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A Photochemical Mechanism for Homochirogenesis

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Theoretical analysis of one-step and multiple-step photoreactions initiated with circularly polarized light shows that the enantiomeric excess of a chiral reactant approaches ± 1 as the amount of unreacted reactant approaches 0. The final product never has a large enantiomeric excess at any stage of its formation and slowly decreases to 0 at the completion of the reaction. For multiple-step reactions the behavior of the intermediate photoproducts is much more interesting. During certain stages of the overall reaction both the size of the enantiomer excess and the amount of a given intermediate photoproduct are large. Furthermore, the sign of the enantiomeric excess of an intermediate may change during the course of the reaction. Multiple-step photoreactions initiated with circularly polarized light may be a method by which the exogenous and endogenous synthesis of optically active molecules occurred in the prebiotic universe.

Introduction

One of the significant unanswered questions in all of science is the origin of optically active molecules in living systems.[1] Because what became biological molecules such as carbohydrates and amino acids were synthesized in the prebiotic world from achiral and racemic substances, they themselves should be racemic unless some type of chiral influence was associated with their formation or destruction. Myriad theories have been proposed to explain what is now called homochirogenesis.[2−10] Most of these theories might operate under ideal or special circumstances, but they usually have flaws that make their implementation unlikely. Some of these theories can be tested in the laboratory, but others cannot be tested because, for example, the time scale of an experiment is much too long or the enantiomeric enrichment of a reaction product is much too small to measure. These issues are exacerbated by the fact that it is not possible to go back to the prebiotic world and see homochirogenesis occur.

The new theory we propose below has features of two other theories that have been described in the literature: the Yamagata hypothesis,[11] and photochemical reactions initiated with circularly polarized light (CPL). A modern version of the Yamagata hypothesis, which takes into account the parity violating energy difference (PVED) of enantiomers and was not known when Yamagata's paper was published in 1966, involves two features: (1) stabilization of D sugars as compared to L sugars due to PVED associated with the weak force of atomic nuclei, and (2) the polymerization of a racemic mixture of a nucleotide such as uridylic acid. In the usual formulation of the hypothesis the D nucleotide condenses with the D nucleotide and L with L. At each stage of the condensation, e.g., monomer to dimer, the rate of L reacting with L is slightly different than D with D because of the previously mentioned PVED between the L sugar and the D sugar. Even though the kinetic effect would be very, very small for each condensation, the effect would be cumulative. Because the polymer with a thousand or more nucleotides will have experienced the kinetic PVED a thousand or more times, there will be slightly more, and perhaps even measurable, amounts of one of the homonucleic acid. Nonetheless, a recent publication has shown in detail that the Yamagata effect is not a likely source of homochirogenesis when amino acids are polymerized in place of Yamagata's nucleotides.[12]

Because there are numerous sources of CPL in the universe, it has been suggested that photochemistry initiated with CPL is the source of homochirogenesis.[2−10,13−22] As will be described below, this is a plausible but not likely scenario for reactions of the type A → B (or A ⇌ B). The reason for this is that the enantiomeric excesses (ee's) generated in A or B are dominated by the asymmetric g factor, which is $(\epsilon_R - \epsilon_S)/\epsilon$, where the numerator is the difference in extinction coefficients for an enantiomer absorbing left-handed and right-handed CPL (determined by circular dichroism) and the denominator ($2\epsilon = \epsilon_R + \epsilon_S$) is the normal extinction coefficient as determined by UV/vis spectroscopy. Although g can range in value from +2 to −2, especially at the single molecule or monolayer level,[23] it is normally quite small in bulk, with values close to zero.

What would occur if one had a series of photochemical reactions of the type A → B → C → etc. initiated with CPL? Would there be enhancement in the ee of a photoproduct after each photoreaction? This is the photochemical equivalent of the Yamagata hypothesis. This idea was first suggested by Henri Kagan but never investigated by him.[24] This paper investigates the consequences of this suggestion.

Results and Discussion

Let us begin by considering the simplest photoreaction A → B. Here A is a racemic mixture of R and S enantiomers, A_R and A_S. At $t = 0$, $A_R + A_S = A_0$ and $A_R = A_S$. If the absorbance of the solution of A is low, the decay of A_R and A_S and the buildup of the enantiomers of B, B_R, and B_S obey first-order kinetics.[25−28] The rate constants for the disappearance of A_R and A_S are identical except for the differences in extinction coefficients ϵ_R and ϵ_S, respectively. Thus, $dA_R/dt = -\epsilon_R k A_R$ and $dA_S/dt = -\epsilon_S k A_S$, where k contains other factors such as path length, light intensity, and quantum yield of the reaction φ ($\phi_{A_R} = \phi_{A_S}$). Kagan has shown that the ee of A ($ee^{(A)}$) goes up (to ±1) as a function of time while the amount of A goes down. How rapidly ee builds up depends on the magnitude of g. How the amount of unreacted A, $ee^{(A)}$, and g are related is shown in eq 1. When ϵ_R is greater than ϵ_S, g is positive; when

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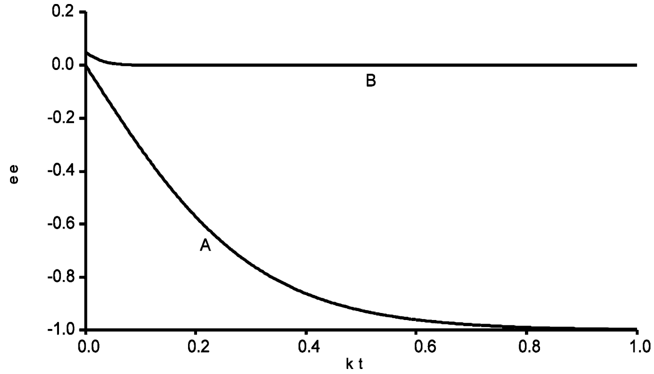

Figure 1. ee of species in a one-step reaction, versus the time function *kt*.

ϵ_R is less than ϵ_S, g is negative. When ϵ_R is greater than ϵ_S, $ee^{(A)}$ is negative because A_R disappears more rapidly than A_S. As mentioned by Kagan in passing, $ee^{(B)} = g/2$ at $t = 0$, which then decays to zero over time.[24] The behavior of a ketone with $g = 0.10$ ($\epsilon_R = 68.25$, $\epsilon_S = 61.75$, the values for 3-methylcyclopentanone at 296 nm[29]) is shown in Figure 1. Because g is usually small, the ee of B is never very large. Nonetheless, if one neglects the signs of $ee^{(A)}$ and $ee^{(B)}$, there is a period of time in which $ee^{(B)}$ is greater than $ee^{(A)}$. $ee^{(A)}$ in fact is numerically equal to $ee^{(B)}$ when half the reaction is over, i.e., $A_R + A_S = A_0/2$. When the reaction is complete, there is no more A and B is completely racemic. In total then, the one-step reaction A → B is an unlikely source of homochirogenesis unless g is very large. Note that in all the subsequent schemes the behavior of the starting material A is identical to what has just been described.

$$\frac{A_R + A_S}{A_0} = \left(\frac{1 + ee^{(A)}}{1 - ee^{(A)}}\right)^{(2+g)/2g}\left(\frac{1}{1 + ee^{(A)}}\right) \qquad (1)$$

Next consider the scheme A → B → C where reactant and photoproducts are chiral. To simplify the mathematics, we will make two assumptions. First, the chirooptical properties of A and B are identical (eq 2). This is not an unreasonable approximation for the symmetry forbidden $n \rightarrow \pi^*$ transitions of carbonyl compounds that include carbohydrates and amino acids. Second, the quantum yields for the two reactions are both equal to 1, which simplifies the mathematics ($k_A = \epsilon(A)\varphi_A k = \epsilon(A)k$). If φ_A is not equal to φ_B, and both are less than 1, the net effect is to reduce the apparent value to the extinction coefficient and thus the effect of the overall reaction ($k_A = \epsilon(A)\varphi_A k = \epsilon(A)'k$, where $\epsilon(A)' \leq \epsilon(A)$). Many conclusions will be derived from these assumptions that will carry over to the more general case to be described later. The behavior of $ee^{(A)}$ in this two-step reaction is identical to that in the one-step reaction described earlier. $ee^{(B)}$ is given in eq 3. At $t = 0$, $ee^{(B)} = g/2$. As time progresses, $ee^{(B)}$ passes through 0 and ultimately reaches -1 at $t = \infty$. The enantiomeric excess of C, the final product, is given in eq 4. At $t = 0$, $ee^{(C)} = 4g/(4 + g)$, and at $t = \infty$, $ee^{(C)} = 0$. ee versus time for A, B, and C using ϵ_R and ϵ_S for 3-methylcyclopentanone is shown in Figure 2. The ee of the three components will be nonzero throughout most of the reaction, but at its completion A and B will be gone and the ee of C will be zero.

$$\begin{gathered} A_R \xrightarrow{\epsilon_R} B_R \xrightarrow{\epsilon_R} C_R \\ A_S \xrightarrow{\epsilon_S} B_S \xrightarrow{\epsilon_S} C_S \end{gathered} \qquad (2)$$

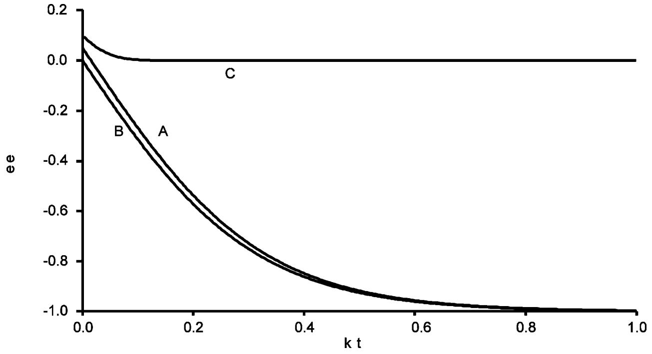

Figure 2. ee of species in a two-step reaction, versus the time function *kt*.

$$ee^{(B)} = \frac{\epsilon_R \exp(-\epsilon_R kt) - \epsilon_S \exp(-\epsilon_S kt)}{\epsilon_R \exp(-\epsilon_R kt) + \epsilon_S \exp(-\epsilon_S kt)} \qquad (3)$$

$$ee^{(C)} = \frac{-\left(e^{-\epsilon_R kt} - e^{-\epsilon_S kt}\right) - \left(\epsilon_R kt e^{-\epsilon_R kt} - \epsilon_S kt e^{-\epsilon_S kt}\right)}{2 - \left(e^{-\epsilon_R kt} + e^{-\epsilon_S kt}\right) - \left(\epsilon_R kt e^{-\epsilon_R kt} + \epsilon_S kt e^{-\epsilon_S kt}\right)} \qquad (4)$$

Is there any amplification of ee in this simplified two-step photoreaction? The answer depends on which stage of the reaction one is considering. For C, the final product, the absolute value of its ee is initially greater than that of A, but it is quickly overtaken by A's. Unfortunately for A, its ee goes up while the total amount of A goes down. For B, its ee is initially positive but $ee^{(A)}$ is never positive as long as ϵ_R is greater than ϵ_S. $ee^{(B)}$ then decreases through zero and becomes negative, as does $ee^{(A)}$. The best way to see if $ee^{(B)}$ has been amplified as compared to $ee^{(A)}$ is to compare the ee of each at the same extent of reaction. This is best accomplished by plotting $(A_R + A_S)/A_0$ and $(B_R + B_S)/A_0$ versus its respective ee. Equation 1 is used for the A versus ee plot and eq 5 for the B versus ee plot. The comparison is shown in Figure 3, again using the extinction coefficients for 3-methylcyclopentanone. Note that in Figure 3 ee on the *x*-axis becomes more negative on going from left to right. Clearly $ee^{(A)}$ becomes more negative as $(A_R + A_S)/A_0$ goes down, as expected. $ee^{(B)}$, on the other hand, is initially positive. As the amount of B increases, $ee^{(B)}$ decreases, reaching $ee^{(B)} = 0$ at B_{max}. Significantly, $ee^{(B)}$ eventually surpasses $ee^{(A)}$. The crossing point occurs at $ee = -0.0859$ and $(A_R + A_S)/A_0 = (B_R + B_S)/A_0 = 0.179$. Thus, $ee^{(B)}$ has been amplified compared to that of A at certain stages of the reaction.

$$\frac{B_R + B_S}{A_0} = -\left(\frac{2 + g}{2g}\right)\left(\ln\left[\frac{1 + ee^{(B)}}{1 - ee^{(B)}} \times \frac{2 - g}{2 + g}\right]\right)\left(\frac{1 + ee^{(B)}}{1 - ee^{(B)}} \times \frac{2 - g}{2 + g}\right)^{(2+g)/2g}\left(\frac{1}{1 + ee^{(B)}}\right) \qquad (5)$$

The ee of B is amplified in eq 2 because the g value in each of the two reactions has the same sign, i.e., $g^{(A)} = g^{(B)}$. What would occur if the g values had the opposite signs? To assess this issue in the simplified case, consider the case where $g^{(A)} = -g^{(B)}$, as shown in eq 6. The behavior for A is again identical to that described above. Surprisingly, $ee^{(B)}$ is constant at $g/2$ at all times. For 3-methylcyclopentanone with $g = 0.10$, for example, $ee^{(B)} = 5\%$ throughout, even when $B_R + B_S$ reaches its maximum value. For 3-methylcyclopentanone, $ee^{(B)}$ is numerically larger than the absolute value of $ee^{(A)}$ until 36.8% of A has been consumed. Interestingly, $ee^{(C)} = 0$ at all times. Clearly going from a g value with one sign to that of the opposite

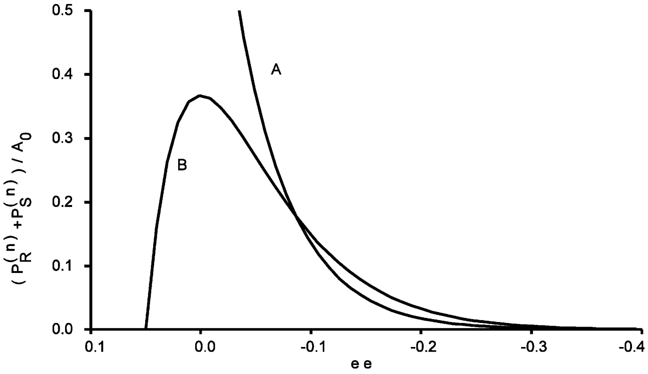

Figure 3. Fraction of reaction in a one-step reaction as a function of ee. The time evolution of each line is along the line, from left to right.

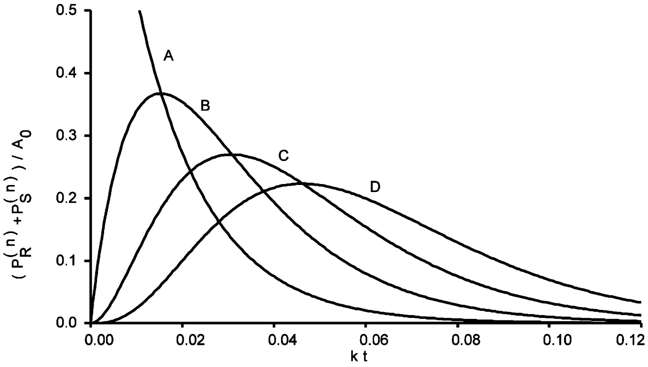

Figure 4. Fraction of each species in a three-step reaction, versus the time function *kt*.

sign has interesting consequences on the ee's of the species involved. The more general case in which the *g*'s are not numerically equal will be described later.

$$A_R \xrightarrow{\epsilon_R} B_R \xrightarrow{\epsilon_S} C_R$$

$$A_S \xrightarrow{\epsilon_S} B_S \xrightarrow{\epsilon_R} C_S \tag{6}$$

Let us now expand the two-step reaction in eq 2 into the general case: A → B → C → D → ..., with each step having the same *g* value and quantum yields. In this case we will call the first product with *R* absolute configuration $P_R^{(1)}$, the second $P_R^{(2)}$, the *n*th $P_R^{(n)}$, and the last $P_R^{(n+1)}$. The products with *S* absolute configuration will be labeled P_S. A plot of $(P_R^{(n)} + P_S^{(n)})/A_0$ versus *kt* for the first four products is shown in Figure 4 and has the well-known characteristics of a sequential series of reactions. $ee^{(n)}$ versus time is given in general by eq 7. At $t = 0$, $ee^{(n)}$ is given by eq 8. As *n* increases, the initial $ee^{(n)}$ also increases. At $t = \infty$, $ee^{(n)} = -1$ for all values of *n*. Thus $ee^{(n)}$ is initially positive, decreases through zero and ultimately reaches -1. The relationship between the amount of P, $(P_R^{(n)} + P_S^{(n)})/A_0$, $ee^{(n)}$, and *g* is given in eq 9. The behavior of the last product, $P_R^{(n+1)}$, as a function of time is given by eq 10; there is a similar equation for $P_S^{(n+1)}$. From $P_R^{(n+1)}$ and $P_S^{(n+1)}$, $ee^{(n+1)}$ as a function of time follows. The initial value of $ee^{(n+1)}$ goes up as the value of $n + 1$ increases but ultimately reaches a limiting value of 0. Thus, at the completion of the reaction all P's except the last one have been consumed and the final product is racemic.

$$ee^{(n)} = \frac{\epsilon_R^n e^{-\epsilon_R kt} - \epsilon_S^n e^{-\epsilon_S kt}}{\epsilon_R^n e^{-\epsilon_R kt} + \epsilon_S^n e^{-\epsilon_S kt}} \tag{7}$$

$$ee^{(n)}(t{=}0) = \frac{\left(\dfrac{2+g}{2-g}\right)^n - 1}{\left(\dfrac{2+g}{2-g}\right)^n + 1} \tag{8}$$

$$\frac{P_R^{(n)} + P_S^{(n)}}{A_0} = \left[\frac{1}{n!}\right]\left[-\frac{2+g}{2g}\right]^n\left[\ln\left\{\left(\frac{2-g}{2+g}\right)^n \times \frac{1+ee^{(n)}}{1-ee^{(n)}}\right\}\right]^n\left[\left(\frac{2-g}{2+g}\right)^n \times \frac{1+ee^{(n)}}{1-ee^{(n)}}\right]^{(2+g)/2g}\left[\frac{1}{1+ee^{(n)}}\right] \tag{9}$$

$$\frac{P_R^{(n+1)}}{A_0} = \frac{1}{2}\left[1 - e^{-\epsilon_R kt}\sum_{r=0}^{n}\frac{(\epsilon_R kt)^r}{r!}\right] \tag{10}$$

Is $ee^{(n)}$ amplified as the value of *n* goes up? The answer depends on which stage of the reaction is being considered. Consider Figure 5, an extension of Figure 3, which has now been extended to include two addition products, C ($=P^{(2)}$) and D ($=P^{(3)}$), neither of which is the final product of the sequence. When the ee's are positive, which can occur at short reaction times, there are regions in Figure 5 where $ee^{(D)} \geq ee^{(C)} \geq ee^{(B)}$ for a considerable part of product evolution. At longer reaction times, where the ee's are all negative, the $ee^{(B)}$, $ee^{(C)}$, and $ee^{(D)}$ curves all cross the $ee^{(A)}$ curve and the corresponding ee's are thus amplified. Even more, each ee is amplified compared to the previous one. This is best seen in the data of Table 1. For ee's more negative than -0.10, the amount of each product at a given ee is in the order D ≥ C ≥ B ≥ A. This scenario corresponds to the photochemical equivalent of the Yamagata hypothesis.

What happens to the ee's of reactants and products when their extinction coefficients and *g* values are different? Consider first the case of three sequential reactions: A → B → C. Because *g* is assumed to be positive in all cases, $ee^{(A)}$ has an initial value of zero that reaches an asymptotic value of -1 when the overall reaction is completed, as observed in the previous examples. $ee^{(C)}$, on the other hand, starts with a small positive value that slowly decreases to zero at the end of the reaction, as also observed in the previous examples. What is of interest is what occurs to $ee^{(B)}$. As above, it also begins with a slightly positive value, which then goes through zero and finally becomes negative. What is important is the question of whether $ee^{(B)}$ eventually exceeds $ee^{(A)}$ for the same extent of reaction; if so, $ee^{(B)}$ has been amplified. If it does not exceed $ee^{(A)}$, then it has not been amplified. Six cases were explored. In the first two, $\epsilon_R + \epsilon_S$ was kept constant at 100 and *g* varied. If *g* for the second reaction is greater than *g* for the first, amplification is observed (Table 2). If the values of *g* are inverted, no amplification of $ee^{(B)}$ is observed. In the second set of two conditions, the difference in extinction coefficients is kept constant at 1 and *g* again varied. As in the first set, if the second *g* is larger that the first, amplification of $ee^{(B)}$ is observed. When the *g*'s are reversed, no amplification is found. In the third set of two conditions, *g* is kept constant at 0.01 and the sum and difference of extinction coefficients varied. Interestingly, when the set second of extinction coefficients is numerically smaller than the first, amplification is observed. When the values are reversed, no amplification is seen.

What occurs when a three-stage reaction, A → B → C → D, is modeled? The trends described for the two-stage reaction in the previous paragraph are observed here as well. There is a distinct correlation between the *g* values of adjacent substrates in the scheme and whether enhancement in ee is observed. When

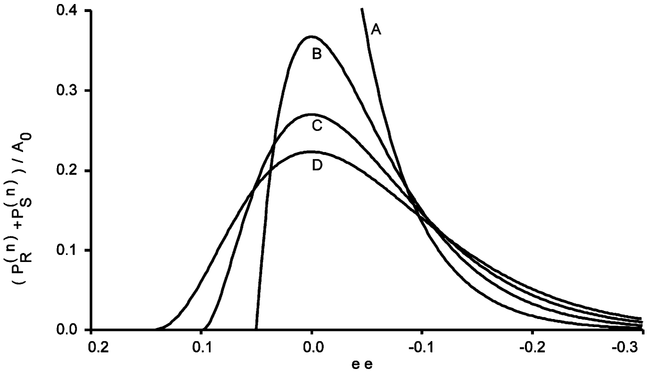

Figure 5. Fraction of reaction in a three-step reaction as a function of ee. The time evolution of each line is along the line, from left to right.

TABLE 1: Amount of Reactant and Products as a Function of ee$^{(n)}$ at −0.10 and Below

ee$^{(n)}$	A/A_0	B/B_0	C/C_0	D/D_0
−0.10	0.135	0.149	0.146	0.140
−0.15	0.049	0.073	0.084	0.089
−0.20	0.018	0.033	0.044	0.051
−0.25	0.006	0.014	0.021	0.028
−0.30	0.002	0.006	0.009	0.014

TABLE 2: Amplification of ee$^{(B)}$ When g and ϵ's Are Varied for A → B → C

entry	kept constant	varied	A → B	B → C	ee$^{(B)}$
1a	$\Sigma\epsilon$ (=100)	g	$g = 0.01$	$g = 0.02$	amplified
1b	$\Sigma\epsilon$ (=100)	g	$g = 0.02$	$g = 0.01$	not amplified
2a	$\Delta\epsilon$ (=1)	g	$g = 0.02$	$g = 0.04$	amplified
2b	$\Delta\epsilon$ (=1)	g	$g = 0.04$	$g = 0.02$	not amplified
3a	g (=0.01)	$\Sigma\epsilon$, $\Delta\epsilon$	$\epsilon_R = 100.5$ $\epsilon_S = 99.5$	$\epsilon_R = 50.25$ $\epsilon_S = 49.75$	amplified
3b	g (=0.01)	$\Sigma\epsilon$, $\Delta\epsilon$	$\epsilon_R = 50.25$ $\epsilon_S = 49.75$	$\epsilon_R = 100.5$ $\epsilon_S = 99.5$	not amplified

$g^{(A)} \geq g^{(B)} \geq g$), for example, ee$^{(C)}$ eventually exceeds ee$^{(B)}$, which in turn exceeds ee$^{(A)}$; when the relative values of g values are reversed, however, no enhancement of the ee of B or C is observed. Likewise, the trend observed in Table 2, entries 3, where g is held constant and the sum and difference in the extinction coefficients is varied, is also observed here. Thus, to observe ee$^{(C)} \geq$ ee$^{(B)} \geq$ ee$^{(A)}$ the following trend in extinction coefficients must be followed: $[\epsilon_R^{(A)} + \epsilon_S^{(A)}] \geq [\epsilon_R^{(B)} + \epsilon_S^{(B)}] \geq [\epsilon_R^{(C)} + \epsilon_S^{(C)}]$. If the magnitudes of the extinction coefficients are reversed, no enhancement of either B or C is seen.

Concluding Remarks

It is clear from the above theoretical analyses of one-step and multiple-step photoreactions initiated with circularly polarized light that it is possible to obtain a significant enantiomeric excess for chiral reactant A. Unfortunately, as the enantiomeric excess of A, ee$^{(A)}$ approaches its maximum value of ±1, the amount of unreacted A, $A_R + A_S$, approaches 0. This dichotomy was first described theoretically and then observed experimentally by Kagan and co-workers in the photochemistry of camphor[22] and more recently by Inoue and co-workers in the photodestruction of amino acids in water.[28] The partial photodestruction of amino acids with circularly polarized light may be the origin of optically active amino acids in the Murchison meteorite.[29,30]

Unlike the reactant, the final product, be it formed in a one-step or multiple-step photoreaction, has its maximum enantiomeric excess when the compound is initially formed and the enantiomeric excess decreases with time until ee = 0 when the reaction is completed. When the reaction is completed, the reactant and intermediate photoproducts are absent and any enantiomeric excess that they may have had is also lost.

The above detailed theoretical analyses have shown conclusively that for a multiple-step reaction the intermediary products may have significant enantiomeric excesses at certain stages of the overall photoreaction. Furthermore, the ee of a succeeding product may be amplified relative to that for the compound that preceded it. This does not apply to the final product, which, as noted above, never has a significant ee. The sign of the individual ee's may also change sign during the course of the reaction.

What is most important about multiple-step photoreactions initiated with circularly polarized light is that one can get large ee's not only of intermediate photoproducts but also in large amounts. This may have been a desirable trait in the prebiotic universe because the purity of the circularly polarized light in the universe may be small. The combination of high concentrations of reactant or product and large ee of reactant or product is not possible in a one-step reaction.

In what class of compounds would one likely see multiple-step photoreactions? We believe that carbonyl-containing compounds are the best choices. There are many instance of aldehydes and ketones, for example, yielding a carbonyl-containing product that, in turn, reacts photochemically to yield a second product. Sugars can be synthesized thermally from formaldehyde in the so-called formose reaction[30] and they can also be built up photochemically from formaldehyde as well.[31] Sugars such as glucose are also photodegraded in steps.[32] A series of carbohydrate-forming and carbohydrate-degrading photoreactions initiated with circularly polarized light may lead to significant enantiomeric excesses of prebiotic sugars.

In a recent review Bailey has described a number of astronomical sources of circularly polarized light.[33] Some sources are quite exotic, others yield weakly polarized light, and still others produce radiation with insufficient energy to induce photochemistry. According to Bailey, significant amounts of circularly polarized light are found in reflection nebulae where star formation occurs and where organic compounds have been detected spectroscopically. As many of these compounds are complex, they may indeed be produced in a sequence of photochemical steps. This behavior may account for the exogenous synthesis of some optically active compounds such as amino acids. Endogenous synthesis of optically active molecules is more problematical because the sun is not a good source of circularly polarized light. The extent of circular polarization of sunlight is small and averages to zero over time. This does not preclude the synthesis of optically active molecules on the earth because the environment of the earth in prebiotic times may have been quite different than what it is today. If homochirogenesis occurred, either exogenously or endogenously, via photochemical pathway, the light source undoubtedly was of short duration relative to the whole time scale of the photochemical processes because, as noted several times above, a photochemical reaction carried to completion yields a single, racemic product.

Let us conclude by returning to the Yamagata hypothesis. Because the reactions described in his original paper may follow first-order kinetics, as do the photochemical reactions described in detail in this paper, the ee's of successive products may be subject to the same complications as do the ee's of the photoproducts.

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Supporting Information Available: Derivations of equations in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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