary units) vs. temperature from MgTPPS ($\approx 10^{-3}$ M) with $K_3Fe(CN)_6$ ($\approx 10^{-2}$ M) in H_2O–Me_2SO. Excitation with argon laser (514.5 nm, 0.8 W); microwave power, 1 mW; field modulation, 0.2 mT at 100 kHz. The maximum signal amplitude corresponds to a free-radical concentration of about 5.5×10^{-4} M.

A study of the temperature dependence of the ESR signal shows that the photostationary radical concentration increases rapidly with decreasing temperture. A plot of the signal intensity vs. temperature, corrected for changes in instrument sensitivity and Curie law dependence, is given in Figure 2. The reduction in triplet ESR signal amplitude gives information on the fraction of porphyrin that has been photooxidized. For this reason, the signal amplitude observed at any given temperature can be linked directly to the free-radical concentration. At the lowest temperature (185 K) for which a data point is given in Figure 2, the photostationary free-radical concentration is 5.5×10^{-4} M, and the radical half-life at that temperature is 0.25 s. Corresponding values at the high-temperature extreme (220 K) are 6×10^{-5} M and 4.5 ms. It is estimated that the quantum yield of the photooxidation reaction at 185 K lies between 50% and 100%. Measurements of the kinetics of growth and decay of the free-radical signal establish that a reduction in temperature is associated with a reduction in rate constants. Kinetic traces obtained at two different temperatures given in Figure 3 illustrate this point. The time required to reach a photostationary state increases strongly with decreasing temperature. For this reason, no attempt was made to measure the temperature dependence below around 180 K. At 100 K, the rate of photooxidation has slowed down to the point that many hours of irradiation may be needed to reach a photostationary state. Because of the temperature dependence of the decay rate, free radicals generated at higher temperatures can be frozen in at low temperature. At 100 K, the free-radical signal does not show a decrease in amplitude over a period of hours in the dark. A similar series of measurements performed on ZnTPPS gave the same results.

Parts A and B of Figure 4 give the rigid matrix ENDOR spectra obtained from the cation radical of ZnTPP generated by chemical oxidation[26] and of the free radical produced photochemically in the ZnTPPS/ferricyanide system. Similar spectra were obtained from the Mg porphyrins. From the ENDOR results, it is evident that the photoinduced doublet radical is indeed formed by electron transfer from the metalloporphyrins to ferricyanide. Both ferri- and ferrocyanide are ESR silent. Neta and Harriman have found

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(23) Mulks, C. F.; van Willigen, H. *J. Phys. Chem.* **1981**, *85*, 1220.

(24) Kirste, B.; van Willigen, H. *J. Phys. Chem.* **1982**, *86*, 2743.

(25) Chandrashekar, T. K.; van Willigen, H. *Chem. Phys. Lett.* **1984**, *106*, 237.

(26) Chandrashekar, T. K.; van Willigen, H., unpublished results.

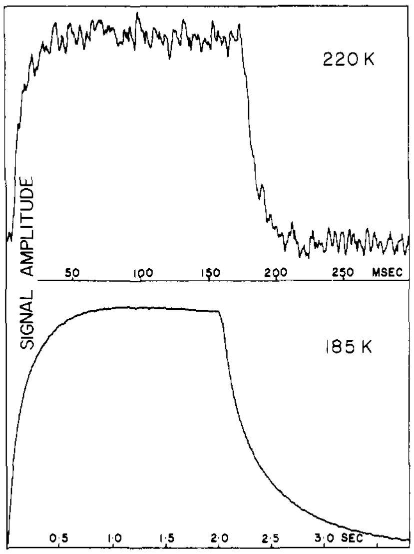

Figure 3. Kinetics of formation and decay of free radicals at 220 and 185 K of MgTPPS ($\approx 10^{-3}$ M)/$K_3Fe(CN)_6$ ($\approx 10^{-2}$ M) in H_2O–Me_2SO. Note the different time scales employed.

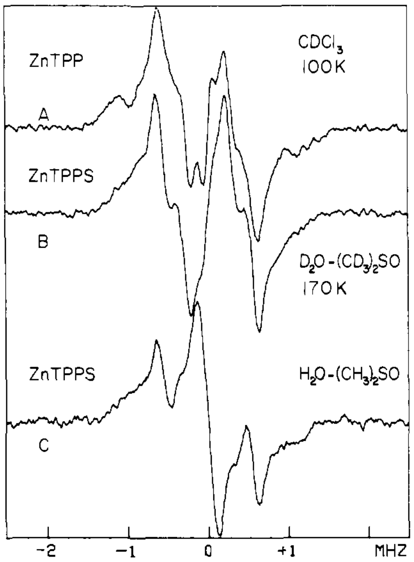

Figure 4. ENDOR spectra of oxidized ZnTPP and ZnTPPS in frozen solution. Microwave power, 2 mW; radio-frequency power, ≈ 100 W; frequency modulation, 50 kHz at 10 kHz; sweep rate, 5 MHz/s; 500 scans. (A) ZnTPP in $CDCl_3$ oxidized with I_2; (B) ZnTPPS with $K_3Fe(CN)_6$ at 170 K photooxidized with 1-W argon laser light in D_2O–$Me_2SO(D_6)$; (C) as B, solvent H_2O–Me_2SO. Frequency scale relative to the free proton Zeeman frequency.

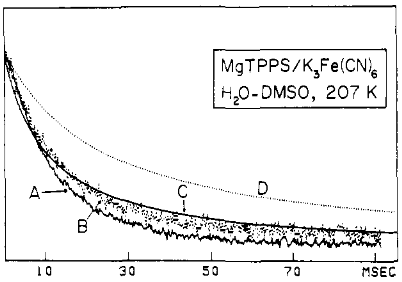

Figure 5. Decay of the ESR signal from the photogenerated π-cation radical of MgTPPS. (A, solid line) Starting radical concentration, 5×10^{-5} M; (B, dotted line) starting concentration, 2.5×10^{-5} M. The two curves have been normalized to the same starting amplitude to emphasize the deviation from second-order kinetics. Theoretical second-order decay curves for the two starting concentrations are given by C and D, respectively.

that the π-radical cation of ZnTPPS is quite persistent in aqueous solution at room temperature.[27] This finding shows that electron transfer involving this water-soluble porphyrin can be fully reversible under the conditions employed in the present study.

The ENDOR spectra presented were taken using deuteriated solvents. With normal solvents the ENDOR spectrum generated by ZnTPPS/$K_3Fe(CN)_6$ exhibits a strong matrix (free proton) signal (cf. Figure 4C) even at temperatures high enough to reduce the free-radical lifetime to well below 1 s. The matrix signal arises because of weak coupling between unpaired electrons associated with the porphyrin molecules and the protons of surrounding solvent molecules.[28] It is known[28] that fluid solution ENDOR spectra do not show a free proton peak due to exchange of solvation shell molecules with bulk solvent molecules and rotational motion of the molecules. Its observation under the present conditions shows that the measurements are made on highly viscous solutions where molecular motion is severely restricted. This suggests the possibility that radical decay involves back electron transfer between originally photogenerated redox pairs rather than electron transfer initiated by random diffusive encounters between redox ions. Figure 5 illustrates the dependence of the kinetics of free-radical decay on the initial concentration of electron-transfer products. The starting concentration of redox ion products was varied by changing the intensity of the laser light. The two experimental decay curves (recorded at 207 K) are for starting radical concentrations of about 5×10^{-5} (A) and 2.5×10^{-5} M (B). The data have been normalized to the same signal amplitude at the time the excitation source is turned off. Included are decay curves (C and D) calculated assuming that second-order kinetics is followed. From the similarity of the decay curves obtained for starting concentrations that differ by a factor of 2, it is evident that the second-order rate law does not apply. The fact that the calculated decay curves do not match the experimental curves supports this conclusion. It follows that electron transfer involving random diffusive encounters between separated redox products can be ruled out as a mechanism for free-radical decay. The data also show small deviations from simple first-order decay. Further studies are necessary to determine whether these deviations reflect details of the mechanism of decay or must be attributed to the temperature modulation associated with square-wave-modulated excitation.

Discussion

From information on the electronic energy levels of Mg- or ZnTPPS and redox potentials of the porphyrins[29] and ferricyanide,[30] it can be estimated that the electron-transfer reaction involving the excited-state porphyrins is exothermic by about 1.5 and 1. eV for the first excited singlet and triplet state, respectively. The free energy of the redox ions lies about 0.5 eV above that of the porphyrin/$K_3Fe(CN)_6$ couple. The optical absorption spectrum shows no evidence of ground-state complexation between donor and acceptor molecules. Except for some quenching, addition of ferricyanide also does not affect the porphyrin triplet ESR spectra. This provides additional evidence for the absence of complexation. It follows that photooxidation in solid solution requires long-range electron transfer. It has been shown that electron transfer between excited donor (or acceptor) molecules and ground-state acceptor (donor) molecules in solid solution can take place over distances as large as 25 Å.[31] The process is reflected in the partial quenching of fluorescence and phosphorescence. The 25% reduction in the porphyrin triplet ESR signal amplitude associated with ferricyanide addition (cf. Figure

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[27] Neta, P.; Harriman, A. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 123.

[28] Hyde, J. S.; Rist, G. H.; Eriksson, L. E. G. *J. Phys. Chem.* **1968**, *72*, 4269.

[29] Kalyanasundaram, K.; Neumann-Spallart, M. *J. Phys. Chem.* **1982**, *86*, 5163.

[30] *Handbood of Chemistry and Physics*; Weast, R. C., ed.; Chemical Rubber Co.: Cleveland, OH, 1977.

[31] Miller, J. R.; Hartman, K. W.; Abrash, S. *J. Am. Chem. Soc.* **1982**, *104*, 4296.

1) is of the order of magnitude expected for electron-transfer quenching.[31,12] However, an increase in the ionic strength of metallotetraphenylporphyrin solutions has been shown to promote porphyrin aggregation.[14,25] This process can account for the reduction in triplet signal amplitude as well.

Earlier studies have shown that the yield of stable redox ions produced by long-range electron transfer in solid solution is very low.[4-6,10-12,31,32] This is because the factors that favor the forward reaction will also favor rapid back electron transfer. A recent paper by Ohta and Kevan[32] on the photooxidation of chlorophyll *a* in the presence of electron scavengers is a good illustration of this point. In their study involving frozen vesicle solutions, irradiation was carried out over a period of an hour or longer to generate ESR-detectable cation-radical concentrations. In the case of Zn(or Mg)TPPS/$K_3Fe(CN)_6$ in a *hard* glass, photooxidation is found to be very inefficient as well. By contrast, virtual quantitative photooxidation can be achieved in seconds by a slight softening of the solvent matrix. In papers on the photooxidation of chlorophyll by Tollin and co-workers[33] and of porphyrins by Bolton and co-workers,[10] reference is made to an effect of solvent viscosity on the rate of radical ion generation and on photostationary radical concentrations. However, the effects noted in those papers are minor compared to the viscosity effect reported here. The striking dependence on solvent viscosity is attributed to two factors. First, the efficiency of the forward electron-transfer reaction must be a function of separation and relative orientation of (excited) donor and acceptor molecules. In a soft glass, donor–acceptor pairs sample a range of configurations during the excited state lifetime. For this reason, electron transfer is more likely to occur than in a hard glass. Second, in a hard glass the configuration that favors electron transfer is frozen in. This makes it likely that the forward reaction is followed immediately by back electron transfer. Molecular motion in a soft glass can serve to trap the electron-transfer products, for instance by reorganizing the solvation shells and changing the relative orientation of the ions. A preliminary study of the photooxidation of ZnTPP in the presence of chloranil in frozen diethyl ether (DEE) or MTHF revealed only a minor temperature effect. This suggests that solvation plays an important role in stabilizing the photooxidation products.

Reports on photoinduced electron-transfer reactions in liquid solution have pointed to the effect of solvent polarity on the yield of redox ion products.[3,8,34] It is found that the yield increases with increasing polarity. The effect has been attributed to solvent-induced dissociation of the ion pairs that are created by electron transfer. Under the experimental conditions maintained in the present study, molecular motion is severely restricted. Therefore, the mechanism of photooxidation differs in a number of important aspects from that found in liquid solution. First, electron transfer does not involve random diffusive encounters between donors and acceptors. Instead, long-range electron transfer generates solvent-separated ion pairs. Second, it is evident from the kinetic data that the back reaction does not involve random encounters between redox ions. The absence of second-order kinetics shows that the photogenerated ion pairs do not diffuse apart. Evidently, the difference in temperature dependence found for ZnTPP/chloranil in DEE or MTHF on the one hand and Zn(Mg)TPPS/$K_3Fe(CN)_6$ in H_2O–Me_2SO on the other cannot be attributed to solvent-induced ion pair dissociation.

Conclusion

Studies of photooxidation of porphyrins in liquid and frozen solutions generally have shown that the yield of redox ion products is very low. The lifetime of redox ions in solution can be increased by a choice of medium that promotes spatial separation of donor and acceptor molecules following electron transfer. Particularly effective in this respect has been the presence of polyelectrolytes in solution.[24] The solubilization of donor or acceptor molecules in organized assemblies such as micelles and vesicles also has proven to stabilize products of electron-transfer reactions.[15,35-37] The results presented in this paper show that a strong degree of kinetic control can be provided as well by the viscosity dependence of long-range electron transfer. The fact that high redox ion concentrations can be generated makes it possible to probe the factors affecting electron transfer with ESR and ENDOR. The efficiency of free-radical generation in the systems studied is high enough to make it possible to perform time-resolved ESR/ENDOR measurements following pulsed laser excitation. This would be of interest because such measurements may reveal chemically induced dynamic electron spin polarization (CIDEP) effects. CIDEP can be of use in probing the spin dynamics associated with the electron-transfer process.[38-40]

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(32) Ohta, N.; Kevan, L. *J. Phys. Chem.* **1985**, *89*, 3070.

(33) Tollin, G.; Green, G. *Biochim. Biophys. Acta* **1962**, *60*, 524.

(34) Harriman, A. In *Energy Resources through Photochemistry and Catalysis*; Grätzel, M., Ed.; Wiley: New York, 1982; pp 163–215.

(35) Ford, W. E.; Otvos, J. W.; Calvin, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 3590.

(36) Infelta, P. P.; Grätzel, M.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 1479.

(37) Infelta, P. P. In *Energy Resources through Photochemistry and Catalysis*; Grätzel, M., Ed.; Wiley: New York, 1982; pp 49–70.

(38) Lepley, A. R.; Closs, G. L. In *Chemically Induced Magnetic Polarization*; Wiley: New York, 1972.

(39) Trifunac, A. D.; Lawler, R. G. *Magn. Reson. Rev.* **1982**, *7*, 147.

(40) Lendzian, F.; Jaegermann, P.; Möbius, K. *Chem. Phys. Lett.* **1985**, *120*, 195.