MCD measurements, have recently proposed the existence of $S = {}^3/_2$ iron in compound c^{37} and some other intermediate oxidation state forms of the oxidase. If the spin of the "silent" iron in the resting oxidase is also assumed to be $^3/_2$ instead of $^5/_2$, as is normally done, the spin relaxation rate would be expected to be much more rapid. A combination of dipolar coupling and a small amount of exchange coupling between the iron and copper could reasonably produce relaxation rates that broaden both signals past the point of experimental observability.[27] The calculated magnetic moment (assuming the remaining iron and copper are both $S = {}^1/_2$) for such a spin system agrees with experimental values reported for the enzyme[4-6] at least as well as the antiferromagnetically coupled high-spin model.[1,38] The major advantage of this intermediate-spin relaxation model is that it avoids the necessity of requiring an exceptionally and possibly unreasonably large Fe–Cu coupling constant while at the same time adequately explaining both the experimental bulk susceptibility and EPR spectrum.

In summary, the trimeric complex reported here exhibits some unusual and unexpected properties. The observed behavior of the model suggests a description for the spin behavior of the oxidase that is different from the explanation that is most generally accepted. The relative merit of these two alternate explanations should now be subjected to an appropriate degree of critical evaluation based on experimental results obtained from the enzyme.

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[38] If consideration is given to the possibility of a spin admixture containing a small percentage of $S = {}^5/_2$ iron, the fit can be made arbitrarily as good as desired.

Dependence of the Yield of a Radical-Pair Reaction in the Solid State on Orientation in a Magnetic Field

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We report the observation that the yield of a radical-pair reaction in the solid state can depend strongly on the orientation of the reactants in a magnetic field. This phenomenon is expected to be quite general for radical-pair reactions in rigid environments where the anisotropic magnetic interactions associated with the individual radicals and with the pair maintain fixed values relative to the field during the evolution of the pair spin multiplicity (typically about 1–10 ns). The particular system being investigated is a bacterial photosynthetic reaction center (RC) depleted of secondary acceptors, where a triplet product is formed by radical ion-pair recombination following photoinduced electron transfer. The reactive components in the RC are immobilized in a hydrophobic protein complex.

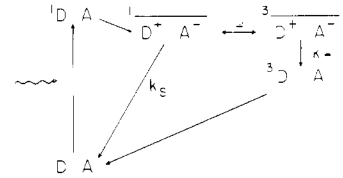

Figure 1. General scheme for photoinduced electron-transfer reactions. In photosynthetic RCs, both D and A are chlorophyll-like chromophores; consequently their radicals are typical aromatic radicals.

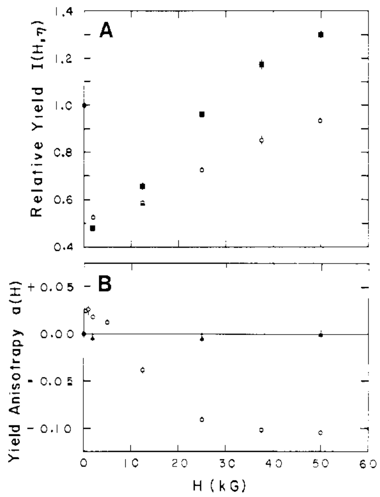

Figure 2. (A) The relative triplet quantum yields, $I(H,\eta)$, for RCs in a viscous buffer: $I(H,0°)$ (○); $I(H,90°)$ (■). The absolute quantum yield at zero field is 0.21.[8] (B) The measured triplet quantum yield anisotropy, $a(H)$ (eq 1) for RCs. $a(H)$ in a viscous buffer (○); $a(H)$ in a nonviscous buffer (▲). Quinone-depleted RCs were suspended in buffer (20mM Tris·HCl, 10 μM EDTA, 0.05% Triton (pH 8.0); nonviscous, 1 cP) or a mixture of this buffer with glycerol (66% glycerol, viscous, ~23 cP), giving a final RC concentration of 10 μM (T = 293 K).

The initial events in photosynthesis following photoexcitation[1] are characteristic of a wide range of electron-transfer reactions (Figure 1). The donor (D) in its first excited singlet state transfers an electron to the acceptor (A) to form a singlet-correlated radical ion pair (RIP). In competition with ion-pair recombination to the ground state (rate constant k_S), the singlet RIP evolves to a triplet RIP, driven by the nuclear hyperfine interactions within each radical and the g factor difference between the radicals. The triplet RIP can then be trapped by the exothermic, spin-allowed recombination reaction to form the molecular triplet ^{3}D, with rate constant k_T. Singlet–triplet mixing is impeded by the triplet splitting due to the isotropic exchange interaction and the anisotropic electron–electron dipolar interaction. The magnitude of the latter depends on the orientation of the RIP in a magnetic field and the distance between the radicals.[2] Likewise, both magnetic interactions which drive singlet–triplet mixing can depend on orientation; the nuclear hyperfine interactions and g factors are each given by their appropriate tensors. Since the contribution of the difference **g** tensor to the rate of singlet–triplet mixing increases linearly with field, whereas the strengths of the electron–electron and electron–nuclear dipolar interactions are field independent, the effects of these anisotropic terms on the triplet quantum yield may vary substantially with the applied field strength, as well as with orientation. Both effects are observed.

Nonoriented quinone-depleted RCs (*R. spheroides*, R-26[3]) were excited essentially isotropically with a subsaturating 8-ns light pulse at 532 nm. The concentration of ^{3}D 3 μs after the flash is conveniently detected with linearly polarized light at 870 nm, where absorption is dominated by the ground state of D. The

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[1] (a) Rockley, M. G.; Windsor, M. W.; Cogdell, R. J.; Parson, W. W. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2251. (b) Kaufmann, K. J.; Dutton, P. L.; Netzel, T. L.; Leigh, J. S.; Rentzepis, P. M. *Science (Washington, D.C.)* **1975**, *188*, 1301. (c) Holten, D.; Hoganson, C.; Windsor, M. W.; Schenck, C. C.; Parson, W. W.; Migus, A.; Fork, R. L.; Shank, C. V. *Biochim. Biophys. Acta* **1980**, *592*, 461. (d) Thurnauer, M. C.; Katz, J. J.; Norris, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3270. (e) Bowman, M. K.; Budil, D. E.; Closs, G. L.; Kostka, A. G.; Wraight, C. A.; Norris, J. R. *Ibid.* **1981**, *78*, 3305.

[2] A more detailed analysis of the dipolar interaction in the primary RIP of RCs is given in: Roelofs, M. G.; Chidsey, C. E. D.; Boxer, S. G. *Chem. Phys. Lett.* **87**, 582 (1982).

[3] Butler, W. F.; Johnston, D. C.; Shore, H. B.; Fredkin, D. R.; Okamura, M. Y.; Feher, G. *Biophys. J.* **1980**, *32*, 967.

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magnitude of the bleach of D when the electric polarization vector of the 870-nm light is at an angle η to $\vec{H}$ is measured as a function of field, and its ratio with the value at zero field defines the relative yield, $I(H,\eta)$. We define a new quantity, the "quantum yield anisotropy", $a(H)$, as

$$a(H) = \frac{I(H,0°) - I(H,90°)}{I(H,0°) + 2I(H,90°)} \quad (1)$$

$I(H,0°)$ and $I(H,90°)$ for a viscous solvent are plotted in Figure 2A; $a(H)$ is plotted in Figure 2B for viscous and nonviscous solvents.[4] The dependence of $a(H)$ on viscosity is simply a consequence of the decay of $a(H)$ due to rotation on the time scale of its measurement, and the observation that $a(H) = 0.00 \pm 0.009$ for a nonviscous solution provides an excellent experimental control.[5]

A quantitative analysis of these data depends on the magnitude of each tensor quantity and its geometric relationship with the direction defined by the transition moment at 870 nm. The remarkable observation that the *sign* of $a(H)$ changes on going from low to high magnetic field implies that there are two or more anisotropic magnetic interactions contributing to $a(H)$. The field dependence of $a(H)$ is due to the *difference* **g** tensor between $D^{+}\cdot$ and $A^{-}\cdot$, while the anisotropy at low field (e.g., 1 kG) is due to the electron–electron and electron–nuclear dipolar tensors. The latter tensors need not be related in magnitude or relative orientation to the *difference* **g** tensor. Also note that $a(H)$ is essentially indpendent of field for fields >40 kG. At extremely high fields we expect the rate of the singlet–triplet mixing to exceed the recombination rate constants (Figure 1) for all orientations in the field. Consequently, the yield would be independent of the mixing rate and orientation, and $a(H)$ would equal zero; i.e., the observed $a(H)$ at 50 kG in Figure 2B is approximately at a turning point.[6]

We have previously derived a theoretical expression for the triplet quantum yield as a function of applied magnetic-field strength considering only isotropic magnetic interactions.[7] This expression is readily generalized for the case of both isotropic and anisotropic interactions; the formalism and details of actual calculations are presented elsewhere.[8] It is found that the anisotropic quantum yield data of Figure 2B can be fit with reasonable values for the anisotropic parameters, placing some limits on RC structures. EPR experiments on trapped, photoselected intermediates ($D^{+}\cdot$, $A^{-}\cdot$, and $D^{+}\cdot A^{-}\cdot$) are currently being performed, and these should augment the $a(H)$ data and allow the determination of several key structural features of the RC.

The new result demonstrated in Figure 2 is that *the yield of a chemical reaction involving radical pairs can depend on the orientation of the reactants in a magnetic field.* This is a natural consequence of the anisotropy of magnetic terms that drive or impede singlet–triplet mixing. This effect can be exploited to probe both magnetic properties of the radicals and structural properties of the short-lived radical pair itself, as the effect depends on the *difference* **g** tensor at high field. Although isotropic magnetic field effects on radical-pair reactions are well-known[9] and entirely predictable based on the CIDNP literature,[10] anisotropic magnetic-field effects have not been reported previously.[11] This is because radical-pair reactions are ordinarily studied in nonviscous solution, where molecular motion leads to a rapid loss of interradical interactions or rotational averaging of anisotropic magnetic terms. Effects similar to those reported here are likely to be important for ion-pair recombination in amorphous solids, for radical-pair reactions in single crystals, for electron-transfer reactions in rigid photosynthetic model systems, and possibly for radical-pair reactions on surfaces or in viscous organized media such as micelles, biological membranes, or polymers.

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(4) $a(H)$ is independent of the angle between the electric polarization direction of the 532-nm exciting light and $\vec{H}$ to within the error limits.

(5) The magnetic field has no detectable effect on the detection system, and there is no evidence for alignment of the RCs in the magnetic field.

(6) Note that the relative yield is observed to saturate at very high field [i.e., the $I(H)$ curve levels off at high field in Figure 2A].

(7) (a) Chidsey, C. E. D.; Roelofs, M. G.; Boxer, S. G. *Chem. Phys. Lett.* **1980**, *74*, 113. (b) Boxer, S. G.; Chidsey, C. E. D.; Roelofs, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 1452. This treatment is valid for the high-field limit, where the electron Zeeman interaction is much greater than the exchange, electron–electron dipolar, and nuclear hyperfine interactions, $H > 300$ G for RCs.

(8) Boxer, S. G.; Chidsey, C. E. D.; Roelofs, M. G. *Proc. Natl. Acad. Sci. U.S.A.*, in press. The isotropic g factor difference between $D^{+}\cdot$ and $A^{-}\cdot$ in RCs is about -1×10^{-3}.[7] The anisotropic quantum yield data at high field can be fit with a difference g tensor having principal values of -14×10^{-4}, -14×10^{-4}, and 1×10^{-4}, which is reasonable for aromatic radicals.

(9) See, for example: Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369.

(10) See, for example: Lepley, A. R.; Closs, G. L., Eds. "Chemically Induced Magnetic Polarization"; Wiley: New York, 1973.

(11) The magnetic-field-dependent delayed fluorescence from single crystals due to an ion-pair reaction with dye molecules adsorbed on the surface exhibits an orientation dependence, which may be due to anisotropic magnetic interactions: Bube, W.; Michel-Beryerle, M. E.; Haberkorn, R.; Steffens, E. *Chem. Phys. Lett.* **1977**, *50*, 389.

Anionic Telomerization of Acrylonitrile Initiated by $^{-}CH_2CN$ in the Gas Phase

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Although the kinetics and mechanism of free-radical-initiated polymerization processes of vinyl monomers have been reasonably understood for years, the same degree of understanding of ionic vinyl polymerization has not been achieved, primarily due to the lack of a method to observe the early stages of the ionic telomerization reaction. We report the first results of an anionic telomerization of a vinyl monomer in the gas phase, specifically acrylonitrile initiated by $^{-}CH_2CN$, where (a) the kinetics of the initiation and propagation steps leading to $NCCH_2\text{–}(CH_2CH(CN))\text{–}_3CH_2CHCN^{-}$ are determined and (b) under these conditions, the termination step of this "living" tetrameric anion is shown to depend on the structure of the anion initiator with intramolecular ion–dipole interactions reducing the reactivity of anionic end of this telomer.

Our approach to the study of gas-phase ionic telomerizations uses a flowing afterglow (FA) apparatus.[1] The initiator, $^{-}CH_2CN$ (m/z 40) was produced in the upstream end of the flow tube by the fast H^{+} transfer reaction[2] between H_2N^{-} and CH_3CN ($k = (4.5 \pm 0.3) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) in helium as the buffer gas ($P_{He} = 0.5$ to 1.2 torr, flow velocity ($\bar{v}$) = 36 to 80 m s^{-1}). Some association of $^{-}CH_2CN$ with CH_3CN occurred to yield the cluster ion $NCCH_2^{-}(CH_3CN)$ (m/z 81). The chemically activated $^{-}CH_2CN$ ions are thermalized to their ground state by numerous collisions with the helium buffer gas in the flow tube prior to reaching the neutral reactant [N] addition port and the ion–molecule reaction commences. The ion composition of the flow is monitored with a quadrupole mass spectrometer as a function of added N. Rate constants (±30% accuracy) for the ion–molecule reactions are calculated by methods previously described.[1]

When $H_2C{=}CHCN$ was added to the helium flow ($P_{He} = 1.1$ torr, $\bar{v} = 36$ m s^{-1}) containing anions m/z 40 and 81, the sequential production of the telomeric anions m/z 93, 146, 199, and 252 was observed (see Figure 1). The rate constants for the decay of m/z 40 and 81 ($\sim 6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) are the same as those

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(1) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491.

(2) Amide ion was produced by dissociative electron attachment to NH_3 at the electron gun.