The Kinetics of the Growth of an Accidentally Created Chiral Biomolecule in the Racemic Prebiotic Medium

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ABSTRACT

A mathematical model is presented to show that a chiral (e.g. L) isomer of a self-replicating biomolecule, created accidentally in the prebiotic medium, could grow rapidly, consuming nearly all L and D forms of nutrients in the medium. A high chiral selectivity is reached in a time comparable to the racemization time of the nutrient species, whose L and D enantiomers were present in equal concentrations at the beginning.

INTRODUCTION

Although a number of plausible schemes have been proposed [1–5], the question of the origin of biochemical right-left asymmetry or chirality remains unsettled [6]. Some of the suggested mechanisms of asymmetry generation are:

(1) Even before the evolution of primary forms of life, an asymmetry was present in the prebiotic medium [1–2]. This implies that the synthesis of organic compounds was stereoselective.

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(2) The chirality began as a result of the spontaneous breaking of the symmetry between L and D enantiomers in parallel autocatalytic reactions biased by universal but minute asymmetric interactions, i.e. beta decaying radioactive materials or weak neutral currents [7–17].

(3) The first forms of life, up to the cellular level or perhaps beyond, were racemic, and the chirality arose from a slight competitive advantage of asymmetric over symmetric ones [6].

(4) The original common progenitor of all life was created accidentally with one handedness [2, 6].

Each of the above ideas has its merits and demerits.

The simplest assumption (1) leads to severe difficulties. As asymmetry can be begotten only from asymmetry, an external chiral influence is necessary for stereoselective synthesis. However, such external influences are small, and because of racemization, the buildup of enantiomers of one handedness is negligible [18].

Scheme (2) is undoubtedly an attractive possibility. When the concentrations of two L and D species capable of autocatalytic reproduction reaches a critical value, an instability sets in and the reaction develops into one of the asymmetric directions. In the presence of even a minute external bias, the probability of symmetry breaking in one sense at different points of the medium becomes greater than 50%. The difficulty here is that the prebiotic compounds which could lead to the envisaged autocatalytic steps have not been identified [6]. Again, spontaneous symmetry breaking could happen at the self-replicating level. However, the simultaneous creation of two complex L and D structures is a highly improbable event.

The formation of complex racemic molecules is more likely than that of chiral enantiomers, but the weak point of option (3) is that the racemic biopolymers are less stable and acts as poorer catalysts.

The chief objection to possibility (4) is that the creation of complex molecules entirely from a selected type of enantiomers is highly improbable, although not as improbable as the production of two complex L and D enantiomeric structures. However, the need for vast expanses of reacting medium and astronomical durations of time suggests that chiral selection and the creation of the first forms of life are indeed improbable events. And chiral selection could be a requirement essential for life, perhaps arising from the necessity of stability, catalytic activity, and information storage. The possibility that the common ancestor of all life was accidentally created as a chiral entity needs serious examination.

Here we present a mathematical model to illustrate that the accidental creation of a self-replicating chiral entity in a racemic background results in its proliferation with removal of nearly all L and D forms of the nutrients in

the medium. Thus a high degree of stereoselectivity is achieved in a short time.

MATHEMATICAL MODEL

We assume that the first self-replicating biomolecule X_L was created in the racemic prebiotic medium as a singular event, involving the interaction of n molecules of the L isomer x_L of some nutrients, i.e.

$$\underset{1}{x_L} + \underset{2}{x_L} + \cdots + \underset{n}{x_L} \rightarrow X_L. \tag{1}$$

Since (1) itself is highly improbable, for the parallel reaction

$$\underset{1}{x_D} + \underset{2}{x_D} + \cdots + \underset{n}{x_D} \rightarrow X_D \tag{2}$$

to occur at the same time is almost impossible. The molecule X_L is also supposed to self-replicate via

$$\underset{1}{x_L} + \underset{2}{x_L} + \cdots + \underset{n}{x_L} + X_L \xrightarrow{a} X_L + X_L. \tag{3}$$

The probability of the catalytic reaction (3) is enormous compared to (1). It is natural to expect that X_L will undergo autolysis to its components, i.e.,

$$X_L \xrightarrow{k} \underset{1}{x_L} + \underset{2}{x_L} + \cdots + \underset{n}{x_L}. \tag{4}$$

In addition there is also interconversion between the isomers of x as a result of racemization, i.e.,

$$X_L \overset{c}{\rightleftharpoons} X_D. \tag{5}$$

X_L's could also undergo partial racemization (the complete racemization of a structure consisting of a number of enantiomeric units is unlikely). However, if the autolysis rate is faster, the effects of partial racemization of X_L on kinetics is negligible.

For the purpose of the model we assume that there is mixing around the point where the reaction (1) has occurred. Equations (2)–(5) leads to

following rate equations:

$$\frac{dX_L}{dt} = ax_L^n X_L - kX_L, \tag{6}$$

$$\frac{dx_L}{dt} = -ax_L^n X_L + cx_D - cx_L + kX_L, \tag{7}$$

$$\frac{dx_D}{dt} = cx_L - cx_D, \tag{8}$$

where the same symbols have been used to denote the concentrations. Equations (6)–(8) satisfy the constraint

$$X_L + x_L + x_D = C \qquad \text{(constant)}, \tag{9}$$

as n molecules of x_L are incorporated into one molecule of X_L. The condition (9) implies mass conservation, i.e., the concentration of the reacting medium in units of x ($x = x_L$ or x_D) remains constant.

Analytical solution of (6)–(8) is impossible. However, the nature of the solution can be understood by examination of the two equilibrium points,

$$X_L = 0, \qquad x_L = x_D = x_0 \,(= C/2), \tag{10}$$

$$X_L = 2x_0 - 2\frac{k}{a}, \qquad x_L = x_D = \frac{k}{a}. \tag{11}$$

The singular event (1) introduces a small inoculum concentration X_L^0 of X_L at time $t = 0$. To examine the subsequent behavior near the point (10) we put

$$\begin{aligned} X_L &= X_L^0 + \delta X_L, \\ X_L &= \frac{k}{a} + \delta x_L, \\ x_D &= \frac{k}{a} + \delta x_D \end{aligned} \tag{12}$$

in (6)–(8), where δX_L, δx_L, δx_D are the deviations of X_L, x_L, and x_D from

the value at time $t = 0$. Solving the resulting equations in the linear approximation, we obtain

$$\delta X_L = X_L^0(e^{gt} - 1), \tag{13}$$

$$\delta x_L = -X_L^0(g + c)(g + 2c)^{-1}(e^{gt} - 1) + X_L^0(2g + 4c)^{-1}(e^{-2ct} - 1), \tag{14}$$

$$\delta x_D = -X_L^0(g + 2c)^{-1}(e^{gt} - 1) - X_L^0 g(2g + 4c)^{-1}(e^{-2ct} - 1). \tag{15}$$

The equilibrium (10) is unstable with X_L increasing and x_L, x_D decreasing provided

$$g > 2c, \qquad \text{or equivalently} \quad x_0 > \left(\frac{k}{a}\right)^{1/n}\left(1 + \frac{2c}{k}\right)^{1/n}. \tag{16}$$

Furthermore, it is easy to see from (14) and (15) that the rate of decrease of x_L is faster than that of x_D. By linearization about the second equilibrium point (11) it is possible to show that when (16) is satisfied, the point (11) is stable. Figure 1 illustrates the time variation of X_L, x_L, and x_D. The model shows that when the initial concentration x_0 of x_L and x_D exceeds the

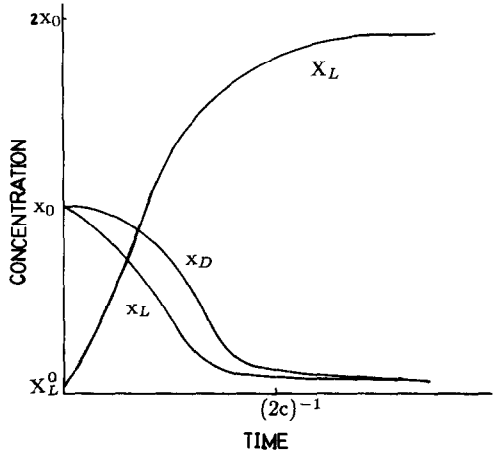

FIG. 1. The time variation of the concentration of the self-replicating molecule X_L and nutrient species x_L and x_D.

critical value given by (16), the self-replicating X_L grows rapidly, converting nearly all x_L and x_D into X_L (if $x_0 \gg k/a$, $X_L \sim 2x_0$). As g^{-1} is the replication time of X_L and $(2c)^{-1}$ is the racemization time of x, the condition (16) indicates that X_L grows only if the replication time is greater than the racemization time. This condition could be easily satisfied, as the racemization time of amino acids in the prebiotic medium is expected to be of the order 10^3 yr [18]. The removal of x_L via the reaction (3) shifts the equilibrium (5) towards the left, converting x_D to x_L, which is consumed to generate X_L. Thus high selectivity (conversion of x_L and x_D to X_L) is achieved in a time interval comparable to the racemization time measured from the time of creation of X_L.

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