SPONTANEOUS BREAKING OF THE L, D SYMMETRY IN PHOTOLYTIC PRODUCTION AND DEGRADATION OF AMINO ACIDS

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(Received May 29, 1990)

Abstract. The radiolysis experiments of amino acids have revealed the presence of bimolecular interaction between like enantiomers which suppress their photodegradation and between opposite enantiomers that enhance the photodegradation. Based on a mathematical model, it is suggested that this phenomenon could have given rise to chiral stereoselection in biochemical evolution.

1. Introduction

The possibility that chiral stereoselection in biochemical evolution is a result of spontaneous breaking of the L, D symmetry in parallel chemical reactions, have received much attention (Frank, 1956; Decker, 1974; Kondepudi and Nelson, 1983; Tennakone, 1984). All models of this type proposed, assumes autocatalytic production of L, D enantiomers, e.g. (Kondepudi and Nelson, 1983).

$$A + B \longrightarrow X_L \qquad [1]$$

$$A + B \longrightarrow X_D \qquad [2]$$

$$A + B + X_L \longrightarrow 2X_L \qquad [3]$$

$$A + B + X_R \longrightarrow 2X_D. \qquad [4]$$

Followed by an inhibitary interaction between L and D species, e.g.,

$$X_L + X_D \longrightarrow C, \qquad [5]$$

where the concentrations of the reactants A, B and C are assumed to be maintained constant. The rate equations for [1] – [5] have an unstable symmetric solution and a stable asymmetric solution. In the presence of even a minute, but universal, right-left asymmetric influence, the selection occurs in the same sense with a high probability (Kondepudi and Nelson, 1983; Mason, 1984). Thus a global symmetry breaking becomes possible. The external chiral factor needed for biasing the symmetry breaking is believed to be weak neutral currents (Letokhov, 1975; Hegstrom, 1985) or polarized radiation from betadecaying radio active materials (Garay, 1968;

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Origins of Life and Evolution of the Biosphere **20**: 515–519, 1990–1991.

Bonner, 1974). Unfortunately the difficulty of the models of this type is that, the molecules likely to have occurred in the prebiotic medium, capable of participating in reactions of the required form are not identified. Self-replicating complex biomolecules will naturally fit into autocatalytic schemes with competitive interactions. However this necessitates simultaneous creation L and D enantiomers of complex biomolecules which is an highly improbable event.

Recently Akaboshi *et al.*, (1990) have observed that in γ-radiolysis of amino acid mixtures, the biomolecular intraction of like enantiomers (i.e. L, L or D, D) suppresses the rate of decomposition, whereas the interaction opposite species enhances each others decomposition rate. In other words, an asymmetric field is found to affect the photodecomposition rate of amino acids. Akaboshi *et al.* (1990) also have suggested that this mechanism could have operated in amplification of L, D asymmetry in biochemical evolution. In this paper we present a mathematical model which illustrate that the effect observed by Akaboshi *et al.* (1990) could have resulted in biochemical stereoselection via spontaneous breaking of the chiral symmetry biased by parity violating interactions.

As is well known uv irradiation of relevant inorganic materials in aqueous medium generate amino acids. Amino acids also undergo photodecomposition and since the rate of decomposition depends on their concentration X, we have,

$$\frac{dX}{dt} = C - kX, \tag{1}$$

where C is the rate of production and k is a constant. Thus,

$$X = C/k + Ae^{-kt} \qquad (\text{A} = \text{Constant}) \tag{2}$$

and an equilibrium concentration $X = C/k$ is reached in a theoretically infinite time. The condition (1) holds in absence of radiation induced bimolecular interactions between L and D enantiomers. The effect observed by Akaboshi *et al.* (1990), implies the presence of second order interactions of the form $X_L{}^2$ ($X_D{}^2$) and $X_L X_D$ of which the former suppresses and latter enhances decomposition rate of $X_L(X_D)$. In this situation, the rate equation for development of two species takes the form.

$$\frac{dX_L}{dt} = C - kX_L + aX_L{}^2 - bX_L X_D \tag{3}$$

$$\frac{dX_D}{dt} = C - kX_D + aX_D{}^2 - bX_D X_L, \tag{4}$$

where a and b are constants and provided $b > a$, Equations (3) and (4) have a symmetric solution.

$$X_L = X_D = X_0 = \frac{-k + [k^2 + 4C(a-b)]^{1/2}}{2(b-a)}. \tag{5}$$

To investigate the stability of the equilibrium (5), we put,

$$X_L = X_0 + \delta X_L \tag{6}$$

$$X_D = X_0 + \delta X_D$$

in (3) and (4), where δX_L, δX_D are the deviations of X_L,X_D from the equilibrium value X_0 and obtain the following linear approximation,

$$\frac{d(\gamma X_L)}{dt} = (2aX_0 - bX_0 - k)\,\delta X_L - bX_0\,\delta X_D \tag{7}$$

$$\frac{d(\gamma X_D)}{dt} = (2aX_0 - bX_0 - k)\delta\, X_D - bX_0\,\delta X_L\,. \tag{8}$$

Equations (7), (8) shows that the equilibrium (5) is unstable when,

$$C > k\,(a + b)\,/\,4a \tag{9}$$

and the solution (7) and (8) yield,

$$\left[\frac{\delta X_L - \delta X_D}{\delta X_L + \delta X_D}\right] = \left[\frac{\delta X_L - \delta X_D}{\delta X_L + \delta X_D}\right]_0 e^{ft}, \tag{10}$$

where

$$f = \frac{-bk + b[k^2 + 4C(b - a)]^{1/2}}{(b - a)}\,. \tag{11}$$

In the presence of an external parity violating influence such as weak neutral currents associated with difference in activation energies of the two enantiomers or polarized radiation from beta-decay (Mason, 1984), the rate constants in (3) and (4) will not be identical and generate a non-zero value for the asymmetry parameter $[(\gamma X_L - \delta X_D)/(\delta X_L + \delta X_L)]_0$ near the point of breaking of the unstable equilibrium. As $f > 0$, the Equation (10) shows that the asymmetry is rapidly amplified (Figure 1). Here the mechanism is identical to previous models that invoke spontaneous symmetry breaking to achieve L, D stereoselection (Frank, 1956; Decker, 1974; Kondepudi and Nelson, 1983; Tennakone 1989). The model can be extended to include the photolytic production and mutual interaction of different kinds of amino acids ($X_L{}^i{}_{(R)}$), here the reate equations take the form,

$$\frac{dX_L{}^i{}_{(R)}}{dt} = \Sigma_i C^j - \sum_i k^i X_L{}^i{}_{(D)} - \Sigma_i a^i X^i{}_{L(D)} X^j{}_{L(D)} - \Sigma_{ji} b_i X^i{}_{L(D)} X^j{}_{D(L)}\,, \tag{12}$$

The stable solutions of the family of Equations ($i = 1$ .....n) (12) in general does not preserve L, D symmetry,

The above model suggests that chiral selection could have occurred at the amino acid level. It may be possible to test this hypothesis experimentally. Amino acid photolysis that simulate [3] and [4] by continuous influx of L and D amino acids

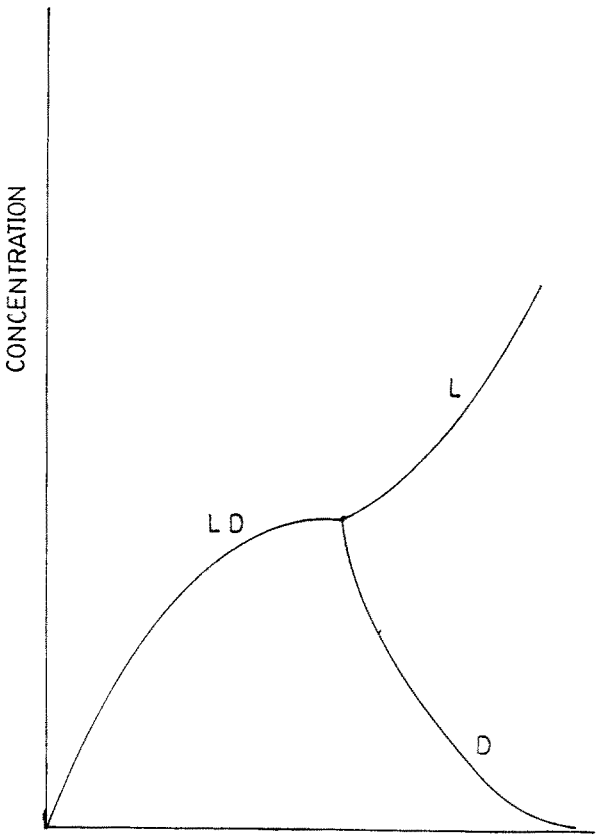

Fig. 1. Schematic diagram illustrating spontaneous breaking of the L, D symmetry of the solution of (3) and (4) in the presence of a slight bias towards L.

at identical rates into a photochemical reactor could be an important experiment. The characteristic time at which the selection would occur is f^{-1} [f is given by equation (11)] and estimation of this quantity requires the values of the rate constants a, b, and k. According to Akaboshi *et al.* (1990), during photolysis of L, D-aspartic acid, L, D – alanine mixtures (initial concentrations 0.5 mM in each case and 2.4 $\times$ 10^4 Gy hr^{-1} Co^{60} γ- source) a L, D selectivity of the order 1% has been achieved when 63% of the material has got photodegraded. Although this is highly significant, data is not sufficient to estimate f^{-1}. Further experiments on γ-radiolysis of amino acid mixtures at varying concentrations could yield information necessary to plan an experiment to test our hypothesis.

Acknowledgment

Author wish to thank Professor Cyril Ponnamperuma, Director Institute of Fundamental Studies for valuable discussions and encouragement.

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