Table III. Arenesulfonate (O_3SAr) Leaving-Group Loss for Solvolysis of Cyclobutyl Arenesulfonates in Several Solvents[21]

entry	solvent	temp, °C	$\beta_{lg}^{CH_3}$ (r)
1	EtOH	40	0.57 (0.994)
2	AcOH	40	0.49 (0.998)
3	TFE[a]	25	0.45 (0.999)

[a] 2,2,2-Trifluoroethanol.

4 and 5). For these cases, lack of nucleophilic solvation is reflected in higher $\beta_{lg}^{CH_3}$ values of around 0.6. The transition state lies on the left vertical boundary of the energy surface of Figure 4. Surprisingly, the extent of leaving-group loss is only marginally greater for the secondary system than for the tertiary one.

When the loss of the leaving group is facilitated by electron donation to the developing cationic center, then lower $\beta_{lg}^{CH_3}$ values result. The $\beta_{lg}^{CH_3}$ values thus obtained can detect charge-stabilizing events like backside solvation (Table II, entry 6), π-participation (Table II, entry 7), and anchimeric assistance (Table II, entry 8)—all points of current interest.

This technique might also be used to evaluate how solvents affect the structure of the activated complex. The methyl-transfer equilibria (eq 3) used as the basis for determining $\beta_{lg}^{CH_3}$ were determined in sulfolane. This dipolar aprotic solvent is not expected to solvate the arenesulfonate anion well, as indicated by the rather large ρ-value of -2.94 for pK_{lg}.[13] However, since each side of the equilibrium equation has an arenesulfonate anion, and since the solvation of different arenesulfonates is thought to be comparable in a given solvent system,[23] then it is reasonable to expect that the equilibrium constants for methyl transfer should not vary greatly in different solvents since the net free-energy difference between the two sides of eq 3 is due to the electronic character of the arenesulfonate ions. If so, then $\beta_{lg}^{CH_3}$ values for a reaction determined in different solvents reflect the extent of leaving-group loss in each solvent and thus serve to illustrate how the solvent changes the transition state.

We applied this technique earlier to imine-forming eliminations and showed that the activated complex is profoundly influenced by the solvent.[12] Literature data suitable for comparison of many reactions are not common, but Table III indicates that the loss of leaving group in cyclobutyl arenesulfonates varies noticeably with solvent. More-polar solvents cause a decreased amount of leaving-group loss at the transition state. This is in accord with the ability of more-polar solvents to stabilize ionic products (upper left of Figure 4) and cause a parallel shift to an earlier transition state. Solvent effects need more systematic study in order to confirm these arguments.

The method developed here for transition-state mapping can be used in a variety of systems to accurately determine the extent of leaving-group loss in the activated complex. It may therefore prove to be a very useful mechanistic tool.

Acknowledgment. We thank the National Science Foundation (CHE-83-04000) for support of this work.

Registry No. p-$BrC_6H_4SO_2OMe$, 6213-85-0; m-$CF_3C_6H_4SO_2OMe$, 103439-12-9; m-$NO_2C_6H_4SO_2OMe$, 6214-21-7; p-$NO_2C_6H_4SO_2OMe$, 6214-20-6; 3,5-$(CF_3)_2C_6H_3SO_2OMe$, 103439-13-0.

---

(23) Kevill, D. N.; Kolwyck, K. C.; Shold, D. M.; Kim, C.-B. *J. Am. Chem. Soc.* **1973**, *95*, 6022.

(24) Morgan, M. S.; Cretcher, L. H. *J. Am. Chem. Soc.* **1948**, *70*, 375.

(25) Kevill, D. N.; Rissman, T. J. *J. Org. Chem.* **1985**, *50*, 3062.

True and False Chirality and Absolute Asymmetric Synthesis

L. D. Barron

Contribution from the Chemistry Department, The University, Glasgow G12 8QQ, United Kingdom. *Received November 12, 1985*

Abstract: The concept of true and false chirality is shown to provide a useful criterion for assessing physical systems proposed as agents for inducing absolute asymmetric synthesis. For example, false chirality is exhibited by colinear electric and magnetic fields, true chirality by a magnetic field parallel to the propagation direction of a light beam of arbitrary polarization. General arguments are presented which indicate that only a truly chiral influence can induce absolute asymmetric synthesis in a reaction mixture at thermodynamic equilibrium, but that true chirality is not necessarily required if equilibrium is not attained.

Absolute asymmetric synthesis refers to the use of an external physical influence to produce an enantiomeric excess in what would otherwise be a racemic product of a prochiral chemical reaction.[1] The subject still attracts much interest and controversy[2] and is also central to the problem of the origin of optical activity in nature.[3] One source of confusion is that there are physical systems which can exist in two distinct mirror-image states and yet are not truly chiral in the fundamental sense described later.

A finite cylindrical helix provides a good example of figures exhibiting what Pasteur[4] called *dissymmetry* if they possess structural forms which "differ only as an image in a mirror differs from the object which produces it". Pasteur's extension of the concept of dissymmetry to other aspects of the physical world[5,6] have had a considerable influence on attempts to induce absolute asymmetic synthesis. For example, he held that the combination of a rotation with a linear motion was expected to generate dissymmetry. And since optical rotation can be induced in any sample by a static magnetic field parallel to the light beam (the Faraday effect), he though that a magnetic field was also a source of dissymmetry. Pasteur also sensed a deep cosmic dissymmetry and so anticipated the modern discovery of parity violation in the weak interactions.[7]

Lord Kelvin[8] coined the work *chirality* as an attribute of a geometrical figure "if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself", and this word has now

---

(1) Morrison J. D.; Mosher, H. S. *Asymmetric Organic Reactions*; American Chemical Society: Washington, DC, 1976.

(2) Mason, S. F. *Int. Rev. Phys. Chem.* **1983**, *3*, 217.

(3) Mason, S. F. *Nature (London)* **1984**, *311*, 19.

(4) Pasteur, L. *Ann. Chim.* **1848**, *24*, 457.

(5) Pasteur, L. *Rev. Scientifique* **1884**, *7*, 2.

(6) Mason, S. F. *Molecular Optical Activity and the Chiral Discriminations*; Cambridge: Cambridge, 1982.

(7) Haldane, J. B. S. *Nature (London)* **1960**, *185*, 87.

(8) Lord Kelvin. *Baltimore Lectures*; C. J. Clay and Sons: London, 1904; p 619.

0002-7863/86/1508-5539$01.50/0

replaced dissymmetry in the literature of stereochemistry. However, the two words are not exactly synonymous in a wider context. Dissymmetry means the absence of certain symmetry elements, improper rotation axes in Pasteur's usage. Chirality is a more positive concept in that it refers to the possession of the attribute of handedness, which has a physical content: in the present context this is the ability to support time-even pseudoscalar observables (see below); in elementary particle physics chirality is defined as the eigenvalue of the Dirac matrix operator γ_5.[9] Although dissymmetry, and the associated enantiomorphism, is sufficient to guarantee chirality in a stationary object such as a finite helix, dissymmetric systems are not necessarily chiral when motion is involved. I have introduced the concept of "true" and "false" chirality to draw attention to this distinction[10-12] but do not intend that this should become standard nomenclature; rather, I suggest that the work "chiral" be reserved in future for systems that I call here truly chiral. It will be appreciated from what follows that true and false chirality correspond to "time-invariant and time-noninvariant dissymmetry (or enantiomorphism)".

We shall see that the combination of a rotation with a linear motion does indeed generate true chirality but that a magnetic field does not. Also, there are physical systems such as stationary rotating cones and colinear electric and magnetic fields that are dissymmetric in the sense of Pasteur's definition above and yet are not truly chiral.

True Chirality

A careful analysis of the natural and magnetic optical activity observables shows that the symmetry classifications of the two are quite different and leads to a more precise definition of a chiral system.[10-12] Thus the *natural* optical rotation observable is a *time-even pseudoscalar*, whereas the *magnetic* optical rotation observable is a *time-odd axial vector*. This means that the nature of the quantum states that can support natural optical rotation is quite different from that of the quantum states that can support magnetic optical rotation: the former have *mixed* parity but *definite* reversality and the latter *definite* parity but *mixed* reversality.[11] In general, the hallmark of a chiral system is that it can support time-even pseudoscalar observables.

However, it is not necessary to understand fully the meaning of these terms in order to follow the rest of this article. Initially, it is only necessary to appreciate that the parity operation P inverts the positions of all the particles in a system through an arbitrary space-fixed origin, and the classical time reversal operation T reverses the motions of all the particles in the system.

These considerations lead to the following definition:[10-12] *True chirality is possessed by systems that exist in two distinct enantiomeric states that are interconverted by space inversion but not by time reversal combined with any proper spatial rotation.*

The validity of this definition is reinforced by a consideration of the parity-violating weak neutral current interaction that lifts the degeneracy of enantiomeric chiral molecules:[13-18] only the space-inverted enantiomers of *truly* chiral systems show a parity-violating energy difference, so parity violation provides a cornerstone for the identification of true chirality.[12] An intriguing implication is that, since the space-inverted enantiomers of a chiral molecule are not strictly degenerate, they are not true enantiomers (the concept of enantiomers implies *precise* opposites). In fact the true enantiomer is the molecule with the opposite absolute configuration but composed of *anti*particles since this has exactly the same energy as the original.[10-12] However, these parity-violating energy differences are many orders of magnitude below current levels of detection, so for normal chemical purposes it is adequate to base the above definition on the conventional space-inverted enantiomers.

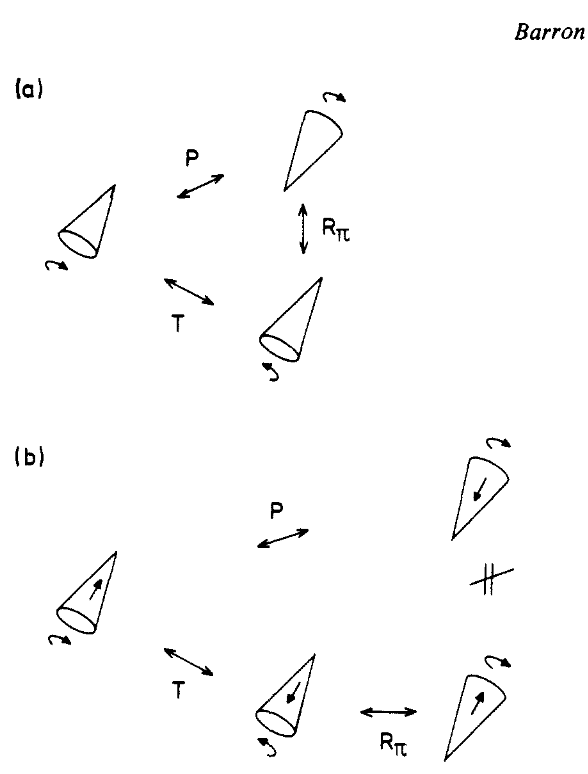


Figure 1. The effect of P, T, and R_π on (a) a *stationary* spinning cone and (b) a *translating* spinning cone.

It is easy to see that stationary objects, such as a finite helix, that are chiral according to the traditional stereochemical definition, are accommodated by the first part of this definition: space inversion is a more fundamental operation than the mirror reflection traditionally invoked but provides an equivalent result (space inversion is equivalent to a reflection in a plane followed by a rotation through 180° about an axis perpendicular to the plane); and the second part of the definition is irrelevant for a stationary object. However, the full definition is required to identify more subtle sources of chirality in which motion in an essential ingredient. A few pertinent examples will make this clear.

(a) Translating Spinning Cones, Spheres, Photons, and Electrons. Consider a cone spinning about its symmetry axis. Since space inversion P generates a version that is not superposable on the original (Figure 1a), it might be thought that this is a chiral system. However, the chirality is false because time reversal T followed by a rotation R_π through 180° about an axis perpendicular to the symmetry axis generates the same system as space inversion (Figure 1a). But if the spinning cone is also translating along the axis of spin, time reversal followed by the 180° rotation now generates a different system to that generated by space inversion (Figure 1b). Thus a *translating* spinning cone exhibits true chirality. In fact the translating spinning object does not need to be a cone. A sphere translating along the axis of spin also shows true chirality, which can be appreciated by looking at just the patterns of arrows in Figure 1b and ignoring the cone.

The photons in a circularly polarized light beam propagating as a plane wave are in spin angular momentum eigenstates characterized by a spin quantum number $s = 1$, with quantum numbers $m_s = +1$ and -1 corresponding to projections of the spin angular momentum vector parallel and antiparallel, respectively, to the propagation direction. The absence of states with $m_s = 0$ is connected with the fact that photons, being massless, have no rest frame and so always move at the velocity of light.[19]

---

(9) Sakurai, J. J. *Invariance Principles and Elementary Particles*; Princeton: Princeton, 1964.

(10) Barron, L. D. *Mol. Phys.* **1981**, *43*, 1395.

(11) Barron, L. D. *Molecular Light Scattering and Optical Activity*; Cambridge: Cambridge, 1982.

(12) Barron, L. D. *Chem. Phys. Lett.* **1986**, *123*, 423.

(13) Rein, D. W. *J. Mol. Evol.* **1974**, *4*, 15.

(14) Letokhov, V. *Phys. Lett.* **1975**, *53A*, 275.

(15) Zel'dovich, B. Ya., Saakyan, D. B.; Sobel'man, I. I. *Sov. Phys. JETP Lett.* **1977**, *25*, 95.

(16) Harris, R. A.; Stodolsky, L. *Phys. Lett.* **1978**, *78B*, 313.

(17) Hegstrom, R. A.; Rein, D. W.; Sandars, P. G. H. *J. Chem. Phys.* **1980**, *73*, 2329.

(18) Mason, S. F.; Tranter, G. E. *Mol. Phys.* **1984**, *53*, 1091.

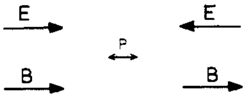
(19) Gottfried, K.; Weisskopf, V. F. *Concepts of Particles Physics*; Clarendon Press: Oxford, 1984; Vol. 1.

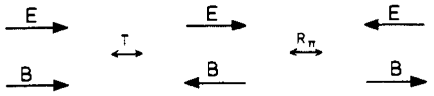
Considerations analogous to those given above for a translating spinning sphere then show that a circularly polarized photon exhibits true chirality.

The case of a spinning electron ($s = {}^1/_2$, $m_s = \pm{}^1/_2$) is somewhat different because, unlike photons, electrons have rest mass. It is clear that, whereas a *stationary* spinning electron is not a chiral system, an electron translating with its spin projection parallel or antiparallel to the propagation direction exhibits true chirality. These considerations expose a link between chirality and special relativity, because the chirality that an observer perceives in a spinning electron depends on the relative motions of the observer and the electron. Indeed, this relativistic aspect of chirality is a central feature of modern elementary particle theory, especially in relation to the weak interactions,[19] and is associated with the very existence of mass.[20]

(b) Electric and Magnetic Fields. It is clear that neither a static uniform electric or magnetic field constitutes a truly chiral influence. A static electric field **E** is a time-even polar vector, so although its direction is reversed by P, a rotation through 180° restores the original sense. A static magnetic field **B** is a time-odd axial vector: this means that, although it is not affected by P, its direction is reversed by T, and a rotation through 180° again restores the original. Likewise, time-dependent uniform electric and magnetic fields are not truly chiral. But if the fields are nonuniform, true chirality becomes a possibility for certain configurations.

Curie[21] appreciated that a uniform magnetic field did not generate spatial dissymmetry but pointed out that colinear elecric and magnetic fields did since one is a polar vector and the other an axial vector. Thus parallel and antiparallel arrangements are enantiomeric in that they are interconverted by space inversion and are not superposable However, **E** is time-even and **B** is time-odd, so they are also interconverted by time reversal combined with a rotation through 180° The apparent chirality here is therefore *false*. Zocher and Török[22] also recognized the flaw in Curie's suggestion: they called the combination of electric and magnetic fields with parallel lines of force a time-antisymmetric enantiomorphism and said that it does not permit a time-symmetric optical activity.





On the other hand, a uniform magnetic field parallel to the propagation vector **k** of a light beam of arbitrary polarization constitutes a truly chiral influence and can generate a new range of phenomena such as magneto-chiral birefringence and dichroism.[23-26] (Parallel and antiparallel arrangements of **B** and **k** are true chiral enantiomers because they cannot be interconverted by time reversal since **k**, unlike **E**, is time-odd).

Absolute Asymmetric Synthesis

We now apply the definition of a truly chiral system given above to assess the various physical influences that have been proposed to induce absolute asymmetric synthesis and to review the associated controversies. The implications are discussed at the end.

(a) Circularly Polarized Radiation and Spin-Polarized Electrons. It was shown above that a circularly polarized photon exhibits true chirality, and following Le Bel's original suggestion in 1874, many examples of the use of circularly polarized electromagnetic radiation as a chiral influence on chemical systems are now known.[1-3,6] An interesting variant has been suggested in the form of circularly polarized radiofrequency radiation to partially resolve racemic fluids by way of the hydrodynamic "propeller effect".[27] It is well-known that an arbitrary chiral body rotating about a fixed axis in a viscous medium is affected by a translational force. Since an electric field applied to a fluid will partially orient the constituent molecules (assuming they are dipolar), the rotating electric field vector of a circularly polarized radiofrequency field will induce angular velocity in the molecules, thereby inducing equal translational forces in opposite directions on the two enantiomers. However, the radiofrequency field is not in fact acting here as a chiral influence since only the circular component of its motion is involved.

Translating spin-polarized electrons also exhibit true chirality and have been much discussed as a possible sources of biological homochirality. For example, spin-polarized electrons emitted in the β-decay of nucleides can give rise to enantio-differentiating radiolysis of racemic mixtures or to the corresponding photolysis by the circularly polarized electromagnetic radiation arising from the progressive retardation of the spin-polarized electron.[28-30]

(b) Electric and Magnetic Fields. In 1975, Gerike claimed to have achieved absolute asymmetric synthesis by performing reactions such as the epoxidation of isophorone in the presence of simultaneous electric and magnetic fields.[31] Nonzero optical rotations were observed in the resulting reaction mixtures for both static and time-dependent uniform fields. Parallel and antiparallel field combinatins seemed to cause opposite rotations.

These observations are puzzling because, as shown above, no combination of a uniform electric and a uniform magnetic field can constitute a truly chiral influence. In fact several years previously, de Gennes[32] had presented a theorem stating the impossibility of asymmetric synthesis in a static electric and magnetic field that was based on the invariance of the Hamiltonian of a molecule in such fields under space inversion and time reversal. Using similar arguments, Mead et al.[33] concluded that "...a simultaneous application of uniform constant electric and magnetic fields cannot affect the equality of the equilibrium enantiomeric populations in a racemic reaction mixture. Hence, whatever the sources of the reported rotations, they cannot have had their origins in uniform applied fields if the reactions had gone to completion". Rhodes and Dougherty[34] extended the argument by pointing out that the conclusions of de Gennes and Mead et al. apply only to reacting systems in a state of complete thermodynamic equilibrium and so are not relevant for reactions that are kinetically, rather than thermodynamically, controlled. However, Mead and Moscowitz[35] found these arguments unconvincing and claimed to show that such kinetic effects are required to be zero by the condition of detailed balancing. De Gennes has returned to the subject[36] and appears to support Rhodes and Dougherty. See also ref 37.

Electric and magnetic fields have been widely discussed as possible sources of optical activity in nature, but none of the suggested arrangements (at least those involving uniform fields) shows true chirality.[38-40]

---

(20) Okun, L. B. *Particle Physics*; Harwood Academic Publishers: Chur, 1985.

(21) Curie, P. *J. Phys. (Paris)* **1894**, *3*(3), 393.

(22) Zocher, H.; Török, C. *Proc. Natl. Acad. Sci. U.S.A.* **1953**, *39*, 681.

(23) Baranova, N. B.; Zel'dovich, B. Ya. *Mol. Phys.* **1979**, *38*, 1085.

(24) Wagnière, G.; Meier, A. *Chem. Phys. Lett.* **1982**, *93*, 78.

(25) Barron, L. D.; Vrbancich, J. *Mol. Phys.* **1984**, *51*, 715.

(26) Wagnière, G. *Z. Naturforsch* **1984**, *39a*, 254.

(27) Baranova, N. B.; Zel'dovich, B. Ya. *Chem. Phys. Lett.* **1978**, *57*, 435.

(28) Ulbricht, T. L. V. *Quart. Rev. Chem. Soc.* **1959**, *13*, 48.

(29) Ulbricht, T. L. V. *Origins Life* **1981**, *11*, 35.

(30) Hegstrom, R. A. *Nature (London)* **1982**, *297*, 643.

(31) Gerike, P. *Naturwissenschaften* **1975**, *62*, 39.

(32) de Gennes, P. G. *C. R. Hebd. Seances Acad. Sci., Ser. B* **1970**, *270*, 891.

(33) Mead, C. A.; Moscowitz, A.; Wynberg, H.; Meuwese, F. *Tetrahedron Lett.* **1977**, 1063.

(34) Rhodes, W.; Dougherty, R. C. *J. Am. Chem. Soc.* **1978**, *100*, 6247.

(35) Mead, C. A.; Moscowitz, A. *J. Am. Chem. Soc.* **1980**, *102*, 7301.

(36) de Gennes, P. G. In *Symmetry and Broken Symmetry in Condensed Matter Physics*; Boccara, N.; Ed.; Editions IDSET: Paris, 1981; p 1.

(37) de Reyff, Chr. *J. Chim. Phys. Phys.-Chim. Biol.* **1983**, *80*, 563.

(38) Mörtberg, L. In *Orgins of Optical Activity in Nature*; Walker, D. C.; Ed.; Elsevier: Amsterdam, 1979; p 101.

(39) Kovacs, K. L.; Kesthelyi, L.; Goldanskii, V. J. *Origins Life* **1981**, *11*, 93.

(40) Thiemann, W. *Origins Life* **1984**, *14*, 421.

(c) Spinning Vessels and Gravity. Even more contentious than mixed electric and magnetic fields have been claims for absolute asymmetric synthesis in a "chiral gravitational field". Dougherty et al.[41-43] reported asymmetric synthesis of isophorone oxide from isophorone in a rapidly rotating vessel, with opposite senses of optical rotation resulting when the vessel is spun clockwise and anticlockwise about an axis perpendicular to the earth's surface but no optical rotation when the vessel is spun about an axis parallel to the earth's surface.

This situation is closely analogous to the case of electric and magnetic fields since here we have the time-odd axial angular momentum vector of the spinning vessel either parallel or antiparallel to the earth's gravitational field, itself a time-even polar vector. The physical influence therefore exhibits *false* chirality. Mead and Moscowitz[35] and Peres[44] criticized these claims, again using arguments based on the invariance of the Hamiltonian.

Similar experiments have been reported in which polymerizing amino acid solutions were stirred in a clockwise and an anticlockwise sense, and the resulting polymerized material was analysed for signs of stereoselectivity.[39] None was found.

A different controversy arose over the use of dissymmetric flow, induced in a conical swirl, to produce a slight enantiomeric excess during the synthesis of a cyanine dye.[45] Although there is no question here that the physical influence is truly chiral (rotation plus translation), it was suggested that the observed optical rotation was actually an artifact due to linear dichroism from accidentally oriented material.[46]

(d) Magneto-Chiral Effects. We saw above that a uniform static magnetic field parallel to the propagation direction of a light beam of arbitrary polarization constitutes a truly chiral influence. Reversing the relative directions of **B** and **k** generates the enantiomeric influence. Thus the early attempts to induce photochemical asymmetric synthesis by using *linearly* polarized light in the presence of an intense magnetic field[47,48] were well-founded, even though they were unsuccessful.

Wagnière and Meier[49] have suggested that these magneto-chiral effects are well worth considering as a source of chirality in molecular evolution because all that is required is a source of light of arbitrary polarization and a static magnetic field which is not perpendicular to the propagation direction.

Discussion

The concept of true and false chirality appears to provide a useful first criterion for assessing systems as candidates for inducing absolute asymmetric synthesis. The alternative approach based on considerations of the invariance properties of the Hamiltonian of a molecule in the presence of the influence[32,33,44] is based on similar fundamental arguments.

However, as demonstrated by the controversy surrounding the reports of absolute asymmetric synthesis in situations where the external influence exhibited false chirality, caution is required in reaching any definite conclusions based solely on whether or not the external influence is truly chiral. Such arguments are essentially applications of Neumann's principle[50-52] which, as reformulated by Curie,[21] states that no dissymmetry can manifest itself in a physical property which does not already exist in the system. But Neumann's principle is only valid in space-time for *static* properties, not for *dynamic* properties such as transport phenomena where a system is permanently in nonequilibrium but has reached a steady state.[51] More generally, Neumann's principle cannot be applied in space-time to a system in which the entropy is changing,[51] which is certainly the case for a reaction mixture that has not been allowed to reach thermodynamic equilibrium. More mundane reservations are that nonuniform fields or forces could be present, and the reacting species might be partially aligned on the walls of the reaction vessel.

A rather different reservation arises in connection with the application of the principle of detailed balancing to the problem.[35] Lifshitz and Pitaevskii[53] have pointed out that, for a system comprising resolved chiral molecules of just one enantiomer, *strict* detailed balancing does not obtain. This because the strict detailed balancing result is obtained by applying space inversion as well as time reversal to the system of colliding particles, which means that a completely different system is generated and so cannot be compared with the original. (See Sakurai[54] for a quantum-mechanical version of the strict detailed balancing result). However, for a system at equilibrium in which *equal numbers* of enantiomeric molecules are present, it appears to follow that strict detailed balancing *can* be invoked if each microscopic collision process between two molecules is balanced by the reverse process involving the *enantiomeric* molecules. Consider an achiral reactant molecule R producing a chiral product molecule M or its enantiomer M*

$$\mathrm{R} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{M}$$

$$\mathrm{R} \underset{k_b^*}{\overset{k_f^*}{\rightleftharpoons}} \mathrm{M}^*$$

Strict detailed balancing in the new sense defined above can be applied provided the reactions have reached equilibrium and $[\mathrm{M}] = [\mathrm{M}^*]$, which will be the case if the external influence is not truly chiral (so that M and M* have the same energy). This enables us to write

$$[\mathrm{R}]k_f = [\mathrm{M}^*]k_b^* = [\mathrm{M}]k_b^*$$

$$[\mathrm{R}^*]k_f^* = [\mathrm{M}]k_b$$

But since R is achiral we can also write $\mathrm{R} = \mathrm{R}^*$ and so obtain

$$k_f/k_f^* = k_b^*/k_b$$

Unlike the result of Mead and Moscowitz[35] ($k_f = k_f^*$ and $k_b = k_b^*$) obtained by using the conventional interpretation of the principle of detailed balancing that disregards whether or not chiral molecules are involved, this allows a difference in rate constants for enantiomeric processes and so does not rule out absolute asymmetric synthesis induced by a falsely chiral influence in a reaction under kinetic control (only *strict* detailed balancing is valid in the presence of a time-noninvariant dissymmetric influence: time reversal alone generates the enantiomeric influence and so is not a symmetry operation for the complete system).

In conclusion, it appears that only a truly chiral influence can induce absolute asymmetric synthesis in a reaction mixture which is isotropic in the absence of the influence and which has been allowed to reach thermodynamic equilibrium. But for reactions under kinetic control, false chirality might suffice.

Acknowledgment. I thank Dr. A. Cooper and C. J. Johnston for valuable discussions and a referee for helpful criticisms.

---

(41) Dougherty, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 380.

(42) Edwards, D.; Cooper, K.; Dougherty, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 381.

(43) Dougherty, R. C. *Orgins Life* **1981**, *11*, 71.

(44) Peres, A. *J. Am. Chem. Soc.* **1980**, *102*, 7390.

(45) Honda, C.; Hada, H. *Tetrahedron Lett.* **1976**, *3*, 177.

(46) Nordén, B. *J. Phys. Chem.* **1978**, *82*, 744.

(47) Radulescu, D.; Moga, J. *Bull. Soc. Chim. Romania* **1939**, *1*, 2.

(48) Pracejus, H. *Top. Curr. Chem.* **1967**, *8*, 54.

(49) Wagnière, G.; Meier, A. *Experientia* **1983**, *39*, 1090.

(50) Neumann, F. E. *Vorlesungen über die Theorie Elastizität der festen Korper und des Lichtäthers*; Teubner: Leipzig, 1885.

(51) Birss, R. R. *Symmetry and Magnetism*; North-Holland: Amsterdam, 1966.

(52) Shubnikov, A. V.; Koptsik, V. A. *Symmetry in Science and Art*; Plenum Press: New York, 1974.

(53) Lifshitz, E. M.; Pitaevskii, L. P. *Physical Kinetics*; Pergamon Press: Oxford, 1981; p 6.

(54) Sakurai, J. J. *Modern Quantum Mechanics*; Benjamin/Cummings: Menlo Park, CA, 1985; p 422.