

PARITY NONCONSERVATION AND THE ORIGIN OF BIOLOGICAL CHIRALITY :  
THEORETICAL CALCULATIONS

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ABSTRACT

Recent theoretical calculations concerning the hypothesized connection between the parity violating weak interactions and the origin of biological chirality are extended in order to assess the relative importance of differential beta radiolysis of enantiomers and the energy difference between enantiomers. It is found that the largest chiral polarizations are produced at lower temperatures where beta radiolysis dominates. At higher temperatures the energy difference between enantiomers dominates but the chiral polarization is appreciably smaller.

The question of the origin of the optical purity of biological molecules has been considered for many years but as yet no definitive answer has been found (1-3). One of the most interesting hypotheses which has been suggested to explain both the origin and the sign of this observed chiral polarization (e.g. L rather than D amino acids) connects it with the weak interaction, one of the four fundamental forces of nature (the other three being electromagnetism, gravity, and the strong nuclear interaction). This weak force is the only one of the four which distinguishes right from left and hence offers the only possible explanation of the sign of the chiral polarization which is based upon natural law rather than upon random initial conditions or statistical fluctuations. Whether or not the effects of the weak interaction on molecular dynamics are sufficiently large to be able to dominate random conditions or fluctuations, however, has not yet been determined.

The purpose of the present work is to take another step toward the solution of this problem by extending the results of recent calculations in order to assess the relative importance of two different effects of the weak interaction on molecular dynamics: (a) a difference in the rates of beta radiolysis of mirror image molecules (the Vester-Ulbricht hypothesis, hereafter designated VU) (4) and (b) an energy difference between mirror image molecules (the Yamagata-Rein hypothesis, YR) (5). Both of these effects can produce a difference  $n_L - n_D$  in the number of L versus D isomers of an optically active compound from an initially racemic mixture. The rate equations for this process have been given by Mann and Primakoff (MP) (6):

$$\begin{aligned}\frac{dn_L}{dt} &= \alpha_L + (\beta_D + \gamma_D S)n_D - (\beta_L + \gamma_L S + \delta_L + \epsilon_L S)n_L \\ \frac{dn_D}{dt} &= \alpha_D + (\beta_L + \gamma_L S)n_L - (\beta_D + \gamma_D S + \delta_D + \epsilon_D S)n_D\end{aligned}\quad (1)$$

where

$\alpha_{L,D}$  = rate of synthesis of L,D isomers (assumed constant)

$\beta_{L,D}$  = thermal racemization rate constant

$\gamma_{L,D} S$  = radio-racemization rate constant

$S$  = strength of radioactive  $\beta$ -ray source (number of  $\beta$  particles per second)

$\delta_{L,D}$  = rate constant for decomposition by heat, electromagnetic radiation, secondary radiolysis, etc.

$\epsilon_{L,D} S$  = rate constant for primary beta radiolysis

Similar rate equations have been considered by Fajszsi and Czége (3). It should be noted that the MP equations are linear ones which describe the combined effect of constant growth, exponential decomposition, and racemization. They hence describe a simple development in time which is characteristic of simple molecules (e.g. monomers), but not more complicated behavior such as autocatalysis or self-replication. The MP equations have been generalized here to include the possibility that each rate constant  $\alpha, \beta, \dots$  is different for L vs. D isomers. The origin of these differences is now considered.

According to the VU hypothesis, beta radiolysis produces an asymmetry

$$A_{\epsilon} \equiv \frac{\epsilon_D - \epsilon_L}{\epsilon_D + \epsilon_L} \tag{2}$$

in the radiolysis rate constant  $\epsilon \equiv (\epsilon_D + \epsilon_L)/2$  because the beta ray electrons, being themselves left handed as a consequence of the parity nonconserving weak interaction which created them in nuclear decay, interact differently with D vs. L molecules. A detailed mechanism for this interaction has been presented recently (7), and order-of-magnitude calculations suggest that the asymmetry  $A_{\epsilon}$  is of order  $10^{-10}$  to  $10^{-11}$  for typical chiral organic molecules and typical beta ray energies (7). Recent measurements of triplet positronium formation rates in amino acids give an approximate limit  $|A_{\epsilon}| < 10^{-8}$  to  $10^{-9}$  (8,9) which is consistent with the theoretical estimate. The sign of  $A_{\epsilon}$  has not yet been determined.

Asymmetries in the other rate constants  $\alpha, \beta, \gamma, \delta$  are possible by the YR mechanism whenever chiral molecules (i) are formed from achiral precursors, (ii) racemize, or (iii) decompose or otherwise react to give achiral products. This is because, due to the small energy difference between the enantiomers, the activation energies will in general be slightly different for the D vs. L isomers. Assuming the Arrhenius form for the rate constants gives e.g. for racemization an asymmetry

$$\begin{aligned} A_{\beta} &\equiv \frac{\beta_D - \beta_L}{\beta_D + \beta_L} \\ &= \frac{\exp \left[ - (E_a - \Delta E)/kT \right] - \exp \left[ - (E_a + \Delta E)/kT \right]}{\exp \left[ - (E_a - \Delta E)/kT \right] + \exp \left[ - (E_a + \Delta E)/kT \right]} \\ &\approx \frac{\Delta E}{kT} \end{aligned} \tag{3}$$

where  $\Delta E$  is the parity nonconserving energy shift,  $k$  is Boltzmann's constant, and  $T$  the absolute temperature. Recent calculations (10-13) suggest that  $\Delta E$  is of order  $10^{-20}$  a.u.  $\approx 4 \times 10^{-38}$  Joules for typical chiral organic molecules, and hence  $A_{\beta} \sim 10^{-17}$  for temperatures near room temperature. The asymmetries in  $\alpha, \gamma,$  and  $\delta$  are expected to have roughly the same order of magnitude.

It is now possible to compare the VU and YR contributions to the chiral polarization, defined as (14):

$$\eta = \frac{n_L - n_D}{n_L + n_D} \quad (4)$$

This is accomplished by solving the MP equations (1) for  $n_L$  and  $n_D$  as a function of time and thereby obtaining an expression for  $\eta$ . One finds that the magnitude of the chiral polarization increases with time from an initial value  $\eta(0) = 0$  (or, if  $\alpha \neq 0$ , changes from an initial value  $\eta(0) = A_\alpha$ ). After a time which is equal to the racemization time  $(\beta + \gamma S)^{-1}$  or the decomposition time  $(\delta + \epsilon S)^{-1}$ , whichever is smaller, an asymptotic value  $\eta_\infty$  is approached which is equal to

$$\eta_\infty = \frac{2\beta A_\beta + 2\gamma S A_\gamma + \delta A_\delta + \epsilon S A_\epsilon + (\delta + \epsilon S) A_\alpha}{2\beta + 2\gamma S + \delta + \epsilon S} \quad (5)$$

where  $\beta \equiv (\beta_D + \beta_L)/2$ ,  $\gamma \equiv (\gamma_D + \gamma_L)/2$ , etc. are the average rate constants and where  $A_\beta$ ,  $A_\gamma$ , etc. are the corresponding asymmetries. For typical cases (e.g. typical amino acids in aqueous solution) it turns out that  $\delta$  is negligible relative to  $\beta$  (15) and  $\gamma$  relative to  $\epsilon$  (6), and in such cases eq. (5) simplifies to

$$\begin{aligned} \eta_\infty &\approx \frac{2\beta A_\beta}{2\beta + \epsilon S} + \frac{\epsilon S A_\epsilon}{2\beta + \epsilon S} \\ &\equiv \eta_\beta + \eta_\epsilon \end{aligned} \quad (6)$$

which explicitly denotes the contributions of the YR and VU asymmetries to the total chiral polarization. (Note that, somewhat paradoxically, starting from a racemic mixture the process of "racemization" alone can induce a chiral polarization.)

To make a quantitative comparison, values must be found for  $\epsilon S$  and  $\beta$ . The value  $\epsilon S \approx 5 \times 10^{-19} s^{-1}$  is taken for the combined  $^{14}C$  and  $^{40}K$  beta sources in the prebiotic ocean (16). The value of the racemization constant  $\beta$  depends on the temperature and can be calculated for a number of amino acids by the Arrhenius parameters given by Williams and Smith (17). Using the values for alanine at pH = 7, which are typical for the amino acids considered in Ref. (17), one obtains the results given in Table I.

It can be seen in Table I that the chiral polarizations are all very small, the largest value  $\eta_\infty = 2 \times 10^{-14}$  occurring for a temperature of  $-20^\circ C$ , just above the freezing point of the ocean (15). The relative contributions of the Vester-Ulbricht

TABLE I. RELATIVE CONTRIBUTIONS OF THE YAMAGATA-REIN AND VESTER-ULBRICHT MECHANISMS TO THE CHIRAL POLARIZATION AS A FUNCTION OF TEMPERATURE. <sup>a</sup>

Temp (°C)	$\beta^{-1}$ (yr)	$A_\beta$	$\eta_\beta$ (YR) <sup>b</sup>	$\eta_e$ (VU) <sup>b</sup>	$\eta_\infty$
-20	$2 \times 10^8$	$1 \times 10^{-17}$	$1 \times 10^{-17}$	$2 \times 10^{-14}$	$2 \times 10^{-14}$
0	$4 \times 10^6$	$1 \times 10^{-17}$	$1 \times 10^{-17}$	$3 \times 10^{-16}$	$3 \times 10^{-16}$
20	$9 \times 10^4$	$1 \times 10^{-17}$	$1 \times 10^{-17}$	$7 \times 10^{-18}$	$2 \times 10^{-17}$
100	2	$8 \times 10^{-18}$	$8 \times 10^{-18}$	$1 \times 10^{-22}$	$8 \times 10^{-18}$

<sup>a</sup>The racemization constants  $\beta$  are for alanine at pH 7. The signs of  $A_e$  and  $A_\beta$  are assumed to be positive (see also Refs. 12, 13).

<sup>b</sup>See eqn. (6).

mechanism and the Yamagata-Rein mechanism are determined by the magnitudes of the products of the rate constants times their corresponding asymmetries, ie  $\epsilon SA_e$  vs.  $2\beta A_\beta$ . For a cold ocean (-20°C to ca 20°C) the VU mechanism is seen to dominate, whereas at a temperature near 20°C the YR mechanism begins to dominate due to the increase in racemization rate constant  $\beta$  with temperature. For a hot ocean (100°C or higher), such as exists today near oceanic thermal vents (18), the YR mechanism dominates completely. For all temperatures considered,  $\beta$  is larger than the corresponding radiolysis rate constant  $\epsilon S = 5 \times 10^{-19} \text{ s}^{-1}$  and hence the asymptotic value  $\eta_\infty$  is reached effectively in a time equal to the racemization time constant  $\beta^{-1}$  which ranges from  $2 \times 10^8$  yr at -20°C to just 2 years at 100°C.

It is concluded that, for simple linear rate laws such as given by eq. (1), the Vester-Ulbricht mechanism can produce larger chiral polarizations than the Yamagata-Rein mechanism provided the temperature is sufficiently low. For the case of <sup>40</sup>K and <sup>14</sup>C beta ray sources in the prebiotic ocean, the value

of  $\eta_{\infty}$  increases with decreasing temperature and for alanine is of order  $\eta_{\infty} \sim 10^{-14}$  at  $-20^{\circ}\text{C}$  (below which the ocean freezes). At higher temperatures (above ca  $+20^{\circ}\text{C}$ ) the YR mechanism dominates but the chiral polarization is appreciably smaller in magnitude.

Finally, it is interesting to ask whether values of  $\eta_{\infty}$  larger than  $\sim 10^{-14}$  could have been produced in prebiotic times. In recent work R. Hegstrom, A. Rich, and J. Van House (19) have reviewed the evidence that intense beta-ray sources were present on the prebiotic earth. Sources which seem likely to have been present are (i) concentrated detrital  $^{235}\text{U}$  deposits with some local concentrations high enough to have produced  $^{235}\text{U}$  fission reactors, and (ii)  $^{26}\text{Al}$  ( $\beta^+$  emitter) accumulated from one or more supernovae. These beta sources are much more intense than the  $^{14}\text{C}$ ,  $^{40}\text{K}$ , etc. sources usually considered and as a consequence they can produce larger chiral polarizations approaching the limiting value  $A_{\infty} \sim 10^{-11}$  [Eq. (6)] in shorter times ranging from  $\sim 100$  years to several hundred million years, depending on the intensity. Chiral polarizations this large will exceed statistical fluctuations if the number of chiral molecules in the irradiated system exceeds  $\sim 10^{23}$  (e.g. 15 grams of alanine). Such a system seems likely to have been realized under conditions commonly believed necessary for the origin of life on the prebiotic earth. Coupled with a suitable amplification mechanism, the system could then have evolved into a chirally pure one of definite sign ( $\eta = \pm 1$ ). Mathematical models of such amplification mechanisms exist (20) (although, to our knowledge, no specific physical mechanism capable of accomplishing this has yet been proposed). Pending further study of amplification processes, one is led to the tentative conclusion that the Vester-Ulbricht hypothesis is viable notwithstanding the small magnitude of the chiral polarization produced by asymmetric radiolysis.

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