Biochemical Chiral Selection in the Presence of Instabilities, Chaos, and Noise

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ABSTRACT

A mathematical model is constructed to illustrate that an arbitrarily small difference in the rate constants for parallel autocatalytic reactions involving L and D isomers is sufficient to cause chiral selection in biochemical evolution. It is shown that the selection is not suppressed by instabilities leading to chaos or heavy external noise.

Models of dynamical systems exhibiting competitive selection have attracted much attention in the context of ecology, evolution, cellular differentiation, and autocatalytic chemical reactions [1–6]. An especially important problem is the competitive interaction between two species in the presence of heavy external noise, when one species has a slight advantage over the other. One of the most interesting puzzles falling into this category is biochemical chiral selection [6–11]. As a result of weak neutral currents [10–11] or the presence of β-radiation from radioactive sources [9–11], the rates of parallel chemical reactions involving L and D isomers could differ by a small amount. If a dynamical system spontaneously breaks the symmetry under the parity operator, i.e., $P(\mathrm{D}, \mathrm{L}) = (\mathrm{L}, \mathrm{D})$, then constant chiral perturbations are expected to cause stereoselection.

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Investigations by Kondepudi and Nelson [6] have shown that selection could result even in the presence of thermal fluctuations in the rate constants. Also, according to their model, for the selection to occur the noise level should not exceed a certain critical limit. The Kondepudi-Nelson [6] model is based on two coupled differential equations governing the time evolution of the concentrations of the L and D isomers. Obviously the actual reaction schemes leading to biochemical chiral selection is much more complicated. Dynamical systems in general exhibit complex behavior giving rise to instabilities and chaos greater than those manifested in models based on two coupled differential equations [12]. In this note we present a model to illustrate the effect of instabilities and chaos on chiral selection in the presence of heavy external noise and conclude that arbitrarily small chiral perturbations could lead to complete stereoselection.

The model is based on two coupled difference equations,

$$\begin{aligned} D_{t+1} &= D_t \exp[r_D(1-L_t)], \\ L_{t+1} &= L_t \exp[r_L(1-D_t)], \end{aligned} \tag{1}$$

where D_t, L_t are the concentrations of D, L isomers at time t, and the rate parameters r_D, r_L are such that $r_L - r_D = \Delta r$, $\Delta r \ll r_L$ ($\Delta r > 0$). When $r_L = r_D = r$, the solution of (1) with the initial condition $D_0 = L_0$ is equivalent to the solution of

$$X_{t+1} = X_t \exp[r(1-X_t)], \tag{2}$$

which is extensively studied as an alternative to the logistic map [13–15].

Solutions of (2) are stable (stable point $X_t = 1$) asymptotically if $0 < r < 1$, and show oscillations about the equilibrium position if $1 < r < 2$. The chaotic region begins (i.e., the point of accumulation of cycles of period 2^n occurs) at $r = 2.6924$, and cycles with period 3 appear at $r = 3.1024$ [14–15]. When $\Delta r \ll r_L$, the initial behavior of the solutions of (1) is almost identical to that of (2), but they have the property $L \to \infty$, $D \to 0$ as $t \to \infty$. The results of a computer experiment with (1) when $\Delta r / r = 10^{-15}$ (the estimate of $\Delta r / r$ for weak neutral current efforts is $\sim 10^{-17}$, and of that originating from β-radiation in the environment is $\sim 10^{-12}$ [9–10]) is presented in Figure 1. If $r < 2$, L and D both increase with t, keeping the difference $L - D$ positive but insignificantly small, until $L \simeq D \simeq 1$, when L begins to increase while D decreases, approaching zero. The number of interactions needed for D to reach the limit of accuracy of the computer (10^{-79}) decreases with the increase of r. When $r > 2$, the trajectories for L and D rapidly diverge from

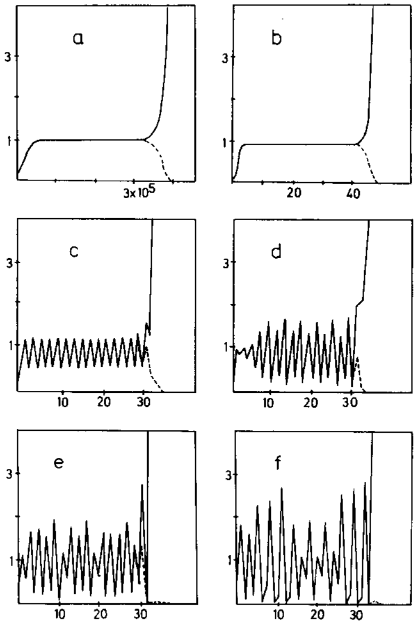

FIG. 1. Plots of time variation of L (full line) and D (dotted line) versus the iteration number (horizontal axis) when $\Delta r = 10^{-15}$ and the initial values are $D_1 = 0.1$, $L_1 = 0.1$: (a) $r = 10^{-4}$, (b) $r = 10^{-1}$, (c) $r = 2.1$, (d) $r = 2.6$, (e) $r = 2.8$, (f) $r = 3.3$. (Initially the two curves are very close to each other and only the full line is indicated.)

each other (i.e., $L \to \infty$, $D \to 0$) with oscillations or chaotic behavior. Figure 2 gives a plot of the number of iterations required for D to reach a value $\sim 10^{-79}$, as a function of r when $\Delta r = 10^{-15}$. It is important to note that in the chaotic region, the curve is noisy but the chaos does not suppress the selection arising from a minute difference in the rate parameters. The phase diagrams for different values of r are presented in Figure 3.

It is interesting to examine the manner in which the selection is affected by external noise. Thermal fluctuations can cause random changes in the rate parameters r_D and r_L many orders of magnitude larger than Δr. To study the effect of such noise we carried out a computer experiment with (1) setting

$$r_X = r + \xi_X(\sigma),$$

$$r_Y = r + \Delta r + \xi_Y(\sigma),$$

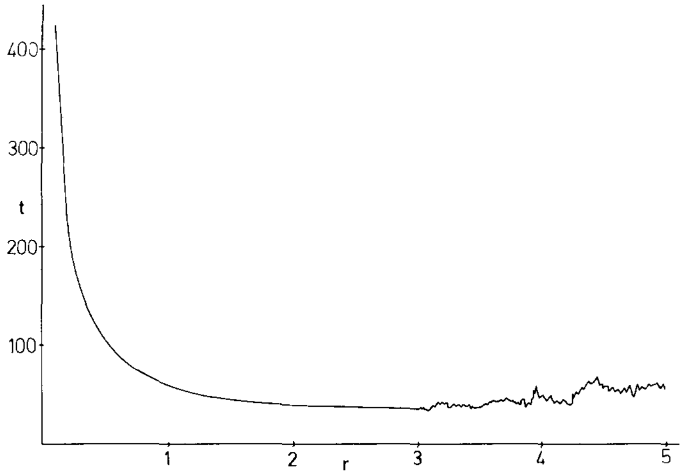

FIG. 2. A plot of t (number of iterations needed to reduce D to a value less than 10^{-79}) versus r when $\Delta r = 10^{-3}$.

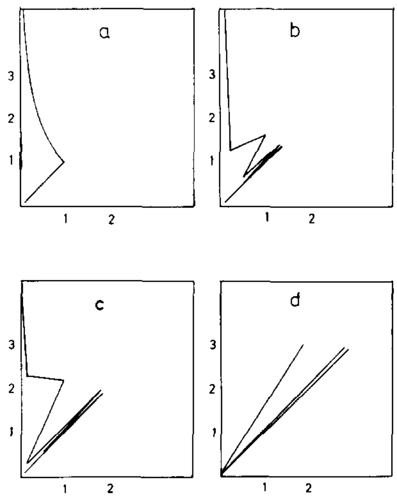

FIG. 3. Phase diagrams, i.e., computer graphics of the plots of L (vertical axis) versus D (horizontal axis) for different values of r when $\Delta r = 10^{-15}$. The initial values are $D_1 = L_1 = 0.1$, and iterations are carried out until $D \sim 10^{-79}$. (a) $r = 0.1$, (b) $r = 2.1$, (c) $r = 2.6$, (d) $r = 3.3$.

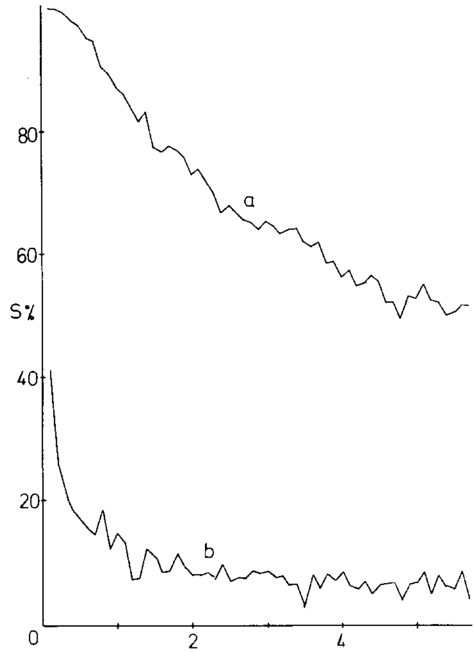

FIG. 4. Variation of the selection parameter S (%) with r. (a) $\Delta r = 10^{-3}$, $\sigma = 10^{-3}$ (b) $\Delta r = 10^{-4}$, $\sigma = 10^{-3}$.

where $\xi_Y(\sigma)$ and $\xi_Y(\sigma)$ are two uncorrelated Gaussian white noises of zero mean 0 and variance σ^2 ($\sigma \geqslant \Delta r$). The result was that in each run either L or D wins, but when the probabilities are worked out, there is a distinct bias towards L. We define the selection probability as

$$S = \left[\frac{N_L - N_D}{N_L + N_D}\right]_{(N_L + N_D) \to \infty}, \tag{4}$$

where N_L (N_D) is the number of instances where L (D) has won the competition. The selection probability depends on r, Δr, and σ, and Figure 4 shows its variation with r. S increases with the decrease of r, and for given r decreases when σ increases. The asymptotically stable region (i.e., $r < 1$) is least sensitive to external noise. Again S remains positive and nonzero for all values of r, including those in the chaotic region. The values of S for different values of r, Δr, and σ are given in Table 1.

TABLE 1

SELECTION PARAMETER S FOR VARIOUS VALUES OF r, Δr, AND σ

r	Δr	σ	n[a]	S (%)
10^{-3}	10^{-15}	10^{-5}	10^{5}	21.4
10^{-1}	10^{-15}	10^{-5}	10^{5}	2.5
10^{-1}	10^{-9}	10^{-3}	10^{5}	4.2
2.2	10^{-15}	10^{5}	10^{6}	0.03
3.3	10^{-15}	10^{-5}	10^{6}	0.01

[a]Number of runs carried out to determine S.

The above model takes into account only the temporal variation of the concentrations of the two species. As $S < 1$, an element of volume of the reacting medium at any instant of time will include points where D has won the competition, in addition to points where L has won, which are in excess. The equations (1) are highly sensitive to small differences in the initial values of L and D (i.e., if $L_0 - D_0 = \delta > 0$, L wins the competition even if $r_L = r_D$). The selection is strongly biased towards L in subsequent iterations. Thus an arbitrarily small difference between r_L and r_D can eventually lead to complete stereoselection even in the presence of heavy external noise. We have also noted that selection biased by Δr or δ persists when noise terms are added to D and L.

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