ON THE MECHANISM OF MAGNETIC FIELD EFFECTS IN BACTERIAL PHOTOSYNTHESIS

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ABSTRACT The recently discovered magnetic field effects in bacterial photosynthesis are discussed by solving a simple model exactly. Analytic expressions are given that permit one to study the influence of the rates of the primary electron transfer reactions and the exchange interaction on the yield of excited triplet states.

INTRODUCTION

Isolating reaction centers of photosynthetic bacteria (e.g., *Rhodopseudomonas sphaeroides*) makes it possible to study the primary electron transfer steps of photosynthesis by nanosecond and picosecond spectroscopy (1–5). Within <10 ps after exciting a bacteriochlorophyll dimer ($BChl_2$) to its first excited singlet state, a radical pair of $BChl_2^+$ and a bacteriopheophytin anion (BPh^-) is found. Then, within 200 ps, the electron is transferred to a ubiquinone-nonheme iron complex. However, if this pathway is blocked by prereducing the ubiquinone chemically, the lifetime of the radical pair is ≃100 times longer, and the final product is either an excited triplet, $^3BChl_2^*$, or $BChl_2$ and BPh in their respective ground states. The bacteriochlorophyll triplet formed that way was also studied by electron paramagnetic resonance (EPR) (6, 7).

A new aspect came into these investigations of the primary photosynthetic steps by the observation (8, 9) that the yield of $^3BChl_2^*$ can, even at room temperature, be strongly influenced by magnetic fields of the order of 100 G. From the low field strengths at which saturation of the effect was reached as well as from the anomalous polarization of the triplet EPR spectrum (6, 7) it was concluded that there is a close analogy to the magnetic field dependence found in a variety of other radical combination reactions (10–15). An explanation of all these effects is provided by the radical pair mechanism (16–18) of chemically induced dynamic nuclear and electron polarization (CIDNP and CIDEP) in which transitions between singlet and triplet states of a radical pair are induced by the magnetic hyperfine interaction of the unpaired electrons with the nuclei. An external magnetic field partially impedes this spin motion and thus has an influence on the combination product yields. It should be noted that this radical pair mechanism is entirely different from intersystem crossing induced by spin-orbit coupling. Triplet states formed via intersystem crossing could show a similar spin polarization (19), but magnetic field effects can only be observed at liquid helium temperature (20).

In this paper, complementing a previous more qualitative study (21), we first present a numerical calculation of the spin motion of the $BChl_2^+/BPh^-$ radical pair, making explicit the time scale of the singlet-triplet transition. Then a simple model with only one representative

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proton is solved analytically and the results are compared with recent numerical work on a two-proton model (22); we also discuss the conditions under which such simplified models can be used to describe the $BChl_2^+/Bph^-$ radical pair.

THE RADICAL PAIR MECHANISM

The interaction of the unpaired electron spins, $\mathbf{S}_1$ and $\mathbf{S}_2$, of a radical pair with the external field $\mathbf{H}$ and the spins of the magnetic nuclei $\mathbf{I}_i$ of radicals (1) and (2), respectively, is described by the spin-Hamiltonian (16–18)

$$\mathcal{H} = g\beta\mathbf{H}\cdot(\mathbf{S}_1+\mathbf{S}_2) + \mathbf{S}_1\cdot\overset{(1)}{\sum_i} A_i^{(1)}\mathbf{I}_i + \mathbf{S}_2\cdot\overset{(2)}{\sum_j} A_j^{(2)}\mathbf{I}_j + J\mathbf{S}_1\cdot\mathbf{S}_2. \tag{1}$$

In the first term, the Zeeman interaction, the g values of the two radicals have been assumed to be identical; this is a very good approximation for aromatic radicals in the low fields of interest here (23). The isotropic hyperfine splittings $A_i^{(1)}$ and $A_j^{(2)}$ are known from the EPR and electron-nuclear double resonance (ENDOR) spectra of the radicals. The last term in Eq. 1 is the exchange interaction, which leads to a splitting J between the singlet and the triplet pair states; its magnitude depends on the overlap between the wave functions of the two radicals. Anisotropic exchange interactions as well as dipolar hyperfine couplings and the magnetic dipole-dipole interaction between the electrons, though not being necessarily smaller than the other contributions to $\mathcal{H}$, have been neglected for simplicity. These terms would lead to interesting anisotropic magnetic field effects in oriented reaction centers that have not been observed so far, however.

The Hamiltonian Eq. 1 does not conserve the total electronic spin, $\mathbf{S}^2 = (\mathbf{S}_1+\mathbf{S}_2)^2$, because of the hyperfine terms. Thus, when a singlet ($S = 0$) pair state is formed from a photoexcited $BCHl_2$ singlet, after some time t the probability T (t) of finding a triplet pair state ($S = 1$) is no longer zero, and accordingly an electron transfer reaction leading to a triplet product becomes spin-allowed. The rate of change from a singlet to a triplet pair is determined by the hyperfine splittings A_i in Eq. 1. For aromatics, they typically are of the order of 10 G (23), which corresponds to $\simeq 10$ ns.

After a derivation that was given elsewhere (24–25) and that is outlined briefly in the appendix, the time dependence of the triplet probability can be expressed as

$$T(t) = \frac{2}{N}\sum_{k,l} |<k|\mathbf{S}^2|l>|^2 \sin^2\left(\frac{1}{2}\omega_{kl}t\right), \tag{2}$$

where $|k\rangle, |l\rangle, \ldots$ are the N eigenstates of $\mathcal{H}$, and $\hbar\omega_{kl} = \mathcal{H}_{kk} - \mathcal{H}_{\ell\ell}$. Similar expressions have been used earlier to calculate the singlet-triplet transition probability for aromatic radicals (12) and photosynthetic reaction centers (22). If the exchange term is neglected in Eq. 1, using the hyperfine splittings of BPh and BChl determined by ENDOR and EPR (26, 27) and employing methods described in reference 28, $T(t)$ for a zero and a very high magnetic field is given by Fig. 1.

It should be noted that, due to the many different frequencies ω_{kl} occurring in Eq. 2, the triplet probability is not an oscillating function. At finite fields H even in the simplest case, where only one magnetic nucleus is present, $T(t)$ is not periodic. At an infinite field the situation is a little more complicated: every given radical pair is oscillating between singlet and

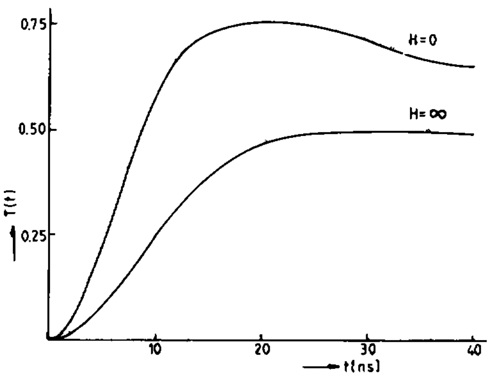

FIGURE 1 Probability $T(t)$ of finding a $BChl_2^+$ / BPh^- radical pair, created at $t = 0$ in the singlet state, in the triplet state at time t for vanishing exchange interaction J.

triplet states, but with a frequency depending on the actual spin orientations of all the nuclei of the pair. Averaging over all possible spin orientations, as done in Eq. 2, again gives a nonperiodic $T(t)$ for the ensemble of radical pairs, as can be seen in Fig. 1.

An important, quite general feature of $T(t)$ is that near the origin the increase is quadratic in time, and that the ratio between the $H = 0$ and $H = \infty$ cases is 3:1 (29). This reflects the fact that at high fields the spin-flip transitions from the singlet to the triplet states T_{+1} and T_{-1} are no longer possible, leaving only the transition between the singlet state and the $S_z = 0$ state T_0. At long times after creation of the pair the magnetic field dependence of the triplet probability is much less pronounced.

THE ONE-PROTON MODEL

In the preceding section we discussed the quantum mechanical motion of the electron spins (from the singlet to the triplet state) of a radical pair under the influence of the spin-Hamiltonian Eq. 1, but without considering the effect of the recombination reactions. Since these reactions in general proceed with different rates for singlet and triplet pairs they strongly disturb the spin motion and must therefore be taken into account in the equation of motion from the outset. The appropriate tool for describing a quantum system disturbed by stochastic processes is the stochastic Liouville equation (30), which takes for a radical pair the form (11, 31, 32)

$$\frac{d}{dt}\rho = -(i/\hbar)[\mathcal{H}, \rho] - \frac{1}{2}k_S(P^S\rho + \rho P^S) - \frac{1}{2}k_T(P^T\rho + \rho P^T). \qquad (3)$$

Here $\rho(t)$ is the density matrix of the radical pair in the space spanned by the eigenstates of the two electronic and all nuclear spins, and P^S and P^T are operators projecting on the singlet and triplet subspaces, respectively.

The first order rate constants k_S and k_T refer to the combination reaction of the radical pair, provided the pair is in a pure singlet or triplet state, respectively. This can be seen by taking the trace of Eq. 3,

$$\frac{d}{dt} Tr\,\rho(t) = -k_S Tr[P^S\rho(t)] - k_T Tr[P^T\rho(t)]. \qquad (4)$$

$Tr\rho(t)$ is the probability that a radical pair created at $t = 0$ has not yet recombined at time t, while $p_S(t) = Tr(P^S\rho(t))$ and $p_T(t) = Tr(P^T\rho(t))$ are the probabilities of finding the pair in the singlet or triplet state, respectively. If $k_S = k_T = 0$ (when $Tr\rho = 1$ at all times) $p_T(t)$ coincides with $T(t)$ as given in Eq. 2. For finite reaction rates $p_T(t)$ and $T(t)$ are generally quite different, in particular at large t where, in contrast to $T(t)$, $p_T(t)$ decays exponentially. The initial increase of $p_T(t)$ at times $t \lesssim k_S^{-1}$, k_T^{-1}, however, is not distorted by the recombination reactions and thus identical with that of $T(t)$. This can readily be seen by inserting a power series expansion of $\rho(t)$ into Eq. 3.

The solution of Eq. 3 for a radical pair with as many nuclei as $BChl_2^+/BPH^-$ would require extensive numerical calculations. Instead of doing this, we now turn to a simple model system with only one representative spin-½ nucleus. As will be seen, this one-proton model has the advantage that it can be solved analytically so that the dependence of the magnetic field effect on the magnetic parameters and rate constants can be discussed directly. Furthermore, this solution approaches the solution with the full Hamiltonian, Eq. 1, at short times. In this region, which is the most important one if the reaction rates are large, $T(t)$ (and thus, as discussed above, $p_T(t)$) can be approximated by (29)

$$T(t) = \frac{1}{4} \sum_{i}^{(1)+(2)} I_i(I_i + 1)(A_i/\hbar)^2 t^2 \tag{5}$$

at magnetic field $H = 0$, and one third of the expression at $H = \infty$.

Thus, if the hyperfine coupling constant in the one-proton model is chosen to be

$$A = \left\{\frac{4}{3} \sum_{i}^{(1)+(2)} I_i(I_i + 1)A_i^2\right\}^{1/2} = 13.23\,\mathrm{G} \tag{6}$$

(using the $BChl_2^+/BPh^-$ data [26, 27]), the model describes well the triplet formation process in the real $BChl_2^+/BPh^-$ pair if k_S or $k_T \gtrsim A/\hbar$ (in frequency units, $A/\hbar = 0.233 \cdot 10^9 s^{-1}$).

The exact solution of Eq. 3 for the one-proton model is given in the appendix. The result for the triplet yield of a radical pair created in the singlet state is at a zero field

$$\Phi_T(0) = 3(A/\hbar)^2 k_T(k_S + k_T)/\{[3(A/\hbar)^2 + 4k_Sk_T](k_S + k_T)^2 + 16\, k_Sk_T(J - A/2)^2/\hbar^2\}, \tag{7}$$

while at an infinite magnetic field strength

$$\Phi_T(\infty) = (A/\hbar)^2 k_T(k_S + k_T)/\{[(A/\hbar)^2 + 4k_Sk_T](k_S + k_T)^2 + 16\, k_Sk_T(J/\hbar)^2\}. \tag{8}$$

The lifetime of the radical pair state, as defined in the appendix, is

$$\tau = (1 - \Phi_T)/k_S + \Phi_T/k_T. \tag{9}$$

As expected, Φ_T in Eqs. 7 and 8 vanishes for $A = 0$ or $k_T = 0$. If $k_S = 0$ the triplet yield is unity, independently of the magnetic field strength. The exchange interaction J impedes transitions between singlet and triplet radical pair states because it introduces an energy difference between them; therefore it appears in the denominator of Eqs. 7 and 8.

The expressions for the triplet yields become simpler in a case that will later be seen to be approximately fulfilled in bacterial reaction centers, namely $J = 0$ and $k_S \ll k_T$:

$$\Phi_T(0) = (A/\hbar)^2/\left\{(A/\hbar)^2 + \frac{4}{3} k_S k_T\right\}, \tag{10}$$

$$\Phi_T(\infty) = (A/\hbar)^2/\{(A/\hbar)^2 + 4\, k_S k_T\}. \tag{11}$$

The magnetic field modulation $\Phi_T(\infty)/\Phi_T(0)$ depends on the ratio $k_S k_T{:}A^2$. If the recombination rates are small, Φ_T tends to unity independently of the field. A modulation of 1:3 is obtained, however, for large reaction rates, because then in $T(t)$ (Fig. 1) the influence of the initial quadratic region becomes dominant.

From Eqs. 10 and 11 this antagonism between large modulation and large triplet yield can be expressed as

$$\Phi_T(\infty)/\Phi_T(0) = [3 - 2\,\Phi_T(0)]^{-1}. \tag{12}$$

This equation has been proposed earlier (8) on the basis of kinetic considerations. From the quantum mechanical derivation we see that it is valid in the case $k_S \ll k_T$ and $J \approx 0$. From an extensive numerical study of a two-proton model (22), which in its essential features is expected to resemble closely the one-proton model, the antagonism expressed in Eq. 12 can also be clearly recognized.

An interesting, perhaps surprising feature of Eqs. 7 and 8, which is retained in the approximate Eqs. 10 and 11, emerges in the limit of large k_T: the triplet yield $\Phi_T \propto A^2 / k_S k_T$, i.e., it decreases with increasing k_T.

This is a direct consequence of the quantum mechanical nature of the spin motion, in a certain sense analogous to the phenomenon of motional narrowing in spin resonance (23). For a qualitative understanding of this effect it must be observed that a large k_T means interrupting the spin motion on the average at a time $\tau_T = k_T^{-1}$, which lies, according to Fig. 1 and Eq. 5, still in the initial quadratic region, so that $T(\tau_T) \propto (A/k_T)^2$. When this triplet probability is multiplied by k_T / k_S, the total number of such interrupts, one arrives at the above relation for Φ_T. An inverse dependence of Φ_T on k_T was also observed in numerical solutions of the two-proton model (22), but was attributed to a dependence of Φ_T on $|k_S - k_T|$.

We have shown above that the one-proton model becomes a good approximation to a radical pair with many nuclei if k_S or $k_T \gg | A/\hbar$. To see whether this condition is fulfilled we consider the experimental data reported for *Rps. sphaeroides* reaction centers at liquid nitrogen temperature (8): $\Phi_T(0) = 0.8$, $\Phi_T(0) = 0.9$, $\tau = 20$–30 ns (we have used 25 ns). Solving the three Eqs. 7–9 for the three unknown quantities of the model one obtains: $k_S = 8.8 \cdot 10^6 \mathrm{s}^{-1}$, $k_T = 3.6 \cdot 10^8 \mathrm{s}^{-1}$, $J = -7.6$ G. The value of k_T is slightly, but not much larger than $A/\hbar = 2.33 \cdot 10^8 \mathrm{s}^{-1}$. This means that the one-proton model is not a very accurate description of the bacterial reaction center, but should at least permit to estimate the order of magnitude of the model parameters. The value of J should be taken as an upper limit, since models with $J = 0$ are possible which match the experimental data not exactly, but still reasonably; with increasing $|J|$, on the other hand, Φ_T would decrease rapidly. We refrain from performing a similar analysis with the reported room temperature data (8, 9); apart

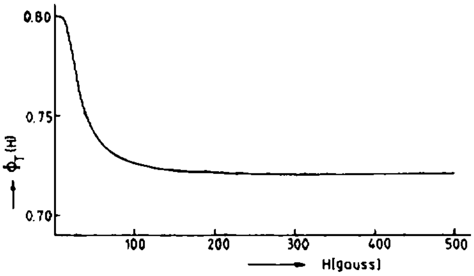

FIGURE 2 Magnetic field dependence of the triplet yield $\Phi_T(H)$ in the one-proton model with parameters $A = 13.23$ G, $k_S = 8.8 \cdot 10^6\,s^{-1}$, $k_T = 3.6 \cdot 10^8\,s^{-1}$, $J = -7.6$ G.

from a dependence of these data on the sample preparation, the limitations inherent in the one-proton model would make a quantitative discussion of the temperature dependence of the rate constants too difficult.

The magnetic field dependence of Φ_T, calculated numerically by methods discussed in the appendix, is shown in Fig. 2 for values of the parameters as in the example considered above. As generally found in magnetic field modulation experiments with radical reactions, the triplet yield decreases and then saturates; the same behavior was found in the experiments with *Rps. sphaeroides* (8, 9). The halfwidth of the $\Phi_T(H)$ curve is determined by the largest one of the quantities A, k_S, k_T and J. Fig. 2 shows a halfwidth of 35 G, which is of the order of that found in some of the experiments. It appears, however, that the halfwidth depends on the sample preparation; with some preparations it was much higher. Possibly relaxation processes that don't change the electron transfer reactions but affect the phase in the coherent spin motion are an explanation of this broadening. Another interesting possibility could be a reversible electron transfer reaction between BChl and BPh (22), which is supported by the observation of a BChl fluorescence decay in parallel to the radical pair decay (33). More experiments clarifying this point would be highly desirable; theoretical studies employing more realistic models for the BChl$_2^+$/BPh$^-$ radical pair and including relaxation processes are currently in progress.

CONCLUSIONS

Our discussion of the magnetic field dependence of the primary steps in the bacterial photosynthetic reaction center is based mainly on an analytically solvable model with only one proton, representing the many magnetic nuclei with which the unpaired electrons in the radical intermediates interact. We have shown, however, that at least the order of magnitude of the reaction rates obtained can be expected to be correct. That the triplet recombination rate found in this analysis is larger than the singlet rate is readily understood within the framework of the theory of electron transfer reactions (34–36), in view of the different exothermicities of the reactions.

Somewhat puzzling is the small value obtained for the exchange interaction. It indicates that the overlap of the wave functions of BChl$_1^+$ and BPh$^-$ is very small; if the interaction between the electrons were mainly of a magnetic nature (which we cannot exclude), the overlap could even be close to zero. On the other hand the electron transfer step leading to the formation of these radicals proceeds extremely rapidly (within 10 ps). Interestingly, there is some evidence that a geometrical change occurs in the reaction center 30 ps (2) after this fast electron transfer step, which perhaps involves an increase of the distance of the radicals. Another possiblility would be a delocalization of one of the unpaired electrons, thus making their average distance in the radical pair state larger.

A model system in which this feature is realized consists of an organic crystal and dye molecules adsorbed at its surface. After excitation by light a radical ion pair is formed, one charge of which may even diffuse into the crystal bulk. The electric current thus generated as well as triplet species formed have been found to be magnetic field dependent (11, 37).

It should be mentioned that at least in some of the photosynthetic bacteria the identification of the anion radical with BPh^-, which we assumed in our analysis, is still under discussion (38). Further, from EPR studies there is evidence (38) for a strong exchange interaction of BPh^- with the Fe-ubiquinone complex. Possibly, because of the very rapid spin relaxation of this complex, the exchange interaction is averaged out at room temperature (38) but is still partly effective at liquid nitrogen temperature. Another explanation of the increase of the triplet yield at lower temperatures could be its antagonistic behavior with respect to the triplet recombination rate.

Interesting anisotropy effects could be expected in oriented reaction centers (or intact chromatophores). Such effects, due to the anisotropic hyperfine interaction, have been studied in the crystal/dye system mentioned above. In the same system appreciable changes of the magnetic-field effects were found by isotopic substitution of either the dye or the crystal (37), inasmuch as different isotopes can have very different nuclear magnetic moments and thus different hyperfine splittings. An interesting possibility would be to slow down the singlet-triplet transition by using reaction centers with perdeuterated pigments. The hyperfine splittings are in this case considerably smaller, such that the lifetime of the radical pair is enhanced; perhaps it could even become possible that way to study the radical pair state by fast EPR methods.

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APPENDIX

The triplet probability $T(t)$ of finding a radical pair in the triplet state, as given in Eq. 2, is obtained by solving the equation of motion of the density matrix (Eq. 3), in the absence of the reaction terms ($k_S = k_T = 0$). Initially the pair is in the singlet state, i.e.,

$$\rho(t = 0) = P^S/TrP^S. \tag{A1}$$

In the frame $|k\rangle, |l\rangle, \ldots$ of the eigenstates of $\mathcal{H}$, using notations as in the text,

$$\frac{d}{dt}\rho_{kl} = -i\omega_{kl}\rho_{kl}, \tag{A2}$$

which has the solution (using Eq. A1)

$$\rho_{kl} = P^S_{kl} \exp(-i\omega_{kl}t)/TrP^S. \tag{A3}$$

The derivation of $T(t) = Tr[P^T\rho(t)]$ is then straightforward, if the relations $N = Tr\ 1$ and $P^S = 1 - (\frac{1}{2})\,S^2$ are used.

To simplify the numerical evaluation of Eq. 2 the experimental hyperfine splittings were slightly modified by omitting very weakly interacting nuclei and enhancing the A values of the strongly interacting ones in such a way that the sum of the squared A's (as in Eq. 6) remained the same. The dimerization of BChl was accounted for by doubling the number of nuclei and halving their A values. The result of this procedure is for $BChl_2^+$: $8 \times A_H = 2.60$ G, $6 \times A_H = 1.82$ G and for BPh^-: $6 \times A_H = 3.32$ G, $2 \times A_N = 2.55$ G.

For the derivation of the triplet yields (Eqs. 7 and 8) observed after completion of the decay of the radical pair, one needs the time-averaged density matrix

$$\bar{\rho} = \int_0^\infty \rho(t)\,dt. \tag{A4}$$

After integrating with respect to time, Eq. 3 can be written as

$$B\bar{\rho} + \bar{\rho}B^+ = \rho(t = 0), \tag{A5}$$

where

$$B = (i/\hbar)\mathcal{H} + \frac{1}{2}k_S P^S + \frac{1}{2}k_T P^T, \tag{A6}$$

and B^+ is its hermitian conjugate. For the one-proton model $\bar{\rho}$, B and P^S are 8×8 matrices. Observing that B commutes with the z component of the total spin $\mathbf{F} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{I}$, the problem can be split into two one- and two three-dimensional equations of the same type as Eq. A5, which is known as the Lyapunov equation and for which a general method of solution is known (39). The magnetic field dependence of Φ_T shown in Fig. 2 has been calculated numerically in this way. In the special cases $H = 0$, when F^2 is an additional good quantum number, and for $H = \infty$, when the z component of the nuclear spin is conserved, this additional symmetry reduces the equations to be solved to a 2×2 problem which can be solved analytically (39). When $\bar{\rho}$ is obtained in this way, the triplet yield is

$$\Phi_T = k_T\, Tr\,(P^T\bar{\rho}), \tag{A7}$$

which for $H = 0$ and $H = \infty$ leads to Eqs. 7 and 8, respectively.

The decay law of the radical is in general not a simple exponential function, and therefore the lifetime is not well defined. We choose the definition $\tau = \mathrm{Tr}\bar{\rho}$, which has the virtue to coincide with the usual one in the case of an expontential decay. Taking the trace of Eq. (A1),

$$k_S\, Tr\,(P^S\bar{\rho}) + k_T\, Tr\,(P^T\bar{\rho}) = 1, \tag{A8}$$

from which, using $P^S = 1 - P^T$ and Eq. A7, Eq. 9 is readily derived.

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