

results of this measurement are also shown in Figure 1. As the data show, the lifetime of singlet oxygen varies in a very simple fashion with the percent benzene and the lifetime for any mixture can be computed simply from the solvent composition and the lifetimes in each of the pure solvents. We, therefore, conclude that the anomalous behavior of the sensitized photooxygenation of anthracene cannot be attributed to anomalies in the lifetime of singlet oxygen. Rather, we conclude that it is the rate of reaction of singlet oxygen with the acceptor which is responsible for the anomaly. In this regard we should point out that only 1% methanol was needed to solubilize the MB in the 25 mol % benzene solution, whereas 1.7% methanol had to be added to the 7 and 60 mol % benzene solutions to dissolve the MB. Even then, we noticed spectral evidence for the dimerization of the MB and precipitation after the solutions had been exposed to light for say 15 min. This may or may not be relevant, but it suggests that the photooxygenation reaction should be reinvestigated.

The results which we have presented in this paper show that there are no important discrepancies between theory

and experiment with regard to the variation of the lifetime of singlet oxygen with solvent or temperature. There is a small temperature dependence to the decay of a singlet oxygen in CHCl_3 , but a number of small effects may account for this. We were able to find some solvent systems in which the lifetime of singlet oxygen approaches 1 msec, but we were unable to discover any "super solvent". The anomalous behavior of benzene- CS_2 mixtures as a solvent system for carrying out sensitized photooxygen reactions is shown not to be due to anomalies in the singlet oxygen lifetime.

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The Chemical Dynamics of Symmetric and Asymmetric Reaction Coordinates

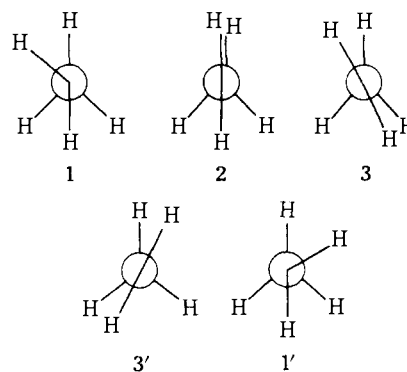
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Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada, the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada, and the Laboratorio C.N.R. dei Composti del Carbonio contenenti eteroatomi, Ozzano E., Bologna, Italy. Received June 4, 1974

Abstract: The question has been posed as to whether a rotation-inversion process that results in the interconversion of two enantiomeric or identical species can be described by a unique asymmetric reaction coordinate. It is shown that the methods of classical kinetics and reaction dynamics are unable to solve this problem rigorously. A quantum mechanical analysis, employing the symmetry properties of the reaction surface, has therefore been developed, and applied to two cases: case I, in which one transition state separates reagents and products; and case II, in which a stable intermediate appears on the reaction coordinate. It is found that no unique path exists for the case I situation, *i.e.*, that all asymmetric reaction coordinates are indistinguishable. This conclusion holds under equilibrium conditions, under nonequilibrium conditions, and under photochemical excitation. The analysis developed to describe the equilibrium situation of case I constitutes a quantum mechanical demonstration of the principle of microscopic reversibility. For the case II situation, it is found that distinguishable asymmetric paths can exist under nonequilibrium conditions. These are related to each other in a diastereomeric sense, in contrast to case I, in which various reaction paths differ in an enantiomeric sense.

In the course of our theoretical studies³ of the properties of systems of type L-MH_2 , in which the ligand L is CH_3 , CH_2^- , CH_2F , NH_2 , PH_2 , OH , SH , SHO , and SHO_2 , and M is a tricoordinate atom such as C^- , N or P, we became interested in the topomerization⁴ of these species. To treat this problem, it was necessary to obtain energy surfaces corresponding to rotation about the L-M bond and pyramidal inversion at the atom M. Topomerization then refers to the process in which structures corresponding to energy minima of such surfaces interconvert. For the case of $^-\text{CH}_2\text{CH}_3$, the rotation-inversion surface associated with the interconversion of the two minima **1** and **1'** was found to have the form shown in Figure 1. It is evident that there exist three modes of topomerization, a symmetric mode from **1** via **2** to **1'**, and two asymmetric modes from **1** via **3** or **3'** to **1'**.

Subsequently it occurred to us that the initial portions of the two asymmetric reaction paths could be sufficiently dif-



ferent to result in the preference of one asymmetric reaction path over the other. Thus, if the path **1** via **3** to **1'** were to be preferred in the forward process, then the path **1'** via **3'** to **1**

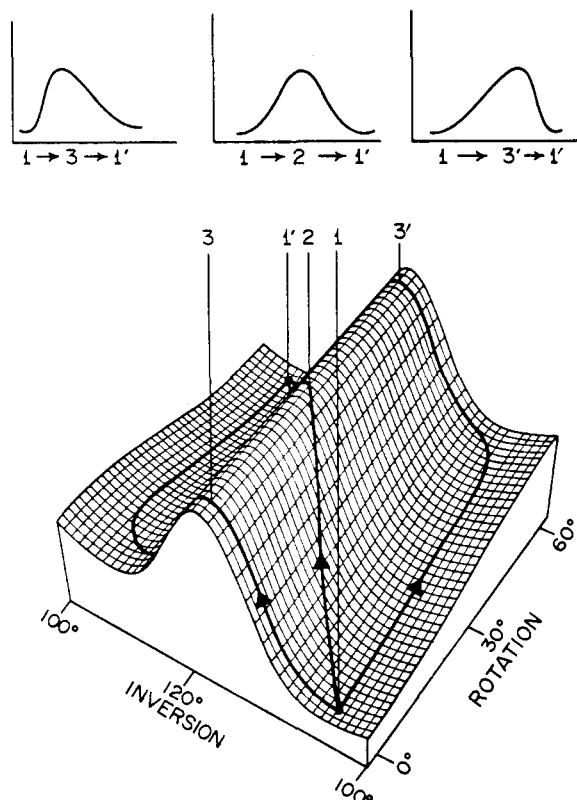


Figure 1. The computed^{3d} rotation-inversion surface of ethyl carbanion, and the symmetric ($1 \rightarrow 2 \rightarrow 1'$) and two enantiomeric asymmetric ($1 \rightarrow 3 \rightarrow 1'$ and $1 \rightarrow 3' \rightarrow 1'$) reaction paths for the interconversion of structures corresponding to the energy minima of this surface (see text for the structures of 1, 2, 3, 3').

would be preferred in the reverse process. This constitutes a chiral topomerization, *i.e.*, $1 \rightarrow 3 \rightarrow 1' \rightarrow 3' \rightarrow 1 \rightarrow \text{etc.}$, by which we mean topomerization proceeding through chiral states exclusively.

Reference to Figure 1 reveals that all pathways are chiral except those which proceed *via* 2, the "achiral point" on the surface. Such reaction paths, proceeding *via* the achiral point, have been discussed recently by McIver⁵ in terms of the symmetry properties of the transition vector. However, chiral topomerization cannot be treated in this way because the transition state lacks the necessary symmetry elements. Moreover, the essential question, of whether a reaction can proceed at different rates along paths that are enantiomeric, cannot be solved by static geometrical considerations alone.

What is described above is, therefore, an *asymmetric reaction*, *i.e.*, a reaction that possesses a set of enantiomeric reaction paths and proceeds at different rates along paths that are enantiomeric. It is well known that many chemical reactions exist in which there is a choice between a symmetrical and various asymmetrical reaction paths.^{6,7} However, to our knowledge there has been no attempt to determine whether a distinction can be made between various asymmetric paths (*i.e.*, whether the conversion from 1 to 1' proceeds preferentially *via* 3 or 3'), presumably because such thinking would appear to require a violation of the principle of microscopic reversibility.¹² Nevertheless, the possibility that chiral topomerization (starting, for example, with 1) might occur preferentially *via* one enantiomeric set of pathways (symbolized by 3 or 3') rather than the other (3' or 3) seemed sufficiently intriguing to warrant detailed investigation.¹³ Two cases have been considered. In the first (case I), one transition state separates enantiomeric or identical

structures. In the second (case II), the reaction coordinate includes a stable intermediate.

Results and Discussion

Classical Treatment of Case I. The relative rates of reaction along the two asymmetric paths can be expressed in terms of transition state theory. The rate constant is given by¹⁴

$$\text{rate constant} = K \frac{kT}{h} \frac{Q^*}{Q_{\text{reag}}^0} \exp\left(-\frac{\epsilon^* - \epsilon_{\text{reag}}^0}{kT}\right) \quad (1)$$

where ϵ^* and ϵ_{reag}^0 are the zero point vibrational energies of the transition state and reagents, respectively, k is Boltzmann's constant, h is Planck's constant, T is the temperature, K is the transmission coefficient, Q_{reag}^0 is the partition function of the reagents, and Q^* is the partition function of the transition state, not including the "unstable" degree of freedom.

We now examine the ratio of the rate constants for two enantiomeric paths (*e.g.*, *via* 3 and 3').

$$\begin{aligned} \frac{\text{rate constant via 3}}{\text{rate constant via 3}'} &= \\ &= \frac{K_3 \frac{kT}{h} \frac{Q_3^*}{Q_{\text{reag}}^0} \exp\left(-\frac{\epsilon_3^* - \epsilon_{\text{reag}}^0}{kT}\right)}{K_{3'} \frac{kT}{h} \frac{Q_{3'}^*}{Q_{\text{reag}}^0} \exp\left(-\frac{\epsilon_{3'}^* - \epsilon_{\text{reag}}^0}{kT}\right)} \\ &= K_3/K_{3'} \quad (2) \end{aligned}$$

Since the transition states are enantiomeric, the Q^* 's are equal, as are the ϵ^* 's. Therefore, according to transition state theory, the ratio of the two rates is equal to the ratio of the two transmission coefficients. Since the transmission coefficients depend upon the detailed shape of the surface about the transition state, the problem has thus not been solved but, rather, restated in a different form. It follows that any rate difference associated with enantiomeric paths must be caused by the dynamics of the reaction and not by the energetics.

The Dynamics of Case I. The simplest manner in which the dynamics of a reaction can be investigated involves the solution of the classical equations of motion for a molecule under the influence of a quantum mechanically derived potential energy surface.¹⁵ Unfortunately, the equations of motion of a molecule on an asymmetric reaction surface cannot, in general, be solved analytically in closed form. Consequently, for an arbitrary distribution of molecules, *no general proof, based on classical dynamics, can be given for the existence or nonexistence of a dynamically-induced difference in the rates along asymmetric reaction coordinates.*

To gain some insight into the behavior of a specific example, a numerical analysis was performed of the dynamics associated with the arbitrary reaction surface

$$V = a(x^4 + y^4) - b(2x^2 + 4y^2 - xy) \quad (3)$$

$$a = 1; \quad b = 1$$

wherein V has the units of energy and x and y are coordinates that define the surface, *e.g.*, differing modes of vibration. As shown in Figure 2, such a surface has the required properties of possessing two identical (or enantiomeric) minima connected by enantiomeric reaction paths.

The equations of motion were integrated numerically using a fifth-order Runge-Kutta procedure. An acceptance-rejection technique was used to select starting points with a Boltzmann distribution in their total energy, from points having a uniform random distribution in position and velocity. Trajectories were computed only for those points having

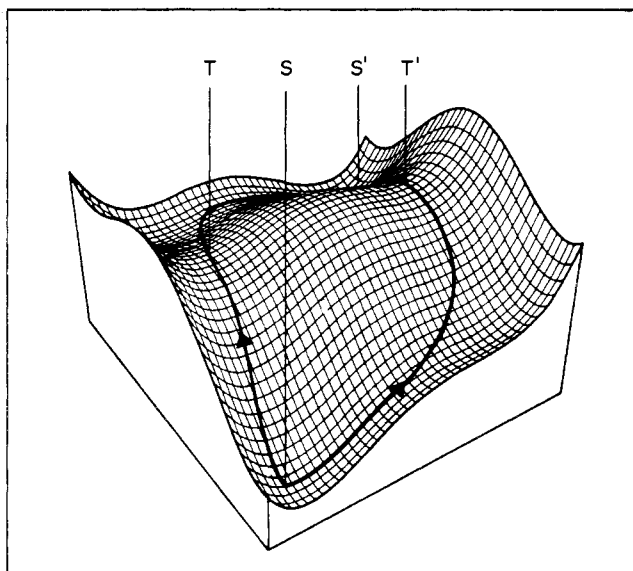


Figure 2. A model reaction surface (eq 3) which illustrates the interconversion of two minima S and S' via enantiomeric reaction paths proceeding over the enantiomeric transition states T and T'.

sufficient energy to cross the saddle points. Integration was carried out for a time corresponding to about 7–10 vibrational periods for a particle in one of the minima. A reaction was considered to have occurred when the point crossed the x axis (*i.e.*, $y = 0$). The number of crossings having a shallow ascent and a steep descent was compared to the number of crossings having a steep ascent and a shallow descent. At the three different temperatures used in the Boltzmann distribution, no significant difference could be detected at the 95% confidence level. Because of the relatively small number of reactions that occurred, differences of less than 10% in the rates could not be resolved. Clearly a general and more precise method for determination of the ratio of the rates must be found.

Quantum Mechanical Treatment of Case I. A full quantum mechanical treatment of topomerization on an asymmetric reaction surface includes, in addition to the non-classical phenomena such as tunnelling, the energetics and dynamics of the problem.¹⁶ A solution of the two-dimensional time-dependent Schrödinger equation for the i th molecule in a real scalar potential $V(\mathbf{r})$ describing the rotation-inversion surface

$$-(\hbar^2/2m)\nabla^2\psi^i + V(\mathbf{r})\psi^i = i\hbar(\partial\psi^i/\partial t) \quad (4)$$

is given in a series expansion

$$\psi^i = \sum_n C_n^i \exp(-i\epsilon_n t/\hbar) \phi_n \quad (5)$$

in terms of the solutions of the time-independent Schrödinger equation

$$-(\hbar^2/2m)\nabla^2\phi_n + V(\mathbf{r})\phi_n = \epsilon_n\phi_n \quad (6)$$

with the eigenfunctions ϕ taken to be real. The square of the coefficients C_n^i denotes the probability of finding the system in state n , $P_n = |C_n^i|^2$. For convenience, a Boltzmann distribution is chosen:

$$P_n = Q^{-1} \exp(-\epsilon_n/kT) \quad (7)$$

$$Q = \sum_n \exp(-\epsilon_n/kT) \quad (7)$$

$$C_n^i = \sqrt{P_n} \exp(i\delta_n^i) \quad (8)$$

The phase factors δ_n^i are chosen to satisfy the initial conditions.

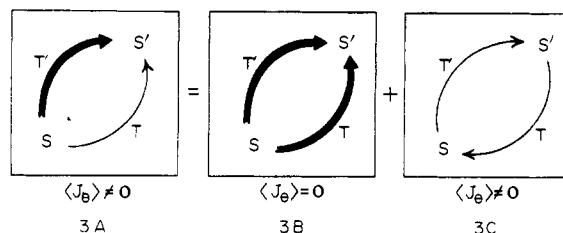


Figure 3. Decomposition of an unsymmetrical flow of reagents to products ($S \rightarrow T' \rightarrow S'$ preferred over $S \rightarrow T \rightarrow S'$) into a symmetrical flow ($S \rightarrow T' \rightarrow S' = S \rightarrow T \rightarrow S'$) and an angular flow ($S \rightarrow T' \rightarrow S' \rightarrow T \rightarrow S$). The symbols S, S', T, T' refer to those shown in Figure 2.

The potential $V(\mathbf{r})$ represents the arbitrary reaction $S \rightleftharpoons T \rightleftharpoons S' \rightleftharpoons T'$ (Figure 2), in which S and S' are enantiomeric minima and T and T' are enantiomeric transition states. Because the surface has C_2 symmetry about the midpoint, it is possible to divide the eigenfunctions into A and B symmetry types and, eventually, to examine various integrals involving functions that belong to these two irreducible representations.

Any net flow of reagents to products ($S \rightarrow S'$) can be determined from the sum over all molecules of the expectation value of the current \mathbf{J} for each molecule. The components may be examined either in Cartesian coordinates, *i.e.*, $\langle \hat{J}_x \rangle$ and $\langle \hat{J}_y \rangle$ or in polar coordinates, *i.e.*, $\langle \hat{J}_R \rangle$ and $\langle \hat{J}_\theta \rangle$. Examination of a hypothetical unsymmetrical flow of reagents to products (Figure 3A) shows that it can be decomposed into a symmetrical flow (B symmetry) of reagents to products (Figure 3B) and an angular circulation (A symmetry) of reagents and products (Figure 3C). It is then evident that a net circulation is characterized by a nonzero $\langle \hat{J}_\theta \rangle$. In addition, the operator \hat{J}_θ can give rise to nonzero integrals only if it connects functions having the same symmetry (both A or both B).

For each molecule, the density function $\rho^i(\mathbf{r}, t)$ and the circulation $\langle \hat{J}_\theta^i \rangle$ are given by

$$\rho^i(\mathbf{r}, t) = \sum_{m,n} \rho_{m,n}^i(\mathbf{r}, t) \quad (9)$$

$$\rho_{m,n}^i(\mathbf{r}, t) = \text{Re} \{ B_{m,n} D_{m,n}^i E_{m,n}(t) \phi_m(\mathbf{r}) \phi_n(\mathbf{r}) \} \quad (10)$$

where

$$B_{m,n} = \exp\left(-\frac{\epsilon_m + \epsilon_n}{2kT}\right) / Q \quad (11)$$

(the Boltzmann weighing factor)

$$D_{m,n}^i = \exp\{-i(\delta_m^i - \delta_n^i)\} \quad (12)$$

$$E_{m,n}(t) = \exp\left\{\frac{i}{\hbar}(\epsilon_m - \epsilon_n)t\right\} \quad (13)$$

and

$$\langle \hat{J}_\theta^i \rangle = \sum_{m,n} L_{m,n}^i \quad (14)$$

where

$$L_{m,n}^i = \text{Re} \{ B_{m,n} D_{m,n}^i E_{m,n}(t) L_{m,n} \} \quad (15)$$

$$L_{m,n} = \left\langle \phi_m \left| \frac{\hbar}{im} \left(\frac{x}{r} \frac{\partial}{\partial y} - \frac{y}{r} \frac{\partial}{\partial x} \right) \right| \phi_n \right\rangle \quad (16)$$

$$= \langle \phi_m | \hat{J}_\theta^i | \phi_n \rangle$$

where the midpoint of the surface is taken as the origin for \mathbf{r} . Macroscopic observables are found by summing over all molecules. Thus

$$D_{m,n} = \sum_{i=1}^N D_{m,n}^i \quad (17)$$

The relative phases of the various molecular wavefunctions are determined by the initial conditions. At equilibrium, we may invoke the postulate of random phases¹⁷ (*i.e.*, the phases δ_m^i are uniformly randomly distributed).

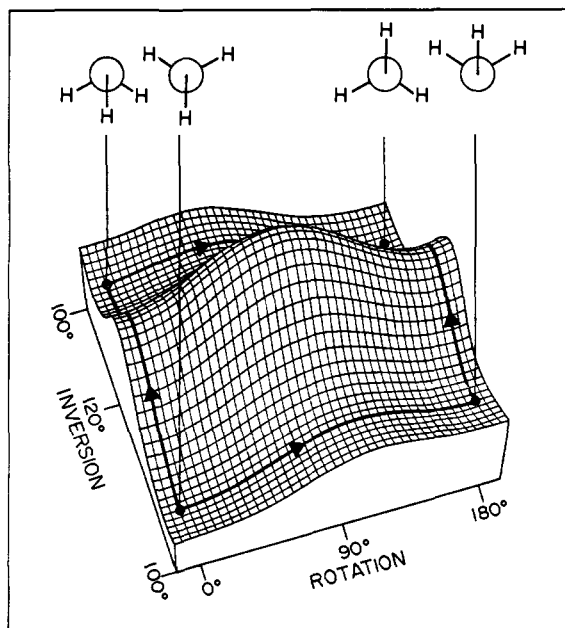


Figure 4. The energy surface of CH_2OH^- corresponding to rotation about the C-O bond and inversion of the carbon valence angles.

$$D_{m,n} = \sum_{i=1}^N D_{m,n}^i = 0 \quad m \neq n$$

$$= N \quad m = n \quad (18)$$

Therefore, only the diagonal elements contribute to the expectation values at equilibrium. However, using eq 18 to simplify eq 14-16 gives

$$\langle \hat{J}_\theta \rangle = \sum_m N B_{m,m} \text{Re}\{L_{m,m}\} \equiv 0 \quad (19)$$

because $L_{m,m}$ is purely imaginary (recalling that the ϕ_m 's are real, and \hat{J}_θ is imaginary).

Therefore, at *thermal equilibrium*, there can be no net unsymmetrical flow of reagents to products. This is the principle of microscopic reversibility (PMR). However, the PMR cannot be invoked for the more interesting case in which no equilibrium exists between reagents and products.

When reagents initially predominate over products, there must be a density function having a mixture of A and B symmetry.

$$\rho(\mathbf{r}, t) = \text{Re}\left\{ \sum_{m,n} B_{m,n}(t) D_{m,n} \phi_m \phi_n \right\} \quad (20)$$

This will be possible if and only if some elements of $D_{m,n}$ are nonzero where m and n refer to functions of different symmetry type. We assume that the reagents and products are the only stable species. Then, since no stable intermediates exist on the reaction path from reagents to products, no special phase relation can exist between ϕ_m and ϕ_n of the same symmetry. Hence summing over all of the molecules, we find that, for m and n of the same symmetry, the $D_{m,n}$ are zero.

$$D_{m,n} \neq 0 \text{ for } \phi_m \text{ and } \phi_n \text{ of different symmetry}$$

$$= 0 \text{ for } \phi_m \text{ and } \phi_n \text{ of the same symmetry } (m \neq n) \quad (21)$$

If we now examine $\langle \hat{J}_\theta \rangle$, and recall that \hat{J}_θ is of A symmetry, we find that

$$L_{m,n} = \langle \phi_m | \hat{J}_\theta | \phi_n \rangle = 0 \quad (22)$$

when m and n refer to functions of different symmetry. Thus, combining the results of eq 21 and 22

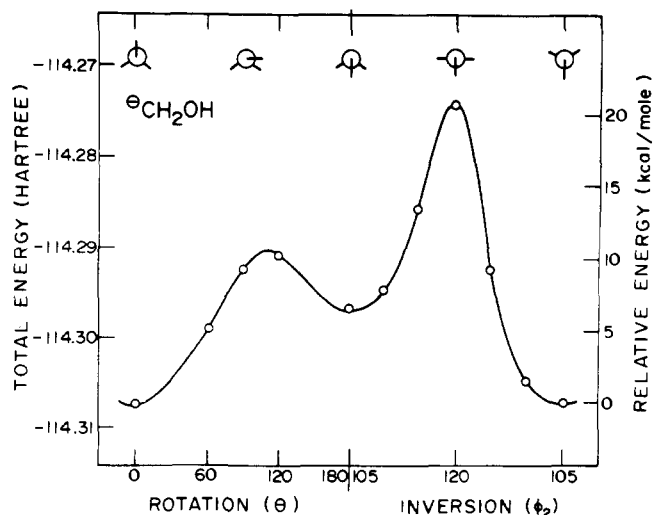


Figure 5. A reaction coordinate illustrating the topomerization of CH_2OH^- ($Y \rightleftharpoons Y$) via a rotation-inversion pathway.

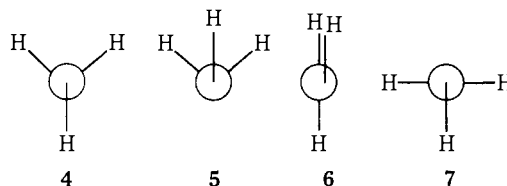
$$\langle \hat{J}_\theta \rangle = 0 \quad (23)$$

Therefore, for the nonequilibrium case as well, no net unsymmetrical flow of reagents to products can occur.

If the system were now to be subjected to an additional time-dependent potential such as thermal or photochemical excitation, the coefficients C_n^i in general become time dependent. However, $B_{m,m} = |C_{m,m}|^2$ remain real, so that $L_{m,m}^i$ remain zero. Hence the above conclusions are valid not only for tunnelling processes that go through the barrier but also for thermally and photochemically initiated processes that go over the transition state.¹⁸

The quantum mechanical treatment of case I has therefore demonstrated that *the rates of interconversion of enantiomers are the same* under equilibrium conditions, under nonequilibrium conditions, and under photochemical excitation for all pairs of enantiomeric reaction paths. Referring to Figure 1, this means that the process $1 \rightarrow 3 \rightarrow 1'$ is indistinguishable from the process $1 \rightarrow 3' \rightarrow 1'$.

Quantum Mechanical Treatment of Case II. The above treatment can be extended without difficulty to the case in which the reaction coordinate includes a stable intermediate. An example of this situation is found in the rotation-inversion behavior of CH_2OH^- . Figure 4 shows a perspective view of the energy surface of this anion³⁸ corresponding to rotation about the C-O bond and inversion of the carbon valence angles. There are four minima and one maximum on this surface. The lower minima correspond to the Y conformation 4 and the higher minima to the W conformation 5. The maximum corresponds to the I conformation 6, and



is 13 kcal/mol higher than the higher of the two saddle points associated with pure rotation or pure inversion. Consequently, the symmetric path via 6 is disfavored energetically with respect to reaction paths, proceeding around the maximum of the surface, in which the T conformation 7 is the highest transition state. One such path is shown in Figure 5 and illustrates the interconversion of two Y conformations via the W conformation as a stable intermediate; this reaction coordinate corresponds to the case II situation.

Equations 18 and 19 hold for case II at thermal equilibrium, so that, under these conditions, the conclusion is the same as before. Once equilibrium has been established between Y and W, or, in the general case, between the energy minima of the reaction coordinate, no asymmetric flow of reagents to products is possible and the principle of microscopic reversibility applies. This means that, at equilibrium, the left-to-right and right-to-left directions shown in Figure 5 are experimentally indistinguishable.

However, under nonequilibrium conditions, the postulate of random phases can no longer be invoked for ϕ_m and ϕ_n of the same symmetry, as was done in eq 18. Certain non-random phase relations must exist between functions of the same symmetry in order to permit reagents to be distinguished from intermediates and products. Hence, for some ϕ_m and ϕ_n of the same symmetry

$$D_{m,n} \neq 0 \quad (24)$$

and, since \hat{J}_θ is of A symmetry,

$$\langle \hat{J}_\theta \rangle \neq 0 \quad (25)$$

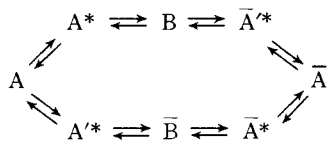
Equation 25 also applies to thermally and photochemically excited systems, because there are no symmetry arguments which require the $B_{m,n}$ to vanish.

The meaning of these results is that there is a condition in which an asymmetric flow of reagents to products is possible. The condition is twofold: *a stable intermediate must exist between reagent and product; and it must be possible to achieve a nonequilibrium distribution of the components (reagent, product, intermediates) in the system.* If the reagent and product are enantiomeric, the intermediate must necessarily be a diastereomeric species.

Conclusions

The interconversion of a species A and its enantiomer \bar{A} , via a single and unique asymmetric transition state, has been found to be impossible because a *kinetically indistinguishable* enantiomeric path must also exist. For a reaction to proceed at different initial rates along two reaction paths having enantiomeric transition states, it is necessary that the initial portions of these paths be diastereomeric. For the case in which interconversion of A and \bar{A} involves an intermediate (case II), this requirement then demands the presence on the reaction path of two enantiomeric intermediates which are diastereomers of A and \bar{A} (e.g., Figure 4). A kinetic model which embodies this requirement is illustrated in Scheme I.

Scheme I



This shows the enantiomerization of A to \bar{A} to proceed via B or \bar{B} , where B and \bar{B} are enantiomeric intermediates in the process, and are diastereomers of A and \bar{A} . Transi-

tion states A^* and \bar{A}^* are enantiomeric as are A'^* and \bar{A}'^* . However, A^* and \bar{A}'^* are diastereomeric, as are \bar{A}^* and A'^* , because $A(\bar{A})$ and $B(\bar{B})$ are diastereomeric, so that the paths $A \rightarrow B \rightarrow \bar{A}$ and $A \rightarrow \bar{B} \rightarrow \bar{A}$ are diastereomeric. It is readily shown, from the solution of Scheme I, that the evolution of the system from the initial condition $[A] = [A]_0$ and $[B] = [\bar{B}] = [\bar{A}] = 0$ leads initially to a greater flow of molecules in the direction of that diastereomer $B(\bar{B})$ which is produced via the lower of the two transition states $A^*(A'^*)$.

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