

Biochimica et Biophysica Acta, 502 (1978) 255–268
© Elsevier/North-Holland Biomedical Press

BBA 47491

ELECTRON TRANSFER AND SPIN EXCHANGE CONTRIBUTING TO THE MAGNETIC FIELD DEPENDENCE OF THE PRIMARY PHOTOCHEMICAL REACTION OF BACTERIAL PHOTOSYNTHESIS

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(Received September 19th, 1977)

Summary

The yield φ_T of triplet products "P_R" generated in reaction centers of *Rhodospseudomonas sphaeroides* in which the "primary" acceptor is reduced had been found to depend on external magnetic fields. The magnetic field dependence varies, however, between different reaction center preparations. By means of a theoretical description of the primary electron transfer processes and hyperfine coupling-induced electron spin motion the factors influencing the magnetic field behaviour of the triplet products are studied. The following quantities characteristic of the primary electron transfer in photosynthesis have a strong effect on φ_T : (1) the rate constants of reversible electron transfer between the initially excited singlet state of the reaction center and an intermediate radical ion pair state; (2) the rate constants of irreversible electron transfer of the radical pair to the ground and excited triplet state of the reaction center; (3) the electron exchange interactions between the radical pair and the "primary" acceptor. From the observed magnetic field dependence of φ_T estimates for these quantities are obtained. A temperature dependence of the magnetic field behaviour of φ_T and a magnetic field effect on the fluorescence quantum yield of the reaction center are predicted.

(1) Introduction

The transformation of light into chemical energy in the photosynthetic apparatus of bacteria is based on the flow of electrons through an oxidation chain. This process originates from photoinduced electron transfer reactions in a

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Abbreviations: BChl, bacteriochlorophyll; BPh, bacteriopheophytin.

membrane-bound complex of pigments and proteins, the reaction center, to which the absorbed light energy is channeled [1]. The electron flow following the excitation of 1P , probably a bacteriochlorophyll dimer (BChl)₂, is started by the formation of a radical ion pair [2–5]:



The electron acceptor I is generally assumed to be bacteriopheophytin (BPh) [5–8]. Under normal conditions the electron is transferred within 100–250 ps [6,7] from I⁻ to a second acceptor X, probably an iron · ubiquinone complex [1,9,10]. Since the short-lived $^2I^-$ escaped observation for so long X had been named the “primary” acceptor. If X is reduced ($^1X \rightarrow ^2X^-$) [1–3] or removed [9,10] the electron transfer is blocked and the lifetime of the initial radical pair ($^2P^* \ ^2I^-$) increases to about 10 ns at room temperature [3]. This time reflects the electron back transfer



The reaction route in Eqn. 2 depends on the spin multiplicity of the radical pair at the instance of the electron transfer. In case the pair is in the singlet electron spin state S_0 , i.e. $^1(^2P^* \ ^2I^-)$, either the singlet ground state ($^1P \ ^1I$) or (if energetically allowed) the singlet excited state ($^1P^* \ ^1I$) are reformed; in case the pair is in a triplet state T_0 , T_{+1} or T_{-1} , i.e. $^3(^2P^* \ ^2I^-)$, the triplet excited state ($^3P^* \ ^1I$), usually referred to as P_R , is populated.

It has been reported recently that the yield ϕ_T of triplet products generated in reaction centers of *Rhodospseudomonas sphaeroides* with a reduced “primary” acceptor X is lowered by weak external magnetic fields [11,12]. The relative magnetic field effect

$$R(B) = 1 - \phi_T(B)/\phi_T(B=0) \quad (3)$$

was found to depend on the preparation of the reaction center sample [11]. In chromatophores of *Rps. sphaeroides* wild type the saturation value of the magnetic field effect on the triplet yield $R(B \rightarrow \infty)$ was determined to be 0.15. For the field strength $B_{1/2}$ at which $R(B)$ takes half its saturation value, i.e. $R(B_{1/2}) = \frac{1}{2} R(B \rightarrow \infty)$, a value of about 250 G had been measured. In reaction centers which lack a functional iron complexed to the primary acceptor ubiquinone $R(B \rightarrow \infty)$ is about 0.4 and $B_{1/2}$ about 35 G. In reaction centers of *Rps. sphaeroides* mutant R26 in which the iron · ubiquinone complex is intact, the $R(B \rightarrow \infty)$ and the $B_{1/2}$ value were measured to be about 0.25 and 50 G, respectively. We want to show in this paper how these differences in magnetic field dependence originate from intermolecular interactions characteristic of the electron transfer processes in the reaction centers.

The magnetic field effect observed can be explained on the basis of the theory of Chemically Induced Magnetic Polarization [13]: Initially, the radical pair is generated in a singlet electron spin state (reaction 1). The lifetime of the pair is long enough to allow the hyperfine interaction between the electron and nuclear spins in $^2P^*$ as well as in $^2I^-$ to perturb the two electron spins from the singlet to the triplet state thereby inducing triplet products (reaction 2). Provided there is no exchange interaction between the $^2P^*$ and $^2I^-$ radicals the S_0 , T_0 and $T_{\pm 1}$ spin states are degenerate at zero magnetic field. In this case the

T_0 and $T_{\pm 1}$ states are populated with equal probability through the hyperfine interaction with the S_0 state. An external magnetic field lifts, however, the degeneracy between S_0 , T_0 and $T_{\pm 1}$, and at sufficiently high fields decreases the population of the $T_{\pm 1}$ states. This gives rise (1) to a reduced overall singlet \rightarrow triplet transition probability and, hence, to the reduction of the yield of triplet products ($^3P^* \ ^1I$), and (2) to an electron spin polarization of the triplet product in the T_0 state which had been inferred before from ESR spectra [1,4,14].

Such magnetic field effects have also been observed previously for electron-hole recombination on crystal surfaces [15] and for radical pair recombination in solution [16–19]. Detailed theoretical studies have shown [20,21] that in solution the $B_{1/2}$ value reflects exclusively the strength of the hyperfine interaction in the radical pair state. Other interactions which influence the electron spin motion, the exchange interaction between the unpaired electrons and the existence of spin-selective electron transfer channels, come into play only during the short collision times of the diffusing radical pair and can be neglected in solution [21]. The primary photosynthetic reaction is to be characterized, however, as a “solid state” process [1]. The $^2P^*$ and $^2I^-$ moieties are in permanent contact and the above interactions contribute permanently to the electron spin motion and therefore to the magnitude and magnetic field dependence of the triplet yield ϕ_T .

(2) Theory

The primary electron transfer processes in photosynthetic reaction centers are summarized in the reaction scheme of Fig. 1. Since the $^2P^*$ and $^2I^-$ moieties are immobile in the reaction center the electron transfer reactions are treated as first-order processes. The rate constant k_c describes the generation of the singlet radical ion pair from the excited singlet state (reaction 1). This process competes with the decay of $^1P^*$ to the ground state accounted for by the rate constant k_f . The electron back transfer (Eqn. 2) to the singlet ground state and the triplet excited state is described by the rate constants k_S and k_T , respectively. Also an electron back transfer to the excited singlet state accounted for by the rate constant k'_S is likely to exist in *Rps. sphaeroides* [22,23]. For the sake of simplicity the treatment of this process will be deferred to below. Here we assume $k'_S = 0$.

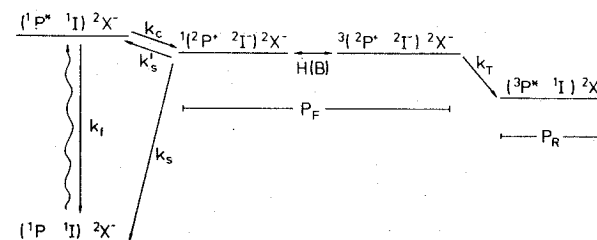


Fig. 1. Reaction scheme for the primary electron transfer processes in bacteriochlorophyll reaction centers with the second acceptor chemically reduced.

The coherent electron-nuclear spin motion of the radical pair ($^2P^+ \ ^2I^-$) is induced by the interactions collected in the Hamiltonian

$$H = \sum_k a_{1k} \mathbf{I}_k \cdot \mathbf{S}_1 + \sum_l a_{2l} \mathbf{I}_l \cdot \mathbf{S}_2 + \mu \mathbf{B} \cdot (g_1 \mathbf{S}_1 + g_2 \mathbf{S}_2 + g_3 \mathbf{S}_3) - J_{PI}(\frac{1}{2} + 2\mathbf{S}_1 \cdot \mathbf{S}_2) - J_{IX}(\frac{1}{2} + 2\mathbf{S}_2 \cdot \mathbf{S}_3) \quad (4)$$

The first two terms represent the isotropic hyperfine coupling between the electron spins \mathbf{S}_1 (\mathbf{S}_2) and the nuclear spins \mathbf{I}_k (\mathbf{I}_l) on radical 1(2). The third term describes the (Zeeman) interaction between the electron spins and an external magnetic field \mathbf{B} . The last two terms account for possible electron exchange interactions between $^2P^+$ and $^2I^-$ and between $^2I^-$ and $^2X^-$, where $^2X^-$ carries the unpaired electron spin \mathbf{S}_3 . The hyperfine coupling constants a_{1k} and a_{2l} of $^2P^+$ and $^2I^-$, respectively, can be derived from ESR spectra. The unknown exchange interaction constants J_{PI} and J_{IX} depend sensitively on the distance and relative orientation of the respective radical pairs. In accord with the solid state character of the reaction centers they are assumed to be constant in time. It will be shown below that information about these quantities can be abstracted from the observed magnetic field dependence of the triplet yield. The spin Hamiltonian (Eqn. 4) neglects anisotropic contributions to the hyperfine coupling which exist since intramolecular motions of $^2P^+$ and $^2I^-$ are supposedly hindered by the membrane environment.

The radical pairs in an ensemble of reaction centers are described by a spin density matrix $\rho(t)$. The diagonal elements ρ_{ii} represent the concentration of pairs in the electron-nuclear spin state labelled by i . The total concentration of pairs is $\text{tr} \rho = \sum \rho_{ii}$. The off-diagonal elements $\rho_{ij} (i \neq j)$ give the phase relations between different spin states i and j necessary to describe the coherent quantum mechanical spin motion. The time evolution of the density matrix is governed by the Liouville equation

$$\frac{d}{dt} \rho = -\frac{i}{\hbar} [H, \rho] - \frac{1}{2} k_S [Q_S, \rho]_+ - \frac{1}{2} k_T [Q_T, \rho]_+ \quad (5)$$

where $[A, B]_{\pm} = AB \pm BA$ and where the operators $Q_S = \frac{1}{4} - \mathbf{S}_1 \cdot \mathbf{S}_2$ and $Q_T = \frac{3}{4} + \mathbf{S}_1 \cdot \mathbf{S}_2$ project out the singlet and triplet states, respectively. The first term in Eqn. 5 describes the spin motion of the radical ion pair. The second and third terms represent the depletion of the singlet and triplet pairs, respectively. The generation of singlet radical pairs is accounted for by the initial condition imposed on the solution of Eqn. 5

$$\rho(0) = Q_S / (\text{tr} Q_S) \quad (6)$$

where $\text{tr} Q_S = \sum_i (Q_S)_{ii}$ is twice the number of nuclear spin configurations. Eqn. 6 states that at time $t = 0$ all pairs ($^2P^+ \ ^2I^-$) are in the singlet electron spin configuration with equal populations of all nuclear spin configurations and the two possible electron spin states of the $^2X^-$ radical. The yield of the reduction of $^2P^+$ to the triplet state is calculated as the time-integral over the third term of Eqn. 5 summed over all nuclear spin configurations (and directions of the $^2X^-$ electron spin)

$$\phi_T(B) = k_T \text{tr} \left\{ Q_T \int_0^{\infty} \rho(t) dt \right\} \quad (7)$$

In the special case of identical rate constants of electron transfer for singlet and triplet radical pairs, i.e. $k_S = k_T = k$, Eqn. 5 has the simple solution

$$\rho(t) = \left\{ \exp\left(-\frac{i}{\hbar} Ht\right) \rho(0) \exp\left(\frac{i}{\hbar} Ht\right) \right\} e^{-kt} = \rho_0(t) e^{-kt} \quad (8)$$

where $\rho_0(t)$ describes the spin motion of the radical pairs in the absence of any reaction. The yield of triplet products can be expressed as

$$\phi_T(B) = k \int_0^{\infty} P_T(t) e^{-kt} dt \quad (9)$$

where

$$P_T(t) = \text{tr} \{ Q_T \rho_0(t) \} \quad (10)$$

is the probability of radical pairs which do not react to be in a triplet state at time t . $P_T(t)$ can be evaluated numerically [21] even for radical pairs with a very large number of electron-nuclear spin states.

In the general case $k_S \neq k_T$ the spin motion cannot be separated from the electron transfer processes. For the ($^2\text{BChl}_2^+ \ ^2\text{BPh}^-$) pair the Liouville equation 5 comprises then large sets of coupled equations which are beyond the reach of numerical solution. In this situation the realistic systems have to be described through model systems with a small number of nuclear spins coupled to the unpaired electron spins. For the evaluation of the total triplet yield it is sufficient to determine $\int_0^{\infty} dt \rho(t) = \hat{\rho}$ which can be obtained directly by solving the algebraic equation

$$-\rho(0) = -\frac{i}{\hbar} [H, \hat{\rho}] - \frac{1}{2} k_S [Q_S, \hat{\rho}]_+ - \frac{1}{2} k_T [Q_T, \hat{\rho}]_+ \quad (11)$$

In order to avoid singularities one has to evaluate in some cases the Laplace transform $\hat{\rho} = \lim_{s \rightarrow 0} \int_0^{\infty} e^{-st} \rho(t) dt$.

(3) Irreversible electron transfer

The irreversible electron transfer processes described by the rate constants k_S and k_T in Eqn. 5 have a marked influence on the magnetic field behavior of the triplet yield. For a demonstration we consider first the case $k_S = k_T = k$ and neglect the exchange interactions J_{PI} and J_{IX} . In order to evaluate the singlet-triplet transition probability $P_T(t)$ the hyperfine coupling constants of the $^2\text{BChl}_2^+ + ^2\text{BPh}^-$ radical ion pair must be specified. Due to the complete electron delocalization in the dimeric cation $^2\text{BChl}_2^+$ one can assume its coupling constants to be one half of those of the monomeric $^2\text{BChl}^+$ cation. These were recently determined from ENDOR measurements in solution [24] (in Gauss):

β -protons:	$1 \times 6.0, 1 \times 5.14, 1 \times 3.5$
methyl groups:	$3 \times 3.23, 3 \times 1.80$
nitrogens:	$2 \times 1.14, 2 \times 0.86$

(protons with coupling constants less than 1 G being omitted). In order to sim-

plify the numerical calculation of the triplet probability $P_T(t)$ (for details see ref. 21) only the β -protons and the three methyl protons with the largest coupling constants were taken into account. This is justified since the initial rise of the triplet probability $P_T(t)$ is determined mainly by the largest coupling constants [21]. Furthermore, we averaged over the coupling constants of similar magnitude, i.e. over two β -protons and over one β -proton and three methyl protons. The coupling constants for the ${}^2\text{BChl}_2^+$ cation obtained in this way (in Gauss)

$$4 \times (a_H = 2.8), 8 \times (a_H = 1.65)$$

were employed in our calculations. The coupling constants of ${}^2\text{BPh}^-$ were also determined recently from ENDOR measurements [25] to be (in Gauss)

$$6 \times (a_H = 3.0), 3 \times (a_H = 2.5), 2 \times (a_N = 2.3)$$

We approximated these coupling constants by the simpler set (in Gauss)

$$9 \times (a_H = 2.65), 2 \times (a_N = 2.65)$$

The g -values used for P^+ and I^- were 2.0026 and 2.0035, respectively.

Fig. 2 presents the time evolution of the triplet probability $P_T(t)$ for the pairs (${}^2\text{BChl}_2^+$ ${}^2\text{BPh}^-$) initially generated in the singlet state at various magnetic fields. Triplet pairs are seen to be formed with a half-time of 8–10 ns. This compares well with the measured decay time of the radical ion pair with the rise time of the triplet state P_R at room temperature [3] demonstrating that the hyperfine mechanism can indeed produce triplet products in the reaction centers of *Rps. sphaeroides*. Fig. 2 illustrates that external magnetic fields reduce the singlet \rightarrow triplet transition probability which leads to the experimentally observed reduction of the triplet yield $\varphi_T(B)$. Hence, measurements of $\varphi_T(B)$ properly analyzed in terms of influences on the spin motion of the radical pair (${}^2\text{BChl}_2^+$ ${}^2\text{BPh}^-$) may yield valuable information on the reaction center micro-environment.

Fig. 3 displays the magnetic field dependence of the relative triplet yield

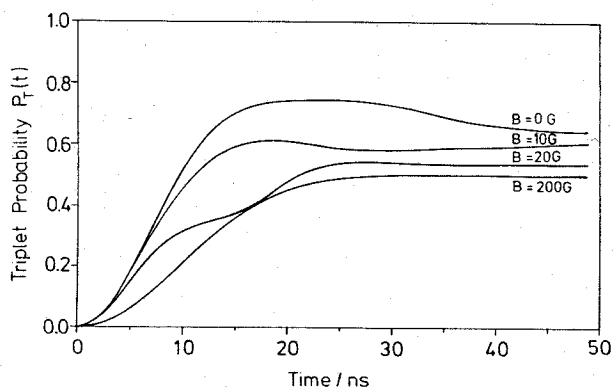


Fig. 2. Time evolution of the triplet probability $P_T(t)$ of the ${}^2\text{BChl}_2^+$ ${}^2\text{BPh}^-$ radical ion pair at various magnetic field strengths. Hyperfine coupling constants are given in the text, $J_{\text{PI}} = J_{\text{IX}} = 0$.

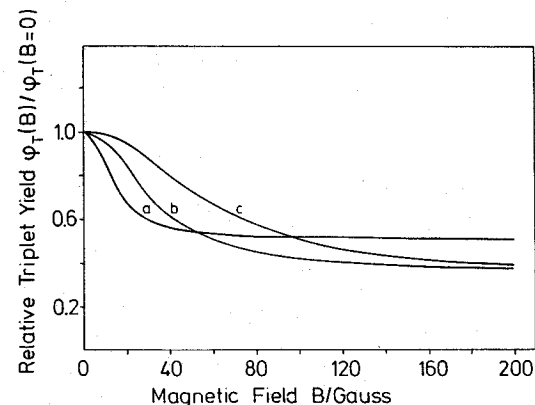


Fig. 3. Magnetic field dependence of the relative yield $\varphi_T(B)/\varphi_T(B=0)$ for the (${}^2\text{BChl}_2^+$ ${}^2\text{BPh}^-$) radical pair for $k_S = k_T = k$: a, $k = 0.1 \text{ ns}^{-1}$; b, $k = 0.5 \text{ ns}^{-1}$; c, $k = 1 \text{ ns}^{-1}$ (other parameters as in Fig. 2).

$\varphi_T(B)/\varphi_T(B=0)$ evaluated according to Eqn. 10 with the triplet probabilities $P_T(t)$ of Fig. 2. The magnetic field modulation ($B_{1/2}$ values) is seen to vary with different choices of k . This is due to the fact that for intermediate fields the triplet probability $P_T(t)$ of the pair ${}^2\text{BChl}_2^+$ ${}^2\text{BPh}^-$ is close to the $B=0$ curve at short times but approaches the $B \rightarrow 200 \text{ G}$ curve at longer times. Fast electron transfer (large k) samples the short time domain of $P_T(t)$ leading to larger $B_{1/2}$ values whereas slow electron transfer (small k) samples also the longer time domain, giving rise to smaller $B_{1/2}$ values. However, this effect cannot be responsible for the different magnetic field behaviour in various preparations of reaction centers. To yield $B_{1/2}$ values above 50 G one needed to assume enormous k values which would correspond to too short a lifetime of the radical pair. Also the absolute triplet yield decreases with increasing k much below the observed yield since for large k most pairs react at short times when they are still in the singlet electron spin state: $\varphi_T(B=0)$ amounts to 36.4, 5.81 and 1.69% for k values of 0.1, 0.5, and 1 ns^{-1} , respectively.

The irreversible electron transfer reactions bring about lifetime broadenings $\hbar k_S$ and $\hbar k_T$ of the energy levels of the singlet and triplet radical pairs, respectively. In the case $k_S \neq k_T$ the different broadenings of the singlet and triplet radical pair states effectively lower the singlet \rightarrow triplet transition probability (this does not necessarily apply in the case $J_{\text{PI}} \neq 0$). The $B_{1/2}$ value is enlarged since for a reduction of the $S_0 \rightarrow T_{\pm 1}$ transition probabilities the Zeeman splitting must overcome the difference in the energy band widths $\hbar|k_S - k_T|$. The $B_{1/2}$ value of 15 G obtained for the rate constant $k = \frac{1}{\tau_F} = 0.1 \text{ ns}^{-1}$ (τ_F is the measured lifetime of the radical pair) should therefore be a lower limit to the $B_{1/2}$ value of experimental systems which generally have different rate constants k_S and k_T .

For the case $k_S \neq k_T$ we have solved Eqn. 11 for a model system with only one nuclear spin $\frac{1}{2}$ on each radical. The hyperfine coupling constants 5 G and 10 G yield for the case $k_S = k_T = 0.1 \text{ ns}^{-1}$ at $B=0$ approximately the same triplet yield ($\varphi_T = 34.6\%$) as for the (${}^2\text{BChl}_2^+$ ${}^2\text{BPh}^-$) pair. This assures that these model calculations approximate well the realistic situation.

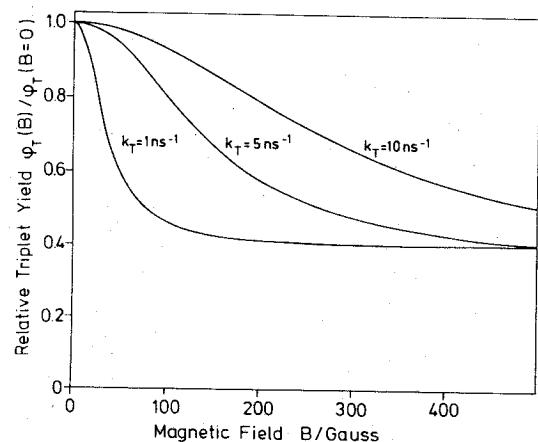


Fig. 4. Magnetic field dependence of the relative triplet yield $\varphi_T(B)/\varphi_T(B=0)$ for a model radical pair (see text) with hyperfine coupling constants $a_1 = 5$ G, $a_2 = 10$ G for various recombination rate constants k_T ($k_S = 0.1$ ns $^{-1}$, $k'_S = 0$, $J_{PI} = J_{IX} = 0$).

Fig. 4 presents the magnetic field dependence of the triplet yield $\varphi_T(B)$ for fixed $k_S = 0.1$ ns $^{-1}$ and k_T values 1, 5 and 10 ns $^{-1}$. The $B_{1/2}$ values are observed to shift to larger fields as k_T increases. This effect could indeed explain the high $B_{1/2}$ value observed in chromatophores. The absolute triplet yields decrease with increasing k_T : $\varphi_T(B=0)$ is predicted to be 19.4, 5.31, and 2.77% for k_T values of 1, 5 and 10 ns $^{-1}$, respectively. This result is explained by the decrease of the singlet \rightarrow triplet transition probability with increasing $h k_S - k_T$.

In Fig. 5 the magnetic field dependence of $\varphi_T(B)$ is compared for various k_S values and fixed $k_T = 1$ ns $^{-1}$. The results demonstrate that k_S exerts only a small influence on the $B_{1/2}$ value but determines crucially the magnitude of the

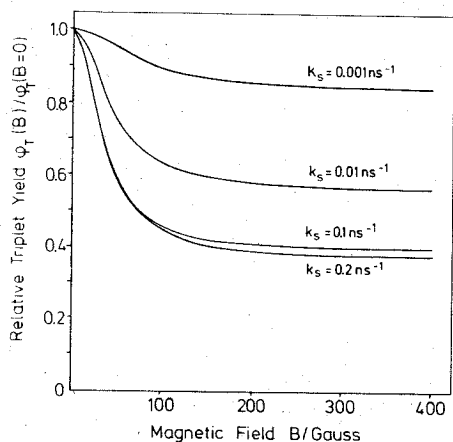


Fig. 5. Magnetic field dependence of the relative triplet yield $\varphi_T(B)/\varphi_T(B=0)$ for various rate constants k_S and fixed $k_T = 1$ ns $^{-1}$ (other parameters as in Fig. 4).

relative magnetic field effect * $\varphi_T(B \rightarrow \infty)/\varphi_T(B=0)$. For $k_S = 0$ one has $\varphi_T(B \rightarrow \infty)/\varphi_T(B=0) = 1$. The ratio $\varphi_T(B \rightarrow \infty)/\varphi_T(B=0)$ decreases with increasing k_S down to a minimum value of about 0.4. As to be expected the absolute triplet yield decreases with increasing k_S : $\varphi_T(B=0)$ is 96.0, 70.9, and 10.1% for k_S values of 0.001, 0.01, and 0.2 ns $^{-1}$, respectively.

(4) Exchange interactions

In order to demonstrate the effects of the exchange interactions J_{PI} and J_{IX} on the magnetic field dependence of the triplet yield we again model the hyperfine coupling in the ${}^2\text{BChl}_2^+$ and the ${}^2\text{BPh}^-$ radicals by just one nuclear spin $\frac{1}{2}$ with coupling constants 5 G and 10 G. The electron transfer rate constants are assumed to be $k_S = 0.1$ ns $^{-1}$ and $k_T = 1$ ns $^{-1}$. The reversible electron transfer will be neglected, viz. $k'_S = 0$.

The exchange interaction J_{PI} between the ${}^2\text{BChl}_2^+$ and the ${}^2\text{BPh}^-$ radical ions separates the S_0 and the $T_0, T_{\pm 1}$ radical pair spin levels by the energy $2J_{PI}$ and thereby suppresses the hyperfine-induced singlet \rightarrow triplet transitions. The observation of a magnetic field modulation of the triplet yield with $B_{1/2}$ values of order 100 G sets an upper bound of $\approx 10^{-6}$ eV on J_{PI} . Fig. 6 shows the magnetic field dependence of the triplet yield $\varphi_T(B)$ for J_{PI} values of 0, 10, 20, 50 and 100 G. The triplet yields at $B=0$ and at high fields decrease rapidly with increasing J_{PI} . However, for field strengths around $B = 2J_{PI}$ there is a resonance type increase of the triplet yield which originates from the crossing of the S_0 and $T_{\pm 1}$ states. Such feature has, however, not been detected by the experimental observations and one can conclude that J_{PI} is negligible.

The relative magnetic field effect $R(B \rightarrow \infty)$ has been found weaker in preparations in which the iron-ubiquinone complex is intact than in preparations where the iron was removed from the ubiquinone acceptor [11]. These experimental findings suggest that the variation of $R(B \rightarrow \infty)$ between 15 and 40% may result from differences in the electron spin exchange interaction between ${}^2\text{BPh}^-$ and ${}^2\text{X}^-$. The occurrence of this exchange interaction has also been concluded from ESR investigations [26].

At the instance of the primary electron transfer process the $({}^2\text{BChl}_2^+ {}^2\text{BPh}^-)$ radical ion pair is formed in a singlet electron spin state. The unpaired electron spin on the neighbouring ${}^2\text{X}^-$ is randomly oriented. An exchange interaction between ${}^2\text{BPh}^-$ and ${}^2\text{X}^-$ replaces the aligned (with respect to the ${}^2\text{BChl}_2^+$ spin) electron spin on ${}^2\text{BPh}^-$ by a random spin and introduces thereby a relaxation of the initial singlet spin state ${}^1({}^2\text{BChl}_2^+ {}^2\text{BPh}^-)$ to a mixture of singlet and triplet states. The result is an increase of the absolute triplet yield φ_T , but as the mechanism is independent of an external magnetic field, a reduction of the relative magnetic field effect $R(B \rightarrow \infty)$. In the light of this argument the small $R(B \rightarrow \infty)$ value of 15% for chromatophores with an intact iron-ubiquinone complex indicates a maximum exchange interaction which is reduced in R26 reaction center preparations with a $R(B \rightarrow \infty)$ value of 25% and is weakest

* $B \rightarrow \infty$ is to indicate a magnetic field large compared to the hyperfine coupling constants (e.g. $B = 1$ kG). The effect of small differences in the g -values of the radicals ${}^2\text{P}^+$ and ${}^2\text{I}^-$ which becomes important at larger fields is neglected.

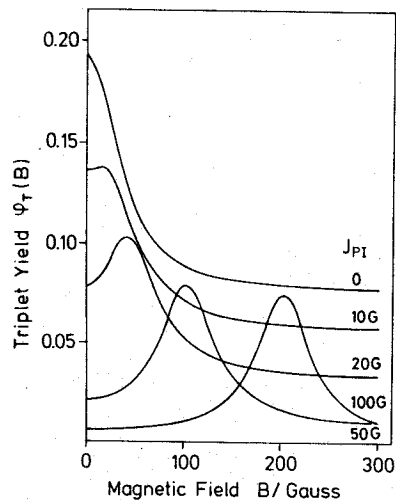


Fig. 6. Magnetic field dependence of the triplet yield $\varphi_T(B)$ for various exchange interactions J_{PI} . $k_S = 0.1 \text{ ns}^{-1}$, $k_T = 1 \text{ ns}^{-1}$ (other parameters as in Fig. 4).

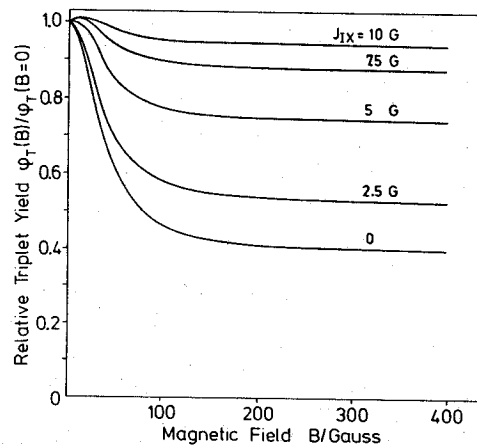


Fig. 7. Magnetic field dependence of the relative triplet yield $\varphi_T(B)/\varphi_T(B=0)$ for various exchange interactions J_{IX} ($k_S = 0.1 \text{ ns}^{-1}$, $k_T = 1 \text{ ns}^{-1}$, $k'_S = 0$, other parameters as in Fig. 4).

in the reaction center preparations which lack the iron complexed to the ubiquinone acceptor with an $R(B \rightarrow \infty)$ value of 40%.

The proposed effect of the exchange interaction J_{IX} on the relative triplet yield $\varphi_T(B)/\varphi_T(B=0)$ is demonstrated in Fig. 7. Rather weak exchange interactions suffice to suppress the magnetic field modulation of the relative triplet yield. As to be expected the absolute triplet yield increases with increasing J_{IX} : $\varphi_T(B=0)$ is predicted to be 19.4, 28.2, 45.1, and 79.2% for J_{IX} values of 0, 5, 10 and 50 G, respectively. The $B_{1/2}$ value is not shifted through the exchange interaction.

In our calculations we have neglected spin lattice relaxation effects. These can be important in the presence of iron bound to the ubiquinone complex since the spin lattice relaxation of Fe is of order 10^{-9} s at 10°K [1]. This relaxation would amplify the predicted effect of the exchange interaction J_{IX} on the magnetic field dependence of the triplet yield. It is possible that the differences of the magnetic field effect in samples with and without Fe originates from such enhanced relaxation rather than from changes in the J_{IX} values.

At low temperatures the absolute triplet yield has been found to be near 100%, i.e. much larger than the 10% yield at room temperature [2,27]. This finding could be explained by a temperature sensitivity of the rate constant k_S (see above). An alternative explanation would be an increase of the exchange interaction J_{IX} with decreasing temperature.

(5) Reversible electron exchange

The following experimental observations are indicative of the reversible electron transfer reaction $(^1P^* \ ^1I) \rightleftharpoons (^2P^* \ ^2I^-)$ described by the rate constants k_c and

k'_S in the reaction scheme of Fig. 1: (1) the fluorescence quantum yield of $^1P^*$ increases by a factor 3–5 when the “primary” acceptor X is chemically reduced [22,28,29]; (2) the $^1P^*$ fluorescence decays in parallel to the radical pair, its quantum yield was found to be temperature dependent indicating an activation energy of 0.12 eV [23].

The reversible electron transfer reaction leads to a coupling of the spin motion of the electrons in the excited singlet state $^1P^*$ and in the radical pair state. For a description of the coupled system one has to introduce the effect of the electron spin exchange interaction in $(^1P^* \ ^1I)$ of order $0.1 \text{ eV} \approx 10^7 \text{ G}$ which exceeds by far the hyperfine coupling and Zeeman energies. This large spin exchange interaction induces extremely rapid oscillations of the phases between different electron spin states. Since the electron transfer reactions are assumed to be random processes this brings about a factual relaxation of the electron spin phases in the radical pair and results in a reduction of the singlet \rightarrow triplet transition probability and, hence, of the triplet yield.

The relaxation of the electron-nuclear spin phases may be introduced directly into the Liouville equation without treating explicitly the electron spin motion in $^1P^*$. We assume that the nuclear spin states are not affected by the electron transfer $(^2P^* \ ^2I^-) \rightarrow (^1P^* \ ^1I)$ and denote by ρ_S the density matrix for the nuclear spin states of $(^1P^* \ ^1I)$. This leads to the equations

$$\dot{\rho}_S = k'_S Q_S \rho Q_S - (k_f + k_c) \rho_S \quad (12a)$$

$$\dot{\rho} = -\frac{i}{\hbar} [H, \rho] - \frac{1}{2} (k_S + k'_S) [Q_S, \rho]_+ + k_c \rho_S - \frac{1}{2} k_T [Q_T, \rho], \quad (12b)$$

which has to be complemented by the initial conditions

$$\rho_S(0) = Q_S / \{\text{tr} Q_S\} \quad (13a)$$

$$\rho(0) = 0. \quad (13b)$$

In our calculations we assume the rate constants k_f , k_c , k_S and k_T to be 0.1, 100, 0.1 and 1 ns^{-1} , respectively. These values are consistent with observations of bacteriochlorophyll reaction centers [1,3,5–7,28,29]. The hyperfine coupling constants on the two radicals are again taken to be 5 G and 10 G mimicking the hyperfine coupling situation in $(^2\text{BChl}_2^+ \ ^2\text{BPh}^-)$. The electron exchange interactions J_{PI} and J_{IX} are assumed to be zero. An upper bound for the k'_S value can be obtained from the measured activation energy of the reaction $(^2\text{BChl}_2^+ \ ^2\text{BPh}^-) \rightarrow (^1\text{BChl}_2^+ \ ^1\text{BPh})$ or 0.12 eV [23] and the rate constant $k_c \approx 100 \text{ ns}^{-1}$ for the reverse reaction for which the activation energy can be neglected:

$$k'_S \leq k_c \exp(-0.12 \text{ eV}/kT) \approx 1 \text{ ns}^{-1} \text{ at } T = 25^\circ\text{C}.$$

In Fig. 8 the magnetic field dependence of the relative triplet yield $\varphi_T(B)/\varphi_T(B=0)$ for $k'_S = 0.5, 1, 5$ and 10 ns^{-1} is presented. Most remarkable is the enormous shift of the $B_{1/2}$ values to large fields with increasing k'_S . In Tables I and II the absolute yields of triplet products φ_T and of fluorescence and radiationless decay (mainly intersystem crossing) φ_f are compared at zero and high fields for various values of k_S and k'_S . As to be expected the triplet yield φ_T decreases with increasing k_S and k'_S . φ_f increases with increasing k'_S but

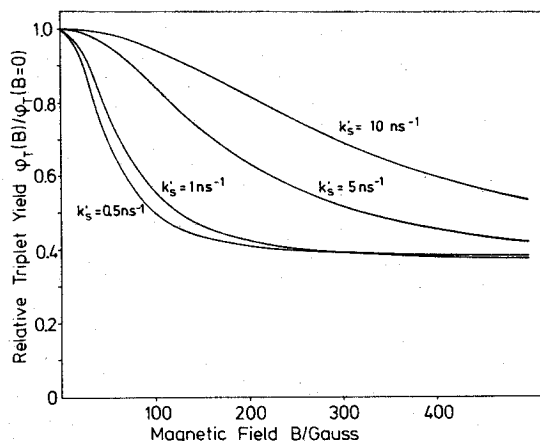


Fig. 8. Magnetic field dependence of the relative triplet yield $\varphi_T(B)/\varphi_T(B=0)$ for various rate constants k'_S ($k_S = 0.1 \text{ ns}^{-1}$, $k_T = 1 \text{ ns}^{-1}$, other parameters as in Fig. 4).

decreases with increasing k_S . Since at high magnetic fields the radical pairs stay longer in the singlet electron spin state than at low fields a positive magnetic field effect on the fluorescence yield is predicted. The magnitude of this effect depends, however, sensitively on the value of k_S .

The radiative lifetime of the fluorescence has been estimated to be 20–30 ns [28,29], that of intersystem crossing to be about 25 ns [11]. The fluorescence quantum yield is therefore approximately one half of the total yield φ_f in Tables I and II. The fluorescence quantum yield of intact reaction centers has been determined to be 0.03–0.04% [28,29]. If the primary acceptor is reduced the yield increases to 0.12–0.15%. The lifetime of the intact state ($^2P^+ ^2I^-$) 1X is about 250 ps corresponding to $k_S = 4 \text{ ns}^{-1}$ *. The fluorescence quantum yield $\frac{1}{3}\varphi_f$ obtained for this value and $k'_S = 0.5 \text{ ns}^{-1}$ (Table I) is in good agreement with the experimental result. This value of k'_S is in harmony with the above estimate $k'_S \leq 1 \text{ ns}^{-1}$. The lifetime of the reduced state ($^2P^+ ^2I^-$) $^2X^-$ is about 10 ns which implies $k_S \leq 0.1 \text{ ns}^{-1}$. Satisfactory agreement between the predicted and experimental fluorescence quantum yields is obtained indeed for the rate constants $k_S = 0.1 \text{ ns}^{-1}$ and $k'_S = 0.5 \text{ ns}^{-1}$. Also the triplet yield $\varphi_T(B=0)$

TABLE I
TRIplet AND FLUORESCENCE QUANTUM YIELDS FOR $k'_S = 0.5 \text{ ns}^{-1}$ (in percent)

Results are evaluated with the parameters: $k_T = 1.0 \text{ ns}^{-1}$, $k_c = 100 \text{ ns}^{-1}$, $k_f = 0.1 \text{ ns}^{-1}$, $a_1 = 5 \text{ G}$, $a_2 = 10 \text{ G}$, $J_{IP} = J_{IX} = 0$ (see text).

k_S (ns^{-1})	$\varphi_T(B=0)$	$\varphi_T(B \rightarrow \infty)$	$\varphi_f(B=0)$	$\varphi_f(B \rightarrow \infty)$	$\varphi_f(B \rightarrow \infty)/\varphi_f(B=0)$
0.001	91.5	67.2	2.90	11.0	3.8
0.01	61.4	31.4	1.93	3.36	1.7
0.1	14.5	5.42	0.52	0.57	1.1
1	1.12	0.38	0.15	0.15	1.0
4	0.13	0.044	0.11	0.11	1.0

* Here we describe by k_S also the decay of the singlet radical pair $^1(2P^+ ^2I^-)^1X \rightarrow (2P^+ ^1I)^2X^-$.

TABLE II
TRIplet AND FLUORESCENCE QUANTUM YIELDS FOR $k'_S = 5 \text{ ns}^{-1}$ (in percent)
Parameters as in Table I.

k_S (ns^{-1})	$\varphi_T(B=0)$	$\varphi_T(B \rightarrow \infty)$	$\varphi_f(B=0)$	$\varphi_f(B \rightarrow \infty)$	$\varphi_f(B \rightarrow \infty)/\varphi_f(B=0)$
0.001	42.5	18.8	47.9	67.7	1.41
0.01	23.4	9.12	25.6	30.3	1.18
0.1	4.26	1.47	4.65	4.78	1.03
1	0.41	0.14	0.59	0.59	1.00
4	0.072	0.024	0.22	0.22	1.00

which is calculated to be 14.5% is in reasonable agreement with the experimental value of 10% (at room temperature) [2]. For smaller k_S values, however, the fluorescence as well as the triplet yields become much larger than the experimental values. These results support strongly the assumption that recombination from the radical ion pair to the singlet ground as well as to the singlet excited state occurs, and that the values 0.1 and 0.5 ns^{-1} are reasonable estimates of the rate constants k_S and k'_S , respectively, describing these processes.

The above discussion applies to reaction center preparations of *Rps. sphaeroides*. In order to explain the large $B_{1/2}$ values of 250 G of the chromatophore preparations one has to postulate a k'_S value of about 5 ns^{-1} for which the yields are given in Table II. In light of the sensitive dependence of k'_S on the energy difference between the ($^1\text{BChl}_2^+ ^1\text{BPh}^-$) $^2X^-$ and the ($^2\text{BChl}_2^+ ^2\text{BPh}^-$) $^2X^-$ state as well as on the distance and orientation of the donor and acceptor groups, such a shift in the k'_S value upon variation of the reaction center preparation is no surprise. It would be of great interest in this respect to measure in different reaction center preparations the fluorescence quantum yield and its magnetic field dependence and, in particular, the temperature dependence of the $B_{1/2}$ value. If k'_S is indeed responsible for the $B_{1/2}$ shift a lowering of the temperature should decrease k'_S and, thereby, shift $B_{1/2}$ to lower fields.

(6) Conclusions

We have demonstrated that intermolecular interactions which are characteristic of the initial electron transfer process contribute to the magnetic field dependence of the primary photochemical reactions in reaction centers of bacterial photosynthesis. The observed shift of the $B_{1/2}$ values of the relative magnetic field effect $R(B)$ have been traced to variations in the rate constant of reversible transfer between the ($^2\text{BChl}_2^+ ^2\text{BPh}^-$) radical pair and the $^1\text{BChl}_2^+$ excited singlet state (see Fig. 1). It has been predicted that this mechanism should induce a shift of $B_{1/2}$ to lower fields with decreasing temperature and give rise to a magnetic field effect on the fluorescence quantum yield. The larger $B_{1/2}$ values in some reaction center preparations may also be explained by the assumption of different rate constants of irreversible electron transfer for singlet and triplet radical pairs which result in a different lifetime broadening of the radical pair singlet and triplet states. The reversible and irreversible electron transfer reactions have only a minor influence on the magnitude of the relative magnetic field effect, viz. $R(B \rightarrow \infty)$. Variations of $R(B \rightarrow \infty)$ can origi-

nate from the electron exchange interaction between the ${}^2\text{BPh}^-$ and the reduced iron-ubiquinone acceptor. From a comparison between observed yields of triplet states, fluorescence yields, $B_{1/2}$ and $R(B \rightarrow \infty)$ values and the results of model calculations we have estimated electron transfer rate constants and electron exchange interaction constants.

Acknowledgements

We like to thank A.J. Hoff for drawing our attention to the subject studied in this paper and placing his results at our disposal prior to publication. The excellent computer facilities of the Gesellschaft für wissenschaftliche Datenverarbeitung mbH Göttingen are acknowledged.

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