Zeitschrift für Physikalische Chemie Neue Folge, Bd. 111, S. 1–5 (1978)

A Biomagnetic Sensory Mechanism Based on Magnetic Field Modulated Coherent Electron Spin Motion

By

Klaus Schulten, Charles E. Swenberg*
and Albert Weller

Max-Planck-Institut für biophysikalische Chemie,
Abteilung Spektroskopie, D-3400 Göttingen, Federal Republic of Germany

(Received July 20, 1978)

Biomagnetism / Electron spin states / Hyperfine interaction

Electron transfer processes which generate radical pairs in coherent electron spin states (singlet or triplet) are affected by weak magnetic fields [Schulten *et al.*, Z. physik. Chem. Neue Folge **101** (1976) 371]. Based on this finding we suggest a reaction mechanism for a chemical compass which exhibits a sensitivity on the orientation of the geomagnetic field originating from an anisotropy of the hyperfine interaction experienced by unpaired electron spins in a redox process. It is argued that such mechanism may explain the ability of many biological species to orient themselves in the geomagnetic field.

Elektronübertragungsprozesse, die Radikalpaare in kohärenten Elektronenspinzuständen (Singlett oder Triplett) erzeugen, können durch schwache Magnetfelder beeinflußt werden [Schulten *et al.*, Z. physik. Chem. Neue Folge **101** (1976) 371]. Diese Beobachtung veranlaßt uns zu dem Vorschlag eines Reaktionsmechanismus für einen chemischen Kompaß, bei dem eine anisotrope Hyperfeinwechselwirkung auf die ungepaarten Elektronenspins eines Redoxprozesses die Empfindlichkeit für die Richtung des Erdmagnetfeldes hervorruft. Es wird dargelegt, daß der vorgeschlagene Mechanismus die Fähigkeit vieler biologischer Spezien zur Orientierung im Erdfeld erklären könnte.

Over the past decade evidence has accumulated that some living organisms are able to detect both the presence and the direction of the earth's magnetic field [1, 2]. In addition to controlled cage experiments with both passerines and non-passerines [3, 4] and homing experiments with pigeons

* Permanent address: Laboratory of Neuropharmacology, National Institute of Mental Health, Saint Elizabeths Hospital, Washington, D.C. 20032.

(Columba livia) [5] Moore has recently reported direct visual evidence that the orientation of free-flying nocturnal migrants is affected by nocturnal fluctuations of the geomagnetic field.

Our study of the modulation of chemical reactions by small magnetic fields of only a few 10 Gauss in solutions [7, 8] and solids [9] based on the hyperfine (and/or fine structure) and Zeeman interaction on unpaired electron spins, and the recent discovery of a similar magnetic field modulation of the primary electron transfer in photosynthesis [10, 11, 12] prompted us to consider the same mechanism to be operative in biomagnetic sensors. In brief, our conjecture is that the biomagnetic sensory mechanism entails either a dark or a light-driven biochemical electron transfer reaction generating radical pairs (in either the singlet or triplet state) in which consecutively an *anisotropic* hyperfine interaction and external magnetic fields induce a coherent electron spin motion. This motion, i.e. the relative orientation of the two unpaired electron spins, determines the spin multiplicity of the radical products appearing through electron back transfer. These products can be modulated by the strength as well as by the direction of an external magnetic field establishing, thus, a chemical compass. The radical process described can either be in series or, as we will assume in the following, parallel with the generation of a chemical X serving as the measure of the field direction.

The following kinetic scheme illustrates our idea:

$$\begin{array}{l} {}^1Z \overset{k_I}{\rightleftarrows} {}^1({}^2A^- + {}^2D^+) \overset{\frown}{\underset{\smile}{H}} {}^3({}^2A^- + {}^2D^+) \xrightarrow{k_T} {}^3T \\ \big\downarrow k_X \\ {}^1X \end{array} \tag{1}$$

${}^1Z$ denotes a singlet precursor (*e.g.* the singlet excited state ${}^1A^* + {}^1D$) from which the radical pair is generated in a singlet state, i.e. ${}^1({}^2A^- + {}^2D^+)$. Electron back transfer either reproduces ${}^1Z$ or produces triplet products ${}^3T$ depending on the spin state of the radical pair. The spin state changes in time due to the hyperfine and Zeeman interaction collected in the Hamiltonian H. The time evolution of the radical pair described by the spin density matrix ϱ is governed by the Liouville equation

$$\frac{\mathrm{d}\varrho(t)}{\mathrm{d}t} = -\frac{i}{\hbar}[H, \varrho(t)]_- + k_I n(t) Q_S - \frac{k_S}{2}[Q_S, \varrho(t)]_+ - \frac{k_T}{2}[Q_T, \varrho(t)]_+ \tag{2}$$

where Q_S and Q_T are the projection operators on the singlet and triplet states, respectively, and where $n(t)$ stands for the concentration of ${}^1Z$ [7, 8]. $n(t)$ obeys the complementary rate equation

$$\frac{\mathrm{d}n(t)}{\mathrm{d}t} = -(k_X + k_I)\, n(t) + \frac{k_S}{2} \operatorname{tr}[Q_S, \varrho(t)]_+ . \tag{3}$$

Eqs. (2) and (3) are to be supplemented by the initial conditions $n(t = 0) = 1$ and $\varrho(t = 0) = 0$. The percentage change of the product X can be written

$$\Delta X = X(t \to \infty) - 1 = k_X\, \tilde{n}(0) - 1 \tag{4}$$

where $\tilde{n}$ denotes the Laplace transform of $n(t)$. We assume for an illustration of our model $k_S = k_T = k$ as in this case Eq. (2) can be solved analytically. Defining the branching ratio of the reaction of ${}^1Z$ to ${}^1({}^2A^- + {}^2D^+)$ and to ${}^1X$ by $\alpha = k_I/k_X$ the solution can be written

$$\begin{aligned} X(t \to \infty) &= \left[1 + \alpha - \alpha \sum_{m,n} \frac{|\langle m|Q_s|n\rangle|^2}{1 + i(\varepsilon_m - \varepsilon_n)}\right]^{-1} \\ &= [1 + \alpha\, T(t \to \infty)]^{-1} \end{aligned} \tag{5}$$

where $|m\rangle$, ε_m are the eigenstates and eigenvalues (in units of k) of the radical pair Hamiltonian and $T(t \to \infty)$ denotes the yield of triplet products ${}^3T$ defined in [1].

We have restricted explicit calculations to radicals having identical isotropic g-values and assumed that only one of the radicals, i.e. either ${}^2A^-$ or ${}^2D^+$, interacts with a single nuclear spin I ($\frac{1}{2}$) characterized by an axial symmetric hyperfine tensor (A_{xx}, A_{xx}, A_{zz}). Thus

$$\begin{aligned} H = {} & g\mu \mathbf{B} \cdot (\mathbf{S}_1 + \mathbf{S}_2) + I_z A_{zz} S_{1z} \\ & + (I_x S_{1x} + I_y S_{1y}) A_{xx} \end{aligned} \tag{6}$$

where $\mathbf{B}$ denotes the earth's magnetic field which we chose 1 Gauss in magnitude. The neglect of any exchange interaction in [6] can be shown to overestimate the percent change of $X(t \to \infty)$ slightly [7]. The inclusion of more than one nuclear spin in [6] is not expected to change the qualitative behaviour of the system.

In Figs. 1 and 2 we have presented some typical results for $X(t \to \infty)$ and $T(t \to \infty)$ as a function of θ, the angle of the magnetic field with respect to the hyperfine symmetry axis (z-axis). It is interesting to note from Figs. 1 and 2 that changes of up to 33 % are obtained for $X(t \to \infty)$, viz. for the choice $A_{xx} = 0$, $A_{zz} = 4$ Gauss). This demonstrates convincingly that an anisotropic hyperfine interaction can be made sufficiently sensitive to angular changes of an external field in order to serve as a chemical compass.

Of interest is the angular acuity predicted by the angular dependence of $X(t \to \infty)$ or $T(t \to \infty)$. When A_{xx} is comparable in magnitude to A_{zz} most of the angular variation occurs over only a narrow range of θ, about 30°. Lacking any knowledge of k and α we have chosen rather arbitrarily the values 10^{-3} ns^{-1} and 10, respectively. We note, however, that increasing the branching ratio enhances the angular acuity (see below) but decreases the absolute concentration of ${}^1X$. Shortening of the lifetime of the radical pair diminishes the angular percentage change, i.e. decreases angular acuity.

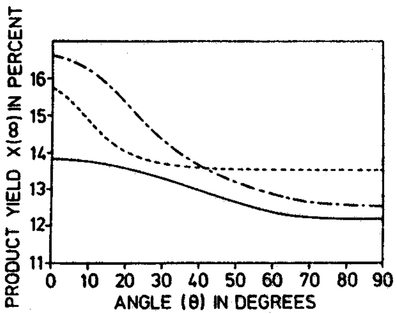

Fig. 1

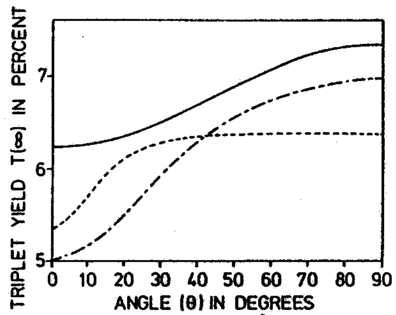

Fig. 2

Fig. 1. Angular dependence of the yield of ${}^1X$; θ is the angle between the field direction and the z-axis. Values of the parameters used are: $k = 10^{-3}\ ns^{-1}$, $\alpha = 10$, $B = 1$ Gauss, $A_{zz} = 4$ Gauss; —— $A_{xx} = 10$ Gauss, ---- $A_{xx} = 5$ Gauss, -·-·- $A_{xx} = 0$

Fig. 2. Angular dependence of triplet yield $T(t \to \infty)$, θ is the angle between the field direction and the z-axis. Same parameters as in Fig. 1

For our model to give an appropriate field effect consistent with experimental data it is necessary that (1) the hyperfine symmetry axis is fixed in direction (relative to the whole organism), and (2) the radical ion pair is characterized by small hyperfine coupling constants, summing together to only a few Gauss. The latter condition implies the prediction that radicals ought to be detected which exhibit very narrow ESR lines. We also predict that the magnetic sensory ability measured as a function of the absolute magnitude of the external field should exhibit a maximum at fields of a few Gauss and vanish at higher fields. Our model also implies that the range of angles discernible is not 360° but only 90°; a reversion of the field direction or reflection with respect to the x,y-plane of the molecule fixed coordinate system would go unnoticed by a sensor based on the hyperfine mechanism. This is in agreement with the observed magnetic field sensitivity of birds which must take advantage of the inclination of the geomagnetic field in order to acquire full orientation.

We have presented in this paper just one realization for a magnetic sensor based on a magnetic field modulation of a coherent spin motion and a spin-selective electron transfer reaction. The model presented is based on anisotropic hyperfine coupling. An anisotropy of the Zeeman interaction would similarly yield a sensitivity on the orientation of the geomagnetic field, particularly in view of the fact that biological electron transfer systems with g-value anisotropies exceeding 2.6 have been observed [13]. The interplay of the strength of the anisotropic hyperfine and Zeeman interaction, the strength of the magnetic field to be detected and the electron transfer rate constants will be discussed in a forthcoming publication.

Acknowledgement

The authors like to acknowledge the computer services of the Gesellschaft für wissenschaftliche Datenverarbeitung mbH Göttingen.

References

1. Neurosciences Research Program Bulletin, Vol. 15, No. 1, Jan. 1977, MIT Press.
2. See for example: *Biological Effects of Magnetic Fields* (M. F. Barnothy ed.), Plenum Press, 1964.
3. S. Emlen, W. Wiltschko, N. Demong and S. Bergman, Science **193** (1976) 505.
4. W. Wiltschko and R. Wiltschko, Science **176** (1972) 62; Z. Tierpsychol. **37** (1975) 337.
5. W. Keeton, Proc. Nat. Acad. Sci. USA **68** (1971) 102. – L. Walcott and R. Green, Science **184** (1974) 180.
6. F. R. Moore, Science **196** (1977) 682.
7. K. Schulten, H. Staerk, A. Weller, H.-J. Werner and B. Nickel, Z. physik. Chem. Neue Folge **101** (1976) 371. – H.-J. Werner, H. Staerk and A. Weller, J. Chem. Phys. **68** (1978) 2419.
8. Z. Schulten and K. Schulten, J. Chem. Phys. **66** (1977) 4616. – H.-J. Werner, Z. Schulten and K. Schulten, J. Chem. Phys. **67** (1977) 646. – K. Schulten and P. G. Wolynes, J. Chem. Phys. **68** (1978) 3292.
9. See for example: C. E. Swenberg and N. E. Geacintov, in: *Organic Molecular Photophysics*, Vol. 1 (J. B. Birks ed.), John Wiley & Sons, New York 1973
10. A. J. Hoff, H. Rademaker, R. van Grondelle and L. N. M. Duysens, Biochim. Biophys. Acta **460** (1977) 547.
11. R. E. Blankenship, T. J. Schaafsma and W. W. Parson, Biochim. Biophys. Acta **461** (1977) 297.
12. H.-J. Werner, K. Schulten and A. Weller, Biochim. Biophys. Acta **502** (1978) 255.
13. J. Rawlings, V. K. Shah, J. R. Chisnell, W. J. Brill, R. Zimmermann, E. Münch and W. H. Orme-Johnson, J. Biol. Chem. **253** (1978) 1001.