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Excited State Electron Transfer in Systems with a Well-Defined Geometry

MASTER

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K. J. Kaufmann

School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

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I. Introduction

We have been studying electron donor-acceptor pairs joined with two covalent linkages to form a dimer with a semi-rigid geometry. One of the compounds we have been studying is a cyclophane formed by joining two meso-pyropheophorbide molecules. Three different cyclophanes have been examined: a) one with two magnesium atoms, b) one which contains no metal atoms, c) a third which has only one magnesium atom. A second type of donor-acceptor complex consists of a porphyrin linked to a quinone. The aim of our work has been to understand the conditions that lead to efficient charge separation in the singlet excited state and the conditions that will stabilize the charge transfer state for a period long enough to extract it to do useful chemical work.

We have used a variety of techniques to understand the dynamics of these molecules. Steady state absorption, steady state fluorescence, circular dichroism, and picosecond fluorescence measurements have been used to determine the amount of interaction between the two macrocycles in the ground and the excited state. Time resolved picosecond absorption spectroscopy was used to determine the extent of charge separation in the singlet excited state and also to detect the nature and the yield of the products formed due to wasteful processes.

II. Photophysics of the Cyclophanes

The Q_Y transition dipoles of the cyclophanes are nearly perpendicular. Thus, Wasielewski et al.[1] noted that the failure to observe the change in the absorption spectrum of the dimetal cyclophane with respect to the monomer is consistent with the first order perturbation treatment of the exciton interaction between the two monomers. A careful examination of the absorption spectra and the emission spectra of the other two cyclophanes suggests that the two macrocycles do not act as two completely isolated chromophores. We have noticed a slight broadening of the absorption and the emission spectra of the cyclophanes in comparison to the monomers. The emission of the metal free cyclophane contains a red tail which is not observed in the monomers.

To obtain addition information on the extent of interaction between macrocycles in the three cyclophanes, we developed a new technique for measuring the relative radiative rates for the fluorescing states. Briefly the method involves measuring the instantaneous emission from the chromophore using a streak camera. When combined with a simultaneous measurement of the intensity of the light used to excite the sample, it is possible to determine the ratio of emission to the number of excited singlet states, hence a relative radiative decay rate. Using this technique the relative radiative rates for the monomers and dimers have been measured. The relative rates can be normalized to a radiative rate (k_r) determined from the fluorescence lifetime and the fluorescence quantum yield of the monomers. These numbers are presented in Table I. For all of the dimers the radiative rates are smaller by about a factor of 2 compared to the monomers. We feel that this decrease in radiative rate is due to an exciton interaction.

A simple exciton calculation[2] was carried out. It was found that if the transition dipoles are at angles about 15-20° away from the orthogonal orientation, a decrease in the rate of about 2 should be observed. However,

the simple calculation indicates that the amount of exciton splitting that should be observed is much larger than what we have found in the steady state absorption and emission studies. This indicates that a more sophisticated theoretical treatment is needed to interpret the exciton interaction in these chromophores.

Another technique that we have started to use to determine the degree of exciton interaction is circular dichroism. Preliminary measurements on the monometal cyclophane indicate the presence of a very weak exciton interaction, much weaker than the simple theory would indicate for a factor of two reduction of the radiative rate. We are presently carrying out additional circular dichroism measurements in all the cyclophanes for several solvents to determine to what degree exciton interaction makes itself felt in terms of a CD spectrum.

III. Photochemistry of the Cyclophanes

The metal free dimer appears to undergo no photochemistry in the singlet excited state because the fluorescence lifetime and the triplet yields are nearly independent of the dielectric strength of the solvent. The dimetal cyclophane appears to show some shortening of the fluorescence lifetime in solvents of moderate dielectric strength such as butyronitrile. The time response of the fluorescence from the monometal cyclophane is strongly dependent on the dielectric strength of the solvent. In all solvents other than toluene the fluorescence decay of the cyclophane with one metal atom is biphasic in behavior. The shortlived component decays in 300 ± 100 picoseconds in all the solvents that have been studied. The long component is somewhat difficult to analyze with our streak camera. It has a lifetime on the order of 2-3 nanoseconds. As the dielectric strength is decreased the ratio of the short to long component increases reaching a maximum at a dielectric strength of about 37 (in dimethyl formamide) and then increasing again as the dielectric strength is raised.

In butyronitrile lowering the temperature has an effect which is equivalent to decreasing the dielectric strength. As the temperature is lowered the amount of fast component compared to the slow component decreases. Presumably this is due to an increase in the dielectric relaxation time of the solvent as the temperature is lowered. Emission from the monometal cyclophane in butyronitrile at 77K is very similar to that observed from toluene at room temperature.

Time resolved absorption studies in the bleaching region of the difference spectrum (655 nm) and in the region where a positive absorbance change is observed (445 nm) were carried out in five different solvents. In all cases, there was a residual absorbance change 30 ns after the laser flash which was assigned to the triplet state of the cyclophane. From the ratio of the

instantaneous bleaching to the long term bleaching a triplet yield could be estimated. These triplet yields are found in Table I. In all cases the absorbance decayed as a single exponential. The decay times were always longer than the decay time of the short component of the fluorescence.

The singlet absorbance decay time coupled with the biphasic fluorescence decay were interpreted in terms of a two state model. After excitation the molecule resides in a singlet state. The short fluorescence component represents decay of the singlet state to a charge transfer state. This charge transfer state decays by a recombination of the charges back to the ground state or by returning to the emissive singlet state. The long term fluorescence is due to this second pathway and it monitors the lifetime of the charge transfer state. Computer simulation of this model gave values for the rate of formation and decay of the charge transfer state. In all systems the rate of electron transfer was found to be exceedingly slow on the order of 2-4 x $10^9 sec^{-1}$ and the decay time of the charge transfer state was found to be on the order of $10^9 sec^{-1}$.

The most important conclusion of the work that we have carried out on the cyclophanes is that electron transfer is slow even when the donor and the acceptor are at a small distance. Presumably this is due to the fact that there is an orientation as well as a distance requirment for the rate of electron transfer.

IV. Photochemistry of the Porphyrin Quinone

In the last two months we have been studying dynamics of a porphyrin connected by two covalent linkages to an anthraquinone molecule. Preliminary data indicate that for the porphyrin quinone complex electron transfer appears to proceed slowly. The porphyrin quinone complex is very unstable in the presence of water or oxygen. The majority of our work with this complex has been devoted to developing techniques to assure that it does not decompose during the experiment and that indeed the samples we are dealing with are pure. We have made great strides in this and have found that when handled properly the complex does not decay after more than 100 excitations of the laser.

V. Time and Effect of the Principal Investigator

The principal investigator devoted 33% of his time to the project. He is expected to devote 33% of his time to the project for the remainder of the contract.

VI. Publications Prepared under This Contract

1) Electron Transfer Reaction in Bis-Chlorophyll Cyclophane Models of Photosynthetic Reactions, by Robert E. Overfield, Michael R. Washielewski and Kenneth J. Kaufmann, J. Am. Chem. Soc., submitted for publication.

2) The Photophysics of Rigid Bis-Chlorophyll Cyclophane Models of Photosynthetic Reaction Centers, by Robert E. Overfield, Michael R. Wasielewski and Kenneth J. Kaufmann, J. Am. Chem. Soc., submitted for publication.

VII. Persons Working on the Contract

1) R. E. Overfield (Postdoctoral Fellow) May - July, 1980
2) Avigdor Scherz (Postdoctoral Fellow) October, 1980 - April, 1981
3) Cindy Teeters (Graduate Student) September 1980 - April, 1981

VIII. Residual Funds

No funds are expected to remain at the expiration of the contract.

References

1) M. R. Wasielewski, W. A. Svec, and B. T. Cope, J. Amer. Chem. Soc. 100, 1961 (1978).

2) I. Tinoco, Rad. Res. 20, 133 (1963).

Table I

	Toluene				Dichloromethane				Butyronitrile			
	τ_f (nsec)	ϕ_f	k_R ($\cdot 10^{-7}$ sec^{-1})	ϕ_T	τ_f (nsec)	ϕ_f	k_R ($\cdot 10^{-7}$ sec^{-1})	ϕ_T	τ_f (nsec)	ϕ_f	k_R ($\cdot 10^{-7}$ sec^{-1})	ϕ_T
Methyl mesopyrochlorophyllide a	7.5	0.60	8.0	--	7.0	0.56	8.0[a]	--	11.0	0.50	6.0	0.40
Methyl mesopheophorbide a	8.0	0.40	6.0	--	7.0	0.46	5.0	--	10.0	0.43	3.9	0.65
Nonmetal Cyclophane	8.0	0.20	3.5	0.45	6.0	0.31	4.2	0.3	6.0	0.33	3.5	0.40
Monometal Cyclophane	6.5	0.17	2.7	0.45	1.5[b] [0.31, 2.6][c]	0.06	4.0	0.02	1.0[b] [0.29, 2.5][c]	0.04	4.1	0.10
Dimetal Cyclophane	8.0	0.26	4.6	0.45	6.3	0.36	6.3	0.40	3.5[b]	0.22	3.8	0.15

a) This value was calculated from ϕ_f and τ_f, and used as a normalizing factor.

b) Best single exponential fit to the fluorescence decay.

c) Best fits to dual exponential.

Table II

Decay Rates Determined by Computer Simulation

Solvent	Rate of Formation of Charge Transfer State (sec^{-1})	Rate of Decay of the Charge Transfer State to the Ground State (sec^{-1})
Methylene Chloride	2×10^9	1×10^9
Butyronitrile	3×10^9	1×10^9
Dimethylformamide	4×10^9	2×10^9
MethylFormamide	4×10^9	2×10^9