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**MAGNETIC RESONANCE STUDIES OF PHOTOINDUCED ELECTRON
TRANSFER IN HOMOGENEOUS AND HETEROGENEOUS MEDIA**

**PROGRESS REPORT
FOR PERIOD JUNE 1, 1993 - MAY 31, 1994**

**HANS VAN WILLIGEN
UNIVERSITY OF MASSACHUSETTS AT BOSTON
BOSTON, MASSACHUSETTS 02125**

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INTRODUCTION

During the past year research has been concerned primarily with the application of cw time-resolved Electron Paramagnetic Resonance (TREPR) and Fourier Transform EPR (FT-EPR) in the study of photoinduced electron transfer reactions. The application of these techniques in this area of research is of interest for a number of reasons:

- Excellent spectral resolution makes it possible to identify paramagnetic molecules unambiguously and to obtain information on interaction with the environment.
- The time development of the spectra generally is strongly affected by Chemically Induced Dynamic Electron Polarization (CIDEP) mechanisms. Identification of CIDEP contributions contributes to the understanding of the reaction involved in free radical formation.
- Data from relaxation measurements can be used to study the effect of temperature and medium on molecular motion.

Topics of research were: (1) the study of oxidative and reductive electron transfer quenching of the photoexcited triplets of C_{60} , (2) the study of the TREPR spectrum of C_{60} triplets in polymer films, (3) the study of the TREPR spectra of porphyrins adsorbed in the pores of silica gel, and (4) the development of instrumentation and software for carrying out pulsed-EPR measurements of electron spin relaxation.

RESULTS

1. Electron transfer quenching of $^3\text{C}_{60}$ (in collaboration with H. Linschitz)

Photoexcited C_{60} in liquid solution gives a narrow EPR signal that has been attributed to triplet state C_{60} . A detailed FT-EPR study of the time development of this signal in the presence and absence of electron transfer quenchers, and of the relaxation characteristics (T_1 and T_2) of the paramagnetic species confirmed this assignment.

In the presence of electron donors, such as hydroquinone (HQ) and tritolylamine (TTA), the triplets lifetime is reduced by electron transfer quenching as is evident from the decay of the $^3\text{C}_{60}$ signal and the appearance of signals from paramagnetic electron transfer products (the neutral semiquinone radical and TTA^+). Since both the precursor triplet and product doublet radicals can be observed, the EPR measurements can give direct information on the efficiency of formation of cage escape products and the effect of solvent polarity on the electron transfer reaction.

Currently, measurements focus on triplet C_{60} quenching by electron acceptors such as chloranil and tetracyanoethylene. Measured electron transfer rates indicate that in some cases complex formation of acceptor molecules with the solvent has a strong effect on the reaction.

2. TREPR spectra of $^3\text{C}_{60}$ in a polymer film

The EPR signal from $^3\text{C}_{60}$ is strongly dependent on molecular motion because of the anisotropic electron spin dipole-dipole interaction. In fluid solution at room temperature the triplets give a signal with a linewidth of less than 0.1 mT because the interaction is averaged out by molecular motion and interconversion between

Jahn-Teller states. In a rigid matrix at low temperature the spectrum covers a range of more than 20 mT. The extreme sensitivity to molecular motion can be used to investigate how molecular motion of C_{60} is affected by incorporation in a solid matrix. This is of some interest because of possible applications as a photosensitizer in heterogeneous media. Studies in progress deal with C_{60} in polymethacrylic acid film. Results obtained so far show that the triplet state molecules have a great deal of motional freedom. Future work will explore the possibility of photoinduced electron transfer between molecules captured in the polymer matrix or across the boundary between polymer and solvent.

3. TREPR study of porphyrin triplets adsorbed on silica gel

In preliminary work it was shown with FT-EPR measurements that electron transfer from photoexcited porphyrins to benzoquinone, where both reactants were adsorbed in the pores of silica gel, could take place if the pores were filled with solvent. With TREPR studies of the porphyrin triplets adsorbed in silica gel pores information will be obtained on the mobility of these molecules under various conditions. This will aid in the interpretation of the electron transfer data.

4. Development of instrumentation and software for relaxation measurements

Until recently, the pulsed-EPR spectrometer build at the University with funding from DOE was used exclusively for FT-EPR measurements. It became evident that the interpretation of CIDEP effects would be aided if information on relaxation times could be obtained. Of course, it has been known for a long time that relaxation measurements also can provide valuable insights with respect to molecular motion of paramagnetic molecules. For this reason, the pulsed-EPR

instrument was programmed to carry out spin-lattice relaxation time and phase memory time measurements. These capabilities were used in the study of $^3\text{C}_{60}$.

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