

A Correct Understanding of Symmetry-Breaking in Chiral Organic Synthesis

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Abstract

In recent years, many scientists have referenced the work of mathematicians D.K. Kondepudi and G.W. Nelson who claim that symmetry breaking states are extremely sensitive to small symmetry breaking interactions, and small external influences can play a role in the selection of one outcome from other possible outcomes. Kondepudi and Nelson have previously concluded that the energy barrier for selecting one outcome over the other should be on the order of 10^{-15} – 10^{-17} kT based on their earlier calculations. Kondepudi and Nelson then studied mathematically the rate equations from a hypothetical chemical reaction to see if symmetry breaking leading to bifurcation could create new homochirality in that chemical reaction. Although symmetry occurs in some chemical reactions that produce chirality, the breaking of that symmetry as it relates to forming new homochirality, the alleged formation of only one outcome and the bifurcation they propose occurs contrary to the chemical literature. For this reason, it was necessary to evaluate their claims because of the potential impact of their discovery if verifiable. Unfortunately, it had to be concluded that the Kondepudi and Nelson math equations for symmetry breaking are not relevant to chemical systems, and their claims for creating new homochirality were only assumed, never substantiated.

The synthesis of organic molecules has always been an important part of organic chemistry, and in recent years, the synthesis of “chiral” organic molecules has received much attention. The word “chiral” is derived from the word “chirality” meaning handedness, and a chiral carbon exists when that carbon atom has four different bonds attached to it. When four different

bonds exist around a carbon, that carbon atom will exist as two distinctly different structures. Those two structures differ only as each being the non-superimposable mirror image of the other and because they are mirror images of each other, hence the term handedness, those images are designated as either the left-handed isomer or the right-handed isomer. In

this paper, the labels “D” or “L” will be used as subscripts to distinguish between the right-handed and left-handed isomers since that was the method used by Kondepudi and Nelson in their published articles.

[**Author’s Note:** In organic chemistry, mirror image isomers are frequently labeled as either “D” or “L” to distinguish between their handedness, but to be correct, “D” or “L” only refer to the direction that isomer rotates polarized light; rotation to the right is given as “Dextrorotatory” and rotation to the left is “Levorotatory.” Unfortunately, there is no correlation between handedness and polarized light rotation.]

Of special interest in chiral organic synthesis is the topic of homochirality; a homochiral molecule is a molecule existing as one of the two possible mirror-image isomers. The synthesis of such homochiral molecules has become increasingly important for understanding the chemistry of life’s chiral systems, and the need for synthesizing a single chiral isomer is more important than ever because all of the chiral molecules found in the human body are essentially 99.9%+ of a single chiral isomer without exception. For this reason, the evolutionary origin of homochiral molecules is the most difficult topic to explain when it comes to understanding the origin of life on Earth. For many scientists, that is the “mystery” keeping them from knowing the origin of life, and this mystery still exists today (Cohen, 1995, pp. 1265–1266). For a discussion of homochirality, see Coppedge (1971), Helmick (1976), and Murphy (2013). Ever since the presence of unique homochirality was discovered in living organisms, scientists have tried, but failed to explain how unique homochirality came to exist in living organisms. There have been many attempts to explain the origin of homochirality, and all these attempts have failed for one reason. There is no natural process that can explain how new homochirality can be formed without some form of pre-existing homochirality already present, a known fact of chemistry.

In chemistry, there are many examples of how the homochirality of a starting material can be transferred to the final product. Either the homochirality of the starting material is directly incorporated into the final structure, or indirectly as other factors influence how the new chiral carbon bonds are formed, but there is not a single example of forming a homochiral product from achiral substrates without some form of asymmetric induction. Therefore, when mathematicians Kondepudi and Nelson claimed that homochiral products might be prepared from achiral substrates after a symmetry breaking process based on conclusions obtained from their math equations, their claim caught the attention of many scientists (Jafarpour et al., 2015, 2017; Michael Stich et al., 2016; Ribo et al., 2017).

Kondepudi and Nelson (1984) claim that symmetry breaking in non-equilibrium systems can occur in several ways, and the breaking of symmetrical states is extremely sensitive

to small interactions. Kondepudi and Nelson extended the general idea of symmetry breaking they saw in their system and applied it to a chemical system, and then compared the sensitivity of symmetry breaking leading to bifurcation with the selective formation of one chiral product being formed from a choice of two possible isomers. In order to extend symmetry breaking and bifurcation to a chemical system, they presented hypothetical chemical reactions and studied the kinetics of the derived rate equations in an effort to show that there was a very real mathematical possibility for creating new homochirality.

Kondepudi and Nelson (1984) further claim that when a chemical system is operated near equilibrium, the left- and right-handed molecules will be produced in equal amounts, but if the system is “far” from equilibrium, molecules of one kind could be produced in much larger quantity than the other, provided the kinetics have appropriate auto-catalytic steps. Because of the many claims that were made, it was necessary to determine if there was a possibility for new homochiral products to be formed in this way.

Symmetry Breaking in a Physical System

The process of “symmetry breaking” described in Kondepudi and Nelson’s publications refers to a “system with symmetry” changing to a “system without symmetry.” Although one can imagine several ways in which symmetry can be broken, the system studied by Kondepudi and Nelson was not a simple system; it was a hypothetical system containing a bifurcation point where, because of bifurcation, there would be two possible outcomes after symmetry is broken. Kondepudi and Nelson further imagined that symmetry breaking initiated simultaneous bifurcation in their system, and once bifurcation occurred, only a single outcome would be possible because of the low energy required to break that symmetry.

Using all of the claims and descriptions made by Kondepudi and Nelson for what their system was supposed to do, their system can best be described as a spherical ball balanced on a fulcrum (see Figure 1).

Even though the ball-on-a-fulcrum description was not presented by Kondepudi and Nelson, this is a classic example of a system at symmetry taken from physics, and fully incorporates the description of the Kondepudi and Nelson system. When this system is balanced and symmetrical, there are two equally possible ways for the ball to fall. In order to understand the concept of “symmetry breaking,” consider

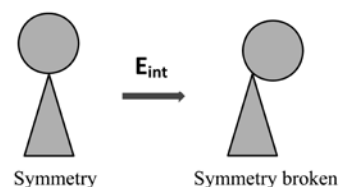


Figure 1. Ball on a fulcrum.

that balanced ball falling off of that fulcrum as shown in Figure 1. Once symmetry is broken by either internal or external forces, bifurcation simultaneously occurs. Although there are two possible outcomes before bifurcation, only one outcome is observed after symmetry was broken. When dealing with a symmetrical state as thus described, it would not take much energy to disturb (break) the symmetry of that ball balanced on a fulcrum. Thus, symmetry breaking leading to a single outcome is a reasonable conclusion in this model.

Symmetry in Chemical Reactions

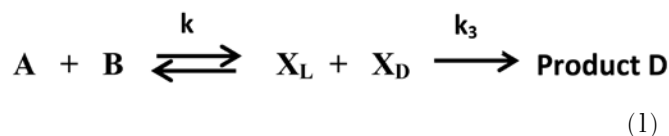
Believing that symmetry breaking can lead to a single outcome in their hypothetical system, Kondepudi and Nelson wanted to extend the concept of “symmetry breaking” to organic chemical reactions forming chirality with the expectation of forming a single homochiral product. The ball-on-a-fulcrum model described above may have many similarities with a chemical reaction forming chirality, and although not an exact representation of a chemical reaction, some organic reactions can possess symmetry and a bifurcation point. Among organic chemists, it is understood that symmetry can be created in a chemical reaction for example when a planar transition state is formed as in S_N1 type reaction mechanisms. Furthermore, the planar transition state creates the opportunity for two possible products to be formed (bifurcation) and bifurcation occurs because reactions on this planar transition state must approach from either the top or the bottom of the plane of symmetry.

Kondepudi and Nelson took the assumptions and conclusions derived from study of their mathematical equations in physical systems, and proposed that symmetry breaking and bifurcation should be expected to occur in chemical reactions as well. It was further believed that since the energy required for breaking symmetry in a physical system is very low, the energy required to selectively form a single chiral product in a chemical system should be equally low. If these assumptions hold true in chemical systems forming chirality, those chemical reactions should be capable of forming only one chiral isomer, a result not expected from the chemical literature.

The Kondepudi-Nelson Reactions

In order to show symmetry breaking and bifurcation in a chemical system, Kondepudi and Nelson created hypothetical chemical equations to prove their hypothesis. According to the Kondepudi and Nelson model, substrates A and B are the two starting materials, each having no chirality, and these substrates can combine chemically to produce a chiral product X at rate k. Product X, being chiral, is a mixture of the left-handed isomer (X_L) and the right-handed isomer (X_D), and since Kondepudi and Nelson expect to see these isomers

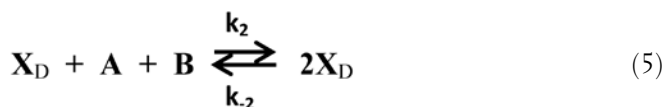
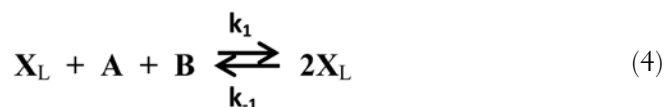
formed unequally, the individual rate constants are shown as k_L and k_D to represent the rate at which each chiral isomer is formed. Kondepudi and Nelson also show X_L and X_D as further reacting to form achiral product D at a rate of k_3 according to the following chemical reaction:



Based on this chemical reaction, Kondepudi and Nelson derived the following rate equations:



Kondepudi and Nelson then assume that X_D and X_L can auto-catalytically reproduce more chiral product at different rates according to these reactions:



Then, X_L and X_D react to form D irreversibly.



From these chemical reactions, one can write the following rate equations:

$$\frac{dX_L}{dt} = k_{1L}AB - k_{-1L}X_L + k_{2L}ABX_L - k_{-2L}X_L^2 - k_3X_LX_D \quad (7)$$

$$\frac{dX_D}{dt} = k_{1D}AB - k_{-1D}X_D + k_{2D}ABX_D - k_{-2D}X_D^2 - k_3X_LX_D \quad (8)$$

If one assumes,

$$\alpha = (X_L - X_D)/2 \quad \text{and} \quad \beta = (X_L + X_D)/2$$

The appearance of asymmetric solutions for $(AB) > (AB)_c$ will occur when:

$$(AB)_c = \frac{s + [s^2 - 4k_2^2k_1]^{1/2}}{2k_2^2}$$

$$\text{when } s = 2k_2k_1 + 4(k_2^2k_1)/(k_3 - k_2)$$

According to Kondepudi and Nelson, when the value of (AB) exceeds the critical value $(AB)_c$ and if the supplemental solution $(k_3 - k_2) \neq 0$ is satisfied, the following asymmetric steady states (α_A, β_A) will appear:

$$\alpha_A = \pm[\beta_A^2 - K_1AB/(k_3 - k_2)]^{1/2} \quad (9)$$

$$\beta_A = (k_2AB - k_1)/2k_2 \quad (10)$$

According to these equations, there is a necessary condition requiring that k_3 must be greater than k_2 (Equation 9) so that α_A and β_A can be real numbers. If this condition is met, there should be a set of reaction parameters where the concentration of $X_D \neq X_L$, and their conclusion of inducing new homochirality as the result of symmetry breaking will have been proved.

Results and Discussion

The addition of hydrogen bromide to 2-butene is an excellent example of the formation of a chiral product from two achiral substrates when we assume 2-butene is substrate A and hydrogen bromide is substrate B (see Figure 2).

The expected product from this reaction would be an equal mixture of the left- and right-handed chiral isomers of 2-bromobutane, and if the Kondepudi and Nelson claims are correct, conditions could be found where symmetry breaking and bifurcation should form a different ratio of products.

In order for Kondepudi and Nelson to prove their claims, they would have to show the factors or conditions that must be met to form an unequal mixture of X_D and X_L . Unfortunately, they made four bad assumptions and two major errors, and consequently, they failed to realize that physical systems do not automatically correlate with chemical systems, that symmetry breaking is different than shifting the equilibrium,

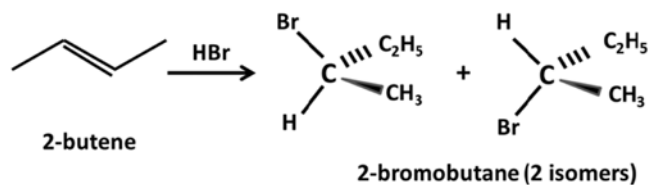


Figure 2. Reaction to form 2-bromobutane as two chiral isomers.

or that bifurcation can selectively choose one chiral isomer over another. Although symmetry and a bifurcation point are present because of the mechanism of the reaction that forms 2-bromobutane, we will learn that it is symmetry that creates the bifurcation point. We will also learn that the breaking of symmetry does not *cause* the reaction to proceed; symmetry is broken as the *result* of the reaction. As mentioned earlier, there are many similarities with Kondepudi and Nelson's physical system, but it was the non-similarities with the chemical reaction that Kondepudi and Nelson failed to consider as being a problem. This paper will show that chiral product formation has nothing to do with symmetry breaking, and un-aided bifurcation is the actual reason why one chiral isomer will never be formed in a chemical reaction.

The Interaction Energy

In their earlier work, Kondepudi and Nelson (1981) claimed that systems that break symmetry are so sensitive that an interaction energy (E_{int}) greater than 10^{-15} – 10^{-17} kT , where k is the Boltzmann constant and T is the temperature, is sufficient to break symmetry. According to Kondepudi and Nelson, such energies are within the range of parity violating weak-neutral-current interactions. Chiral interaction energies due to a combination of electric, magnetic, gravitational and centrifugal fields, even when high field strengths are considered, are found to be less than $10^{-19}kT$. Therefore, if the concept of symmetry breaking could be applied to a chemical system, that interaction energy should be more than enough to promote strong chiral selectivity.

Unfortunately, the energy requirements of the Kondepudi and Nelson system and a chemical reaction are very different. In a chemical reaction, the required symmetry must be created in the transition state, and the creation of the symmetrical transition state requires additional activation energy for such a reaction to proceed. In the Kondepudi and Nelson system, symmetry is already present with no mention of the energy required to get the system to a point of symmetry, and they assume that their estimated interaction energy (E_{int}) is enough

to initiate and complete any chemical reaction. *This is their first bad assumption.* In the Kondepudi and Nelson model, the sequential process of symmetry breaking, bifurcation and single outcome formation was a domino effect aided by the ball's initial potential energy and the downward force of gravity; none of which would be present in a chemical reaction. The Kondepudi and Nelson system may have provided the results they wanted to achieve, but there is no reason to believe that results from their physical system will correlate with a chemical system.

Shifting the Equilibrium

To achieve their goal, Kondepudi and Nelson say that symmetry breaking must occur under non-equilibrium conditions, and when the equilibrium is shifted "far" from equilibrium, bifurcation will occur in a physical system. To claim symmetry breaking in a chemical system, they must be assuming that a ball balanced symmetrically on a fulcrum is analogous to a chemical reaction at equilibrium, and by analogy, they must be assuming that symmetry breaking is the result of shifting that equilibrium. However, *this is their second bad assumption.* A chemical reaction at equilibrium means that there is a forward reaction converting starting materials into product, and there is a backwards reaction converting products back into starting materials. When a reaction is at equilibrium, there is a steady state concentration of starting materials and product and that concentration does not change. In chemistry, it is well known that pressure, volume, temperature, and concentration changes can shift the equilibrium of a reaction, but not to a point of bifurcation. Plus, the shifting of the equilibrium cannot be shifted to a point where the reaction is no longer non-reversible, and the shifting of equilibrium never breaks any symmetry if symmetry is present. The idea of shifting equilibrium to a point of bifurcation may be a theoretical exercise in math, but it is not a practical exercise in chemistry.

In a chemical system, the reaction is either at equilibrium or it is not, and it is the reaction mechanism that determines whether or not a reaction is at equilibrium. Furthermore, the ability to create new homochirality can *only* occur when the chemical reaction is NOT at equilibrium. Kondepudi and Nelson created their own problem when they wrote Reactions 2 and 3 as being at equilibrium, a fact not consistent with their original assumption of needing to be "far from equilibrium." By including the reverse reactions in the kinetic equations, Kondepudi and Nelson unnecessarily complicated the reaction equations they were trying to solve. By writing the reactions in this manner, they failed to realize that there is *not* a single example of homochiral products being formed by a reaction at equilibrium, and their math equations have done nothing to suggest otherwise.

Formation of Product D

The stated objective of the Kondepudi and Nelson paper (1984) was to show that symmetry breaking and bifurcation can lead to a homochiral product, and to accomplish this purpose, Kondepudi and Nelson (1984) wrote a hypothetical chemical reaction to simulate symmetry breaking leading to bifurcation in a chemical system. However, since their reaction was not based on an actual chemical reaction, they failed to realize that the rate equations they wrote did not represent the chemical reaction they were trying to perform. According to the written chemical reaction (Equation 1), the only product that will be formed by this reaction is achiral product D, especially if k_3 is greater than the reverse reactions forming products X_D and X_L . *The inclusion of product D in the chemical reactions is their third bad assumption.* The reaction in Equation 6 shows X_D and X_L reacting equally and irreversibly to form product D, and as long as k_3 is greater than k_2 from Equation 9, product D will always be the final product, but what is product D? If the goal of the paper was to create new chirality, why would you want to include a reaction that would take away any new chirality after it has been formed? Kondepudi and Nelson show product D as a secondary product of the reaction between X_D and X_L and the only mention of product D in the Kondepudi and Nelson original paper (although not specifically mentioned as product D) was to incorporate an element of "competition" or "source of mutual destruction" into the kinetics. The fact that Reaction 6 is included in the reaction is a huge problem that will always prevent the formation of a homochiral product formation.

As the rate equations are written, components X_D and X_L will always be formed from their starting substrates A and B, but X_D and X_L are also being constantly removed by the reaction to form product D. Since product D is never removed by any reaction, the ONLY product that will accumulate is product D. Since product D was supposed to be a source of "competition" for X_D and X_L , it did its job so well that it completely negated the Kondepudi and Nelson's intention of forming one chiral isomer. And even if you consider the possibility that an unequal mixture of X_D and X_L might remain after formation of product D, the reverse reactions (in Equations 2 and 3) would quickly remove that inequality. This is an excellent example of what can happen when writing hypothetical chemical reactions or rate reactions not based on real chemical reactions. In chemistry, the written chemical reaction is supposed to be an exact representation of what is occurring within the chemical reaction, not in a math equation.

Presence of Auto-Catalysis

Kondepudi and Nelson claim that the unequal formation of X_D and X_L can result when auto-catalysis is working. Auto-catalysis (or self-catalysis) is the idea that the product of a chemical reac-

tion can catalyze the formation of itself. Kondepudi and Nelson are assuming that since auto-catalysis is working in a chirality forming reaction, and as the left-handed chiral isomer is formed by the reaction, the presence of that left-handed isomer will catalyze the formation of new left-handed isomers beyond its uncatalyzed formation rate. Of course, the same would be true for the right-handed isomer. Kondepudi and Nelson incorrectly assume that when left- and right-handed isomers are present in the same reaction mixture, those chiral isomers will unequally catalyze the formation of their respective chiral products, even though no verifiable evidence was provided to support that claim. *This is their fourth bad assumption.*

In the Kondepudi and Nelson model, Equations 4 and 5 are trying to show the unequal formation of products X_D and X_L where each product catalyzes the formation of itself unequally by separate and different rates of catalysis. Unfortunately, there are problems with these equations. First of all, Kondepudi and Nelson are assuming that auto-catalysis is a well-established fact of chemistry and is presented as if it is universally accepted by all chemists, but neither statement is correct. Secondly, Equations 4 and 5 should not have been written to include the catalyst as a substrate of the reaction because the way those Reactions 4 and 5 are written shows X_D and X_L as reacting stoichiometrically with substrates A and B instead of catalytically. Besides making the rate equation unnecessarily complicated, there is another problem. Once you remove their so-called catalyst as a substrate, Equations 2 and 3 and Equations 4 and 5 become identical, and being identical, Equations 4 and 5 showing auto-catalysis become unnecessary. Kondepudi and Nelson failed to realize that the reactions in Equations 2 and 3 and reactions in Equations 4 and 5 cannot both be working at the same time. As quickly as components A and B react to form product X_D or X_L as in Equations 2 and 3, the reactions given in Equations 4 and 5 have already begun to take place. Although one might argue that both reactions were taking place at the same time, Kondepudi and Nelson failed to realize that the rate constants in Equations 2 and 3 and the rate constants in Equations 4 and 5 cannot both be working at the same time. The rate constant is defined as the "total" amount of product formed in a specified period of time, and for this reason, the rate constants k_1 and k_2 cannot be forming products "in addition to" the rates for k_D and k_L . Since only one set of rate constants can be working at one time, rate constants k_1 and k_2 are unnecessary making Equations 4 and 5 redundant, and these auto-catalytic reactions should not have been included in their analysis.

Although Kondepudi and Nelson claim that the uncatalyzed reaction (Equations 2 and 3) occurs with one set of rate constants and the catalyzed reaction (Equations 4 and 5) occurs with a second set of rate constants, there is still no reason to believe that two enantiomers could ever be formed unequally

in their reaction. Contrary to the Kondepudi and Nelson claims, the idea of auto-catalysis forming unequal mixtures of X_D and X_L is contradicted by every known chemical reaction that forms chiral products as equal mixtures. In the chemical literature, there are hundreds of examples where mirror image chiral isomers react with other substrates at exactly the same rate forming equal mixtures of chiral products. The Kondepudi and Nelson math equations has not provided any reason to accept their claims of auto-catalysis and to overlook the chemical literature, confirming again that the written chemical reactions are supposed to be an exact representation of what is occurring within the chemical reaction.

In chiral organic synthesis, the only way to form the enantiomers unequally is by adding an additional catalyst; a technique called asymmetric induction (discussed later). It is likely that Kondepudi and Nelson are confusing auto-catalysis with asymmetric induction. In their paper, Kondepudi and Nelson (1984) tried to use the rhodium catalyzed hydrogenation with a chiral phosphine ligand as an example of auto-catalysis, but this is a perfect example of asymmetric induction. As a general rule, the expectation to form X_D and X_L unequally is only possible when one of the original substrates of the reaction is chirally enriched or when a third component is added to the mixture to influence product formation at the planar transition state, but Kondepudi and Nelson did neither. In the absence of chirally enriched substrates, Kondepudi and Nelson falsely assume that in Equations 4 and 5, the mere presence of X_D or X_L acts as its own catalyst unequally forming new chiral products from substrates A and B. As the Kondepudi and Nelson chemical reactions were written, no additional catalyst was ever present and therefore asymmetric induction cannot be working. Kondepudi and Nelson may have assumed that auto-catalysis was working in their reactions and they may have included it in their math equations as if it was a proven fact, but in reality, no such auto-catalysis was ever present or has ever been proved to be working in a chemical reaction.

Problem of Bifurcation

Kondepudi and Nelson claim that the breaking of symmetry will cause the chemical reaction to reach a bifurcation point. A bifurcation point means that there will be a point where division occurs; a division point that provides the option for two possible outcomes. However, Kondepudi and Nelson are also assuming that at the exact instance the symmetry of a physical system is broken; the forces that cause symmetry to break also cause bifurcation to proceed in only one direction. This result may be true with a ball on a fulcrum because the ball is already balanced on the bifurcation point, but this is not true in a chemical reaction. *This is their first major error* because with a ball on a fulcrum, the energy required to break sym-

metry does not tell the ball which way to fall off the fulcrum. Kondepudi and Nelson may have thought that bifurcation created the final outcome, but in reality, it was only “chance” that provided that single outcome.

In the Kondepudi and Nelson model, symmetry is already present, but in a chemical reaction symmetry must be created in the intermediary transition state. In the Kondepudi and Nelson model, the bifurcation point (the fulcrum) is already present, but not so in a chemical reaction. Kondepudi and Nelson may want to believe that in a physical system the “breaking” of symmetry causes bifurcation to occur, but in a chemical reaction it is the “formation” of symmetry itself that causes bifurcation. Kondepudi and Nelson may observe bifurcation creating a single outcome in their model system, but bifurcation is the problem that “prevents” the creation of a single outcome in a chemical reaction. In a physical system, the fulcrum is the bifurcation point that creates the option for the ball to fall to one side or the other. Once symmetry was broken, it was only chance, not bifurcation, that determined to which side of the fulcrum the ball will fall.

In a chemical reaction forming chirality, symmetry must be created in an intermediate transition state, and bifurcation occurs at the plane of symmetry that is created in that transition state. Once a chemical reaction has reached its symmetrical transition state, it is this plane of symmetry that provides the option for two possible outcomes (the plane of the chiral carbon is the bifurcation point). As the fourth bond to a carbon is being formed, that new bond can only approach from the top or from the bottom of the plane created in the transition state, and the final outcome is only determined by chance (see Figure 3). Because of chance, the product will always be a 50/50 mixture of both isomers.

Kondepudi and Nelson are assuming that one instance of symmetry breaking in a physical system is equivalent to one chiral isomer being formed by a chemical reaction; this may sound logical, *but this is very wrong*. In chemistry, the chemical reaction describes what happens to the individual “molecules” as they react. Each “molecule” will go through that planar transition state and each “molecule” will have the option to form one of two possible outcomes. With only one instance of symmetry breaking of a ball on a fulcrum, it is easy to get a single outcome. However, there are 6.023×10^{23} molecules per mole of any chemical substance, and when all molecules have reacted, there will be a 50/50 mixture of the two possible outcomes. To expect a different result is to deny the legitimacy of the laws of probability.

The Necessary Condition

Kondepudi and Nelson (1984) found two equations (Equations 9 and 10) where, if the rate constants and substrate concen-

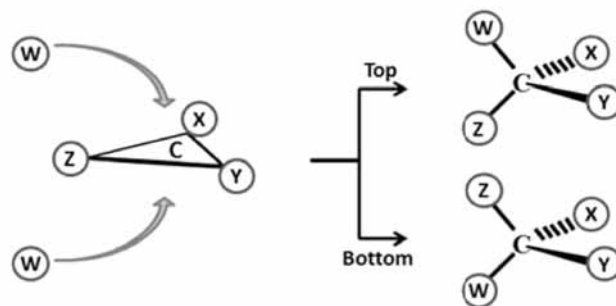


Figure 3. Bifurcation leading to chiral isomers.

trations are real and those values are attainable, there would be proof to suggest that symmetry breaking and bifurcation could induce new homochirality. Within Equation 9, we see the value $(k_3 - k_2)$ in the denominator of the equation, and mathematically, this value cannot be negative or zero because of its location in the denominator of the equation under a radical. Mathematically, this condition must be met for α_A of Equation 9 to be real, but there is another problem. Knowing that k_3 is the rate of product D formation and k_2 is the rate of the reverse auto-catalytic reaction, it is equally important to make sure that rate constants k_3 and k_2 also represent real rate values in a chemical reaction (this is their second major error). For this reason, *the condition that k_3 must be greater than k_2 poses the biggest problem of all* even if we assume all their other assumptions were correct. Since auto-catalysis does not exist in any reaction and the need for product D formation in their rate equations is certainly questionable, then the rate values for k_3 and k_2 are not real numbers. If k_3 and k_2 are not real numbers in Equation 9, then there are no parameters that would allow for unequal formation of X_D and X_L , and if true, there is no proof for their concept of symmetry breaking leading to bifurcation and the formation of a single chiral outcome.

A Correct Understanding of Chirality Formation

In general, chemical reactions can only proceed to a product according to a mechanism, and it is this reaction mechanism that dictates how the substrates interact, combine, and proceed towards product formation. In a chemical reaction, it is the reaction mechanism that creates the symmetrical intermediate, and it is this symmetrical intermediate that becomes the bifurcation point. This is where the Kondepudi and Nelson logic fails because bifurcation (without asymmetric induction) does not ever form just one of two possible outcomes. And two, the determining factor for the existence of symmetry is

the reaction mechanism, not the shifting of the equilibrium. The reaction mechanism is what provides the opportunity for symmetry to be created, but there can be other geometric changes that can occur during a chemical reaction. It is also well known that a carbon atom will change its geometry in order to place the carbon atom in a favorable electronic state. This change of geometry will occur whenever there is a change in the number of other atoms attached to the central carbon atom. The change in geometry occurs because the bonds around carbon want to be as far from each other as possible. The geometry will be “linear” if a carbon atom has two other attached atoms; it will be “planar” if there are three other attached atoms, and “tetrahedral” if there are four other attached atoms to that carbon.

In the reaction of 2-butene with hydrogen bromide, after the proton from hydrogen bromide (H^+) adds across the double bond of 2-butene, the circled carbon in the reaction intermediate below has only three other attached bonds and therefore that carbon will have planar geometry regardless of the number of bonds present in the original substrate. Once the reaction with the bromide ion is complete, the product now has four attached bonds and the circled carbon becomes tetrahedral in shape (see Figure 4).

Because the intermediate transition state has planar geometry, the bromide ion (analogous to element W in Figure 3) must approach from either the top side of plane or the bottom side of plane. In a chemical system, the plane of the carbon atom is the bifurcation point that forces the fourth bond to approach from one side or the other. In the absence of an outside influencing force, there is an equal probability of approach from the top or from the bottom of the plane by the bromide ion. Therefore, the product will always be an equal mixture of two chiral products.

In order to create new homochirality, the chemical reaction must NOT proceed through a bifurcation point. In the chemical literature, there are many reactions capable of introducing new homochirality into an organic molecule, but in every one of those reactions, the mechanism did not proceed through a planar intermediate. Without a planar intermediate, there is no

bifurcation. When there is no bifurcation, only one product is possible from the reaction, which is the desired outcome when creating new homochirality. However, when planar symmetry is present, there will always be a bifurcation point. It is the process of bifurcation that provides the opportunity for multiple outcomes in a chemical system. Whenever the reaction proceeds through a planar intermediate, the equal formation of X_D and X_L is the only possible result. Even if one started with a homochiral substrate (A^* or B^*), as long as the chemical reaction proceeded through a symmetrical intermediate, the product will never contain any new homochirality because all pre-existing homochirality would be lost because of the symmetry of the planar intermediate. These are the facts that Kondepudi and Nelson were trying to overcome by the use of symmetry breaking. Symmetry breaking leading to bifurcation may be a valid observation in the system they imagined, but in chemical reactions, the breaking of symmetry does not occur and it is the symmetry that is created that forces a bifurcation point preventing the actual formation of new homochirality.

Asymmetric Induction

In the system by Kondepudi and Nelson, a single outcome was achieved by the design of the system, but when chemical reactions proceed through a planar transition state, the product will always be an equal mixture of chiral isomers. In the absence of chiral substrates A^* or B^* , the only way for an unequal mixture of chiral isomers to be formed (meaning $k_L \neq k_D$) is by the addition of a third optically active component to the reaction mixture; this process is called asymmetric induction. This third component either by incorporation, complexation or steric hindrance causes unequal access to the plane of the carbon, and unequal access means unequal mixture of products. In certain types of reactions, asymmetric induction can be accomplished by the addition of an optically active catalyst Z because that catalyst forms the product at a rate catalytically faster than those products can be produced naturally (meaning $k_{cat} > k_D$ or k_L). The rhodium catalyst with a chiral phosphine ligand mentioned by Kondepudi and Nelson is an excellent

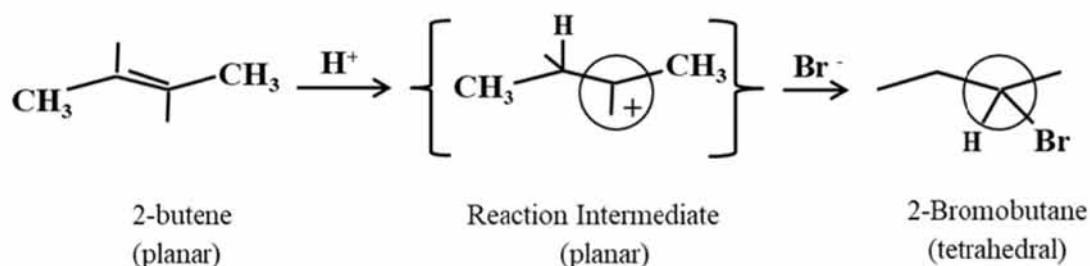
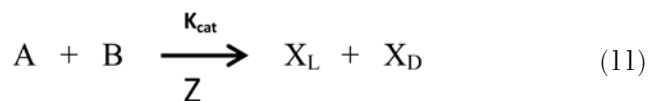


Figure 4. Symmetry changes due to geometric changes.

example of such a catalyst. It is the unequal catalytic effect provided by catalyst Z that allows for the unequal formation of X_D and X_L in the product as shown in Equation 11.



If asymmetric induction is present, $X_L \neq X_D$
 If not present, $X_L = X_D$

Yes, there are two possible outcomes, but it was the catalyst Z that provided the mechanism for unequal formation of X_D and X_L , not bifurcation. Without an additional substrate like catalyst Z, the products X_D and X_L can only be formed in equal proportions due to the equal probability of approaching a two-sided plane of symmetry.

The Correct Chemical Reactions

Since the chemical reactions need to be written in such a way that the actual products of those reactions are the products we desire to see and study, we need to remove the reaction-forming product D, the reactions showing auto-catalysis and all reverse reactions from the Kondepudi and Nelson equations. By removing these reactions, we are left with Equations 12 and 13 below. Consequently, there are only two equations that need to be evaluated, and coincidentally, these two equations are totally consistent with equations known from the chemical literature and they are the exact equations that a scientist would write for the formation of X_L and X_D as products of this reaction (see Figure 5).

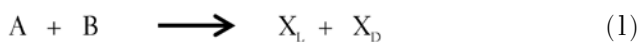


Figure 5. Correct rate equations from chemical reaction.

These new equations show the formation of X_L and X_D at rates k_L and k_D using much simpler rate equations. In order to show that an unequal mixture of X_L and X_D can be formed, one only needs to show that X_L and X_D are formed at different rates (meaning $k_L \neq k_D$), but this is exactly the same problem that

Kondepudi and Nelson set forth to solve by incorporating symmetry breaking and bifurcation in the first place. Unfortunately, these reactions still confirm what was already known; that new homochirality cannot be created without some form of asymmetric induction (pre-existing homochirality). By removing those unnecessary reactions, the final reaction equations were greatly simplified, but even after simplifying these equations, it was still impossible to create new homochirality without some form of pre-existing homochirality (catalyst Z) already present. Contrary to their expectations, Kondepudi and Nelson were unable to solve the problem of creating new homochirality, which not surprisingly, explains why evolutionists cannot solve the mystery of homochirality; life and homochirality are not the result of chemical reactions.

Conclusions

Although the original intent of Kondepudi and Nelson was to show that new homochirality could be formed by a process of symmetry breaking leading to bifurcation, that result was only assumed theoretically and never proven practically. Kondepudi and Nelson may see bifurcation leading to only one outcome in a physical system, but in chiral organic synthesis, bifurcation is the reason why one chiral isomer will never form. Their conclusions are totally contrary to the chemical literature, and nothing was presented to suggest that symmetry breaking leading to bifurcation could ever form just one chiral isomer in a chemical reaction. Kondepudi and Nelson want to believe that their mathematical analysis and more specifically their derived necessary condition proved the possibility of their claim, but unfortunately, a proper analysis of their “necessary condition” does more to prove the impossibility of creating new homochirality than the possibility of forming a single homochiral isomer.

There is a very good reason why the homochirality found in our bodies and life in general was never formed from chemical reactions as evolutionists suggest. The homochirality found in our bodies is there because the homochiral chemical molecules found in our bodies were supernaturally created to have that homochiral structure; they were created to be the way they are found. In chemistry, the formation of new homochirality always requires the pre-existence of another homochiral molecule. This is not just a statement of fact; it also means that existing homochirality, whenever observed, was never formed by a natural chemical reaction. The fact that homochirality exists anywhere means that chemical reactions did not form those homochiral molecules. This is why the origin of life and the subject of homochirality is a mystery to the evolutionists. It is a huge mystery because they have no answer to the question... How did that “first” homochiral molecule get into the “first” living organism if there is no God who created homochirality? To a Bible believer, it is easy. God created those molecules to

be the way they exist because there is no process capable of doing it naturally. Questions like these are easy to answer when you have God's Word telling us that...*all things were created by Him*, and because of the homochirality found in our bodies, we can believe that we are not the product of a chemical reaction, i.e., we are not an accident of nature; *we are fearfully and wonderfully made* in the image of our Creator.

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