and the other, silylene,

$$R_3Si + CH_3SiH_2 \rightarrow R_3SiH + CH_3SiH$$

The data in Table II for self-disproportionation refer to the silaethylene-yielding reactions, and those for cross disproportionation, to the sum of the silaethylene- and silylene-producing reactions.[15]

Thus, we conclude that disproportionations of silyl radicals are of general occurrence and further detailed studies are warranted.

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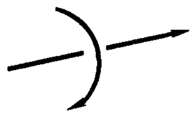
Chemical Geometrodynamics: Gravitational Fields Can Influence the Course of Prochiral Chemical Reactions

Sir:

The following discussion will show that, in principle, the dynamics of geometry in prochiral chemical reactions can be controlled by the macroscopic geometry of chiral physical fields in which the reactions proceed. Prochiral chemical reactions are capable of producing chiral products; however, without dissymmetric catalysts, solvents or physical fields, or extremely unusual statistics, the reactions would produce only racemic products.

The question of the potential effect of parallel (chiral) combinations of electric, **E**, and magnetic, **B**, fields on prochiral chemical reactions has been the subject of three recent reports.[1-3] We originally asserted that it would be possible to obtain asymmetric synthesis using chiral **E** and **B** fields, if the prochiral reactant had an intrinsic magnetic moment, and if it were possible to select one of the two magnetic species [A (j) or A (−j)].[3] It appears from the theorem by deGennes[1] that it would be impossible to select one of the magnetic species using only **E** and **B** fields. Thus, for electric and magnetic fields, asymmetric synthesis must depend on nonadiabatic currents in the transition state.[3] A realistic estimate of the magnitude of possible nonadiabatic currents and their contribution to asymmetric synthesis suggests that an enantiomeric excess of 1 ppb is all that one could expect with readily attainable fields.[4]



A

The three other physical fields that could be considered for use in field-directed, asymmetric synthesis are strong, weak, and gravitational. Both strong and weak fields have ranges much less than molecular diameters; so neither of these fields could contribute to a chiral macroscopic field structure. The remaining field is gravitational.[5] In the following paragraphs we will show that, in principle, it is possible to direct an asymmetric synthesis with a chiral physical field, the polar component of which is gravitational.

In constructing a chiral field containing a gravitational component the gravitational field can be either continuous or quantal (gravitons or gravitational phonons). In the former case a chiral gravitational field can be represented by the vector diagram A in which the polar vector represents linear acceleration and the axial vector represents centrifugal motion. Molecules moving under the influence of this field structure would have both linear momentum, p, and angular momentum, σ. Parity, P, and time reversal, T, operators are used to illustrate the possibility of asymmetric synthesis in this chiral field. The arguments are directly analogous to the case of the electromagnetic field.[1-3]

Given a molecule, M, moving in a chiral gravitational field such that it has a linear momentum, p, and angular momentum, σ, application of the parity operator, P, to this system will give the enantiomeric molecule, M*, with enantiomeric momenta:

$$(\mathrm{M}, p, \sigma)\ P\ (\mathrm{M}^*, -p, \sigma)\ T\ (\mathrm{M}^*, p, -\sigma) \qquad (1)$$

Application of the time reversal operator T will leave both the molecule and the chirality of the momenta unchanged (1). It is well known that collision velocities can influence the rates of chemical reactions. Thus it appears that a chiral gravitational field which will impart chiral momenta to reacting species could cause asymmetric synthesis.

It is possible to construct a macroscopic analogue for the change in the energy of a chiral transition state caused by a chiral field. Imagine a right- and a left-handed propeller in separate wind tunnels, designed to produce the chiral field in A by gas motion. The right-handed propeller would rotate at a higher rate than the left-handed one.

Consideration of a chiral field in which the gravitational component is quantal, **G**, is entirely analogous. In this case the axial vector field might be magnetic, **B**. Application of the parity operator to the molecule, M, and chiral field will give the enantiomeric molecule M* and the enantiomeric field (2). Neither the molecule nor the field structure will be altered by the time reversal (2), a situation which is compatible with asymmetric synthesis.[6] Gravitational phonons should influence molecular translation.

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$$(\mathbf{M}, \mathbf{G}, \mathbf{B})\, P\, (\mathbf{M}^*, -\mathbf{G}, \mathbf{B})\, T\, (\mathbf{M}^*, \mathbf{G}, -\mathbf{B}) \qquad (2)$$

In principle, the results in (1) and (2) indicate that both types of chiral fields would be capable of perturbing both enantiomeric equilibria and reaction rates.

The amount of energy required to introduce chiral order into a prochiral chemical reaction to the extent of 1-100 ppm depends on the nature of the fields that introduce the order. If the fields are continuous, they must alter the free energies of the *pro-R* and *pro-S* transition states by the amount required to produce the observed enantiomeric excess. In this case classical partition functions can be used to estimate the enantiomeric excess that will be generated for a given field strength. If chiral order were introduced into the *pro-R* and *pro-S* reaction coordinates by a **B** field and a parallel quantal **G** field, classical partition functions will not apply. If the imposed quantal field influenced motion in the reaction coordinate, it would not alter the electronic energy of the system if there was no breakdown of the Born-Oppenheimer approximation. The influence of the field on relative reaction rates would then be found in changes in the frequency for crossing the transition-state barrier.

If we assume that the free energies of the *pro-R* and *pro-S* transition states are the same, as they must be in the magnetic field alone, then it is possible to calculate the amount of energy that would be required to order the *R, S* binary array to the extent of 1-100 ppm. The order-disorder contribution to the entropy of a binary array is given by

$$S = -\left\{\frac{dA}{dT}\right\}$$

$$= \tfrac{1}{2}Nk[(1 + s)\ln(1 + s) + (1 - s)\ln(1 - s) - 2\ln 2]$$

where s is the order parameter. The change in entropy associated with 1-ppm ordering corresponds to 3.5×10^{-26} erg/molecule at 255 K. For ordering to the extent of 100 ppm at the same temperature, the energy required is 1.8×10^{-22} erg/molecule. These calculated energies do not take into consideration the fact that the magnetic field only partially orders the *pro-R* and *pro-S* transition states. For a magnetic field strength of 1 T, a transition-state magnetic moment of 2 μ_B which would be realistic for reaction of a solvated electron with a prochiral radical for example, and a temperature of 255 K, the energies above become 2×10^{-24} and 1×10^{-20} erg/molecule for 1 and 100 ppm, respectively. These numbers should be reduced by a factor of 2 because the ordering effect will act equally on the *pro-R* and *pro-S* transition states driving one toward products and one toward reactants. The estimate of the energy required in this case is 1×10^{-24} and 5×10^{-21} erg/molecule for ordering of the extent of 1 and 100 ppm, respectively. Strictly speaking, Boltzman statistics is not applicable to this system because any chiral population is metastable. The numbers above are highly approximate and only indicate general orders of magnitude.

The thermal energy of the reaction system, kT, is of the order of 3.5×10^{-14} erg/molecule at 255 K. The thermal energy is randomly oriented, and any energy producing asymmetric synthesis must be directed. In spite of the fact that the random motions are large compared to the ordering motions, a shift in the centroid of the random motions will be observable as chiral ordering in the reaction products. Prochiral chemical reactions may be one of the most sensitive energy detectors yet devised. The amounts of energy required for observable, asymmetric synthesis in accessible magnetic fields are within the range anticipated for gravitons.

It is possible that the chirality of the prebiotic metric contributed to the selection of the enantiomeric molecules of biology. The effect would have been larger than presently observable if gravitational acceleration has been decreasing with time as suggested by P. A. M. Dirac.

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(5) Pasteur first investigated the possibility of gravitationally directed, asymmetric synthesis by use of a centrifuge. The experiment was not successful as the motion of molecules in a centrifuge is not chiral.

(6) It is interesting to note that charge inversion, *C,* following *P* and *T* in (2) would produce ($^{+}\mathbf{M}^*$, **G, B**). The positron enantiomer, $^{+}\mathrm{M}^*$, would have the same energy in the same field structure as the electron molecule, M. This is not true for charge reflection in (1).

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Asymmetric Synthesis in a Confined Vortex: Gravitational Fields Can Cause Asymmetric Synthesis

Sir:

This paper records the observation of asymmetric synthesis of isophorone oxide which resulted from conducting the reaction in the chiral gravitational field[1] of a confined vortex.

The chiral gravitational field was obtained by placing the reaction mixture in a 30-mm double-walled Pyrex tube which had been capped and placed in a double-ended turbine (Figure 1). The turbine was driven by air at pressures between 37 and 47 psi. The turbine assembly could be oriented so that the tube would spin clockwise or counterclockwise (from the top) when perpendicular to the earth's surface or the tube could be spun parallel to the earth's surface. The rotational rates for the tube varied between 6000 and 14 000 rpm and were generally within the range of 10 000 and 12 000 rpm.

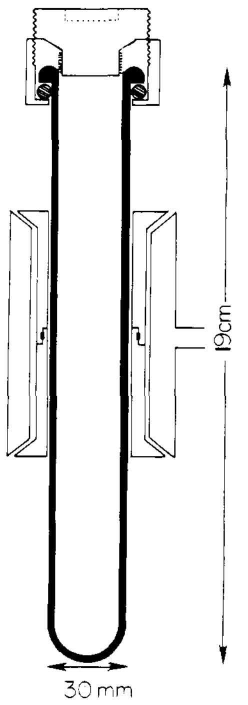

Figure 1. Double-ended turbine spinner assembly. Materials: housing, aluminum; rotor, "Rulon"; plug, "Teflon".

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