DOE/ER/13242-7

MAGNETIC RESONANCE STUDIES OF PHOTO-INDUCED
ELECTRON TRANSFER REACTIONS

DOE/ER/13242--7

DE91 006813

PROGRESS REPORT

FOR PERIOD JUNE 1, 1990 - DECEMBER 31, 1990

HANS VAN WILLIGEN

UNIVERSITY OF MASSACHUSETTS AT BOSTON

BOSTON, MASSACHUSETTS 02125

DECEMBER 1990

PREPARED FOR

THE UNITED STATES DEPARTMENT OF ENERGY

AGREEMENT NO. DE-FG02-84ER13242

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

INTRODUCTION

During the period covered by this report research has been concerned with the application of Fourier Transform Electron Paramagnetic Resonance (FT EPR) in the study of photo-induced electron transfer reactions. Donor molecules used in this investigation have been various porphyrins, whereas quinones were used as acceptor molecules.

Excited-state electron transfer reactions are of interest from a fundamental point of view as well as in connection with applications in photosensitization, photopolymerization, and solar energy conversion. Porphyrins are particularly well suited for the study of the factors that play a role in photo-induced electron transfer reactions. Upon excitation with visible light they readily engage in electron transfer reactions with a variety of acceptor (or donor) molecules. The synthesis of porphyrins with a wide range of substituents is straightforward. Generally, the molecules are very stable. Furthermore, photochemical and -physical characteristics have been well documented. 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.

Our work is concerned with the investigation of the factors that affect the efficiency with which excited porphyrins can generate electron transfer products. The fact that the primary products are free radicals makes it possible to measure

effects of solvent changes, variation in porphyrin substituents, and heterogeneous environments on electron transfer kinetics with time-resolved EPR techniques. Until recently applications of EPR in this field of research have made use almost exclusively of the direct-detected cw EPR method. The development of FT-EPR instrumentation during the last few years has led to time-resolved studies with this novel technique.

With FT EPR one can measure the kinetics of growth and decay of paramagnetic species with nanosecond time resolution. Free radicals can be identified unambiguously using information on hyperfine couplings and g factors. These parameters can be a sensitive function of solvent-solute interactions so that the FT-EPR spectra can be used to get information on the environment the free radicals find themselves in. Finally, signal amplitudes are not simply a function of free radical concentration, but also reflect the spin selectivity of the photophysical and -chemical processes involved in excited-state electron transfer. Spin selective processes give rise to Chemically Induced Dynamic Electron Spin Polarization (CIDEP) effects. With an analysis of CIDEP exhibited in time-resolved spectra detailed information can be obtained on the characteristics of precursor paramagnetic molecules such as porphyrin photo-excited triplets and radical pair intermediates.

Our work has focused on the following topics:

1. The development of software for FT-EPR instrument control and numerical analysis of pulsed-EPR data. Evaluation of kinetic models that can be used to quantitatively account for the time-evolution of

FT-EPR spectra displaying Chemically Induced Dynamic Electron Spin Polarization (CIDEP) effects.

2. Measurement of the FT-EPR spectra from benzoquinone anions (BQ^-) generated by pulsed-laser induced electron transfer from Zn tetraphenylporphyrin (ZnTPP) both in homogeneous solution and in micellar solutions.
3. Study of the time evolution of $[ZnTPP^+...DQ^-]$ radical pairs. (Here DQ denotes duroquinone.)

RESULTS

1. FT-EPR Data Analysis Software

In FT EPR measurements the photochemical 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 (15 ns) microwave pulse. Following this pulse the Free Induction Decay (FID) of the magnetization in the plane perpendicular to the magnetic field direction is measured. The FID represents the time-domain representation of the paramagnetic species present at the time of the microwave pulse.

Compared with the direct-detection cw EPR technique, FT EPR has a number of advantages. First, the time evolution of the signal is probed in the absence of a perturbing microwave field. This simplifies the data analysis methodology and gives a more direct insight into the factors that affect growth and decay of the signals. Second, the method is much more sensitive so that its range of potential applications is broader than that of the

cw method.

Of interest is the delay-time dependence of the amplitudes of all hyperfine components in the EPR spectrum. In addition, the frequencies, phases, and linewidths (T_2) of these components carry information pertinent to the electron transfer process. It was found that simple Fourier transformation of the time-domain signals does not give reliable numerical data. This is because instrument deadtime can have a strong effect. Also, linewidth and phase measurements are difficult to carry out in frequency domain spectra. For this reason software was developed for the analysis of the FID's with the linear prediction - singular value decomposition (LP/SVD) method. LP/SVD analysis of an FID gives frequency, amplitude, phase, and damping (T_2) of all hyperfine components in the spectrum. Application on a series of FID's obtained with different laser pulse-microwave pulse delay-time settings generates a data array which gives direct access to information on the delay-time dependence of all spectral parameters.

As noted earlier, the time dependence of the parameters that characterize the EPR spectrum of an electron transfer product reflects the chemical kinetics as well as CIDEP effects. Spin polarization can be generated by transfer of triplet precursor spin polarization to product molecules (Triplet Mechanism CIDEP). It can also be caused by the spin-state evolution that takes place during the lifetime of acceptor-donor radical pairs (Radical Pair Mechanism CIDEP). A quantitative analysis of TM and RPM CIDEP effects and how they are affected by changes in structure of donor and/or acceptor and solvent medium

gives an insight, at the molecular level, into the electron transfer mechanism. A kinetic model was developed that made it possible to quantitatively relate the EPR signal development over a time regime extending from 100 nanosecond to 100 μ s to all the parameters that control the spin state dynamics. The model was tested on FT-EPR data from the acetone ketyl radical formed by photo-induced hydrogen abstraction from 2-propanol.

2. ZnTPP-benzoquinone

The photo-induced electron transfer from ZnTPP to benzoquinone has been subject of a number of optical as well as magnetic resonance studies. The fact that a great deal is known about the mechanism and kinetics of the reaction makes it a suitable model system for the application of FT EPR. Of interest is the additional insights given by the fact that the time evolution of the signal reflects spin state dynamics in precursor triplet state molecules and radical pairs.

A detailed kinetic analysis of FT-EPR signals from the benzoquinone anion formed in electron transfer from photo-excited triplet ZnTPP in ethanol was completed. It gives information on the characteristics of the ZnTPP triplets and radical pair generated CIDEP. A solvent change from ethanol to acetonitrile shows that the EPR spectra reveal subtle solvation effects. It is apparent from the data that the presence of stoichiometric quantities of hydrogen bonding solvents changes spectral as well as kinetic parameters. The data base generated by the study of this model system is being used in the interpretation of results obtained with measurements of electron transfer from

cationic and anionic porphyrins in ethanol-water mixtures.

FT EPR has been used as well to investigate the changes induced in electron transfer dynamics and mechanism when reactants are solubilized in micellar solutions. Micellar media are of interest because the spatial arrangement of donor and acceptor molecules may be such that back electron transfer is strongly inhibited. It is found that the magnetic resonance data can be used to get information on the spatial distribution of reactants and redox ion products. So far measurements have been made on ZnTPP/BQ in solutions of cationic and neutral surfactants. On-going work will deal with the effect of charged substituents on donors and/or acceptors.

3. Radical pairs

FT EPR measurements on ZnTPP/BQ and ZnTPP/DQ revealed significant phase shifts of the FID's for short delay time settings (<200 nanoseconds). This effect can be attributed to the presence of what have been labeled spin correlated radical pairs (SCRPs) in solution at the time the microwave pulse is delivered. The exchange interaction between the two unpaired electrons in the pair causes a characteristic 90° phase shift of the transverse magnetization. This is reflected in the FID of the radicals after cage escape. With the LP/SVD method of data analysis this dispersive signal component can be separated from the in-phase signal component. The time dependence of the amplitude of this signal contribution reflects the kinetics of formation and decay of radical pairs.

A detailed study was made, in collaboration with Dr.

Dinse at Dortmund University, of the SCRP lifetime for ZnTPP/DQ in ethanol at various temperatures. It was found that the lifetime is considerably longer than that expected if cage escape is diffusion controlled. The temperature dependence of the SCRP lifetime indicates that the pairs are "trapped" in a shallow potential well generated by the Coulombic interaction between the redox ions. Signals from SCRP's were observed as well in the case of the acetone/2-propanol system. In this case the pair consists of two (identical) neutral radicals. In accordance with expectations it was found that its lifetime is diffusion controlled.

The lifetime of the radical pair is expected to play an important role in determining the photo efficiency of cage-escape product formation. The fact that FT-EPR measurements can be used to directly probe radical pair characteristics, therefore, is of considerable interest. In future work the effect of solvent dielectric constant on SCRP lifetime will be investigated. The effect of charged substituents will be studied as well.

PUBLICATIONS

M. Plüschau, A. Zahl, K. P. Dinse, and H. van Willigen,
"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.

P. R. Levstein, H. van Willigen, and M. Ebersole,
"FT-EPR STUDY OF PHOTOINDUCED ELECTRON TRANSFER IN A
MICELLAR SYSTEM", Mol. Cryst. Liq. Cryst. **1990**, in press.

G. Kroll, M. Plüschau, K. P. Dinse, and H. van Willigen,
"FT-EPR SPECTROSCOPY OF CORRELATED RADICAL PAIRS",
J. Chem. Phys. **1990**, in press.

P. R. Levstein and H. van Willigen, "FT-EPR STUDY OF THE
PHOTOCHEMICAL REACTION OF ACETONE WITH 2-PROPANOL",
J. Phys. Chem. **1990**, submitted for publication.

END

DATE FILMED

02 / 08 / 91