MAGNETIC RESONANCE STUDIES OF PHOTOSYNTHETIC REACTION CENTERS
AND PORPHYRINS

DOE/ER/13242--6

DE91 000597

FINAL REPORT

FOR PERIOD JUNE 1, 1987 - NOVEMBER 15, 1989

HANS van WILLIGEN

UNIVERSITY OF MASSACHUSETTS AT BOSTON

BOSTON, MASSACHUSETTS 02125

NOVEMBER 1989

PREPARED FOR

THE UNITED STATES DEPARTMENT OF ENERGY

AGREEMENT No. DE-FG02-84ER13242

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

LB

INTRODUCTION

During the period covered by this report research has been concerned with the study of photo-induced electron transfer reactions from porphyrins to acceptor molecules with time-resolved Electron Paramagnetic Resonance (EPR) methods.

Excited-state electron transfer reactions are of importance from a fundamental point of view and in connection with applications in homogeneous and heterogeneous photosensitization, photopolymerization, and solar energy conversion. For this reason, the study of photo-induced electron transfer reactions is of considerable interest.

Porphyrins are particularly well suited for this field of research. Upon excitation with visible light they readily engage in electron transfer with a variety of molecules. Their synthesis is straightforward and it is possible to introduce a wide range of substituents so that the effect of geometric and electronic structure on the electron transfer process can be investigated.

The structural relationship with chlorophylls suggests that porphyrins may find use in man-made solar energy conversion and storage devices that mimic the photosynthetic apparatus in plants and photosynthetic bacteria. This application requires a detailed knowledge of the factors that affect the efficiency with which excited porphyrins can generate electron transfer products. It has been established that spin selection rules can have a significant effect on the quantum efficiency of this

3
reaction. For instance, electron transfer involves a transient donor/acceptor radical pair (RP) and the probability of cage escape of electron transfer products is a function of the electron spin state of the RP. The efficiency can be modified by changing the conditions that control the original spin state of the RP and its time evolution during the RP lifetime. Time-resolved EPR measurements provide a means to get direct information on such spin state dependent processes. They also make it possible to identify paramagnetic products and can be used to characterize the excited state involved in the charge transfer reaction. Finally, the measurements can give data on electron spin relaxation which can serve as a probe of molecular motion. Evidently, EPR measurements can contribute valuable knowledge that complements that derived from studies performed with other spectroscopic techniques.

Our work has been concerned with the time evolution of EPR signals following pulsed-laser excitation. Studies were performed with cw EPR equipment adapted for time-resolved studies. The Fourier Transform (FT) EPR equipment constructed by Professor K. P. Dinse's research group at the Physics Institute of Dortmund University (FRG) was also used in the investigations. This collaborative work established that this novel technique is uniquely suited for studies of spin-state evolution in pulsed-laser generated transient free radicals. Currently, FT-EPR studies are carried out as well with an instrument constructed in the laboratory of the PI with funding from the DOE Instrumentation Program.

EXPERIMENTAL RESULTS

Time-resolved cw EPR

With the acquisition of an excimer-laser-pumped dye laser it became possible to monitor the time-evolution of photo-induced EPR signals with a time-resolution in the nanosecond range. A conventional EPR spectrometer was adapted for direct signal detection (no field modulation) using a boxcar integrator. This equipment was used to study the EPR signals generated by photoexcitation of porphyrin-quinone solutions as function of delay time between laser pulse and boxcar detection.

With the cw EPR instrument useful data could be obtained over a delay time ranging from 500 nanoseconds to about 20 microseconds. With shorter delay times off-resonance contributions cause considerable linebroadening. The upper limit is set by instrumental sensitivity. It is estimated that the radical ion concentration generated under the conditions of the experiment is in the 10^{-5} range. This, combined with the inherent lack of sensitivity of the direct detection method, means that signals can be detected only in the time span that the radicals are spin polarized.

Measurements on Zn tetraphenylporphyrin (ZnTPP)-benzoquinone (BQ) in ethanol, over a temperature range from 20°C to -20°C, unambiguously established the reversible photogeneration of the ZnTPP cation and BQ anion radical¹. The time-resolved spectra display strong spin-polarization that originates from two mechanisms. The first is the Triplet

Mechanism (TM), it gives rise to enhanced absorption signals and is due to spin polarization transfer from the porphyrin triplet precursor. The second is the Radical Pair Mechanism (RPM) which stems from the spin state dependence of the probability of cage escape of free radical products. In the BQ anion radical, the RPM causes the four low field hyperfine lines to be in emission. The polarization pattern observed experimentally is a function of the relative contributions of these two mechanisms. It can be modulated by changes in: (1) delay time between laser pulse and EPR detection, (2) BQ concentration, and (3) temperature. This is because the triplet spin polarization decays within $1\mu\text{s}$ so that a reduction in triplet quenching rate diminishes the TM contribution. Moreover, temperature changes are expected to affect the spin state evolution of the RP and this will result in a change in the RPM contribution as well.

Similar time-resolved measurements were performed on a series of other ZnTPP-quinone solutions in ethanol.² The objective was to investigate whether a variation in structure of the acceptor molecule has a significant effect on the characteristics of the electron transfer process. Of particular interest was the question whether or not the RP spin state evolution is affected. The fact that two mechanisms contribute to the observed spin polarization proved useful in this comparative study. The spin polarization of the ZnTPP triplet precursor is unaffected by a change in acceptor molecule. Hence, experimentally observed changes in the relative contributions of TM and RPM spin

6

polarization in the EPR spectra of free radical products must stem from a change in triplet quenching rate and/or change in the spin state evolution of the RP. Our measurements did not reveal significant changes in the spin polarization pattern for the series of quinones investigated.²

On the other hand, a measurement of the effect of porphyrin dimerization on the spin polarization pattern showed a pronounced effect. In photosynthetic bacteria the primary donor is a pair of bacteriochlorophyll molecules. Numerous research efforts have been concerned with the question of what the significance of this dimer structure is for the photo-induced charge separation process. For this reason studies of the excited state electron transfer properties of model dimer systems is of interest. The molecule studied is ZnTPP with crown ether substituents (ZnTCP). Addition of trace amounts of cations (K^+ , NH_4^+) to a solution of ZnTCP causes quantitative dimerization.^{3,4} A cw time-resolved EPR study of the effect of dimerization on the spin polarization of the benzoquinone anion radical generated by electron transfer from the crownporphyrin showed a pronounced increase in the relative importance of the RPM spin polarization contribution. This can signify a reduction in triplet quenching rate and/or an increase in the rate of spin state evolution of the RP. It is expected that time-resolved FT-ESR measurements on this system will provide the data that will establish the reason for the dimerization effect.

From the point of view of utilization in solar energy conversion devices the photochemical properties of water-soluble porphyrins are of special interest. This has prompted conventional EPR studies of photoexcited triplets of anionic and cationic tetraphenylporphyrins.^{5,6} We have also reported on an EPR study of the photooxidation of tetrasulfonated ZnTPP (ZnTPPS) by benzoquinone.⁷ Presently, time-resolved EPR methods are being applied in the study of the ZnTPPS-BQ system. Preliminary results show significant differences compared with the ZnTPP-BQ. To what extent this can be attributed to changes in solvent composition is subject of on-going work.

Time-resolved Fourier Transform EPR

The power of the FT-EPR method in time-resolved studies of photo-induced electron transfer was first demonstrated in collaborative work involving the research group of Professor Dinse in Dortmund and the PI.⁸⁻¹¹ In the FT-EPR measurements the electron transfer reaction is initiated by a laser pulse. After a delay that can be as short as 10 nanoseconds or as long as milliseconds, the sample is exposed to a short microwave pulse. Following this pulse, the Free Induction Decay (FID) of the magnetization induced in the plane perpendicular to the field direction is sampled. Fourier transformation of the FID gives the EPR signal from the paramagnetic molecules present at the time of the microwave pulse.

The FT-ESR method has a number of advantages over the time-resolved cw EPR method. In the cw method the microwave field affects spin populations in the time period between laser excitation and detection. This complicates the analysis of the time evolution of the signal. Also, for short delay times, cw spectra show line broadening due to off-resonance signal contributions which precludes meaningful measurements during the radical generation period which covers the first few hundred nanoseconds. The FT-EPR method does not suffer from these disadvantages so that the kinetics of the forward electron transfer reaction can be measured. Since the microwave field is off except for the brief (≈ 20 ns) period that the $\pi/2$ pulse is given, the FT-EPR measurements gives direct information on spin polarization evolution unperturbed by a microwave field. The sensitivity of the pulsed technique is much higher than that of the cw method. This makes it possible to follow the course of the reaction into the back reaction time domain where the spin system has reached thermal equilibrium.

A study was made of the photo-induced electron transfer from ZnTPP to duroquinone (DQ).^{8,9} A detailed analysis of the growth and decay of the EPR signal of the DQ anion radical gave data on the rate of the forward electron transfer reaction and the spin lattice relaxation time of the porphyrin triplet and BQ^- doublet radical.⁹ It is of interest that the measurements give indirect information on the spin polarization and spin-lattice relaxation time of the triplet precursor that is involved in the charge separation reaction.

In fluid solution it is not possible to get information on these characteristics by direct measurement. In this respect it is noteworthy that spectra obtained from TPP(free base)-BQ shows a polarization pattern that differs fundamentally from that given by ZnTPP-BQ. This can be attributed to the fact that the spin selective intersystem crossing pathways that govern spin polarization in the ZnTPP and TPP triplets differ.

The award of a DOE Instrumentation Grant in 1988 made it possible to construct a FT-EPR instrument at the University of Massachusetts. Assembly of the hardware was completed in Spring 1989. Some software development is still required before the instrument can be used for all the envisioned applications. Even so it has already proven a powerful tool in investigations of photo-induced electron transfer involving porphyrins. On-going work performed in the PI's laboratory and in Dortmund in collaboration with Professor Dinse deals with the following topics: (1) a study of the ZnTPP-BQ system, (2) a study of electron transfer involving water-soluble porphyrins, (3) a study of the effect of porphyrin dimerization, (4) a study of excited electron transfer in organized assemblies (micelles, microemulsions).

In the study of ZnTPP-DQ an unusual phase effect in short delay time ($<300\text{ns}$) spectra was noted. A similar, but more pronounced effect was found in FT-EPR spectra from ZnTPP-BQ. Since the effect is found with measurements performed in Dortmund as well Boston it is unlikely that it is due to an instrumental artifact. The signal is attributed

10

to the presence of $\text{ZnTPP}^+-\text{Q}^-$ radical pairs at the time of the microwave pulse. A method has been worked out to extract this contribution from the regular signal and this provides a time profile of the growth and decay of the radical pair.¹¹ It is anticipated that this method can be applied in a systematic study of RP characteristics. For instance, it has been proposed that RP lifetimes are affected by electrostatic interactions between donor and acceptor molecules. Introduction of charged substituents on donors and/or acceptors then are expected to change the time evolution of the FT-EPR signal attributed to the RP.

In recent years numerous studies have been devoted to the study of photo-induced charge separation reactions in organized assemblies such as micelles and vesicles. In terms of research in the area of solar energy conversion these systems are of interest for two reasons. First, in homogeneous solution the rate of charge transfer quenching of singlet excited states generally is too slow to compete with singlet state decay processes. For this reason, photo-induced electron transfer usually involves (longer-lived) excited triplet states. This results in a reduction of the fraction of photon energy that can be stored in the form of an electrochemical potential. Heterogeneous systems can be designed in which donor and acceptor molecules are closely spaced so that electron transfer can compete with normal singlet excited state decay. As a consequence, a larger fraction of the light energy can be converted. Second, in homogeneous media the back electron transfer reaction

11

constitutes an important energy waste pathway. The heterogeneous environment can be tailored so as to promote charge separation and suppress the energy wasting back reaction.

Time-resolved EPR measurements should prove a useful tool in studies concerned with the elucidation of the structure of these organized assemblies. The FT-EPR technique has been used to measure photogenerated BQ^- free radicals in a system consisting of ZnTPP-BQ solubilized in TRITON X-100 micelles and a microemulsion. Initial data show a polarization pattern that deviate strongly from those found in homogeneous solution. In part this may be due to singlet excited state participation in the electron transfer process. Further studies are required before a definitive interpretation of the observations can be given. It is noteworthy and encouraging that FT-ESR spectra have good signal to noise even though porphyrin concentrations are low ($\sim 10^{-5}M$).

REFERENCES

- 1) van Willigen, H.; Vuolle, M.; Dinse, K. P. J. Phys. Chem. **1989**, 93, 2441.
- 2) Vuolle, M.; van Willigen, H. **1988** unpublished results.
- 3) Chandrashekar, T. K.; van Willigen, H. J. Am. Chem. Soc. **1983**, 105, 6323.
- 4) van Willigen, H.; Chandrashekar, T. K. J. Am. Chem. Soc. **1986**, 108, 709.
- 5) Chandrashekar, T. K.; van Willigen, H.; Ebersole, M. H. J. Phys. Chem. **1984**, 88, 4326.
- 6) van Willigen, H.; Das, U.; Ojadi, E.; Linschitz, H. J. Am. Chem. Soc. **1985**, 107, 7784.
- 7) van Willigen, H.; Ebersole, M. H. J. Am. Chem. Soc. **1987**, 109, 2299.
- 8) Prisner, T.; Dobbert, O.; Dinse, K. P.; van Willigen, H. J. Am. Chem. Soc. **1988**, 110, 1622.
- 9) Dinse, K. P.; van Willigen, H.; Dobbert, O.; Prisner, T. in PULSED EPR: A NEW FIELD OF APPLICATIONS, eds. Keijzers, C. P.; Reijerse, E. J.; Schmidt, J.: North Holland, Amsterdam **1989**, 89.
- 10) Plüschau, M.; Zahl, A.; Dinse, K. P.; van Willigen, H. J. Chem. Phys. **1989**, 90, 3153.
- 11) Dinse, K. P.; Plüschau, M.; Kroll, G.; Prisner, T.; van Willigen, H. Bull. Magn. Res. **1989**, in press.

PAPERS ACKNOWLEDGING DOE SUPPORT

Dinse, K. P.; Plüschau, M.; Kroll, G.; Prisner, T.; van Willigen, H. "PHOTO-INDUCED ELECTRON TRANSFER REACTIONS STUDIED BY FOURIER-TRANSFORM ESR", Bull. Magn. Res. **1989**, in press.

Dinse, K. P.; van Willigen, H.; Dobbert, O.; Prisner, T. "PULSED ESR INVESTIGATION OF ELECTRON TRANSFER PROCESSES IN SOLUTION" in **Pulsed EPR: A New Field of Applications**; eds. Keijzers, C. P.; Reijerse, E. J.; Schmidt, J., Amsterdam: North Holland, **1989**, 89-95.

Plüschau, M., Zahl, A.; Dinse, K. P.; van Willigen, H. "FT-ESR STUDY OF SPIN-POLARIZATION GENERATED BY TRIPLET-AND RADICAL PAIR MECHANISMS IN A PHOTOINDUCED ELECTRON TRANSFER REACTION", J. Chem. Phys. **1989**, 90, 3153-3158.

van Willigen, H.; Kirste, B. "ENDOR STUDY OF BIRADICALS RANDOMLY ORIENTED IN A RIGID MATRIX", Israel J. Chem. **1989**, 29, 93-98.

van Willigen, H.; Vuolle, M.; Dinse, K. P. "TIME-RESOLVED ESR STUDY OF PHOTOOXIDATION OF ZINC TETRAPHENYLPORPHYRIN BY BENZOQUINONE", J. Phys. Chem. **1989**, 93, 2441-2444.

Prisner, T.; Dobbert, M.; Dinse, K. P.; van Willigen, H. "FOURIER TRANSFORM ESR STUDY OF PHOTOINDUCED ELECTRON TRANSFER", J. Am. Chem. Soc. **1988**, 110, 1622-1623.

van Willigen, H.; Ebersole, M. H. "ESR AND ENDOR STUDY OF THE PHOTOOXIDATION OF Mg AND Zn TETRAKIS(4-SULFONATOPHENYL) PORPHYRIN", J. Am. Chem. Soc. **1987**, 109, 2299-2302.

ABSTRACTS OF PAPERS ON DOE SUPPORTED RESEARCH

Ebersole, M. H.; van Willigen, H. "TIME-RESOLVED ESR STUDY OF PHOTO-INDUCED ELECTRON TRANSFER", Abstract 31st Rocky Mountain Conference, Denver (CO) 1989.

Ebersole, M. H.; van Willigen, H. "PHOTOOXIDATION OF WATER-SOLUBLE PORPHYRINS",

van Willigen, H.; Dinse, K. P.; Vuolle, M.; Dobbert, O.; Prisner, T. "TIME-RESOLVED ESR STUDIES OF PHOTOINDUCED ELECTRON TRANSFER FROM PORPHYRINS TO QUINONES", Abstracts 7th International Conference on Photochemical Conversion and Storage of Solar Energy, Evanston (IL) 1988.

PERSONNEL INVOLVED IN RESEARCH

Dr. Mikko Vuolle, visiting scientist (on sabbatical from the University of Jyväskylä, Finland), 100% of time, October 1987 through October 1988.

Professor V. Krishnan, visiting scientist from the Indian Institute of Sciences Bangalore, 100% of time, May 1989 through July 1989.

Dr. Frans Pijpers, visiting scientist from the University of Nijmegen, The Netherlands, 100% of time, July 1989.

Dr. Patricia Levstein, postdoctoral fellow, 100% of time, since July 1989.

Marie H. Ebersole, graduate student, 80% of time, since 1987.

ESTIMATE OF UNOBLIGATED BALANCES

It is estimated that no funds will remain unencumbered at the end of the current ant period.

END

DATE FILMED

11 / 07 / 90