EXPLORING FAST ELECTRON TRANSFER PROCESSES BY MAGNETIC FIELDS

KLAUS SCHULTEN AND ALBERT WELLER, *Max-Planck-Institut für*
Biophysikalische Chemie, Abteilung Spektroskopie,
D 3400 Göttingen, Germany

ABSTRACT Photoinduced electron transfer generates radical pairs which recombine within 10^{-9}–10^{-8} s by electron back-transfer to either singlet or triplet products. The product distribution determined by the spin motion of the unpaired electrons in the radical pairs is affected by external magnetic fields. The analysis of the magnetic field effect furnishes new information about electron transfer processes. Light-induced electron transfer in polar solvents and in the bacterial photosynthetic reaction center are discussed as examples.

INTRODUCTION

Unpaired electron spins in radicals experience various interactions (e.g. spin-orbit, exchange, hyperfine, Zeeman) and as a result carry out coherent and stochastic motions. In aromatic radicals without heavy atom substituents the electron spin motion over short periods of about 100 ns is coherent, because of the intramolecular hyperfine interaction between the unpaired electron spins and their surrounding nuclear spins. This motion entails the precession of the unpaired electron spins around an axis given by a combination of the nuclear magnetic moments with a frequency of 10^7–10^9 s^{-1}. An additional precession can be induced through the Zeeman interaction by an external magnetic field.

When radical pairs are generated in a pure quantum state, e.g. by a photon-induced electron transfer in a singlet spin state, this motion can be observed through the radical recombination products, the spin multiplicity of which is determined by the relative orientation of the electron spins at the instant of recombination (e.g. electron back-transfer). External magnetic fields alter the electron spin motion and, thereby, also the yields of (singlet versus triplet) recombination products (1). An analysis of the hyperfine coupling-induced recombination yields and their magnetic field modulation furnishes valuable information about the existence of a short-lived radical pair and its microscopic diffusion in a solvent-mediated force field, and about the reaction propensities to form singlet and triplet products (1–3).

The transformation of light into chemical energy in the photosynthetic apparatus of bacteria and plants originates also from a photoinduced electron transfer reaction. In the case of the bacterium *Rhodopseudomonas spheroides* under conditions that enforce electron back-transfer, the reaction processes are also affected by external magnetic fields (4–6). These magnetic field effects originate from the hyperfine coupling in the

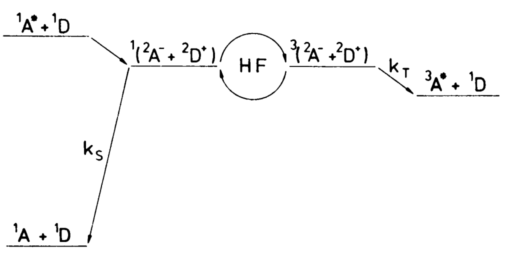

FIGURE 1

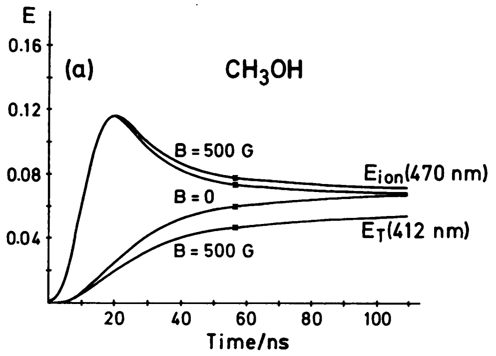

FIGURE 2

FIGURE 1 Reaction scheme for the primary electron transfer processes of electron donor-acceptor systems in polar solvents. Singlet, doublet, and triplet states are indicated by the left-hand side superscripts 1, 2, and 3, respectively.

FIGURE 2 Time evolution of the radical ion ($E_{\mathrm{ion}} = 10.8 \times 10^3\, C_{\mathrm{ion}}$[mol/liter]) and triplet ($E_T = 8.7 \times 10^3\, C_T$[mol/liter]) extinction of the system pyrene/*N*,*N*-dimethylaniline in methanol with and without an external magnetic field of 500 G. Error bars indicate standard deviations obtained from 8–10 measurements.

radicals but, more interestingly, depend also on other spin-dependent interactions characteristic of the primary electron transfer in photosynthesis.

ELECTRON TRANSFER PROCESSES IN SOLUTION

The electron transfer system employed in the study described in this chapter is presented in Fig. 1 by its relevant energy levels. In polar solvents (e.g. methanol, acetonitrile) electron acceptor molecules A (pyrene) are excited by a nanosecond laser flash from the singlet ground state ${}^1A$ to the singlet excited state ${}^1\overset{*}{A}$. Upon excitation the electron affinity of the acceptor molecules is increased so that when they collide with a donor molecule ${}^1D$ (*N*,*N*-dimethylaniline) an electron is transferred, resulting in the formation of a radical ion pair (${}^2A^- + {}^2D^+$). In this pair the electron can be transferred back. For this process there are, however, two possibilities in which either the singlet ground state (${}^1A + {}^1D$) or the triplet excited state of the acceptor (${}^3\overset{*}{A} + {}^1D$) is produced. The state obtained depends on the relative alignment of the two unpaired electron spins at the moment of the electron back-transfer: singlet alignment leads to the singlet ground state and triplet alignment to the triplet state.

Actually the recombination (i.e. electron back-transfer) takes place over two different time periods. A slow, so-called homogeneous, recombination occurs after separation of the initially formed radical ion pairs. Because of the small concentration of the initial pairs, the radicals have to diffuse for about 10 μs before they encounter other free radical ions with subsequent electron transfer. In these random encounters of radicals the electron back-transfer can result in singlet as well as triplet products. Since the relative orientation of the electron spins of ${}^2A^-$ and ${}^2D^+$ is random, one has a 25% probability for singlet and a 75% probability for triplet alignments. Hence predominantly triplet products are to be expected in the homogeneous recombination phase of the radical pairs.

A fast so-called geminate recombination results from the direct back-transfer of the electron within the initially formed radical pairs. These pairs, however, are generated from singlet precursors and it is, therefore, to be expected that they are produced in a singlet spin state, i.e. ${}^1({}^2A^- + {}^2D^+)$. Hence, only singlet products ${}^1A + {}^1D$ should result from the electron back transfer, except if during the lifetime of the pairs the hyperfine interaction succeeds in bringing the electron spins to a triplet alignment, i.e. ${}^3({}^2A^- + {}^2D^+)$.

The question of whether triplet products are formed in recombinations of radical ion pairs can be settled by observing the concentration of the ions ${}^2A^- + {}^2D^+$ and the triplet products ${}^3\overset{*}{A}$ by means of time-resolved absorption spectroscopy. Fig. 2 shows for the acceptor/donor system pyrene/*N*,*N*-dimethylaniline in the solvent methanol the observed radical ion and triplet concentrations obtained from the absorption of ${}^2A^-$ (at 470 nm) and ${}^3\overset{*}{A}$ (at 412 nm). The radical ion signal shows a very rapid rise after the laser flash and a decay in two time domains, a fast process lasting for several nanoseconds and a slow one extending over much longer times. The different decay modes of the radical ions entail the geminate and the homogeneous recombination (1). It is clearly seen in Fig. 2 that triplet products are formed at short as well as longer times. The early triplet products originate from the geminate phase of the radical ion pair recombination.[1] This implies that the hyperfine induced spin motion leading from singlet to triplet alignments takes place within the time the radicals spend in each other's neighborhood before they separate. Fig. 2 also demonstrates that the radical ion as well as the triplet product concentrations are affected by an external magnetic field. In a field of 500 G the triplet product concentration is reduced and the radical ion concentration slightly increased. This effect originates from the influence of the magnetic field on the electron spin motion and is demonstrated schematically in Fig. 3. For radical pairs with predominating hyperfine interaction (zero-field-splitting in the triplet radical pair and exchange interaction [J] negligible) the singlet and three triplet spin states are virtually degenerate at zero field and the hyperfine-induced transitions between these states occur at optimum rate. However, an applied external magnetic field lifts the degeneracy of the two triplet levels $T_{\pm 1}$ and, thereby, reduces the transitions from the initially occupied S_0 state to the $T_{\pm 1}$ states, until at fields which exceed appreciably the sum of the hyperfine coupling constants in the radicals (i.e. ca. 100 G for the pyrene/*N*,*N*-dimethylaniline system) these transitions are totally abolished.

The magnetic field reduction of the triplet yield is seen in Fig. 2 to build up during the geminate phase and to remain constant during the later homogeneous phase, i.e. the magnetic field modulation filters out the most interesting fast geminate process of the radical recombination. To abstract from the observations presented in Fig. 2 information on the detailed dynamics of geminate electron transfer processes, a theoreti-

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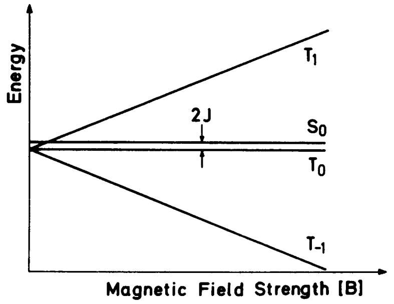
[1] The fast decay of the ion signal at short times does also reflect the disappearance of an exciplex ${}^1(A^- D^+)$ by intersystem crossing to give ${}^3\overset{*}{A} + {}^1D$.



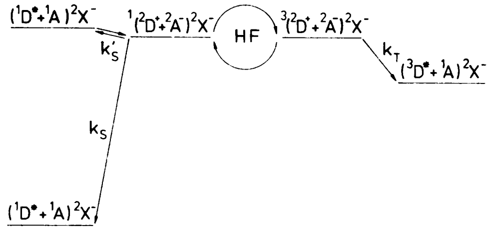


FIGURE 3 Magnetic field dependence of the radical ion pair singlet and triplet state energies (J = exchange interaction energy). The observed magnetic field effects demonstrate that the hyperfine interaction coupling, inducing coherent $S \rightleftarrows T$ transitions in the radical pairs, is predominant.

FIGURE 4 Reaction scheme for the primary electron transfer processes in bacteriochlorophyll reaction centers with reduced primary acceptor X. Singlet, doublet, and triplet states are indicated by the left-hand side superscripts 1, 2, and 3, respectively.

cal analysis is necessary (2, 3). Two results of such an analysis should be mentioned here. Firstly, one can show that any intrapair exchange interaction between the ${}^2A^-$ and ${}^2D^+$ radical ions exceeding the weak intramolecular hyperfine interaction abolishes singlet $\rightleftarrows$ triplet transitions. The observed magnetic field effect, hence, provides unequivocal evidence for the formation of free radical ions after the photoinduced electron transfer which engage in a Brownian motion in their respective Coulomb fields before they interact. Secondly, theory predicts that isotopic replacement changes the hyperfine interaction and shifts the magnetic field modulation (3). This could be confirmed experimentally by using the perdeuterated pyrene/*N*,*N*-dimethylaniline system, where the magnetic field modulation occurs at considerably lower fields than with the protonated system (7).

ELECTRON TRANSFER PROCESSES IN BACTERIAL PHOTOSYNTHESIS

The transformation of light energy in the photosynthetic apparatus of bacteria is based on a photoinduced electron transfer reaction in a membrane-bound complex of pigments and proteins, the reaction center. The reaction system is presented in Fig. 4. The primary electron transfer follows in this case excitation of the donor ${}^1D$, probably a bacteriochlorophyll dimer. The electron acceptor ${}^1A$ is generally assumed to be bacteriopheophytin. Under normal conditions the electron is being transferred within 100–250 ps from ${}^2A^-$ to a second acceptor X, probably an iron-ubiquinone complex (8). If X is reduced chemically (${}^1X \rightarrow {}^2X^-$) or removed, the electron transfer is blocked and the lifetime of the initial radical pair (${}^2D^+ + {}^2A^-$) increases to about 10 ns, this time reflecting the electron back transfer to ${}^2D^+$. The spin multiplicity of the donor molecule in the reaction center, i.e. (${}^1\overset{*}{D} + {}^1A$), (${}^3\overset{*}{D} + {}^1A$), (${}^1D + {}^1A$) depends in this case again on the relative alignment of the two electron spins at the instance of the electron jump, the system behaves very similarly to donor-acceptor pairs in solution. In fact, the yield of triplet products $({}^3\overset{*}{\mathrm{D}} + {}^1\mathrm{A})$ generated in the reaction centers of ***Rhodopseudomonas spheroides*** with a reduced X is also lowered by external magnetic fields (4, 5). It was found, however, that the relative magnetic field effect depends sensitively on the preparation of the reaction center samples (5). This dependence originates from intermolecular interactions characteristic of the electron transfer processes in the reaction center.

The magnetic field effect on the geminate recombination process of radical pairs in solution reflects solely the intramolecular hyperfine coupling. 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 are therefore not influential. The photosynthetic reaction center is, however, a "solid-state" system, the ${}^2\mathrm{D}^+$ and ${}^2\mathrm{A}^-$ moieties are in permanent contact, and the above interactions influence the electron spin motion continuously and, therefore, contribute to the magnetic field dependence of the yield of triplet products ${}^3\overset{*}{\mathrm{D}}$. For a theoretical demonstration, one can consider the case where the reversible electron transfer $({}^1\overset{*}{\mathrm{D}} + {}^1\mathrm{A}) \rightleftarrows ({}^2\mathrm{D}^+ + {}^2\mathrm{A}^-)$, as well as exchange interactions, can be neglected and where for the rates k_S and k_T of irreversible electron transfer holds: $k_S = k_T = k$. Fig. 5 displays the predicted magnetic field dependence of the relative triplet yield $\phi_T(B)/\phi_T(B = 0)$ for various values of k. One finds that with increasing k the magnetic field modulation shifts slightly to higher fields. The reason for this behavior is that fast electron transfer (large k) samples the short time domain of the spin motion when larger fields are needed to affect the spin motion. However, this effect cannot account solely for the high field effects observed by Hoff et al. (5).

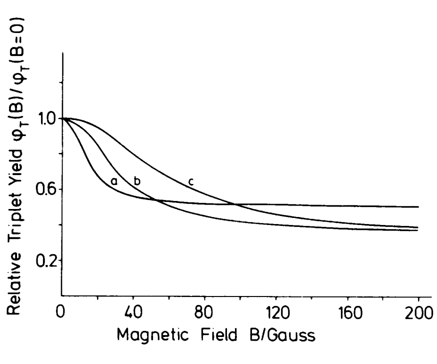


FIGURE 5 Magnetic field dependence of the relative triplet yield $\phi_T(B)/\phi_T(B = 0)$ from the $({}^2\mathrm{D}^+ + {}^2\mathrm{A}^-)$ radical pairs calculated with the sums of the hyperfine coupling constants $\Sigma a_{D^+} \sim 24$ G (for the bacteriochlorophyll radical) and $\Sigma a_{A^-} \sim 32$ G (for the bacteriopheophytine radical) and with $k_S = k_T = k$ for a, $k = 0.1 \times 10^9\ \mathrm{s}^{-1}$; b, $k = 0.5 \times 10^9\ \mathrm{s}^{-1}$; c, $k = 1.0 \times 10^9\ \mathrm{s}^{-1}$ (exchange interactions $J_{\mathrm{D,A}} = J_{\mathrm{A,X}} = 0$).

The irreversible electron transfer processes $^3(^2D^+ + {}^2A^-) \rightarrow {}^3(^3D + {}^1A)$ and $^1(^2D^+ + {}^2A^-) \rightarrow {}^1(^1D + {}^1A)$ bring about lifetime broadenings $\hbar k_S$ and $\hbar k_T$ of the energy levels of the singlet and triplet radical pair states, respectively. Higher magnetic fields are necessary in order for the Zeeman splitting to overcome the relative energy band width $\hbar(k_S - k_T)$, separating sufficiently the S_0 and $T_{\pm 1}$ states and inducing a reduction of triplet products. The reversible electron transfer $(^1\overset{*}{D} + {}^1A) \rightleftarrows (^2D^+ + {}^2A^-)$ has a similar effect as high $k_S = k_T = k$ values in that it restricts the spin motion to the short time regime, thereby shifting the magnetic field modulation up-field. Further effects on the electron spin motion are exerted by the exchange interaction between $^2D^+$ and $^2A^-$ and between $^2A^-$ and $^2X^-$. The first interaction tends to abolish the magnetic field modulation. The fact that a magnetic field modulation of the triplet yield is observed implies that this exchange interaction is smaller than the weak intramolecular hyperfine coupling, a finding with important ramifications with respect to the electron transfer mechanism. The exchange interaction between $^2A^-$ and $^2X^-$ has the net effect of donating a random spin to the $(^2D^+ + {}^2A^-)$ pair and, thereby, giving rise to a magnetic field independent formation of triplet pairs. From a comparison between observed yields of triplet states, their magnetic field modulation, and results of model calculations one can estimate electron transfer rate constants and the magnitude of the exchange interactions in the bacterial photosynthetic reaction centers (6).

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NOTE ADDED IN PROOF

Photoinduced electron transfer processes produce in a picosecond to nanosecond time range high energy intermediates: exciplexes, radical ion pairs, and separated free radical ions. The fast processes involved are fundamental for oxidation-reduction processes as they occur in chemical, electrochemical, and biological (for example photosynthesis) systems. Since these reactions involve the motion of an electron, they should be extremely fast ($\sim 10^{-15}$ s) except that they are coupled to slower degrees of freedom, which are rate-limiting and, therefore, the focal point of most studies. Degrees of freedom coupled to electron transfer are those of the microenvironment, of internal vibrations, and of the relative distance of the reactants (Fig. 1).

Electron transfer reaction between electron donors, (e.g. dimethylamiline)$_*$in the ground state, D, and electron acceptors (e.g. pyrene) in the excited singlet state, $^1\overset{*}{A}$, produce the following intermediates (sequentially):

singlet exciplexes   radical ion pairs   free radical ions
(in the overall singlet state with unrelated spins)

$$^1(A^-D^+) \;\rightarrow\; ^1(^2A^- + {}^2D^+) \;\rightarrow\; ^2A^- + {}^2D^+.$$

From these triplet products are formed via three different pathways: (*a*) intersystem crossing in the exciplex; (*b*) germinate (or intrapair) recombination of the solvated radical ion pairs; (*c*) homogeneous (or interpair) recombination of the free radical ions.

Only the germinate triplet production (pathway *b*), due to the hyperfine coupling between the

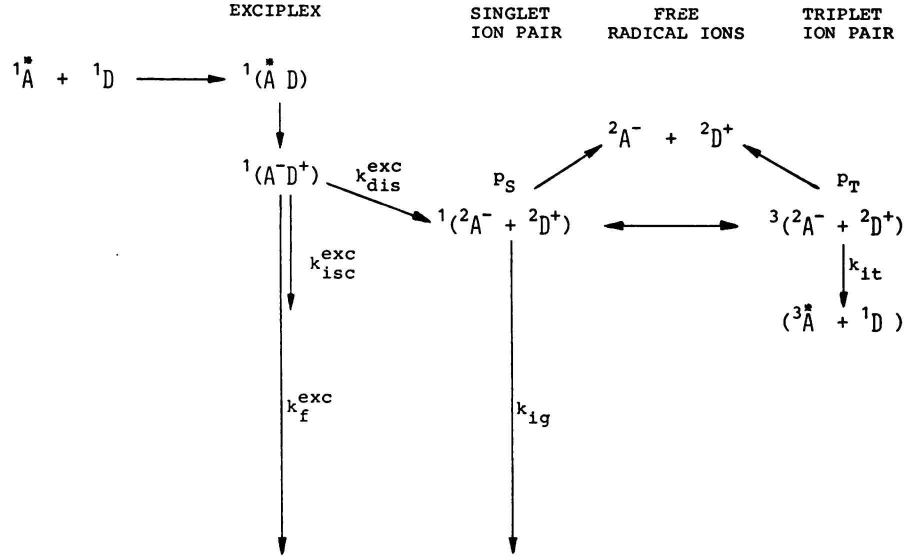

FIGURE 1 Reaction scheme for electron transfer involving exciplex formation followed by radical ion pair formation; only the electron spin motion in the radical ion pairs is influenced by external magnetic fields which modulate the hyperfine coupling-induced (singlet versus triplet) recombination yields.

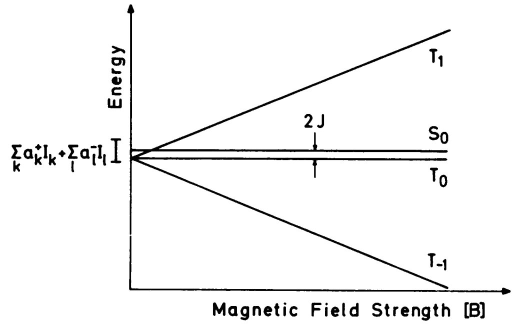

FIGURE 2

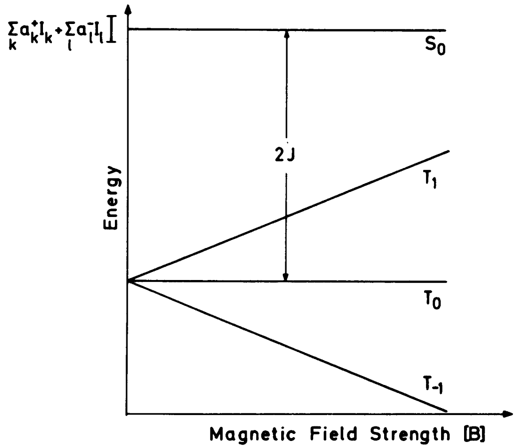

FIGURE 3

FIGURE 2 Magnetic field dependance of the radical ion pair singlet and triplet state energies (J = exchange interaction energy).

FIGURE 3 Magnetic field dependence of the radical ion pair singlet and triplet state energies under the condition that the exchange interaction energy, J, is much greater than the hyperfine coupling energy, E_{hfc} (indicated by the energy bar ⌶).

nuclear spins and the unpaired electron spin in each radical, is reduced by weak external magnetic fields between 0 and 100 G (Fig. 2).

This reduction of the germinate triplet production is based on the fact that at zero magnetic field strength the three triplet states T_{+1}, T_0, T_{-1} are degenerate and can all be populated within the hyperfine coupling energy range (indicated by the bar ⌶) from the initially populated singlet state S_0, which can lead to a maximum of 75% triplet population, whereas at higher magnetic field strengths only T_0 can be populated from S_0, which leads at the most to only 50% triplet population.

It is important to point out that triplet production from the exciplex and triplet production through homogeneous recombination of the free radical ions are not affected by weak magnetic fields. Therefore, from the magnetic field-modulated signal of the recombination products inferences can be drawn about the mechanistic aspects of the radical ion recombination process.

An important aspect is the magnitude of the exchange interaction between the radicals in the radical ion pair (Fig. 3).

The hyperfine interaction energy (indicated by the bar ⌶) may be typically of the order of 50 G, which corresponds to a rate of 1.4×10^8 s^{-1}. Now, if J is 100 times greater (i.e. 5,000 G), population of T_{+1}, T_0, T_{-1} from S_0 by the hyperfine mechanism is not possible anymore. The repopulation now requires that an energy of the order of $2J$ (10,000 G) be exchanged between the spin-system and the heat bath environment. The required spin-lattice relaxation time, T_1, to do that is of the order of 1 μs, so that the triplet population rate now is only $T_1^{-1} \approx 10^6$ s^{-1}. Thus no triplets are formed from the germinate radical pair because its lifetime is too short by at least one or two orders of magnitude.

It should be pointed out that the value assumed here for J, namely 5,000 G or 0.6×10^{-4} eV, is still very small. A very rough guess suggests that it corresponds to a radical pair center to center distance of about 5Å (Fig. 4).

Bacterial photosynthesis in three different preparations investigated by Hoff and co-workers (5) shows a magnetic field effect, in that the relative triplet yield decreases with increasing

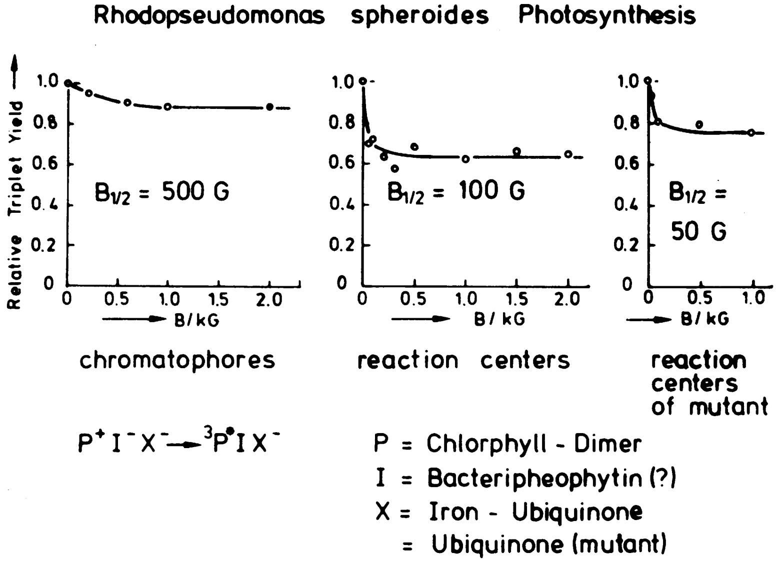

FIGURE 4 Magnetic field dependence of the yield of bacteriochlorophyll triplets generated in reaction centers of *Rhodopseudomonas spheroides* with reduced acceptor X (from Hoff et al., ref. 5).

magnetic field by 15–60%, depending on the type of the reaction center and its preparation. This shows that the electron exchange interaction $J_{P^+I^-}$ (between oxidized bacteriochlorophyl [dimer] and reduced bacteriopheophytin) must be smaller than 100 G or 10^{-6} eV. This small value is very remarkable in view of the "solid state" character in the membrane environment of the reaction centers, in which the electron cannot be transferred over large distances within the short times available except by tunneling.

In the exchange interaction $J_{I^-X^-}$ between reduced bacteriopheophytin (I^-) and the reduced iron-ubiquinone complex (X^-), the aligned electron spin on I^- (aligned with respect to the spin on P^+) is replaced by a random spin (from X^-) and thus introduces more triplet character to the P^+I^- systems thereby reducing the relative magnetic field effect. Since the chromatophore preparations still have an intact iron-ubiquinone complex, one may assume that with the chromatophores $J_{I^-X^-}$ is greater than with the other reaction center preparations so that the magnetic field effect is weaker, but that $J_{I^-X^-}$ is still not great enough to wipe out the magnetic field effect completely.

DISCUSSION

SWENBERG: I would like to know whether the overall photosynthetic yield is affected by an external magnetic field.

WELLER: Under normal photosynthetic conditions the previously formed radical ion pair in its overall singlet state decays in about 120 ps, according to Kaufmann, by donating the electron to a secondary acceptor, ubiquinone. There does not seem to be any substantial leakage through which the primarily formed radical ion pair would go over into the bacteriochlorophyll triplet state. In other words, the lifetime of the primary formed radical ion pair, 120 ps, is much too short for a magnetic field effect to be operative under normal photosynthetic conditions.