Title

MAGNETIC FIELD EFFECTS ON PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS

Permalink

https://escholarship.org/uc/item/8vt6s4hz

Authors

Wamser, C.C.
Otvos, J.W.
Calvin, M.

Publication Date

1981

LBL-12361
UC-63a

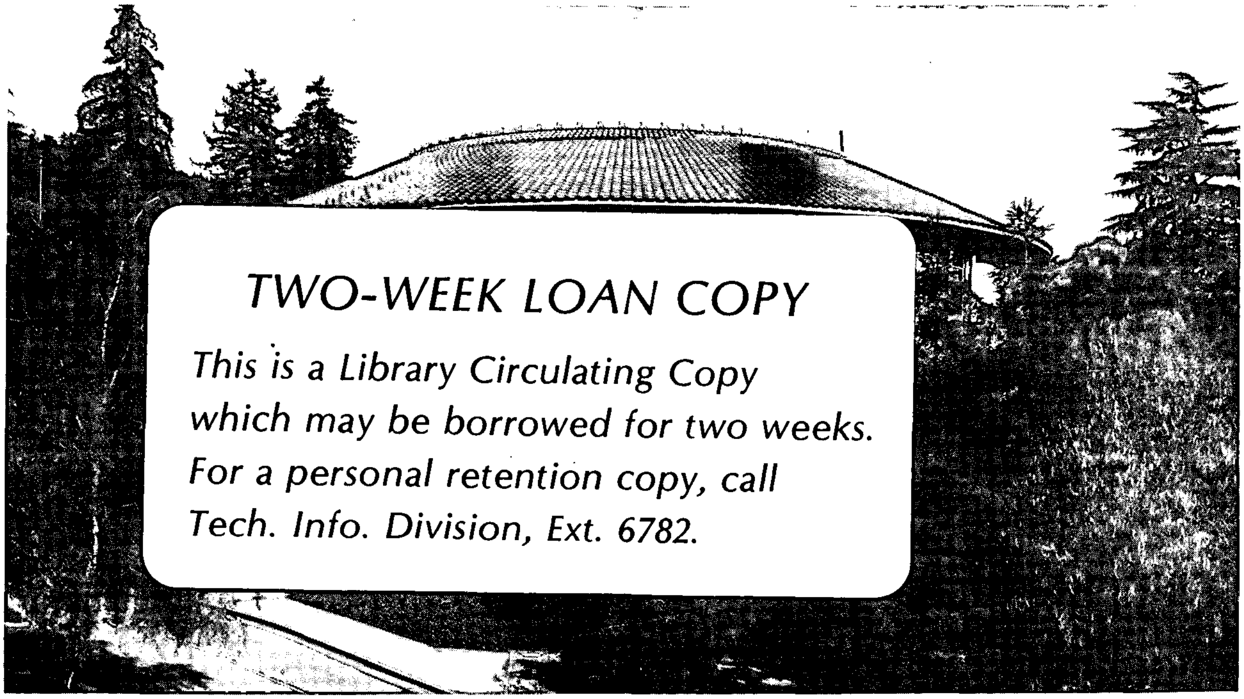
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL BIODYNAMICS DIVISION

MAGNETIC FIELD EFFECTS ON PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS

Carl C. Wamser, John W. Otvos, and Melvin Calvin

January 1981



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

MAGNETIC FIELD EFFECTS ON PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS

Carl C. Wamser, John W. Otvos, and Melvin Calvin

Laboratory of Chemical Biodynamics
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

January 1981

Abstract: Reactions which proceed through the intermediacy of a triplet radical pair can be affected by the application of an external magnetic field of relatively low intensity (100-1000 gauss). Since many of the photoreactions utilized in solar energy schemes are electron transfer reactions involving triplet radical pairs, experiments were performed with representative photoreactions to determine if such effects could enhance reaction efficiency. No magnetic field effects were observed in any of the experiments, which included the photosensitized reduction of dimethyl viologen sensitized by $Ru(bipy)_3^{+2}$ or by various porphyrins, in homogeneous aqueous solution or in reversed micelles (water in toluene) or on silica particles. Apparently the magnetic field effects reported in the literature are observable only under specific conditions. Under the conditions normally utilized for typical solar energy photoreactions, magnetic field effects do not appear to be useful for optimizing efficiency.

The work was supported, in part, by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract W-7405-ENG-48.

Table of Contents

Introduction: Two electrons that are unpaired (in different orbitals) but correlated (interacting with one another) may exist as either a singlet state or a triplet state depending upon the relative orientation of the angular momenta of the electron spins. Any interconversion between a singlet and a triplet state is called an intersystem crosssing and requires either a spin rephasing or a spin inversion. Since most molecules are singlet ground states, with paired electrons, photochemical processes which involve triplet states as intermediates necessarily include an intersystem crossing step to generate a triplet excited state from a singlet excited state. Since the return of the triplet state to a ground state, either a product ground state or regeneration of the starting material, requires another intersystem crossing, triplet states typically have longer lifetimes than the corresponding singlet states, and this longer lifetime is often helpful in facilitiating photochemical reactions.

The photochemical reactions used in artificial photosynthesis solar energy schemes are typically electron transfer reactions. When the photoreaction involves a triplet excited state, electron transfer gives a triplet radical pair. Separation of this radical pair is the desired reaction. The requirement for an intersystem crossing to regenerate the ground singlet state should make reverse electron transfer (the back reaction) less favorable from a triplet radical pair than from a singlet radical pair. This will enhance the efficiency of separation of the initial radical pair and to greater overall efficiency of the photoreaction. Figure 1 shows a generalized mechanism for an artificial artificial photosynthesis scheme which involves electron transfer, and which features a correlated triplet radical pair as a key intermediate.

Recent reports in the literature[1-4] have indicated that applied magnetic fields may be an additional parameter available to affect the rates of photochemical reactions, specifically those which involve intersystem crossing. Magnetic field effects are caused by the splitting in energy of the three sublevels of a triplet state in the presence of an external magnetic field. The three spin sublevels of a triplet state may be designated T_+ ($\alpha + \alpha$), T_- ($\beta + \beta$), and T_o ($\alpha + \beta$), where α and β denote the two possible spin angular momenta orientations, and where the singlet state would be correspondingly designated S_o ($\alpha - \beta$). In the absence of a magnetic field, all four levels are essentially degenerate, and this degeneracy tends to facilitate interconversion between the sublevels (including intersystem crossing). In the presence of a magnetic field, the relative energy levels of S_o and T_o remain unchanged and degenerate, but T_+ and T_- move either up or down in energy, depending upon their orientation relative to the direction of the applied magnetic field. The magnitude of the energy separation is extremely small - for example, 0.3 cal/mole for a field of 1000 gauss. Although the magnetic field effect upon the energetics of a chemical reaction is clearly negligible, the

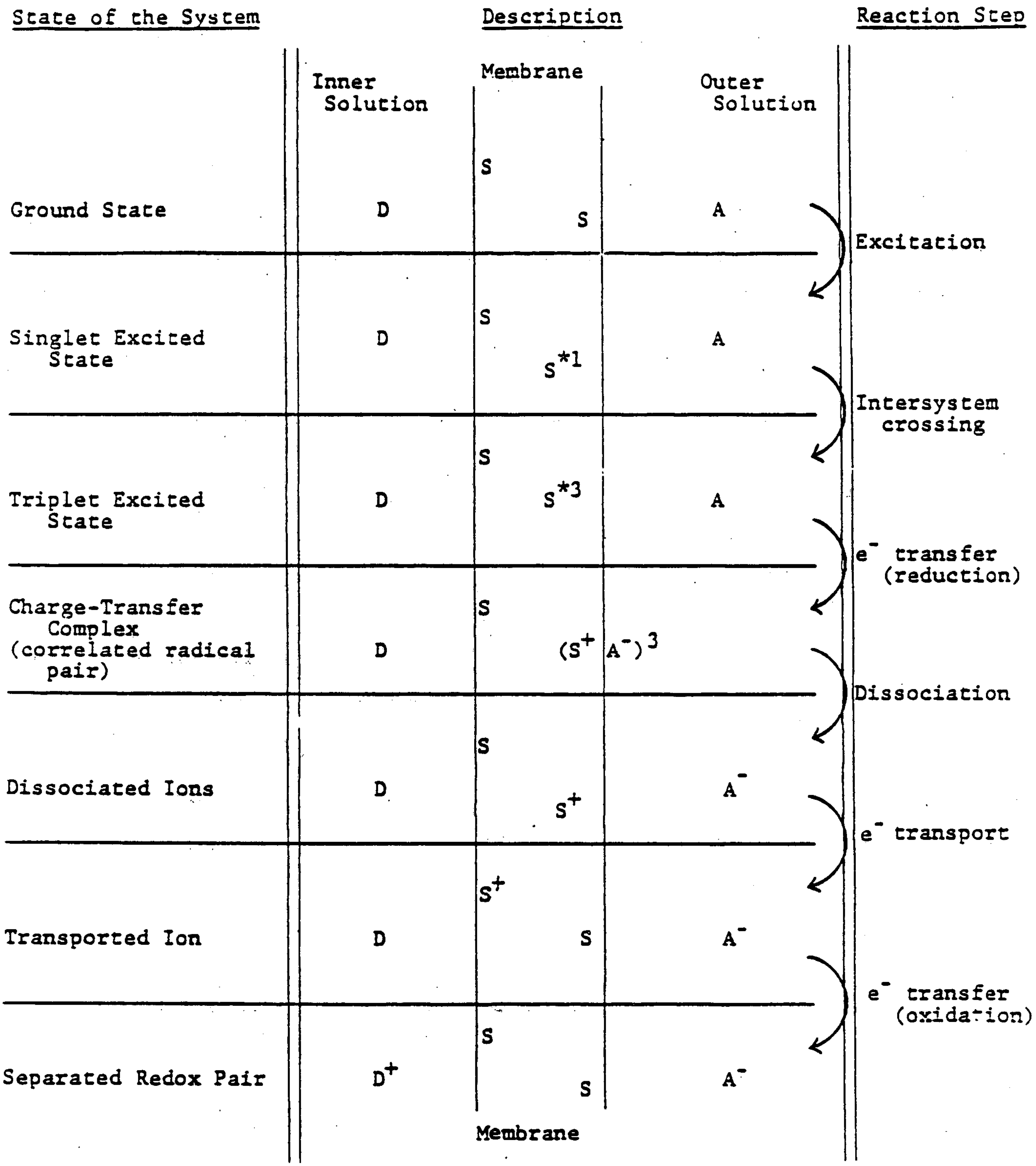


Figure 1

Photosensitized Electron Transfer Across a Membrane Boundary removal of degeneracy can create a substantial entropic effect. Intersystem crossing to a nondegenerate state simply becomes more difficult and this shows up as a reduced frequency factor in the rate constant. Figure 2 illustrates the splitting of the sublevels in an external magnetic field and defines the various rate constants of interest.

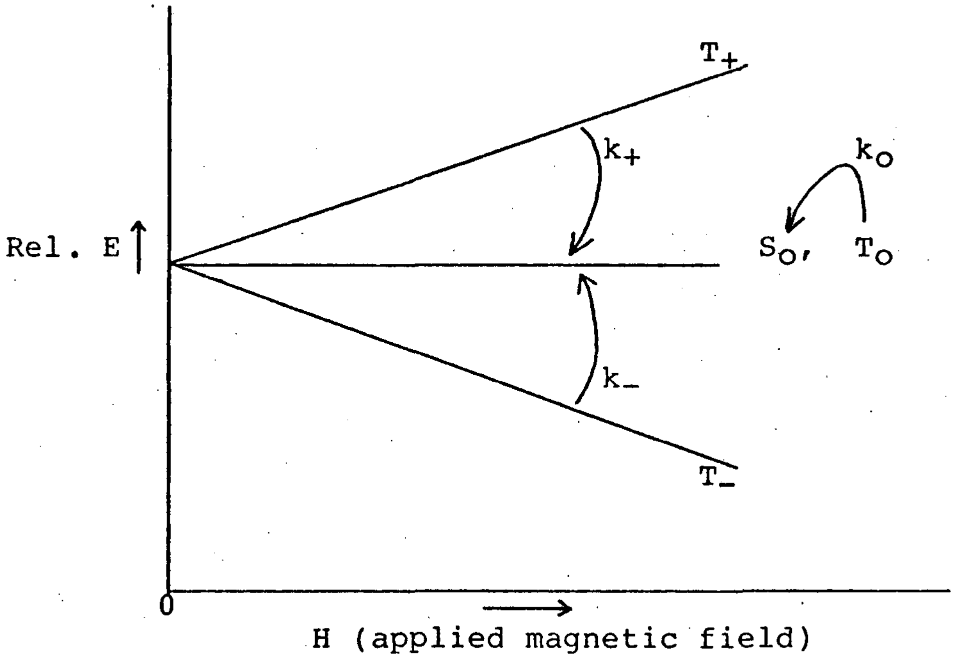


Figure 2 - Energy Levels in an Applied Magnetic Field

k_o = Rate ($T_o \rightarrow S_o$)

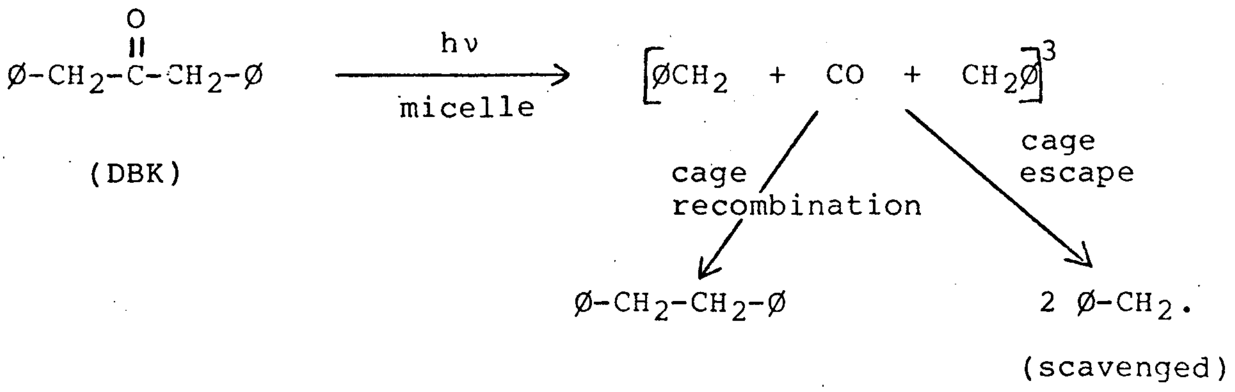
k_- = Rate ($T_- \rightarrow S_o$)

k_+ = Rate ($T_+ \rightarrow S_o$)

No Magnetic Field	Applied Magnetic Field
$k_+ \approx k_-$	k_o unaffected
but $k_o \neq k_+$ or k_-	k_+, k_- decreased

Magnetic field effects reported in the literature have all been observed in micellar systems. The micelle provides a physical containment of the correlated radical pair for a relatively extended time period, thereby enhancing the chances of observing a competitive rate effect. Radical pairs become uncorrelated once they separate, and if rapid separation processes are available, the likelihood of observing small rate effects in competing reactions is reduced.

Turro's initial work dealt with the photolysis of dibenzyl ketone (DBK). Both an external magnetic field effect[2] and a nuclear magnetic isotope effect[5] were observed to affect the relative extent of cage recombination versus cage escape for a correlated pair of benzyl radicals. An initial cage effect of 32% could be reduced to 20% by the application of a modest magnetic field (1000 guass).[2] Cage effects of different magnitudes were observed with C-13 and D-substituted DBK, but these also responded to magnetic field effects in the same range to give a reduction in cage recombination.



A flash photolysis kinetic study by Sakaguchi, et al., has provided specific rate constants for intersystem crossing rates at different applied magnetic fields.[4] Benzophenone was photolyzed in an SDS micelle and the decay of the benzophenone ketyl radical was followed. The ketyl presumably results from hydrogen abstraction from the hydrocarbon chain of the micelle components, a well-known reaction of triplet benzophenone. Thus the benzophenone ketyl and the hydrocarbon radical form a correlated triplet radical pair, encapsulated within a micelle. The decay rate shows two components, a faster rate constant (4×10^6 sec^{-1}) assigned as the rate of recombination from the T_0 sublevel and a slower component (1.6×10^6 sec^{-1}) assigned as the rate of recombination from the T_+ and T_- sublevels. An applied magnetic field (up to 700 gauss) does not affect the fast component but reduces the slow component even further (to 0.9×10^6 sec^{-1}).

Thus these reports of magnetic field effects suggest that such effects may be useful in enhancing the separation of a radical pair. A triplet radical pair is a common feature of many solar energy schemes based on electron transfer photoreactions, and the separation of the initial radical pair is one of the key limitations to the efficiency of such reactions. (Both of these points are discussed in more detail in the accompanying report on kinetics of photosensitized electron transfer reactions).

Experimental: Magnetic field effects were tested on typical electron transfer photoreactions which are commonly used in solar energy schemes. The magnets employed were two alnico horseshoe magnets. The photolysis cell was always a 1 cm square cell placed between the poles of the two magnets in an orientation shown in Figure 3. Measurement of the magnetic field strength was done with a Bell 120 gaussmeter (borrowed from Professor Pines' group) and later with a Bell 240 gaussmeter which had a much smaller probe (available in LCB). Each gave consistent readings of 400-600 gauss in the area within the cell between the poles of the two magnets.

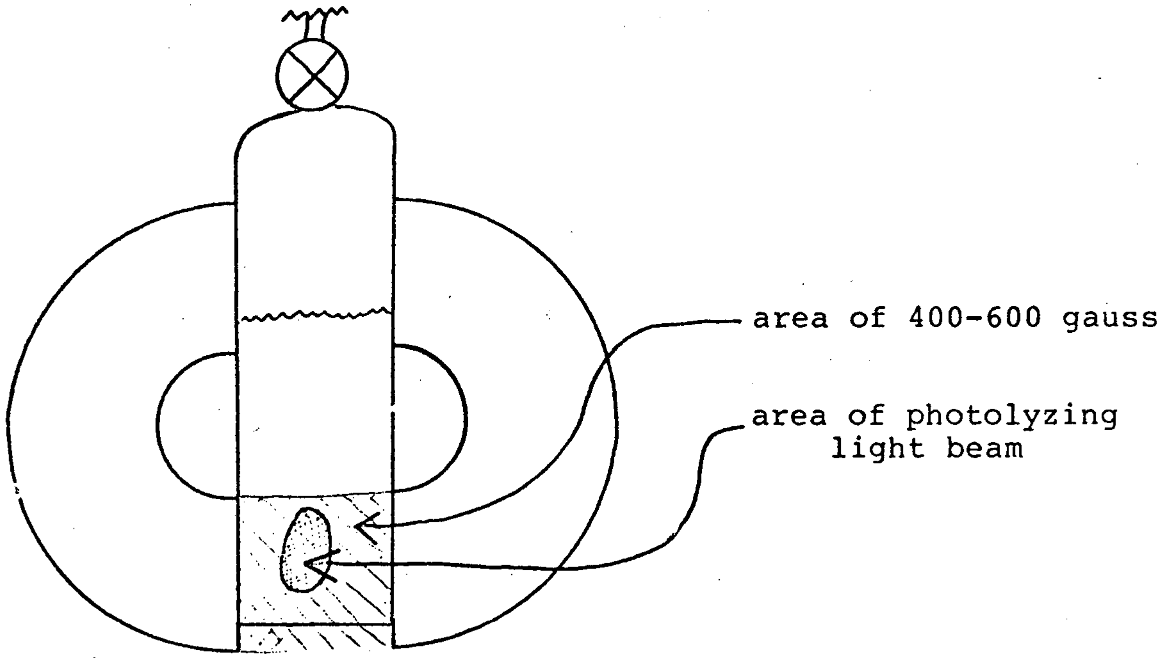


Figure 3 - Arrangement for Photolysis in a Magnetic Field

Samples for the photolysis runs were always deoxygenated by three cycles of evacuation and argon bubbling and closed under positive argon pressure. Control experiments were performed by preparing a double batch of solution and photolyzing equal volumes (typically 3.0 ml) in the same cell in the same location in front of the lamp (Oriel C-50-60 1000 watt xenon lamp), once with the magnets present and once with the magnets absent. In addition, the magnets were occasionally applied during a control run or removed during a magnetic field run to check for any variation in rate. Rates of the photochemical reactions were followed in all cases by spectrophotometric monitoring of the visible absorption of reduced viologen at 602 nm. In none of the experiments was any significant difference in the rates observed between the control and the magnetic field runs.

Homogeneous Systems - A solution was prepared to contain 1×10^{-4} M $Ru(bipy)_3^{+2}$, 1×10^{-3} M propyl viologen sulfonate, and 1×10^{-3} M EDTA. Irradiation was with light unfiltered except for $CuSO_4$ and pyrex. There was no difference in the rates with and without the magnetic field present. It was considered that ruthenium, as a heavy atom with high spin-orbit coupling, may interfere with the desired effects on intersystem crossing rates.

A solution was prepared to contain 1.2×10^{-5} M tetracarboxyltetraphenylporphyrin (TCPP), 0.08 M EDTA, and 0.01 M MV^{+2}, buffered to pH 9.2. Irradiation was with light filtered only by $CuSO_4$ and pyrex. In this reaction there was a suggestion that the initial rate was faster with magnets present. During the first two readings, at one-half and one minute, the O.D. (730nm) rose to 0.185 and 0.260 with magnets and only 0.145 and 0.195 without magnets, but the rates were essentially identical thereafter. The reaction was repeated using somewhat different concentrations and a 420 nm interference filter. The rates were identical with and without the magnetic field present.

Reversed Micelle Systems - Water in toluene microemulsions (reversed micelles) were prepared from 2.9 ml of toluene per 0.1 ml of aqueous solution, plus sufficient dodecylammonium propionate surfactant to visibly clarify the emulsion upon vortex mixing. Thiophenol was used as the electron donor in the bulk organic phase, with the aqueous micelle containing the sensitizer and MV^{+2}.

A microemulsion was prepared to contain an aqueous solution which was 3 x 10^{-3} M in both $Ru(bipy)_3^{+2}$ and MV^{+2} (equivalent to 1 x 10^{-4} M in bulk concentration) and buffered at pH 4.5. The toluene phase contained 0.1 M thiophenol. Irradiation was with $CuSO_4$ and pyrex filtering only. The rates of MV^+ production were essentially identical with and without the magnetic field.

A microemulsion was prepared to contain an aqueous solution of 2 x 10^{-4} M TCPP (bulk concentration 6 x 10^{-6} M) and 3 x 10^{-2} M MV^{+2} (bulk concentration 1 x 10^{-3} M), buffered at pH 7. The toluene phase contained 0.01 M thiophenol. Irradiation was through a 420 nm interference filter. There was no difference in rate with or without the magnets present.

Silica Particles - In collaboration with Itamar Willner, one experiment was performed using silica particles as the medium for attachment of the sensitizer. A solution of 0.1% negatively charged silica particles were prepared in aqueous solution at pH 10. A positively charged porphyrin sensitizer was used: zinc tetra(4-methylpyridinium)porphyrin, $(ZnTMPyP)^{+4}$, at a concentration to generate O.D. = 0.45 at λ_{max} = 420 nm. The electron donor was 1×10^{-3} M triethanolamine and the acceptor was 1×10^{-3} M propyl viologen sulfonate (PVS), a neutral acceptor which becomes negatively charged after electron transfer and therefore repelled from the silica and the sensitizer. Irradiation was with $CuSO_4$ and a 430 nm cut-off filter. There was a slight difference in rates with the initial rate somewhat faster in the presence of a magnetic field, but the difference is not outside of experimental error.

Discussion: Although the literature provides cases for which magnetic field effects can offer improvements in reaction efficiency up to a factor of about 2, it does not appear that these effects are detectable under the conditions typically used for solar energy electron transfer photoreactions. The magnetic field effect should depress the rate of the reverse electron transfer within the initial radical pair, and this is considered one of the key steps which limits the overall reaction efficiency. The lack of a significant effect must mean that other competing processes for deactivation of the radical pair remain much faster than the portion which is susceptible to magnetic field effects.

Acknowledgement: This work was performed during the fall semester of 1980 while Carl C. Wamser was on sabbatical from California State University, Fullerton. The work was supported, in part, by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract W-7405-ENG-48.

References:

1. N.J. Turro and B. Kraeutler, *Accts. Chem. Res.*, **1980**, *13*, 369.
2. N.J. Turro, M.-F. Chow, C.-J. Chung, G.C. Weed, and B. Kraeutler, *J. Amer. Chem. Soc.*, **1980**, *102*, 4843.
3. N.J. Turro, M.-F. CHow, C.-J. Chung, and C.-H. Tung, *J. Am. Chem. Soc.*, **1980**, *102*, 7391.
4. Y. Sakaguchi, S. Nagakura, and H. Hayashi, *Chem. Phys. Lett.*, **1980**, *72*, 420.
5. N.J. Turro and B. Kraeutler, *J. Amer. Chem. Soc.*, **1978**, *100*, 7432.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720