Hypothesis

MECHANISM OF TRIPLET FORMATION IN PHOTOSYNTHESIS VIA HYPERFINE INTERACTION

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Introduction

From picosecond work [1–3] on reaction centers of photosynthetic bacteria a state emerges as an intermediary between the excited singlet of the light absorbing pigment and the appearance of a reduced electron acceptor, X^-. Although there is convincing evidence for the view that this intermediary is a radical ion-pair [3,4], its connection to the triplet-state, detected via ESR [5] is not clear. Furthermore the origin of the triplet's strong spin-polarization [6,7] as observed in high magnetic fields is not understood.

It is the purpose of this paper to explain the almost exclusive population of the (m = 0) polarized triplet-state, T_0, in terms of decoupling of electronic and nuclear spins of a spin-correlated radical pair in the external magnetic field. In zero field, however, the hyperfine interaction is here shown to lead to the population of all three sublevels of the triplet in agreement with the recent experimental finding [8]. It has been conjectured earlier [9] that the radical pair might play a role in the singlet–triplet transition in photosynthetic reaction centers. The hyperfine mechanism given here provides an explicit mechanism for this. Finally we will outline how the hyperfine mechanism can be put to test by a study of the magnetic field-dependence of the absorption of transients (radical ions, triplet-state) within the lifetime of the radical pair.

Discussion

Mechanism of triplet formation by hyperfine interaction

The general kinetic scheme (fig.1) summarizes the more recent results of experiments with reaction centers isolated from *Rps. sphaeroides*.

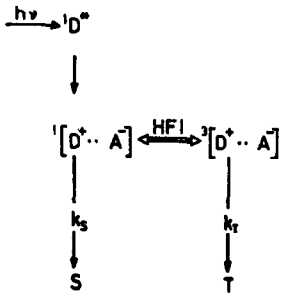

Fig.1. Kinetic scheme for the triplet-formation through hyperfine interaction.

Following the excitation of pigment molecules D into an excited singlet state, $^1D^*$, the radical pair is generated within a few picoseconds [1–3]. D^+ is taken to correspond to an oxidized bacteriochlorophyll dimer (BCl··BCl) [10], A^- to a reduced bacteriopheophytin (BPh) molecule [4]. If the final acceptor X (not indicated in the scheme) has been chemically reduced so as to block the electron-transfer from A^- to X, the radical pair decays with an approximate half-time of 10 ns at 295°K [11] into a metastable-state, obviously identical [3,12] with the triplet identified by ESR [6,9].

It is of crucial importance for the occurrence of magnetic field effects that it be recognized that the orientation of the electron spins is unaffected when the electron is transferred between the molecules, D and A. The spin-lattice relaxation is slower than the reaction rates in fig.1. Thus, the radical pair is initially formed in a singlet-state, $^1[D^+\cdot\cdot A^-]$, from which – to

a first approximation – only the singlet ground-state S of D and A can be reached (with the rate constant k_S). However, due to the hyperfine interaction between electronic and nuclear magnetic moments, the total electronic spin can change, and the radical pair attains an increasing amount of triplet character. The triplet radical pair, $^3[D^+\cdot\cdot A^-]$, decays to the lowest triplet-state T of either D or A (with the rate constant k_T).

A quantitative theory of triplet formation by hyperfine interaction [13] has to start from the spin Hamiltonian, $\mathcal{H}$, used also in the radical pair theory of chemically induced dynamic nuclear polarization (CIDNP) [14].

$$\mathcal{H} = g\beta(\vec{S}_1 + \vec{S}_2)\cdot\vec{H} + \vec{S}_1 \sum_l A_l^{(1)}\cdot\vec{I}_l^{(1)} + \vec{S}_2 \sum_{l'} A_{l'}^{(2)}\cdot\vec{I}_{l'}^{(2)}$$

$\vec{S}_1$ and $\vec{I}_1$ are the electronic and nuclear spins of radical 1, $A_l^{(1)}$ is the hyperfine coupling tensor of the lth nucleus of radical 1. For the radical 2 corresponding notations have been employed. The g-values for BCl and BPh are scalars, close to the one for the free electron [4].

In addition to the external field H, the hyperfine interaction causes small magnetic fields h (of the order of 10–100 G). Since these fields are in general different for $\vec{S}_1$ and $\vec{S}_2$, the mutual orientation of the unpaired electron spins is changed, as shown in fig.2. In the absence of an external field, H, all three components of h are effective, though due to the anisotropy of the A tensors, not necessarily equally strong. This explains why in zero-field magnetic resonance experiments all three sublevels have been found to be populated, with rates differing only by a factor of about 6[8]. These different rates could be attributed to the nitrogen nuclei which usually exhibit a very strong hyperfine interaction for spin-orientations perpendicular to the plane of the system [15]. The exclusive population of the T_0 sublevel, observed in ESR experiments [6,7] is readily understood in terms of the hyperfine mechanism of triplet-formation, taking into account that the x- and y-components of h are averaged out due to the rapid precession in a high external field H (fig.2). This is equivalent to a partial suppression of the spin-precession from the singlet- to the triplet-state by an external field, and is in fact the physical idea underlying the novel experimental approach sketched below. Assuming an effective hyperfine coupling constant of the order of 10 G [4], corresponding to a time constant for the S–T-transition in the radical pair of the order of 10 ns, the hyperfine mechanism could well account for the triplet-yield observed [11].

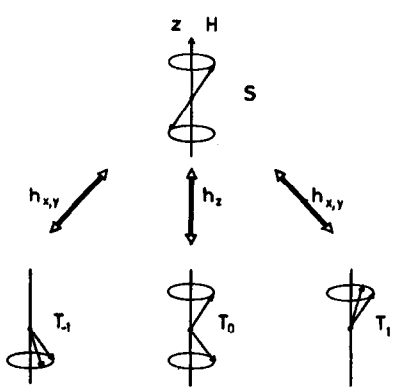

Fig.2. Mixing of singlet-state S with the triplet sublevels, T_{-1}, T_0, T_1, by the components of the hyperfine field h.

Since picosecond experiments have conclusively shown that the first product of the photochemical transformation in bacterial reaction centers is indeed the radical pair and not a triplet-state, the selective T_0-population through spin–orbit coupling inducing intersystem crossing, $^1D^* \rightarrow {}^3D^*$, as an alternative to the radical pair mechanism can be neglected. Moreover, such a 'triplet' mechanism could hardly explain why in zero-field the relative populations of the triplet sublevels [14] are 30-fold smaller than the relative populations observed in high-fields [6,7].

Nevertheless, recent CIDEP (chemically induced dynamic electron polarization) experiments in the more complex photosystems I [16] and II [17] of chloroplasts have been interpreted within the framework of the 'triplet' mechanism of CIDEP [18] implying that a spin-polarized triplet-state precedes the radicals.

The alternative radical pair mechanism of CIDEP, has been discarded with the argument that the molecules in the two photosystems are not free to diffuse. In the view of our analysis, this would mean that the basic mechanism of the primary reaction in bacterial reaction centers and in photosystems of chloroplasts are completely different. Therefore, we would like

to emphasize that the diffusive motion of the unpaired electrons is not at all a necessary condition for the hyperfine or radical pair mechanism to occur. It is sufficient that the separation of the radicals with respect to the unpaired electrons is sufficiently slow [19]. From this it follows that a triplet-state precursor for the radical pair is not favoured. Furthermore this assumption could be tested by the excitation of the pigment ($D \rightarrow {}^1D^*$) with polarized light which can only influence the CIDEP signal if the radicals are created from a spin-polarized triplet-state [20].

On the other hand, an important feature of the hyperfine mechanism of triplet-formation is that the total yield of triplets depends on the external magnetic field. Recent experiments [21] with organic electron donors and acceptors showed a 10%-modulation (80 G) of the triplet-yield obtained through radical recombination in a polar liquid. Since in bacterial reaction centers the separation of radicals by diffusion is negligible as compared to a non-viscous liquid as used in ref. [21], even larger modulations can be expected here as shown in experiments [19(b)] *.

A detailed theory [13] shows that the probability of the radical pair to be in the triplet-state, in proportion increases to t^2 in time, such that the amount of triplets present follows a t^3- rather than a linear t-dependence as expected in ordinary kinetics. This unusual time-dependence together with the saturation of magnetic field effects below 500 G are typical indications for the hyperfine mechanism described. The half-width of the saturation reflects – in appropriate units – either the mean hyperfine constant or the decay-rate of the pair, whichever is larger. The saturation of magnetic field effects, at relatively low field strengths, allows one to discriminate between the hyperfine interaction and singlet-fission as a possible alternative [22].

As a side remark, we propose an explanation for the unusually fast triplet-relaxation-rate (corresponding to $T_2 \sim 5\ \mu s$), observed even at liquid helium temperatures [6]. There is evidence [23] that the triplet-state is delocalized over a 'special' BCl-pair. Since the two BCl molecules have different orientations, excitation transfer [24] provides a very efficient relaxation mechanism similar to the relaxation of triplet-excitons in molecular crystals [25].

*The hyperfine modulation of the triplet-yield obtained through recombination of adsorbed dye anions with anthracene cations at the crystal surface amounts to 50%.

Conclusion

The dependence of the transient absorption (radicals and triplet-states) on the external magnetic field provides a valuable tool both for the qualitative identification of paramagnetic species (with overlapping absorption spectra in complex reaction schemes) and for the quantitative determination of the rate constants, k_S and k_T. The method is essentially temperature-independent since during the spin-precession in the radical pair the spins are not coupled to the environment. Finally, we want to emphasize that this method of time-resolved control of initial and final molecular states bridges the experimental gap between the conventional spectroscopy on the nanosecond or subnanosecond time-scale and electron spin resonance studies on radical- and triplet-intermediates which are restricted to times longer than microseconds.

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References

[1] Kaufmann, K. J., Dutton, P. L., Netzel, T. L., Leigh, J. S. and Rentzepis, P. M. (1975) Science 188, 1301.
[2] Rockley, M. G., Windsor, M. W., Cogdell, R. J. and Parson, W. W. (1975) Proc. Natl. Acad. Sci. USA 72, 2251.
[3] Dutton, P. L., Kaufmann, K. J., Chance, B. and Rentzepis, P. M. (1975) FEBS Lett. 60, 275.
[4] Fajer, J., Brune, D. C., Davies, M. S., Forman, A. and Spaulding, L. D. (1975) Proc. Natl. Acad. Sci. USA 72, 4956.
[5] Dutton, P. L., Leigh, J. S. and Reed, D. W. (1973) Biochim. Biophys. Acta 292, 654.
[6] Leigh, J. S. and Dutton, P. L. (1974) Biochim. Biophys. Acta 357, 67.
[7] Uphaus, R. A., Norris, J. R. and Katz, J. J. (1974) Biochem. Biophys. Res. Commun. 61, 1057.

[8] Hoff, A. J. (1976) Biochim. Biophys. Acta 440, 765.
[9] Thurnauer, M. C., Katz, J. J. and Norris, J. R. (1975) Proc. Natl. Acad. Sci. USA 72, 3270.
[10] Norris, J. R., Druyan, M. E. and Katz, J. J. (1973) J. Am. Chem. Soc. 95, 1680.
[11] Parson, W. W., Clayton, R. K. and Cogdell, R. J. (1975) Biochim. Biophys. Acta 387, 265.
[12] Parson, W. W. and Cogdell, R. J. (1975) Biochim. Biophys. Acta 416, 105.
[13] Haberkorn, R. (1977) Chem. Phys. in press.
[14] Chemically Induced Magnetic Polarization (1973) (Lepley, A. R. and Closs, G. L. eds) Wiley.
[15] Carrington, A. and McLachlan, A. D. (1967) in: Introduction to Magnetic Resonance, Harper and Row.
[16] Blankenship, R., McGuire, A. and Sauer, K. (1975) Proc. Natl. Acad. Sci. USA 72, 4943.
[17] McIntosh, A. R. and Bolton, J. R. (1976) Nature 263, 443.
[18] Pedersen, J. B. and Freed, J. H. (1975) J. Chem. Phys. 62, 1706.
[19] (a) Atkins, P. W. (1973) Chem. Phys. Lett. 18, 290. (b) Haberkorn, R. and Michel-Beyerle, M. E. (1975) Mol. Crystl. Symp. Nikko, Japan.
[20] Adrian, F. J. (1974) J. Chem. Phys. 61, 4875.
[21] Michel-Beyerle, M. E., Haberkorn, R., Bube, W., Steffens, E., Schröder, H., Neusser, A. J., Schlag, E. W. and Seidlitz, H. (1976) Chem. Phys. 17, 139. Haberkorn, R. and Michel-Beyerle, M. E. (1976) Z. Naturf. 31a, 499.
[22] Swenberg, C. E. and Geacintov, N. E. (1973) in: Organic Molecular Photophysics, (Birks, J. B. ed) Wiley.
[23] Katz, J. J., Oettmeier, W. and Norris, J. R. (1976) Phil. Trans. R. Soc. London B 273, 227.
[24] DeGroot, M. S., Hesselman, I. A. M. and Van der Waals, J. H. (1969) Mol. Phys. 16, 61.
[25] Suna, A. (1970) Phys. Rev. B 1, 1716.