

anticipate that IV might also be trapped by H_2O solvent. If this should have occurred, then pseudobase rather than III would have resulted as product. From the pH of the experiment (4.6) and pK_R , it can be calculated¹⁹ that $k_f = 10^7 k_r$. Since pseudobase was not observed, it must be assumed that $k_3[\text{I}] \gg k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] < 10^2 \text{ s}^{-1}$.

It is reasonable to suppose that changes in the substituents on the 1,5-dihydroisoalloxazine ring system might decrease ΔG^\ddagger relative to ΔG^* and thereby result in the formation of $\text{Fl}_{\text{radical}}$ and O_2^- as discrete intermediates. Apparent ΔG^\ddagger values for the bimolecular reaction of $^3\text{O}_2$ with seven assorted 1,5-dihydroflavins (Va-Vg) at pH 4.6 were obtained from initial rate constants (eq 1a).¹¹ The potentials E_1 and E_2 (eq 2a and 2b) were determined for each flavin and corrected to pH 4.6 (as in the case of the 1,10-ethano-5-ethylumiflavin system loc. cit.).²⁰ From the calculated values of ΔG^\ddagger , ΔG^1 , and ΔG^2 ,¹⁴ there may be constructed the averaged cartoon of Figure 2. Inspection of Figure 2 reveals that $\text{Fl}_{\text{radical}} + \text{O}_2^-$ exists in a potential well. Return to the starting state is associated with a potential barrier of $19.7 \pm 3 \text{ kJ m}^{-1}$. The barrier for formation of products from $\text{Fl}_{\text{radical}} + \text{O}_2^-$ cannot be greater than that for return to the starting state and in the cartoon has been set equal to this value. The free-energy difference of 19.7 kJ M^{-1} corresponds to a diffusion-controlled rate constant of $2.6 \times 10^9 \text{ s}^{-1}$.²¹ Thus, the moieties $\text{Fl}_{\text{radical}}$ and O_2^- may diffuse from the $\{\text{Fl}_{\text{radical}}, \text{O}_2^-\}$ radical pair, and the former are true intermediates. One may conclude that the $^3\text{O}_2$ oxidation of the 1,5-dihydroflavins Va-Vg¹⁵ occurs by two consecutive one-electron transfer steps. The driving force for the reaction(s), overall, is provided by ΔG^2 (product stability). Changes in the potentials of eq 2a, 2b, and 2c and the rate constant for the reaction of eq 1a with pH will change the reaction-coordinant cartoon. Other data^{1f} indicate, however, that the values of ΔG^1 remain less than ΔG^* so that the one-electron transfer reaction from 1,5-reduced flavin to $^3\text{O}_2$ is allowed at other pH values.

We have shown in this investigation that: (i) dependent upon 1,5-dihydroflavin structure, the reaction of these compounds with $^3\text{O}_2$ involves a transition state closely resembling a flavin radical plus O_2^- or a flavin radical and O_2^- as discrete intermediates; (ii) a covalent intermediate is required in the $^3\text{O}_2$ oxidation of 1,5-dihydroflavin to flavin plus hydrogen peroxide in water.

Acknowledgment. This work was supported by grants from the National Institutes of Health and the National Science Foundation.

Registry No. I, 80720-87-2; **III,** 80720-88-3; **Va,** 76030-63-2; **Vb,** 64910-62-9; **Vc,** 50387-36-5; **Vd,** 50635-52-4; **Ve,** 64910-61-8; **Vf,** 80720-89-4; **Vg,** 79075-88-0; O_2 , 7782-44-7.

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(20) (a) 5-Ethyl-10-(2',6'-dimethylphenyl)-3-methyl-1,5-dihydroisoalloxazine (Va) (ΔG^\ddagger (kJ/M) = 70.6, $\Delta G^1 = 52.4$, $\Delta G = -28.5$; E^1 (mV) [pH 4.6, NHE] = 365 mV, $E^2 = 233$ mV). 10-(2',6'-Dimethylphenyl)-3-methyl-1,5-dihydroisoalloxazine (Vb) ($\Delta G^\ddagger = 54.0$, $\Delta G^1 = 37.2$, $\Delta G = -76.5$; $E^1 = 25$, $E^2 = 75$). 5-Ethyl-3-methyl-1,5-dihydroisolumiflavin (Vc) ($\Delta G^\ddagger = 64.4$; $\Delta G^1 = 49.1$, $\Delta G = -21.2$; $E^1 = 474$, $E^2 = 199$).^{14b} 3-Carboxymethylumiflavin (Vd) ($\Delta G^\ddagger = 59.1$, $\Delta G^1 = 25.6$, $\Delta G = -102.6$; $E^1 = -125$, $E^2 = -45$).^{14c} 7-Cyano-3,10-dimethyl-1,5-dihydroisoalloxazine (Ve) ($\Delta G^\ddagger = 54.9$, $\Delta G^1 = 39.1$, $\Delta G = -71.7$; $E^1 = 55$, $E^2 = 95$). 7-Chloro-3,10-dimethyl-1,5-dihydroisoalloxazine (Vf) ($\Delta G^\ddagger = 55.7$, $\Delta G^1 = 40.5$, $\Delta G = -68.9$; $E^1 = 70$, $E^2 = 110$). 5-Ethyl-3-methyl-1,5-dihydro-1-deaza-1-carbaflavin (Vg) ($\Delta G^\ddagger = 65.4$, $\Delta G^1 = 42.9$, $\Delta G = -44.7$; $E^1 = 295$, $E^2 = 135$). (b) Calculated from values obtained by: Draper, R. D.; Ingram, L. L. *Arch. Biochem. Biophys.* **1968**, *125*, 802. (c) E_m obtained by Schug are about 70 mV lower: Schug, C. "Diplomarbeit"; Konstanz, Germany, 1978.

(21) For the individual 1,5-dihydroisoalloxazines investigated (compounds Va-Vg¹⁰), the calculated rate constants for partitioning of the $\text{Fl}_{\text{radical}} + \text{O}_2^-$ to initial state vary from 4×10^7 to $2.6 \times 10^{10} \text{ s}^{-1}$. Dissociation rate constants have been shown to range from $\sim 10^{12}$ to $\sim 10^8 \text{ s}^{-1}$ (see ref 16 and literature citations therein).

Use of Large Magnetic Fields To Probe Photoinduced Electron-Transfer Reactions: An Example from Photosynthetic Reaction Centers

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Received July 27, 1981

We will outline an experimental approach that uses large magnetic fields and simple optical methods, combined with a method of data analysis, that is ideally suited for studying the mechanism of rapid photoinduced electron-transfer (ET) reactions over a very wide range of conditions. Results are presented from experiments on the primary photochemistry in photosynthetic reaction centers (RCs), along with predictions for a variety of chemically interesting ET reactions.

Many investigators are attempting to prepare photosynthetic analogues, including covalently connected donor-acceptor pairs,¹ organized assemblies (micelles, bilayers, surfaces),² and solid-state materials such as amorphous silicon.³ Time-resolved optical data are widely used to study charge separation in these systems; however, the absorption spectrum of the primary photoproduct, a radical-ion pair (RIP), is frequently difficult to distinguish from that of excited singlet and triplet intermediates. In order to resolve this ambiguity and prove the intermediacy of RIPs, it is important to demonstrate that the intermediates possess spin angular momentum. For long-lived radicals, ESR is the method of choice, but this fails when the lifetime of the RIP is less than about 200 ns. Indirect magnetic resonance methods, such as reaction yield detected magnetic resonance (RYDMR) can also be applied when the conditions are favorable.^{3,4}

A fairly general description of the kinetics in a singlet ET reaction is shown in Scheme I. Donor D is excited to its singlet state and forms a RIP with acceptor A. This pair recombines to the ground state with the magnetic-field-independent rate constant k_S . If k_S is sufficiently slow, the phase of the unpaired spins in the correlated RIP may evolve to the triplet RIP. Spin-allowed recombination in the latter can produce ^3D (or ^3A), providing the reaction is sufficiently exothermic. Such long-lived triplet products are a useful probe of the short-lived RIP.

The effects of *small* magnetic fields on the yields of reactions of this type have been widely discussed.^{5,6} As illustrated in Figure 1, if the exchange interaction (J) in the RIP is small relative to the interactions that mix radical-pair singlet and triplet states, then application of a small field (typically less than 500 G) will *decrease* the yield of ^3D (ϕ_T), because the field removes the T_+ and T_- levels from the vicinity of S. However, certain systems suspected to undergo ET show negligible triplet formation at low

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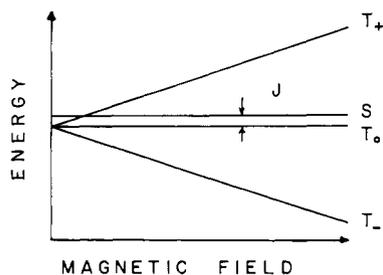


Figure 1. Schematic energy level diagram for a radical pair in a magnetic field. J is the isotropic electron exchange interaction (anisotropic electron dipolar coupling is omitted).^{14,15}

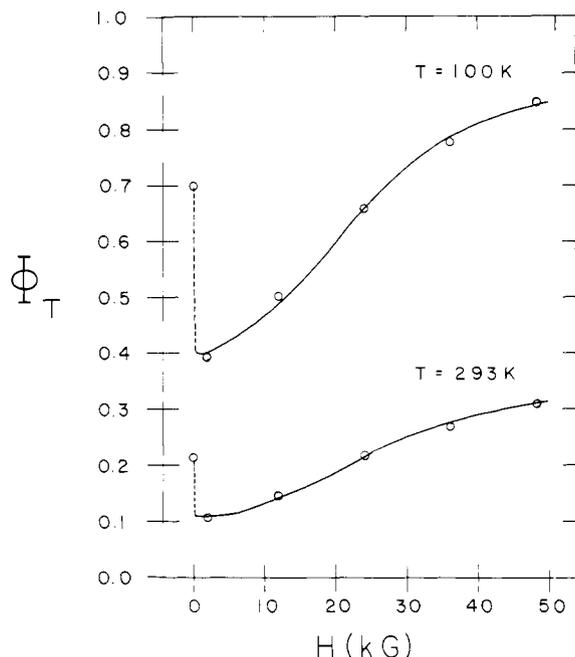
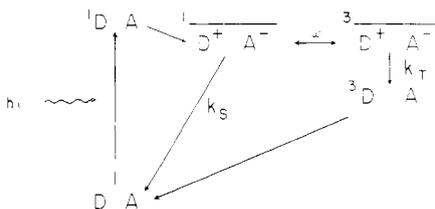


Figure 2. Quantum yield of triplets detected optically in quinone-depleted RC's from *R. spheroides*, R-26 mutant, as a function of applied magnetic field strength and temperature. (O) experimental data; (—) calculated ϕ_T . No attempt was made to fit the intermediate field region ($0 < H < 2$ kG), indicated by a dashed line.¹⁵ The absolute quantum yield was measured at 293 K. At 100 K relative yields were scaled to fit calculated yields. Yields were calculated as in ref 13. At 293 K, $k_S = 2.1 \times 10^8$ s⁻¹, $k_T = 1.2 \times 10^8$ s⁻¹, $\Delta g = 0.0011$, $J = 0$, and $\sigma\hbar/g_e\beta = 8$ G.¹⁴ At 100 K, $k_S = 3.4 \times 10^7$ s⁻¹, $k_T = 3.1 \times 10^8$ s⁻¹, $\Delta g = 0.0011$, $J = 0$; and $\sigma\hbar/g_e\beta = 8$ G. J is likely to be nonzero. Values of $|J/g_e\beta| < 6$ G have little effect on the fits at high field.

Scheme I



field, either because J is too large or the singlet RIP lifetime is too short (k_S fast).^{1d,e}

The essential features of the effects of large magnetic fields are well-known from CIDNP theory.⁷ Providing that D^+ and A^- have different g factors, the difference in their precession frequencies will increase linearly with increasing field as $\Delta g\hbar$ without limit. Thus, the frequency of $S-T_0$ mixing (ω in Scheme I) can be made arbitrarily large, and so long as ω does not greatly

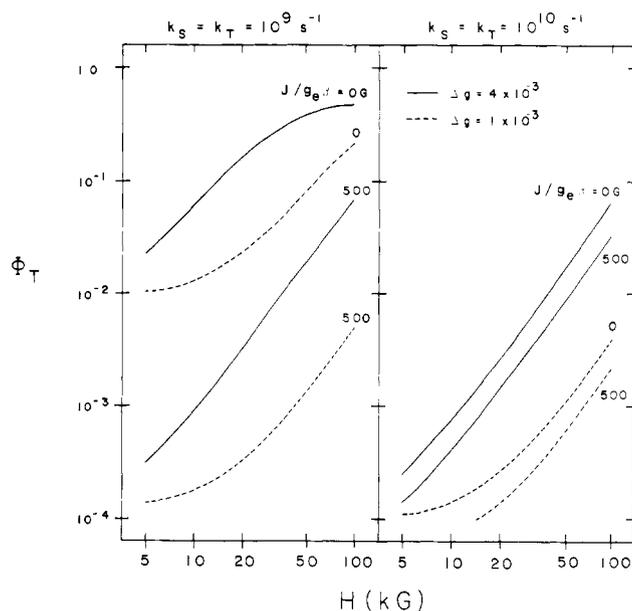


Figure 3. Theoretical plots of ϕ_T as a function of applied magnetic field strength for the indicated values of magnetic and kinetic parameters ($\sigma = 8$ G¹⁴).

exceed k_T , ϕ_T should increase with increasing field. As ω exceeds k_T , ϕ_T becomes independent of field strength and approaches the limiting value $k_T/(k_S + k_T)$.

An example of all these effects is shown in Figure 2 (open circles) for ϕ_T in photosynthetic RCs.⁸ It is evident that ϕ_T changes enormously with field and that ϕ_T becomes field independent at high field, as was predicted qualitatively above.¹¹ We have presented elsewhere¹³ a detailed theoretical treatment of the mechanism at high field, which provides an analytical expression for ϕ_T as a function of field in terms of the g -factor difference (Δg), J , the distribution of hyperfine energies in the radicals, and the recombination rate constants k_S and k_T . The explicit expression is¹⁴

$$\phi_T(H) = \frac{k_T}{k_S + k_T} \left(\frac{1}{N} \sum_{k=1}^N \frac{1}{1 + (\kappa/\omega_k)^2} \right) \quad (1)$$

where $\kappa^2 = k_S k_T [1 + 4(J/\hbar)^2 / (k_S + k_T)^2]$ and $\omega_k = (1/\hbar)[\Delta g\beta H + \sum_i A_{i1} m_{i1}^k - \sum_i A_{i2} m_{i2}^k]$; A_{ij} is the isotropic hyperfine coupling

(8) RC's from *R. spheroides*, R-26 mutant, were prepared by standard methods.⁹ Quinone depletion and analytical methods for assessing purity were as described by Feher et al.¹⁰ 10 μ M RCs [50/50: 20 mM of Tris-HCl, 10 μ M of EDTA, 0.05% Triton (pH 8.0)/glycerol] were placed in a temperature-controlled (100–298 K) 1-mm path-length cell in the bore of a superconducting magnet (variable H from 0 to 50 kG) or a Helmholtz coil (0–500 G). The sample was excited with a subsaturating flash at 532 or 600 nm from a frequency-doubled YAG pumped dye laser (8 ns, fwhm; 100–200 μ J/cm² pulse) and was probed with a laser diode (860 nm) at 2 μ s. Details of the experimental apparatus are discussed elsewhere.¹²

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(11) We have observed that ϕ_T changes by as much as 300% between 2 and 50 kG in reduced RC's containing quinone, by far the largest magnetic field effect on a chemical reaction reported to date.¹²

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(14) This is a simplification of eq 5, ref 13, which collects kinetic (κ) and magnetic (ω_k) parameters. This expression is rigorously correct at fields for which the electron Zeeman energy is much greater than either the hyperfine or exchange energies (typically 1 kG). Anisotropic interactions are not considered here. See: Boxer, S. G.; Chidsey, C. E. D.; Roelofs, M. G. *Proc. Natl. Acad. Sci. U.S.A.*, in press. Given the large number of nuclear hyperfine interactions in a typical π radical, we can approximate the sum over discrete nuclear states with an integral over a Gaussian distribution for ω_k , centered at $\Delta g\beta H$, with a second moment σ^2 ($\sigma\hbar/g_e\beta = 8$ G for RCs¹³).

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constant for nucleus i on radical j , m_{ij}^k is the axial quantum number for nucleus i on radical j in the k th state, and β is the Bohr magneton. The data shown in Figure 2 were fitted to this function for $H > 2$ kG,¹⁵ giving the excellent fit shown with the solid line for the parameters in the figure caption. These values for kinetic and magnetic parameters compare very favorably with previous kinetic and ESR data on RCs,^{13,16} making us confident of the validity of the method. The details of this analysis and its implications for photosynthesis are the subject of a separate paper.¹²

The key point we wish to stress is that the analysis and method presented here should be generally applicable to many chemically interesting ET reactions. Figure 3 illustrates selected calculations of the dependence of ϕ_T on magnetic field strength between 5 and 100 kG for various values of Δg , J , and the recombination rates. It is evident that an appreciable ϕ_T can be generated at high field, even when ϕ_T is negligible at low field. In model systems, Δg and the hyperfine energies are generally known, thus it is straightforward to extract both recombination rate constants and exchange interactions from experimental data, as well as prove that ET must have occurred. This is a versatile method since the measurement of either ground-state absorption, triplet-triplet absorption, or delayed fluorescence provides the same information, and the method can be applied to the system in any physical state or at any temperature. Photosynthetic model systems are being investigated.

Acknowledgment. We thank Varian Corp. for loaning us the superconducting magnet used in these experiments. This work is supported by the NSF and the Science and Education Administration of the USDA under grants PCM7926677 and 78-59-2066-0-1-147-1, respectively. C.E.D.C. is an NSF Predoctoral Fellow and S.G.B. is a Sloan and Dreyfus Fellow.

(15) At 293 K the field ($B_{1/2}$), which gives a ϕ_T decreased from the zero-field value by half the low-field variation, is 42 G. ϕ_T at low field and the role of dipolar coupling are discussed elsewhere: Roelofs, M. G.; Chidsey, C. E. D.; Boxer, S. G. *Chem. Phys. Lett.*, in press.

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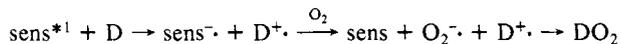
Photooxygenation via Electron Transfer.

1,1-Dimethylindene

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Only a few examples of photooxygenation via electron transfer are known.¹⁻⁵ Although a variety of mechanisms are involved in these examples,^{1-3,5} reactions between a radical cation and



superoxide, formed by electron transfer from a sensitizer radical anion to oxygen, have been the most extensively studied.²⁻⁵ This area is currently of interest because it appears that photooxygenations involving electron-transfer processes may be more

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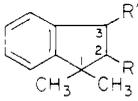
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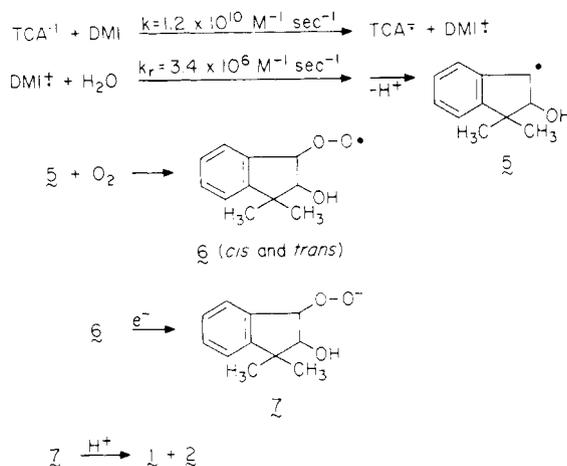
Table I. NMR Data of the Photoproducts and Their Reduction and Acetylation Products in C_6D_6 ^a



R	R'	trans			cis		
		H-2	H-3	$J_{2,3}$	H-2	H-3	$J_{2,3}$
OH	OOH	4.33	5.53	6.6	4.08	5.45	5.1
OH	OH	3.95	5.09	7.2	3.75	4.85	5.2
OCOCH ₃	OCOCH ₃	5.20	6.35	5.6	5.48	6.41	5.5
OCH ₃	OOH	3.85	5.45	5.5	3.33	5.32	5.1
OCH ₃	OH	3.39	5.00	6.9	3.24	4.90	5.1
OCH ₃	OCOCH ₃	3.69	6.40	5.9	~3.30	6.22	5.4
OOH	OCH ₃	4.50	4.71	5.8			
OH	OCH ₃	3.92	4.60	6.6			
OCOCH ₃	OCH ₃	5.46	4.72	4.7			

^a The H-3 signals are distinguished from those of H-2 by slight broadening due to long-range coupling with the aromatic proton(s). The structure of the cis diol was confirmed by comparison with an authentic sample prepared by OsO_4 oxidation of DMI.¹⁰ Reaction of the epoxide of DMI with NaOCH_3 gave a product identical with the reduction product of 12.

Scheme I



diverse and ubiquitous than the extensively studied singlet-oxygen processes. To define the scope of photooxygenation via electron transfer, we investigated the reactions of the cyclic, asymmetric olefin 1,1-dimethylindene (DMI)⁶ and report an electron-transfer-sensitized photooxygenation that is preceded by nucleophilic addition to the olefin radical cation⁷ and that gives products with regiochemistry opposite to that of products from a comparable singlet-oxygen reaction.

Irradiation of DMI, sensitized by 2,6,9,10-tetracyanoanthracene⁸ (TCA), in acetonitrile in the presence of oxygen and

(6) The dimerization of this olefin via its radical cation was investigated earlier: Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* 1973, 677.

(7) A similar sequence of reactions has been postulated as a minor reaction path in the photooxygenation of 1,1-diphenylethylene in methanol; ref 5.

(8) This sensitizer was first used to study the photosensitized electron-transfer reactions of phenylacetylene: Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* 1980, 126. It was prepared by allowing 2,6,9,10-tetrabromoanthracene (Grandmougin, E. C. R. *Hebd. Seances Acad. Sci.* 1921, 173, 1176) to react with 10 equiv of cuprous cyanide in refluxing *N,N*-dimethylacetamide for several hours. The copper complex of the product was destroyed with hydrogen sulfide, and the black solid which was collected by filtration was extracted repeatedly with boiling toluene. Concentration of the combined toluene extracts yielded crude 2,6,9,10-tetracyanoanthracene (TCA), which was purified by several recrystallizations from nitromethane: mp >345 °C; NMR (CF_3COOH) δ 8.21 (H-3), 8.86 (H-4), 9.20 (H-1) (ABX spectrum, $J_{1,3} = 1.5$ Hz, $J_{1,4} = 0.7$ Hz, $J_{3,4} = 9.05$ Hz); IR (KBr) 2225, 1625, 1460, 1365, 1258, 1172, 910, 822, 590, 438 cm^{-1} ; absorption spectrum ($\text{C-H}_3\text{CN}$) λ_{max} 428 nm ($\epsilon = 11000$); mass spectrum, m/e (rel intensity) 279 (23, M + 1), 278 (100, M⁺), 252 (8), 251 (8), 250 (22, M - H₂CN), 249 (6), 224 (11), 223 (11), 222 (6), 200 (11), 199 (7); exact mass 278.0582 (calcd for $\text{C}_{18}\text{H}_6\text{N}_4$, 278.0592).