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The Triplet State of Chlorophylls[1]

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Abstract: The triplet state zero-field splittings and rates of intersystem crossing for the individual triplet spin sublevels in chlorophyll a, chlorophyll b, and zinc-substituted chlorophylls are presented. Whereas there are only small differences in zero-field splitting parameters among the chlorophylls, their kinetics show significant differences. The general trends in the chlorophyll intersystem crossing rate constants of the triplet spin sublevels may be explained qualitatively by a consideration of the one-center spin–orbit and spin–vibronic coupling activity of the chlorophyll ring system and the effect of side-chain substituents on these coupling mechanisms.

I. Introduction

An understanding of the properties of the triplet state of chlorophylls as revealed by EPR studies is of importance from several points of view. First, since chlorophyll molecules contain large conjugated units, the mechanisms of intersystem crossing active in these molecules and their derivatives provide new tests for existing models of radiationless transitions in multi-ring organic systems. For studies of triplet state intersystem crossing in organic molecules, magnetic resonance spectroscopy has proven to be a most useful tool.[2-5] Second, in recent low-temperature EPR experiments on both the intact cells of photosynthetic bacteria and the reaction centers extracted from the cells, photoexcited triplet state EPR signals have been observed under conditions where electron-transfer processes have been blocked by chemical reduction of the electron acceptors.[6-8] These experiments have renewed interest in the possible role of the excited triplet state of chlorophylls in the initial photophysical processes of photosynthesis, although further work is necessary to clearly identify the function of the triplet state in photosynthetic mechanisms.[9] Finally, since triplet states are paramagnetic, an understanding of their magnetic properties and the changes which can occur in these properties would allow the use of the triplet state as a magnetic probe into chlorophyll-containing systems, providing information concerning the structure and molecular interactions within such systems. As has been shown in previous work from our laboratories,[10,11] the population and decay of chlorophyll (and derivatives) triplet states are sensitive to relatively small changes in molecular structure and surrounding environment. A characterization of the factors influencing chlorophyll triplet dynamics in isolated molecules is useful in understanding the changes in triplet properties which occur in more complex chlorophyll systems.

In the present work we attempt to detail the general features of chlorophyll triplet state intersystem crossing as revealed through EPR measurements over a range of temperatures, in varied solvent systems, and with metal center and substituent changes in the chlorophyll molecule. The methods used to obtain the data presented for discussion are high-field EPR on chlorophyll systems showing spin polarization[11] and zero-field optically detected EPR,[10,12] both of which have been detailed in previous publications from our laboratories. The discussion presented in this paper attempts to provide a description of the mechanisms active in the intersystem crossing of chlorophyll molecules and the effect of intra- and intermolecular interactions on these mechanisms.

II. Results and Discussion

A. The Zero-Field Splittings. Table I contains the triplet state spin Hamiltonian parameters $|D|$ and $|E|$ for the mole-

Table I. Zero-Field Splitting Parameters of the Lowest Triplet States of Chlorophylls

	$\|D\|$, cm^{-1}	$\|E\|$, cm^{-1}
Chlorophyll a[a]	0.0280 ± 0.0003	0.0038 ± 0.0003
Chlorophyll b[a]	0.0320 ± 0.0010	0.0041 ± 0.0006
Pheophytin a[b]	0.0341 ± 0.0005	0.0033 ± 0.0003
Pheophytin b[b]	0.0358 ± 0.0010	0.0046 ± 0.0005
Zn chlorophyll a[a]	0.0306 ± 0.0003	0.0042 ± 0.0003
Zn chlorophyll b[a]	0.0328 ± 0.0003	0.0032 ± 0.0003

[a] In *n*-octane at 2 K. [b] In MTHF at 103 K.

cules to be discussed. Zero-field splittings for the pheophytins have not previously been reported; the chlorophyll values are in agreement with those reported by several previous high-field EPR measurements.[13,14]

Both pheophytin a and pheophytin b exhibit larger $|D|$ values than the corresponding metal-substituted chlorophylls. Such a difference has also been noted in a comparison of free-base porphyrins and their metal salts,[15,16] although the difference is not as pronounced in the chlorophylls. The difference in $|D|$ between metal-free and metal-containing chlorophylls presumably reflects restricted delocalization around the chlorin ring system when the central protons are present.

The zero-field splitting parameters in Table I show a consistent trend when one compares molecules with the chlorophyll a structure with those of the chlorophyll b structure (see Figure 1). In each case the molecule derived from the chlorophyll b structure has a larger $|D|$ value than its counterpart with the chlorophyll a structure, the difference being smaller for pheophytin a and b than the corresponding chlorophylls. Since the substituent change on the chlorin ring involves the presence of a CHO in chlorophyll b instead of the CH_3 group found in chlorophyll a, the electron-withdrawing nature of the aldehyde substituent on the chlorophyll ring must decrease the extent of triplet delocalization around the ring system. This produces a somewhat greater electron spin density in the vicinity of the CHO unit, resulting in an increased spin-spin interaction in molecules with the chlorophyll b structure. Overall, the difference among zero-field parameters for the compounds listed in Table I are not large and do not provide the differentiation that one might desire in using these molecules as photoexcited probes of photosynthetic systems.

B. The Intersystem Crossing Rates. Table II presents the results of all experiments performed on intersystem crossing dynamics of chlorophylls in the two laboratories including data which had been previously published.[10,11,27] Perhaps the most obvious feature of the data presented in Table II is the fact that, unlike the zero-field splittings, the triplet intersystem crossing rate constants are highly sensitive to detailed changes in the structure of the molecule. Understanding the differences among these values and the changes which occur as one examines the molecules in different environments may prove to be the most valuable feature of triplet state EPR measurements in vitro.[14]

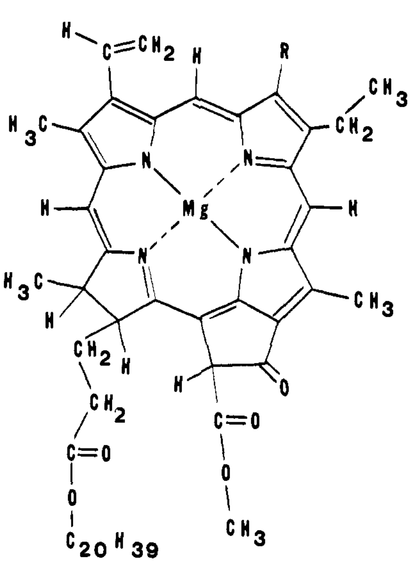

Figure 1. The molecular structure of chlorophyll. In chlorophyll a R is a CH_3 group; in chlorophyll b R is a CHO group.

The most general trend in the intersystem crossing rates in Table II is the dominance of the *x* and *y* (the arbitrarily designated in-plane molecular axes) spin sublevels in the deactivation of the triplet states of all the systems listed, with the exception of the zinc-substituted chlorophylls. The trend is also observed in the relative populating rates into the triplet spin sublevels. These data suggest that the intersystem crossing of chlorophyll a and b may be described in terms of models advanced for radiationless transitions in planar aromatic hydrocarbons,[5,17,18] with spin orbital contributions of the magnesium atom relatively unimportant in the mechanism of triplet population and decay. The rate of deactivation from spin sublevel i of triplet state T_1 into an isoenergetic vibrational level of the ground state, $S_{0,\nu}$, can be written as

$$k_i(T_1{}^i \rightarrow S_{0,\nu}) = (2\pi/\hbar)|\langle T_1{}^i|\Omega|S_{0,\nu}\rangle|^2\rho(E) \qquad (1)$$

where Ω is the level shift operator capable of mixing the states $T_1{}^i$ and $S_{0,\nu}$, and $\rho(E)$ is the density of states. Identification of the mixing operator with the spin-orbit coupling interaction operator and straightforward expansion of $S_{0,\nu}$ and $T_1{}^i$ as pure-spin adiabatic Born-Oppenheimer states leads to a simplification of the rate expression for planar aromatic hydrocarbons which has been shown[17,18] to essentially reduce to the following expression for *x* and *y*

$$k_i(T_1{}^i \rightarrow S_{0,v}) \propto |\delta/\delta Q\langle S_0|H_{so}|T_1{}^i\rangle|^2(\text{F.C.}) \qquad (2)$$

a product of Franck-Condon factor (F.C.) which is the same for all spin sublevels i and a spin-vibronic coupling term $\delta\langle S_0|H_{so}|T_1{}^i\rangle/\delta Q$ (Q is the nuclear displacement coordinate and H_{so} is the spin-orbit coupling operator for the molecule) which depends strongly on the spin-orbit coupling mechanisms available to each triplet spin sublevel. Work by Metz et al. has shown that for planar aromatic systems one would expect that in calculating the spin vibronic coupling term, the spin sublevels corresponding to the in-plane molecular axes (*x* and *y*) associated with a $\pi\pi^*$ triplet state derive their intersystem crossing activity from first-order, one-center spin-orbit coupling with singlet $\sigma\pi^*$ and $n\pi^*$ levels in eq 2, whereas the *z* spin sublevel must utilize higher order one-center terms to gain appreciable activity; therefore, the population and decay rates for the *z* level will always be smaller than for *x* and *y*.[18] The dominance of the *x* and *y* spin sublevels in the chlorophyll triplet state dynamics suggest that spin-vibronic coupling between the chlorophyll $\pi\pi^*$ triplet state[13] and $n\pi^*$ singlet states derived from nitrogen and oxygen centers around the chlorin ring, as well as singlet configurations involving σ electrons, is sufficient to account for the overall observed intersystem crossing kinetics without the necessity of invoking any magnesium involvement in the coupling scheme. In contrast, when Mg is replaced by Zn, a complete redirection of the spin sublevel intersystem crossing activity takes place, leading to a dominance of the *z* (out-of-plane molecular axis) spin sublevel in population and decay. The introduction of zinc into the chlorophyll ring system introduces new one-center spin-orbit coupling terms to the evaluation of the integrals in eq 2, involving mixing of the d orbitals of the zinc atom into the π orbitals of the ring system.[19,21] Such metal-center terms have been shown to enhance the *z* spin sublevel activity in the Zn porphin triplet state

Table II. Rate Constants for Triplet State Deactivation in Chlorophylls (in s^{-1})

Molecule	Solvent	k_x[a]	k_y[a]	k_z[a]	$P_x:P_y:P_z$	Temp, K
Chlorophyll a	*n*-Octane	661 ± 89	1255 ± 91	241 ± 15	0.3:1.0:0.1	2[b]
Chlorophyll a	MTHF	400 ± 150	1250 ± 50	200 ± 50	0.47:1.0:0.2	95[c]
Chlorophyll a	Ethanol	710 ± 100	2710 ± 100	370 ± 30	0.38:1.0:0.15	95[c]
Chlorophyll b	*n*-Octane	268 ± 34	570 ± 54	34 ± 4	0.3:1.0:0	2[b]
Chlorophyll b	MTHF	270 ± 30	570 ± 30	40 ± 20	0.6:1.0:0.07	95[c]
Chlorophyll b	Ethanol	310 ± 30	850 ± 30	65 ± 20	0.4:1.0:0.1	95[c]
Zn chlorophyll a	*n*-Octane	346 ± 50	330 ± 32	660 ± 70		2[b]
Zn chlorophyll b	*n*-Octane	122 ± 13	250 ± 50	622 ± 47	0.3:0.7:1.0	2[b]

[a] Axis designations: x,y refer to (arbitrarily assigned) in-plane molecular axis, z to out-of plane molecular axis. The x axis is taken as the top zero-field spin sublevel, y the middle zero field, the z the lowest energy zero-field level. [b] ODMR experiment. [c] High-field transient EPR experiment.

compared with free-base porphin[19-21] and may be expected to contribute to the Zn chlorophyll triplet state rate constants in a similar manner. The triplet state wave functions for chlorophyll a and chlorophyll b would, therefore, seem best expressed in terms of the electronic structure of the aromatic ring system and its substituents, with little contribution from Mg-centered terms to the spin-orbit coupling. Such a relatively minor role for magnesium has also been observed in the triplet state dynamics of magnesium mesoporphyrin dimethyl ester.[22]

C. Chlorophyll a vs. Chlorophyll b Dynamics. A detailed comparison of the dynamics of the chlorophyll a and the chlorophyll b structures reveals a consistent difference in deactivation rates observed with the structural change of a CHO group (chlorophyll b) for a CH_3 group (chlorophyll a). The chlorophyll b type molecules have consistently smaller decay rate constants than the corresponding chlorophyll a derivative. The difference appears to be an intrinsic feature of CHO substitution, since the differences are retained in a variety of solvents and at widely different temperatures (see Table II). It should be noted that earlier EPR[13] and phosphorescence[23] measurements on the overall triplet state lifetime also reported a longer triplet lifetime for chlorophyll b than for chlorophyll a. Table III shows that for chlorophyll the largest effect of CHO substitution is in the deactivation rate of the spin sublevel corresponding to the out-of-plane molecular axis. There is an appreciable solvent effect on the chlorophyll depopulation rates measured in ethanol, which increases the rates for the three spin sublevels, but, as seen in Tables II and III, the solvent interaction does not alter the essential features of the differences in dynamics between chlorophyll a and chlorophyll b.

A qualitative explanation for these differences may be found in the influence of the aldehyde unit of chlorophyll b on the rate expression given in eq 2. There are several contributions from the CHO unit. One is an overall effect on the triplet state lifetime due to the electron-withdrawing nature of the aldehyde unit; a second is due to the additional one-center spin-orbit coupling contributions from the carbonyl unit to the electronic term in eq 2 for each spin sublevel. If the effect of aldehyde substitution on the chlorophyll ring system is to reduce electron delocalization around the ring, as suggested by the trends in the zero-field splittings, one might expect such a reduction or redistribution of electron spin density in the ring system toward the aldehyde unit to affect those carbon atoms bonded to hydrogen atoms around the ring perimeter. The spin-vibronic coupling terms in eq 2 are expected to be dependent on vibrational modes, Q, which involve C-H motions, as had been shown in calculations on radiationless deactivation of organic molecules[17,24] and, most recently, in experiments on the triplet state deactivation of free-base porphin and zinc porphin.[19] The effect of an electron density reduction around the ring by withdrawal of electrons by the aldehyde group, therefore, will be to reduce the efficiency of radiationless deactivation which is dependent on coupling through C-H vibrations for each of the triplet spin sublevels in the chlorophyll b type molecules, compared with the corresponding chlorophyll a structure, as is observed.

Table III. Ratio of Triplet State Deactivation Rate Constants for Chlorophylls

System[a]	Solvent	$k_x{}^a/k_x{}^b$	$k_y{}^a/k_y{}^b$	$k_z{}^a/k_z{}^b$
Chlorophyll	*n*-Octane	2.5	2.2	7.1
Chlorophyll	MTHF	1.5	2.2	5.0
Chlorophyll	Ethanol	2.3	3.2	5.7

[a] Labels a and b attached to k_i (i = x,y,z) refer to the a and b forms of the photosynthetic pigment.

A second effect of CHO substitution is the spin-orbital coupling activity centered on the aldehyde unit introduced into eq 2. If the CHO unit lies in the plane of the chlorin ring system (as would be expected, since such a geometry would be stabilized by conjugation with the ring system), additional one-center spin-orbit coupling terms at the carbonyl oxygen become available for the rate constant expressions in eq 2. Since the largest one-center spin-orbit coupling terms in carbonyl systems is known to involve coupling of 2p orbitals at the oxygen center through orbital angular momentum operators directed along the C=O bond axis (operators which transform as axial vectors or rotations along the C=O bond),[25,26] these integrals can contribute *only* to the rate expression for k_x and k_y. Thus, the overall effect of aldehyde substitution is to reduce the chlorophyll triplet state deactivation rates, but less for the x and y spin sublevels than for z, since the reduction is modified for the in-plane levels by additional C=O spin orbit coupling terms not available for k_z. The ratios of rate constants given in Table II presumably reflect this situation. In the case of the Zn chlorophylls, the x and y decay rates also show the CHO-induced reduction of the depopulation rate constants for the b form compared with the a form. However, the values of k_z are the same in Zn chlorophyll a and b (within experimental error), presumably due to the dominance in the rate expression for k_z of the spin-orbit coupling interaction involving the metal center in both molecules.

CHO substitution into the chlorin ring and subsequent alteration in electron distribution around the ring may produce effects on the intersystem crossing rates in addition to those described above which would also contribute to the differences in k_i between chlorophyll a and chlorophyll b. A reduction in electron density in the region of the central nitrogen atoms, making them more positive, will shift the $n\pi^*$ levels associated with these nitrogens to higher energy in chlorophyll b compared with chlorophyll a.[28] The shift to higher energy will reduce the spin-orbit mixing of singlet $n\pi^*$ states (which depends on the energy separation of the mixing levels[17]) into the three spin sublevels of T_1. This reduction will lower the intersystem crossing rate constants for each spin sublevel by about the same amount, since each sublevel can couple via one-center spin–orbit coupling terms—the z sublevel at a higher order than x or y[18]—to the nitrogen $n\pi^*$ levels. Thus, the reduced coupling to nitrogen $n\pi^*$ singlet states in chlorophyll b compared with chlorophyll a also contributes to the increased overall lifetime in chlorophyll b and, when combined with the aldehyde spin–orbit coupling, is consistent with the trends in chlorophyll a and chlorophyll b intersystem crossing rates for each spin sublevel. Other possible effects of CHO substitution in chlorophyll b, such as a rotation of principal axes or a distortion away from planar symmetry, may also affect the intersystem crossing rates, but the essential features of intersystem crossing seem adequately explained by the points detailed above.

III. Conclusions

From a comparison of new and published experimental data on the chlorophyll triplet state zero-field splittings and intersystem crossing rates several points emerge which provide a basis for a qualitative understanding of the nature of the triplet state in chlorophyll. The general trends in the chlorophyll intersystem crossing rate constants of the triplet spin sublevels may be explained by consideration of the one-center spin–orbit and spin–vibronic coupling activity of the chlorophyll ring system, as has been done successfully in simple planar aromatic molecules.[5,18] Implicit in this description is the suggestion that the magnesium atom coordinated in the center of the chlorophyll ring system is relatively unimportant in the description of chlorophyll triplet state dynamics. Thus, the chlorophylls prove to be another example of in-plane spin sublevel dominance of the population and decay processes in $\pi\pi^*$ triplet states, as suggested by Metz et al.[19] for the triplet states of *all* planar aromatic systems. In contrast, the replacement of magnesium with zinc results in a redirection of spin sublevel activity away from planar aromatic behavior, due, most likely, to important spin–orbit coupling interactions involving mixing of Zn orbitals into the chlorophyll ring system and a dominance of the z spin sublevel in population and decay.

An important influence on chlorophyll triplet state properties is found in substituent changes on the chlorophyll ring system. Aldehyde substitution on the chlorin ring, forming the chlorophyll b molecule (Figure 1), produces a substantial change compared with chlorophyll a in the depopulation rate constants, which is intrinsically intramolecular as evidenced by the retention of the changes in a variety of solvents and over a wide temperature range. The explanation of the differences in triplet state dynamics upon the relatively small change in structure of substituting a CHO group for a methyl group in chlorophyll b compared with chlorophyll a is again possible within the framework of the spin–vibronic coupling activity of the ring system and the electron-withdrawing ability of the aldehyde unit. The combined effect of reduced electron density within the ring system with a subsequent increase in the $|D|$ values and the change in one-center spin–orbit coupling activity by the introduction of the aldehyde unit results in a reduction of the overall chlorophyll b triplet lifetime compared with chlorophyll a; however, the lifetime reduction is greater for the z spin sublevel (corresponding to an out-of-plane molecular direction) than for the x or y spin sublevels whose intersystem crossing rates are enhanced over that for z by additional in-plane carbonyl spin–orbit coupling terms. Thus, it seems possible to explain qualitatively the essential features of the triplet state EPR investigations of chlorophyll a and chlorophyll b on the basis of the simple models for radiationless transitions in aromatic systems and the electronic nature of the ring substituents.

Further work on the intersystem crossing mechanisms on chlorophyll and pheophytin derivatives and model compounds is presently underway in both laboratories to verify the qualitative schemes proposed for the radiationless processes in the triplet state of chlorophyll, both as an isolated molecule and in aggregated systems.

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