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Effect of magnetic fields on the triplet state lifetime in photosynthetic reaction centers: Evidence for thermal repopulation of the initial radical pair

(photosynthesis/electron transfer/magnetic field effects)

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ABSTRACT **The *lifetime* of the molecular triplet state formed by recombination of the radical ion pair in quinone-depleted bacterial photosynthetic reaction centers is found to depend on applied magnetic field strength. It is suggested that this magnetic field effect results from thermally activated repopulation of the same radical ion pair that generates the triplet. Consistent with this hypothesis, the magnetic field effect on the triplet lifetime disappears at low temperature where the triplet state decays exclusively by ordinary intersystem crossing. This activated pathway for the decay of the triplet state can explain the strong temperature dependence of the triplet decay rate. A detailed theoretical treatment of the problem within a set of physically reasonable assumptions relates the observed temperature dependence of the triplet decay rate to the energy gap between the radical ion pair intermediate and the triplet state. This energy gap is estimated to be about 950 cm^{-1} (0.12 eV). Combined with an estimate of the energy of the donor excited state, we obtain an energy gap between the excited singlet state of the donor and the radical ion pair of 2,250 cm^{-1} (0.28 eV).**

The examination of magnetic field effects has provided a great deal of insight into the initial chemistry of photosynthesis (for a review, see ref. 1). Magnetic fields influence the outcome of the initial photochemistry by modifying the electron-spin evolution of the initially formed radical ion pair, thus affecting the competition between spin-state-dependent decay pathways.

The initial photochemistry in reaction centers (RCs) from the bacterium *Rhodopseudomonas sphaeroides* R-26 mutant, when subsequent electron transfer is blocked by removal or prior reduction of ubiquinone, can be modeled by the reaction scheme shown in Fig. 1. The primary electron donor, P, is excited to its first singlet state, ^{1}P, and transfers an electron to the primary electron acceptor, I, forming the singlet-correlated ion pair, $^1(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$. $^1(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ can decay by three routes: activated recombination to the precursor, ^{1}PI; recombination to the ground state, PI (rate k_S); and evolution to the triplet-correlated radical pair, $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$. $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ either decays by recombination to generate the excited triplet state of P, ^{3}P (rate k_T), or it evolves back to $^1(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$. The rate of interconversion between the singlet and triplet radical-pair states is characterized by a magnetic field-dependent parameter, $\omega(H)$. At zero magnetic field, the nuclear hyperfine interaction causes interconversion of the singlet radical-pair state and all three triplet radical-pair states. When the magnetic field is increased from 0 to about 1 kG (1 gauss = 1 × 10^{-4} tesla), the rate of interconversion decreases because of loss of the near degeneracy of the singlet and two of the triplet radical-pair states; as the field is increased beyond 1 kG, $\omega(H)$ increases because the g-factor difference between P$^{\dot{+}}$ and I$^{\dot{-}}$ becomes the dominant mechanism for interconversion. It is evident that the applied magnetic field, by varying the interconversion rate, may affect the quantum yields of states produced from the radical pair and the lifetimes of states that decay through the radical pair. The effects of magnetic fields on the fluorescence lifetime and quantum yield (2), on the radical-pair decay rate (2, 3), and on the quantum yield of ^{3}P have been reported (4–10).

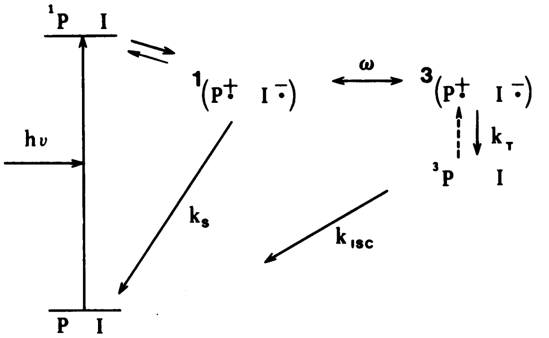

FIG. 1. Kinetic scheme for the initial photochemistry in quinone-depleted *R. spheroides* RCs. Activated formation of $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ from ^{3}PI (dotted arrow) is the new pathway considered in this paper.

In this paper we report the observation that the *lifetime* of ^{3}P depends on the applied magnetic field. If the scheme in Fig. 1 is modified to include the thermally activated reformation of $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ from ^{3}P as indicated by the dotted line, it is evident that the decay of ^{3}P also could depend on the magnetic field because of decay through $^1(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$. One expects that the observed triplet decay rate would decrease as the field strength is raised from 0 to 1 kG because of the decrease in the interconversion rate and that the decay rate would increase at higher fields as $\omega(H)$ increases in much the same manner as the observed dependence of the triplet quantum yield on field. This effect should go away at lower temperatures as the thermally activated route becomes inaccessible, leaving only the intersystem-crossing decay path (rate constant k_{isc}). These effects are precisely what we observe.

EXPERIMENTAL

RCs from the bacterium *R. sphaeroides* R-26 mutant were prepared by standard procedures (2). Quinone-depleted RCs were obtained as described by Okamura *et al.* (11). Quinone-containing RCs were reduced (Q$^{\dot{-}}$) by anerobic addition of

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Abbreviation: RC, reaction center.

sodium dithionite. Q^{2-} RCs were prepared by irradiation in the presence of cytochrome *c* and sodium dithionite (11). The RCs were suspended in buffer (10 mM Tris·HCl, pH 8.0/0.1% Triton X-100 (TT buffer) or 65% (wt/vol) ethylene glycol/TT buffer). All samples were deoxygenated by repeated cycles of evacuation followed by addition of N_2. The samples were held in a 1-mm pathlength variable-temperature cell (temperature control ± 1°C) in a Helmholtz coil (0–500 G) or a superconducting magnet (0–50 kG). Both the triplet lifetime and quantum yield of P were studied by monitoring the change in absorption at 868 nm after subsaturating 8-ns excitation flashes (532 nm, 10 Hz). The time resolution was about 1 μs. Triplet lifetimes were obtained by fitting the decay data to a single exponential. Relative triplet quantum yields were obtained from the relative amplitudes of the transmission changes 3 μs after the excitation flash. A small correction was made for the ^3P decay after the excitation flash.

RESULTS

The effect of an applied magnetic field on the observed triplet decay rate, $k_{obs}(H)$, in quinone-depleted RCs at room temperature is shown in Fig. 2; it is compared with the effect of the field on the relative quantum yield of ^3P. These results constitute a signature that the decay of ^3P, as well as its formation, involve the radical-pair intermediate.

The effects of temperature on k_{obs} as a function of magnetic field are shown in Fig. 3. The magnetic field effect disappears to within the noise level at lower temperatures, as expected if repopulation of $P^{+}I^{-}$ is thermally activated.

The triplet lifetime in reduced, quinone-containing RCs (Q^{-}) is 6.5 ± 0.5 μs. No magnetic field effect on this lifetime was observed between zero and 500 G (data not shown). Finally, the triplet lifetime of Q^{2-} RCs at room temperature and zero field was 49 μs; this value increased to 66 μs at 1 kG and decreased to 48 μs at 50 kG (data not shown).

THEORY

A quantitative analysis of this new effect requires some information about RCs that is not yet available. Nonetheless, a simplified model can be developed using the following approximations.

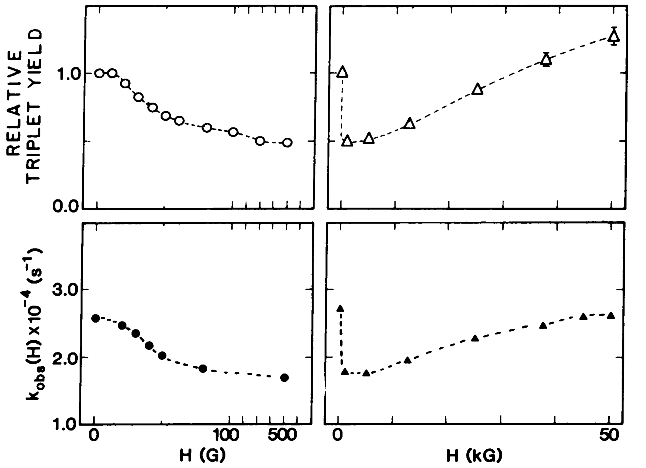

FIG. 2. Relative ^3P quantum yield and observed ^3P decay rate, $k_{obs}(H)$, in quinone-depleted RCs at room temperature as a function of magnetic field (H). The relative quantum yields and decay rates were obtained on different samples. All data are for RCs in TT buffer except the high-field quantum yield data, in which the RCs were in a 65% (wt/vol) ethylene glycol/35% TT buffer. The error in $k_{obs}(H)$, based on uncertainty in the fits of the decays to exponentials, is less than the size of the symbols. Note the change in scale at 100 G in the low-field plots and the vertical offset in plots of $k_{obs}(H)$.

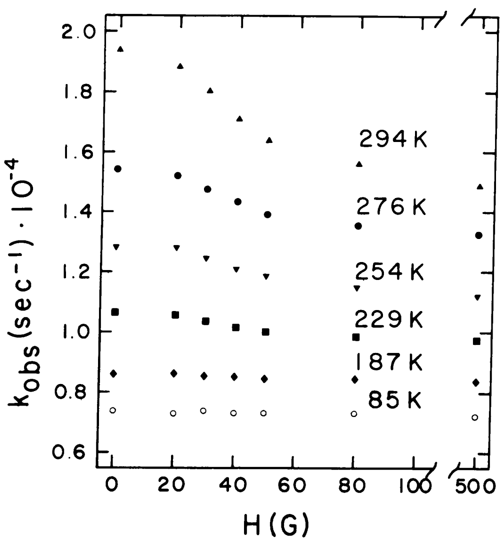

FIG. 3. ^3P decay rate, $k_{obs}(H)$, in Q-depleted RCs as a function of magnetic field at low field for various temperatures (65% ethylene glycol/35% TT buffer).

(*i*) Fig. 1 describes all relevant states and pathways.

(*ii*) Only singlet–triplet mixing in $P^{+}I^{-}$ is magnetic field dependent.

(*iii*) The entropies of the states ^3P and $^3(P^{+}I^{-})$ are equal at all temperatures. The back-reaction rate constant from ^3P to $^3(P^{+}I^{-})$ can then be expressed as $k_T\exp(-\Delta H\beta)$, where ΔH is the difference in enthalpy between $^3(P^{+}I^{-})$ and ^3P, and $\beta = 1/kT$, where k is the Boltzmann constant and T is the absolute temperature.

(*iv*) Electron and nuclear spin-lattice relaxation in ^3PI is rapid compared with the ^3PI decay rate at all fields and temperatures.

(*v*) The dependence of singlet–triplet mixing on the orientation of the RC in the magnetic field will be ignored (1, 12). Alternatively, the same results can be derived if the RC is taken to rotate much more rapidly than ^3P decays.

(*vi*) The steady-state approximation is made for the radical-pair states after the initial decay of $P^{+}I^{-}$.

With these approximations it can be shown (see *Appendix*) that the observed ^3P decay rate is given by:

$$k_{obs} = k_{isc} + \frac{1}{3}k_S\Phi_T e^{-\Delta H\beta}, \qquad [1]$$

where Φ_T is the quantum yield of ^3P. The model predicts that, except for a constant (k_{isc}), the observed rate of ^3P decay should be proportional to the observed ^3P yield as a function of magnetic field. Furthermore, this component should show an activation energy equal to the $^3(P^{+}I^{-})$ − ^3P enthalpy difference assuming k_{isc}, k_S, and Φ_T to be temperature independent.

DISCUSSION

The observed ^3P decay rate decreases on application of small fields in parallel with the observed triplet yield. Half the decrease is reached at about 50 G, similar to the value for the triplet yield data (42 ± 2 G). The decay rate of ^3P begins to rise in parallel with the yield on application of larger fields. The major disagreement between the predictions of the simple model (Eq. 1) and the data appears to occur at high field where the rate of ^3P decay begins to level off as a function of field, while the relative ^3P yield continues to rise, albeit with

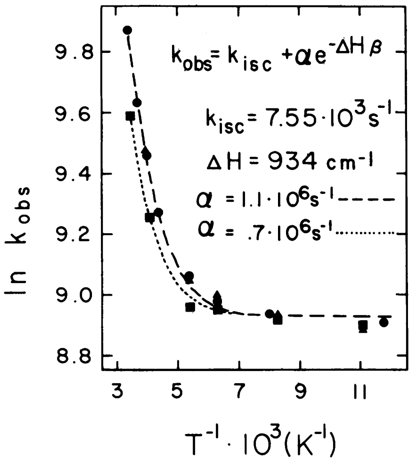

FIG. 4. Arrhenius plots of ^{3}P decay rate as a function of temperature at several magnetic field strengths in Q-depleted R-26 RCs (65% ethylene glycol/35% TT buffer). Data points: ●, at zero field; ■, at 5kG; ▲, at 45kG. The data were fit to Eq. **1** with $\alpha = \frac{1}{3}k_S\Phi_T$.

a diminished slope.

The temperature dependence of the ^{3}P decay rate was fitted to the expression developed above (Eq. **1**) by using a least-squares fit to a single exponential plus a constant (k_{isc}) at several magnetic fields as shown in Fig. 4. The value obtained for k_{isc} is about $7 \cdot 10^3$ s^{-1}. The value of ΔH for the process $^3\mathrm{P} \rightarrow {}^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ is 950 ± 50 cm^{-1} (0.12 ± 0.01 eV). The data in Fig. 4 could be slightly better fit by including a weak temperature dependence for the component associated with k_{isc} (Arrhenius plot slope = 0–10 cm^{-1}), with slight changes in the value of ΔH.

One can calculate the expected value of the preexponential, $(1/3)k_S\Phi_T(H = 0)$, by using values of the quantities involved obtained from independent experiments [k_S = 3–$5 \cdot 10^7$ s^{-1}; $\Phi_T(H = 0)$ = 0.25–0.35, at room temperature] (3, 13): $(1/3)k_S\Phi_T(H = 0)$ = 2.5–$5.8 \cdot 10^6$ s^{-1} (calculated). This value compares reasonably well with the observed preexponential factor of $1.1 \cdot 10^6$ s^{-1} at zero field. This factor is sensitive to small changes in the value of ΔH used in the fit.

One can estimate the enthalpy of $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ by subtracting the $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ − ^{3}P enthalpy difference obtained here of 950 cm^{-1} from the ^{1}P − ^{3}P enthalpy difference of 3,200 cm^{-1} (0.40 eV) obtained by Shuvalov and Parson (14). This places $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ about 2,250 cm^{-1} (0.28 eV) below ^{1}P or, with 11,000 cm^{-1} as the energy of the ^{1}P state, 8,750 cm^{-1} (1.1 eV) above the ground state. The activation energy of the delayed fluorescence from quinone-depleted RCs should provide an independent check on this estimate for the ^{1}P − $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ enthalpy difference if the model scheme describes all states. Woodbury and Parson (15) have recently obtained a value of 0.15 eV at room temperature for Q$^-$–RCs using this method. The fluorescence data is complicated by multiple components of uncertain origin, but we are encouraged that a comparable value was obtained with an entirely different set of assumptions.

The observations for RCs with reduced quinones can be readily explained within the framework of the simple model. The triplet lifetime in $\mathrm{Q}^{\dot{-}}$-containing (paramagnetic) RCs is much shorter than in Q-depleted or Q^{2-}-containing RCs (both diamagnetic). This rapid decay minimizes the opportunity for ^{3}P to reform $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$; consequently, a much smaller magnetic field effect is expected, and none was observed. In Q^{2-}-containing RCs, where the triplet lifetime is longer, a field effect was observed as expected.

Although the simple model qualitatively describes the observed effects, a number of the assumptions we have made are known to be incorrect for RCs, while others are at best reasonable guesses. It is useful to evaluate these assumptions in order to see how they affect the quantitative conclusions we have drawn.

Measurements from several laboratories show that Φ_T is not temperature independent (10, 14, 16, 17). Φ_T increases by more than a factor of 2 as the temperature is decreased over the temperature range we have studied. The exact origin of this change is not known, but it may be due to a decrease in k_S or a change in $\omega(H)$ with temperature. The lifetime of $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ increases by a factor of 1.5 on decreasing the temperature from 293K to 200K (2). As much of the decay is by the singlet channel at room temperature, this suggests that k_S is temperature dependent. Since k_S and Φ_T appear as a product in Eq. **1**, their opposite temperature dependences could offset each other to some extent. If $k_S\Phi_T$ decreases as the temperature is lowered, then the value for ΔH obtained from a simple fit to Eq. **1** overestimates the actual value, and vice versa. It should be noted that magnetic field effects are observed for the triplet quantum yield at low temperatures (10), where the magnetic field effect on the triplet decay rate is entirely suppressed (Fig. 3), indicating that it is the reactivation process that shuts down at low temperatures, rather than the spin rephasing.

The assumed temperature and field independence of k_{isc} receives support in the specific case of RCs from the data at low temperature. This result is not unlike other measurements of molecular triplet state lifetimes in the solid state, when care is taken to exclude bimolecular quenching (18).

The assumption of rapid electron and nuclear spin equilibration during the ^{3}PI lifetime (30–150 μs) at all temperatures and fields is unlikely to be true. Electron spin relaxation in ^{3}P is probably dominated by electron–dipole electron–dipole interactions, modulated by the motion of the RC. The magnitude of this relaxation rate is unknown, and few measurements in other molecules at high temperature and over a wide range of magnetic fields are available for comparison (19). It is likely that electron spin relaxation in nonviscous buffer is fast relative to ^{3}P decay at room temperature; however, at 120K spin polarization in the EPR spectrum of ^{3}P attests to the fact that the electron spin sublevels are not fully equilibrated (20). If electron relaxation is slow in ^{3}P, RCs will tend to repopulate the same substate of $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ from which they initially decayed. At high magnetic fields (>1 kG), there would be a higher proportion of recreated radical pairs capable of rephasing to the $^1(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ state, and a higher value of k_{obs}, than predicted by the simple model. This effect would vary with temperature and magnetic field.

Nothing is known at the present time about the nuclear spin-lattice relaxation rate in ^{3}PI. The nuclear spins in I will relax slowly, since I is diamagnetic. Nuclear relaxation in ^{3}P will be faster but may still be slow compared to the ^{3}PI decay rate. It is likely that the mechanism of nuclear spin relaxation in ^{3}P involves electron–dipole nuclear–dipole interactions, which are typically about 1–2 orders of magnitude smaller than the electron–dipole electron–dipole interaction in ^{3}P. Therefore, it is likely that nuclear spin-lattice relaxation is slower than electron spin-lattice relaxation at a given temperature and field, making this the weakest assumption. If nuclear spin relaxation is slow in ^{3}PI, then the nuclear spin polarization of ^{3}PI produced during the singlet–triplet mixing process will be retained when the radical pair is reformed. The hyperfine field experienced by the radicals in $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ reformed from ^{3}PI will then be larger in general than for the radicals formed from ^{1}PI (essentially the equilibrium distribution), resulting in a larger effective value of ω for the reverse reaction and a k_{obs} greater than that predicted by Eq. **1**. At low and moderate magnetic fields, singlet–triplet interconversion is largely driven by the nuclear hyperfine interaction. At high magnetic fields, the *g*-factor difference becomes the dominant mechanism for interconversion, and since the *g*-factor difference in $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ should be the same irrespective of precursor state, we expect that k_{obs} would start to approach the value predicted by Eq. 1 as the field is increased. In this case, we would expect the change in Φ_{T} upon going to high magnetic fields to be more than the change in k_{obs}. This is what we observe, and it is possible that the breakdown of the assumption that the nuclear spins are at equilibrium in the ^{3}P state may explain the discrepancy between Eq. 1 and the data.

Finally, Fig. 1 may not represent all of the kinetic pathways. We and others (13) have neglected to consider activated reformation of ^{1}PI from $^1(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$, whereas some workers have explicitly considered this pathway (2, 5, 8, 15). It is straightforward to include this pathway theoretically; however, our current knowledge of the actual importance of this pathway is limited so that its impact on our analysis is unclear. A second assumption is the simple decay of $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ to ^{3}PI in Fig. 1. We have provided evidence that only a fraction of the $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ decay generates ^{3}PI, the rest rapidly reforming PI (3). A branching in the decay of $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ between ^{3}P and PI would also affect the reformation of $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ from ^{3}P. Qualitatively such a path would provide a third possibly temperature-dependent but field-independent pathway for ^{3}P decay.

In conclusion, the magnetic field dependence of the ^{3}P decay rate in Q-depleted RCs indicates that at room temperature the triplets decay largely by reformation of the radical ion pair. An analysis of the temperature dependence of the ^{3}P lifetime using the model developed here yields an enthalpy difference of 950 ± 50 cm^{-1} between $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$ and ^{3}PI. Combined with enthalpies for ^{1}P and ^{3}P, this yields an enthalpy difference of about 2,300 cm^{-1} for the initial electron-transfer step, $^1\mathrm{PI} \rightarrow {}^1(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$. We note that for activationless electron-transfer processes, such as $^1\mathrm{PI} \rightarrow {}^1(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$, the energy gap is equal to the reorganization energy. Our estimated value of about 0.28 eV is quite small and is comparable to estimates for the inner-sphere reorganization energy associated with electron transfer between rigid macrocycles, such as those that participate in the initial steps of photosynthesis. Therefore, it appears that the outer-sphere reorganization energy is very small, suggesting that minimal change of the protein environment accompanies the initial electron-transfer step.

APPENDIX

The time dependence of [^{3}P], the number density of ^{3}P normalized to the amount of sample excited, is given by

$$\frac{d[^3\mathrm{P}]}{dt} = -k_{\mathrm{isc}}[^3\mathrm{P}] - k_{\mathrm{T}}e^{-\Delta H\beta}[^3\mathrm{P}] + k_{\mathrm{T}}\mathrm{tr}[P^{\mathrm{T}}\rho], \quad \textbf{[A1]}$$

where ρ is the density matrix describing $(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$, P^{T} is the triplet projection operator, tr denotes trace, and $\mathrm{tr}[P^{\mathrm{T}}\rho]$ represents the effective concentration of $^3(\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}})$.

The time evolution of ρ is given by

$$\dot{\rho} = \frac{-i}{\hbar}[H, \rho] - \frac{1}{2}k_{\mathrm{S}}(P^{\mathrm{S}}\rho + \rho P^{\mathrm{S}}) - \frac{1}{2}k_{\mathrm{T}}(P^{\mathrm{T}}\rho + \rho P^{\mathrm{T}}) + \frac{k_{\mathrm{T}}e^{-\Delta H\beta}[^3\mathrm{P}]}{\mathrm{tr}[P^{\mathrm{T}}]}P^{\mathrm{T}}, \quad \textbf{[A2]}$$

where H and P^{S} are the matrices that represent the field-dependent radical-pair spin Hamiltonian and the singlet projection operator, respectively.

Using the steady-state assumption and setting $\dot{\rho} = 0$ in Eq. **A2**, we obtain

$$\frac{k_{\mathrm{T}}e^{-\Delta H\beta}[^3\mathrm{P}]}{\mathrm{tr}[P^{\mathrm{T}}]}P^{\mathrm{T}} = B\rho + \rho B^{\dagger}, \quad \textbf{[A3]}$$

where

$$B = \frac{i}{\hbar}H + \frac{1}{2}k_{\mathrm{T}}P^{\mathrm{T}} + \frac{1}{2}k_{\mathrm{S}}P^{\mathrm{S}}, \quad \textbf{[A4]}$$

and $B^{\dagger}$ is its hermitian adjoint.

The solution of Eq. **A3** for ρ is (21):

$$\rho_{ij} = \frac{k_{\mathrm{T}}e^{-\Delta H\beta}}{\mathrm{tr}[P^{\mathrm{T}}]}\left\{\sum_{\substack{kl\\mn}} \frac{U_{im}U^{-1}_{mk}P^{\mathrm{T}}_{kl}V_{ln}V^{-1}_{nj}}{\lambda_m + \mu_n}\right\}[^3\mathrm{P}], \quad \textbf{[A5]}$$

where $[U^{-1}BU]_{ij} = \lambda_i\delta_{ij}$, $[V^{-1}B^{\dagger}V]_{ij} = \mu_i\delta_{ij}$, and λ_i and μ_i are the eigenvalues of B and $B^{\dagger}$, respectively. Substituting this expression into Eq. **A1**, we get

$$\frac{d[^3\mathrm{P}]}{dt} = -k_{\mathrm{obs}}[^3\mathrm{P}], \quad \textbf{[A6]}$$

where

$$k_{\mathrm{obs}} = k_{\mathrm{isc}} + k_{\mathrm{T}}e^{-\Delta H\beta}\left\{1 - \frac{k_{\mathrm{T}}}{\mathrm{tr}[P^{\mathrm{T}}]}\sum_{\substack{ij\\kl\\mn}} \frac{P^{\mathrm{T}}_{ji}U_{im}U^{-1}_{mk}P^{\mathrm{T}}_{kl}V_{ln}V^{-1}_{nj}}{\lambda_m + \mu_n}\right\}. \quad \textbf{[A7]}$$

We can express this observed quantity in terms of another observable, the initial triplet yield of $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$, Φ_{T}, when $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ is initially formed in the singlet state. Following previous workers (7), we have

$$\Phi_{\mathrm{T}} = k_{\mathrm{T}}\mathrm{tr}[P^{\mathrm{T}}\bar{\rho}], \quad \textbf{[A8]}$$

where $\bar{\rho}$ is the time integral of ρ subject to the initial condition,

$$\rho(t = 0) = \frac{P^{\mathrm{S}}}{\mathrm{tr}[P^{\mathrm{S}}]}. \quad \textbf{[A9]}$$

The expression for the time dependence of ρ can be integrated subject to this initial condition to yield

$$B\bar{\rho} + \bar{\rho}B^{\dagger} = \frac{P^{\mathrm{S}}}{\mathrm{tr}[P^{\mathrm{S}}]}. \quad \textbf{[A10]}$$

The term representing reformation of $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ from ^{3}P is not included in Eq. **A10** to exclude multiple counting of reaction centers returning to the ^{3}P state.

This equation can be solved in the same way as Eq. **A3**:

$$\Phi_{\mathrm{T}} = \frac{k_{\mathrm{T}}}{\mathrm{tr}[P^{\mathrm{S}}]}\left\{\sum_{\substack{ij\\kl\\mn}} \frac{P^{\mathrm{T}}_{ji}U_{im}U^{-1}_{mk}P^{\mathrm{S}}_{kl}V_{ln}V^{-1}_{nj}}{\lambda_m + \mu_n}\right\}. \quad \textbf{[A11]}$$

In complete analogy to the above, we can obtain the yields of $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ decay by the singlet and triplet routes—Φ'_{S} and Φ'_{T}, respectively—when $\mathrm{P}^{\dot{+}}\mathrm{I}^{\dot{-}}$ is initially formed in the triplet state:

$$\Phi'_{\mathrm{T}} = \frac{k_{\mathrm{T}}}{\mathrm{tr}[P^{\mathrm{T}}]}\left\{\sum_{\substack{ij\\kl\\mn}} \frac{P^{\mathrm{T}}_{ji}U_{im}U^{-1}_{mk}P^{\mathrm{T}}_{kl}V_{ln}V^{-1}_{nj}}{\lambda_m + \mu_n}\right\} \quad \textbf{[A12]}$$

and

$$\Phi'_{\mathrm{S}} = \frac{k_{\mathrm{S}}}{\mathrm{tr}[P^{\mathrm{T}}]}\left\{\sum_{\substack{ij\\kl\\mn}} \frac{P^{\mathrm{S}}_{ji}U_{im}U^{-1}_{mk}P^{\mathrm{T}}_{kl}V_{ln}V^{-1}_{nj}}{\lambda_m + \mu_n}\right\}. \quad \textbf{[A13]}$$

Substituting Eq. **A12** in Eq. **A7** and using the fact that $\Phi'_S = 1 - \Phi'_T$, we can express k_{obs} as

$$k_{obs} = k_{isc} + k_T \Phi'_S e^{-\Delta H \beta}. \qquad \textbf{[A14]}$$

In a basis set in which H, P^S, and P^T are real (as for instance, $|S, S_z, M_1, \ldots M_j>$, where M_i is the z projection of the spin of nucleus i), $B^\dagger = B^*$, $V = U^*$, and $\mu_i = \lambda_i^*$. By interchanging indices, the expressions in brackets in Eqs. **A11** and **A13** can be expressed as complex conjugates of each other. Since the quantum yields must be real, the two expressions must be equal. We can then express Φ_T as

$$\Phi_T = \frac{k_T}{k_S} \frac{\mathrm{tr}[P^T]}{\mathrm{tr}[P^S]} \Phi'_S. \qquad \textbf{[A15]}$$

Substituting this expression into Eq. **A14** and using the fact that $\mathrm{tr}[P^S]/\mathrm{tr}[P^T] = 1/3$, we obtain

$$k_{obs} = k_{isc} + \frac{1}{3} k_S \Phi_T e^{-\Delta H \beta}. \qquad \textbf{[1]}$$

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