Thermal sigmatropic [1,j] shifts in cyclic systems: a perturbation approach and INDO calculations

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References and Notes

(1) (a) NATO Fellow, 1975; on leave from the University of Pavia, Italy; (b) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Recipient, 1972–1977; Alfred P. Sloan Foundation Fellow, 1975–1977.
(12) Calculations were carried out by setting matrix elements corresponding to 2p_x–2p_y interactions equal to 0; H. L. Hasse and A. Schweig, Tetrahedron, 29, 1759 (1973).
(17) This type of reasoning was proposed for AH3 molecules by C. C. Levin, J. Am. Chem. Soc., 87, 5649 (1975).
(18) NOTE ADDED IN PROOF. Optimizations by 4-31G give the following HCN angles for nitrilium betaines: ylide, 123°; imine, 180°; oxide, 180°.
(19) A planar geometry with a COC angle of 129° has been found from an STO-3G optimization: G. Leroy, M.-T. Nguyen, and M. Sana, Tetrahedron, 32, 1529 (1970).

Abstract: Some fundamental aspects of sigmatropic shifts are discussed with the help of INDO calculations and perturbation theory. In cyclic systems the degeneracy of the highest occupied molecular orbital is lifted in the transition state. A suprafacial H shift is determined by a combination of the 1s orbital of the migrating hydrogen with the symmetric MO of the system and an antarafacial shift by a combination with the antisymmetric MOs. The used perturbation model offers the possibility to reconcile somewhat the concepts of "allowed" and "forbidden". Formally forbidden reactions which, however, have been found experimentally can be explained with this model. Many "forbidden" reactions are in fact "allowed", but they proceed with a higher activation energy. Some transition state geometries have been calculated and the occurring charge transfer is explained in terms of aromaticity.

In 1965 Woodward and Hoffmann postulated their concept of orbital symmetry rules governing pericyclic reactions. In the particular case of sigmatropic reactions, the transition state is thought to be determined by the migrating group and the HOMO or LUMO of the radical-like species left behind, after splitting off the migrating group in thermal and photochemical rearrangements, respectively. In principle, the symmetry properties of the HOMO or LUMO were considered for acyclic polyenes. The major part of the experimental work reported in the last ten years is in agreement with the predictions. Curiously enough, this applied also to a host of cyclic systems. Whereas the description of acyclic systems is relatively straightforward, cyclic systems have, so far, defied a truly general explanation. The major problem has been the fact that in these systems all but the lowest molecular orbitals are doubly degenerate in the transition state. In 1968 Anastassiou tried to work out the degeneracy problem in C9H17 monocycles. It was postulated that the presence of the migrating group will disturb the symmetry of the radical, thereby lifting the degeneracy. It was then concluded that the migrating group will combine with the "genuine" HOMO again.

In our opinion, however, the real perturbation is formed by a hydrogen nucleus in the transition state in contrast with Anastassiou’s approach in which the perturbation was applied to the reactant. This leads to an entirely different result (see also next section).

There are no compelling reasons to confine the discussion to the HOMO, as already suggested by Berson and, in a more elaborate way, by Anh and Fukui, who worked out the application of perturbation theory to pericyclic rearrangements. The implications of this method have, so far, not been discussed in detail for sigmatropic rearrangements. In general, the nomenclature and selection rules derived for acyclic systems are used without modifications for cyclic polyenes as well.

Here we wish to present evidence that simple perturbation theory allows one to predict several aspects of [1,1] rearrangements in simple systems in a relatively simple fashion. The results are substantiated by INDO calculations. Before specific examples are discussed, it should be realized that a migrating hydrogen, involved in a suprafacial shift, will have to interact with symmetric molecular orbitals. On the other hand, in antarafacial rearrangements the interaction necessarily originates from combination with asymmetric orbitals.
These statements apply to both cyclic and acyclic systems. However, antarafacial shifts in small cyclic systems are only feasible when the hydrogen shifts are along the edge of the ring, i.e., from one carbon atom to a neighboring carbon atom, such as the antara [1,3] and [1,5] shifts in cyclopropene and cyclopentadiene, respectively. In the transition state of these shifts the migrating hydrogen resides in the plane of the ring, a situation in which no interaction with the σ framework will exist. The only remaining interaction is with the σ framework. In larger rings Möbius arrangements of the polyene fragment are possible, enabling formal antarafacial shifts to occur relatively easy. Möbius-type transition states presumably are also responsible for antarafacial rearrangements in acyclic systems.

For suprafacial rearrangements, the migrating group will interact with a linear combination of molecular orbitals which have a suitable symmetry. For edge-type rearrangements the position of the migrating group may be derived from a simple inspection of the Hückel orbitals. However, in face-type shifts (across the ring) the proper position can only be found by taking recourse to Hückel orbitals. Furthermore, it will be shown that even for shifts in acyclic polyenes molecular orbitals of a cyclic transition state have to be considered. It will also be discussed why some Woodward/Hoffmann "forbidden" reactions occur.

Finally, the limitations of the present approach will be outlined.

Perturbation Treatment

The parameter determining whether or not a particular H shift will occur is the activation enthalpy. We will derive that the activation enthalpy is predominantly determined by the orbital symmetry at migration origin and terminus. We postulate that the following restrictions can be made when considering the transition state: (a) The discussion is confined to the π electrons plus the two electrons of the σ-H bond that is shifting. These electrons participate in the overall conjugation of the system. (b) The π MO's are approximated by the perturbed π MO's of the initial system, the perturbation being the hydrogen nucleus. (c) For the unperturbed π MO's we take the Hückel MO's.

The perturbation treatment consists of two parts: the perturbation of the energy levels and the perturbation of the MO's.

Rayleigh-Schrödinger perturbation theory gives for energy and wave functions:

$$E_n = E_n^0 + \langle n | V | n^0 \rangle + \sum_m \frac{|m| V | n^0 \rangle^2}{E_m^0 - E_n^0}$$

$$|n\rangle = |n^0\rangle - \sum_m |m\rangle \frac{\langle m | V | n^0 \rangle}{E_n^0 - E_m^0}$$

The prime indicates the skipping of m = n. We take as zero-order functions the π MO's of the intermediate state and the 1s orbital of the hydrogen atom. The perturbation is constituted by the interaction between the π MO's and the 1s orbital. This interaction will be appreciable if the orbitals overlap. The first-order correction to the energy (n|V|n^0) will be about the same for the different π MO's (and in the same direction), because it arises through the electrostatic effect of the presence of the hydrogen nucleus, without any mixing of orbitals.

The second-order correction to the energy depends on both the interaction element (n|V|m^0) and the energy difference E_m^0 - E_n^0 of the interacting orbitals. The numerator is always positive with the effect that the energy will be lowered/raised depending on whether the perturbing level is higher/lower than the level being perturbed.

The first-order correction to the wave function depends on both the interaction and the energy difference. In fact the only relevant interaction element is:

$$V_{mn} = \langle m^0 | V | n^0 \rangle = \int \phi_{hn}^*(r) \cdot |r_{1H} - r|^{-1} \cdot \phi_n(r) \ dr$$

where r is the electron position vector, r_{1H} is the position vector of the hydrogen nucleus, \(\phi_{hn}\) is the 1s orbital of hydrogen, and \(\phi_n\) is the π MO of the system. \(\phi_{1H}\) will be zero everywhere, except in the neighborhood of the H nucleus. So the p orbitals, where the contribution of the 1s orbital is dominant, are the p orbitals of the C atoms in migration origin and terminus (for the possible effect of the other p orbitals, see next section).

V_{nn} then becomes:

$$V_{nn} \approx [c_n(C_0) - c_n(C_1)]^2 + [c_n(C_1) \times |r_{1H} - r_{C_1}|]^{-1}$$

where C_0 is the carbon atom at the migration origin, C_1 is the carbon atom at the migration terminus, c_n(C_0) is the coefficient of p_2 on atom C_0 in MO n, and c_n(C_1) is the coefficient of p_2 on atom C_1 in MO n.

In the transition state it follows that \(|r_{1H} - r_{C_1}| = |r_{1H} - r_{C_0}|\) (symmetrical transition state). Thus \(V_{nn}\) will be maximal when both c_n(C_0) and c_n(C_1) are maximal and of the same sign. Coefficients of equal magnitude but different sign will cause \(V_{nn}\) to be zero. In the transition state the migrating hydrogen will be most involved in the MO which is able to cause the greatest \(V_{nn}(E_n^0 - E_n^0)\). Qualitative examples will be given in the next section. Quantitative evidence is given by our INDO calculations.

Results

In this section we will present the implications of the use of perturbation theory to some specific examples.

(1) The Cyclopropene System. The Hückel MO's are as depicted below:

The suprafacial [1,3] H shift from Cl to C_3 is described by the function in which \(\phi_{1s}\) and the symmetrical MO's \(\psi_3\) and \(\psi_4\) are involved.

$$\chi_{\text{supra}} = a\phi_{1s} + b\psi_3 + c\psi_4$$

where \(\phi_{1s}\) is the 1s hydrogen orbital.

The perturbed energy levels are thus determined by two contributions:

$$E_n = E_n^0 + \langle n | V | n^0 \rangle + \sum_m \frac{|m| V | n^0 \rangle^2}{E_m^0 - E_n^0}$$

Thus, the real situation will be as follows:

Perturbation theory predicts the hydrogen to shift along the edge C_1-C_3 of the ring, because of the "wrong" coefficient on C_3 in \(\psi_3\). The relative energy differences predict the combination with \(\psi_3\) to prevail.

These predictions are in agreement with the INDO results. The calculated geometry of the transition state is given in Table I and Figure 1. In the transition state a partial charge transfer occurs from the ring system to the migrating hydrogen. The electron density on the migrating hydrogen \(\rho_{1H} = 1.18\). This is in excellent agreement with the aromaticity rules: the tran-
...tion state contains a 2π-electron contribution. The transition state can be described as a hybrid of two configurations, the former of which is aromatic; the latter, too, has an appreciable resonance energy:

\[ \psi_1 \propto a \phi_1 + b \psi_3 + c \psi_4 \]

Any suprafacial shift can be described by the function:

\[ \chi_{supr} = a \phi_1 + b \psi_3 \]

The contribution of \( \psi_3 \) will be most important, because \( |E_{\psi_3} - E_{\phi_1}| \) is relatively small.

In principle, two suprafacial shifts should be considered in this system: (a) a [1,5] shift from C3 to C4; (b) a [1,3] shift from C3 to C5. The former shift will be of the edge type, avoiding overlap with C2 and C4 ("wrong" coefficients in \( \psi_2 \) and \( \psi_3 \)). The latter shift is of the face type. Perturbation theory predicts the C3-C4 part of the molecule to bend away in the transition state to avoid overlap. This situation corresponds more or less to the transition state that has been calculated by Ustynyuk. However, considering the magnitude of the C3-C4 coefficients and the relatively small interaction with "wrong sign" carbon atoms, the edge-type rearrangement will be favored. The calculated activation enthalpy for the edge-type state is no longer "the HOMO" in an absolute sense. The term the cyclopolyene, the newly formed orbital in the transition state, contains a 2π-electron contribution. The transition state can be described as a hybrid of two configurations, the former of which is aromatic; the latter, too, has an appreciable resonance energy:

\[ \psi_1 \propto a \phi_1 + b \psi_3 + c \psi_4 \]

Any suprafacial shift can be described by the function:

\[ \chi_{supr} = a \phi_1 + b \psi_3 \]

The contribution of \( \psi_3 \) will be most important, because \( |E_{\psi_3} - E_{\phi_1}| \) is relatively small.

In principle, two suprafacial shifts should be considered in this system: (a) a [1,5] shift from C3 to C4; (b) a [1,3] shift from C3 to C5. The former shift will be of the edge type, avoiding overlap with C2 and C4 ("wrong" coefficients in \( \psi_2 \) and \( \psi_3 \)). The latter shift is of the face type. Perturbation theory predicts the C3-C4 part of the molecule to bend away in the transition state to avoid overlap. This situation corresponds more or less to the transition state that has been calculated by Ustynyuk. However, considering the magnitude of the C3-C4 coefficients and the relatively small interaction with "wrong sign" carbon atoms, the edge-type rearrangement will be favored. The calculated activation enthalpy for the edge-type shift is indeed smaller than for the face-type shift (difference: 51 kcal/mol).12

In cyclic polyenes with an even number of double bonds \( (C_{4n+1}H_{4n+2}) \) an interesting phenomenon occurs. Whereas the \( \phi_1 \) function of the migrating hydrogen combines with the highest occupied symmetric molecular orbital (s-HOMO) of the cyclopolyene, the newly formed orbital in the transition state is no longer "the HOMO" in an absolute sense. The term POMO (penultimate occupied molecular orbital) is more appropriate. It should be emphasized, however, that in transition states derived from cyclopolyenes with an odd number of double bonds \( (C_{4n+1}H_{4n}) \), the HOMO of the cyclopolyene

**Table I. The Transition State Geometry of the Cyclopropene System**

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>Angle</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2, Å</td>
<td>1.44</td>
<td>125.9</td>
</tr>
<tr>
<td>S-Ho, Å</td>
<td>1.058</td>
<td>125.3</td>
</tr>
<tr>
<td>α, deg</td>
<td>76.0</td>
<td>107.0</td>
</tr>
<tr>
<td>β, deg</td>
<td>81.2</td>
<td>17.2</td>
</tr>
<tr>
<td>γ, deg</td>
<td>84.2</td>
<td>0.86</td>
</tr>
</tbody>
</table>

**Table II. The Transition State Geometry of the Cyclopentadiene System**

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>Angle</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2, Å</td>
<td>1.471</td>
<td></td>
</tr>
<tr>
<td>S-Ho, Å</td>
<td>1.058</td>
<td></td>
</tr>
<tr>
<td>α, deg</td>
<td>76.0</td>
<td></td>
</tr>
<tr>
<td>β, deg</td>
<td>81.2</td>
<td></td>
</tr>
<tr>
<td>γ, deg</td>
<td>84.2</td>
<td></td>
</tr>
</tbody>
</table>

The coefficients of the POMO and HOMO were calculated by means of the INDO method and are shown in the following figure:

The calculated geometry of the transition state is depicted in the next diagram:

The calculated charge transfer is from the migrating hydrogen to the ring system, which complies again with the aromaticity rules: a transition state containing a 6π-electron contribution.

**Table III. The Transition State Geometry of the Cycloheptatriene System**

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>Angle</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2, Å</td>
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<td></td>
</tr>
<tr>
<td>S-Ho, Å</td>
<td>1.058</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
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<td>81.2</td>
<td></td>
</tr>
<tr>
<td>γ, deg</td>
<td>84.2</td>
<td></td>
</tr>
</tbody>
</table>

The coefficients of the POMO and HOMO were calculated by means of the INDO method and are shown in the following figure:

The calculated geometry of the transition state is depicted in Figure 2 and compiled in Table II. The calculated charge transfer is from the migrating hydrogen to the ring system, which complies again with the aromaticity rules: a transition state containing a 6π-electron contribution.

**Table IV. The Transition State Geometry of the Cycloheptatriene System**

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>Angle</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2, Å</td>
<td>1.471</td>
<td></td>
</tr>
<tr>
<td>S-Ho, Å</td>
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<td></td>
</tr>
<tr>
<td>α, deg</td>
<td>76.0</td>
<td></td>
</tr>
<tr>
<td>β, deg</td>
<td>81.2</td>
<td></td>
</tr>
<tr>
<td>γ, deg</td>
<td>84.2</td>
<td></td>
</tr>
</tbody>
</table>

The coefficients of the POMO and HOMO were calculated by means of the INDO method and are shown in the following figure:

The calculated geometry of the transition state is depicted in Figure 2 and compiled in Table II. The calculated charge transfer is from the migrating hydrogen to the ring system, which complies again with the aromaticity rules: a transition state containing a 6π-electron contribution.

**Table V. The Transition State Geometry of the Cycloheptatriene System**

<table>
<thead>
<tr>
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<th>Angle</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
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<td>C1-C2, Å</td>
<td>1.471</td>
<td></td>
</tr>
<tr>
<td>S-Ho, Å</td>
<td>1.058</td>
<td></td>
</tr>
<tr>
<td>α, deg</td>
<td>76.0</td>
<td></td>
</tr>
<tr>
<td>β, deg</td>
<td>81.2</td>
<td></td>
</tr>
<tr>
<td>γ, deg</td>
<td>84.2</td>
<td></td>
</tr>
</tbody>
</table>

The coefficients of the POMO and HOMO were calculated by means of the INDO method and are shown in the following figure:

The calculated geometry of the transition state is depicted in Figure 2 and compiled in Table II. The calculated charge transfer is from the migrating hydrogen to the ring system, which complies again with the aromaticity rules: a transition state containing a 6π-electron contribution.

**Table VI. The Transition State Geometry of the Cycloheptatriene System**

<table>
<thead>
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<th>Angle</th>
<th>Energy</th>
</tr>
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<tbody>
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</tr>
<tr>
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<td>1.058</td>
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</tr>
<tr>
<td>α, deg</td>
<td>76.0</td>
<td></td>
</tr>
<tr>
<td>β, deg</td>
<td>81.2</td>
<td></td>
</tr>
<tr>
<td>γ, deg</td>
<td>84.2</td>
<td></td>
</tr>
</tbody>
</table>
The interaction element between $\phi_1$ and $\psi_1$ will be most important. The most favorable shift will be the [1,5] shift from C$_1$ to C$_5$:

$$x_{\text{supra}} = a\phi_{1s} + b\psi_1 + c\psi_3 + d\psi_5$$

The comparable fully optimized transition state as calculated by means of INDO yields the coefficients as depicted below for the highest molecular orbital, containing the $\phi_{1s}$ function of the migrating hydrogen atom.

$$\alpha = 106.0^\circ \quad \beta = 50.3^\circ \quad \gamma = 0.2^\circ$$

The geometry of the nonplanar transition state as calculated by the INDO method is given in Figure 3 and Table III. The charge transfer in this system is calculated to be approximately zero: 0.99 electron density on the migrating hydrogen, a result expected for an open pentadienyl system. In this case, however, the pentadienyl system is perturbed by an ethene moiety, which results in the particular MO as depicted. Further evidence for this situation is yielded by the $\pi$ bond order between the atoms C$_6$ and C$_7$ (or C$_4$ and C$_5$), which is approximately zero.

The Huckel MO's have been given already in the section "cycloheptatriene". Again the [1,5] H shift should be described with the function:

$$x_{\text{supra}} = a\phi_{1s} + b\psi_1 + c\psi_3 + d\psi_5$$

Somewhat to our surprise, INDO calculations on this system yield a picture which deviates in certain aspects from the above mentioned completely open pentadienyl fragment. The symmetries of the various MO's comply with a (homo)cyclopentadienyl rather than an open pentadienyl moiety. In addition, the $\pi$ bond orders between C$_1$ and C$_5$ are appreciable. The calculations further show that the migrating hydrogen is involved mainly in the POMO, the coefficient for the $H_1$s function being zero in the HOMO. The electron density on the migrating hydrogen is calculated to be 0.81.

There is no reason to assume that this phenomenon will be restricted to the 1,3-pentadienyl system. In fact, every open 1,3-dienyl system will probably follow this pattern. This conclusion is corroborated quite elegantly by the results obtained for the 1,3-cyclohexadiene system. Even in this case the shift also proceeds via a homocyclopentadienyl transition state as depicted in Figure 4 and Table IV. Electron density on the migrating hydrogen: 0.95.

A similar procedure can be envisaged for larger cycloalka-1,3-dienes. Qualitative predictions regarding relative activation energies are also possible. In open systems [1,5] antarafacial shifts are to be considered.
as well (vide supra). In 1,3-pentadiene this is described by the function:

$$X_{antiar} = a\psi_1 + b\psi_2 + c\psi_3$$

In order to enable this shift, the pentadiene fragment will be forced into a Möbius arrangement. As a consequence, positive overlap is only possible with asymmetric subjacent molecular orbitals. This, in turn, will decrease the interaction elements because of the increased energy difference between the polyene molecular orbitals and the hydrogen 1s function, as compared with the suprafacial case. The result is that the activation enthalpy of the antarafacial shift is considerably higher than for the suprafacial shift. Both activation enthalpies have been calculated by Bingham and Dewar: 28.3 kcal/mol for the suprafacial [1,5] H shift in 1,3-pentadiene, and 37.0 kcal/mol for the antarafacial [1,5] H shift in the same system.

**Discussion, Scope, and Limitations**

The literature on sigmatropic shifts reveals several examples of nominally “forbidden” rearrangements which nevertheless occur. On the other hand, some “allowed” shifts have never been observed. The present perturbation treatment sheds more light on these phenomena. An “allowed” transition state can be hampered by the absence of a suitable (from a symmetry viewpoint) molecular orbital within a reasonable energy distance from the orbital of the migrating group. Further, interaction of the migrating group with subjacent orbitals of the π moiety might assist a migrating group in following a “forbidden” pathway, as already pointed out by Berson:

In a similar way “forbidden” antarafacial shifts are possible in a Möbius arrangement via asymmetric orbitals (the symmetric orbitals have a negative overlap in this Möbius arrangement), for example, the antarafacial [1,5] H shift in 1,3-pentadiene.

The present treatment shows that even in formally allowed transitions subjacent molecular orbitals are involved in the determining MO of the transition state.

Another interesting aspect of the method is the possibility of predicting molecular conformations in the transition state from simple inspection of the Hückel MO’s. Molecular parts with “wrong” signs of the coefficients will tend to avoid overlap with the migrating group. This was demonstrated in cyclohexadiene and cycloheptatriene where our calculations show that those parts of the framework bend away from the migrating group.

Quite obviously, the complexity of the molecular orbitals and the accompanying possibilities of combination grow rapidly with polyenes of increasing chain length. An example is formed by the 1,3,5-heptatriene system. The Hückel MO’s are:

In principle, several shifts are possible in this system. Considering symmetry and coefficients, for example, shifts are possible via $\psi_3$ and $\psi_5$ from C1 to C7 or via $\psi_4$ from C1 to C5.

Meaningful predictions are difficult to make. In cases like this the more sensible approach will be to take recourse to INDO calculations right from the start. The perturbation theory combined with the Hückel orbitals will now serve mainly to indicate logical starting points. For example, a [1,5] H shift in 1,3,5-heptatriene will require a transition state as follows, in which interaction with the lone double bond might occur:

On the other hand, a [1,7] shift will require a homocycloheptatrienyl system. In order to determine which shift will be favored, the respective transition states of different pathways will have to be compared by way of INDO calculations. The suprafacial [1,7] H shift will be a hydride-like shift, comparable with the suprafacial [1,3] H shift in cyclopropene. The difference in absolute magnitude of the charge transfer calculated for the cyclopropenyl and cycloheptatrienyl systems seems relevant and is to be ascribed to the difference in ionization potentials. This way of comparing charge transfers is similar to the use of differences in electron affinities between the cyclopentadienyl, homocyclopentadienyl, and open pentadienyl systems.

Another very obvious extension of the present approach is the treatment of homogenous catalysis of rearrangements by transition metals. Two possibilities are to be distinguished: acceleration of allowed transitions and transformation of forbidden rearrangements into allowed ones. By interaction of the migration framework with the metal, the orbitals of both
will be affected. As a result, also the interaction terms with potential migrating groups will be altered.

Recently, a similar theory of catalytic activity has been worked out.11

References and Notes

(1) (a) R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965); (b) ibid., 87, 2046 (1965); (c) ibid., 87, 2511 (1965).
(12) The experimental and theoretical activation enthalpies are in good agreement. See ref 8.
(13) The geometry of the cyclopentadiene transition state has been optimized with respect to eight variables (see Table II). A fully optimized transition state as calculated by Ustynyuk et al. shows no essential difference. Our optimization resulted in an approximately symmetric structure as can be derived from Table II, which shows (6) approximately equal to (γ and δ are group constants). Consequently for all other cyclic systems the symmetry plane was assumed, while optimizing all other variables. In all systems it was assumed that the transition state has only one negative force constant.
(14) The reason for the cyclic symmetry properties in the present case is probably to be ascribed to the enhanced flexibility of the system. This enables a closer approach between migration origin and terminus in the transition state as compared to cycloheptatriene. In the acyclic pentadienyl system therefore the problem of an orbit overlap and terminus overlap in order to form a partial π bond in the cycloheptatriene system, the two carbon atoms involved are held apart by the rather rigid ethylene moiety.
(15) NOTE ADDED IN PROOF. In reality the H₂ level lies about 1.3 (δ = -2.4 eV) below the zero level, but this does not affect any of the conclusions.

Global Topology of Triatomic Potential Surfaces

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Abstract: A new coordinate system for describing triatomic molecules is introduced. Within this coordinate system various topological features of importance are discussed. Particular emphasis is placed on the Jahn-Teller theorem and the resulting branch-cuts on the potential surface.

Potential surfaces are of importance in chemistry for explaining geometry, spectra, and chemical reactions. Triatomic potential surfaces (especially for excited states) have recently become of even greater interest because of work in plasmas, lasers, and atmospheric pollution associated with various aspects of the energy crisis. Unlike diatomic molecules which are fairly well characterized, polyatomic potential surfaces are only vaguely understood. While the general features expected for a diatomic molecule potential curve over the whole range of possible molecular conformations are well known, such a global topology for triatomic molecules is not usually discussed.

General Considerations

A potential surface, for the purpose of the present discussion, will be a function \( U(X_1, \ldots, X_K) \) generated as one of the solutions to an electronic (Born-Oppenheimer) Schrödinger equation

\[
H \psi(r_1, \ldots, r_N; X_1, \ldots, X_K) = U(X_1, \ldots, X_K) \psi(r_1, \ldots, r_N; X_1, \ldots, X_K) \quad (1)
\]

where the \( r_i \) are electronic coordinates and the \( X_j \) are coordinates for describing the conformation of the nuclei in the molecule. The operator \( H \) in the simplest approximation is just the usual electronic hamiltonian involving electronic kinetic energy and coulomb interactions,

\[
H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - e^2 \sum_{i} \sum_{A} Z_A r_{iA}^{-1} + e^2 \sum_{A \neq B} Z_A Z_B r_{AB}^{-1} + e^2 \sum_{i \neq j} r_{ij}^{-1} \quad (2)
\]

For discussing a potential surface \( U \) it is sufficient to pick the complete set of coordinates \( X \) which affect the shape or size of the molecule but not its position or orientation in space. Hence for three or more atoms \( K = 3N_A - 6 \) where \( N_A \) is the number of atoms (for a global discussion of \( U \) the question of whether the molecule is "linear" or not does not enter).

The Schrödinger equation for a molecule actually defines an infinite family of potential surfaces, of course. Because of the possibility of intersections, great care must be exercised in identifying a surface. In general, there are certain elements of symmetry such as electron spin which are global in nature (i.e., commute with \( H \) for all values of the \( X_j \)). Diatomic molecules are always linear and triatomics are always planar, while larger polyatomics have no global geometric symmetry. In any case, the electronic wave functions and associated potential surfaces can be labeled with whatever global symmetry is present. Beyond that, at each set of nuclear coordinates \( X \) the potential surfaces of the same global symmetry are simply numbered in order of increasing energy. With this convention the \( k \)th potential energy surface of symmetry \( \Gamma \), \( U_k(\Gamma) \), will be a continuous function of the \( X \). For diatomic molecules this convention is known to lead to smooth (differentiable) functions \( U_k \) (except for the \( 2s_2g \) and \( 3d_3g \) curves1 for \( H_2^+ \)) which do not intersect other curves of the same symmetry \( 2 \) in the open interval \( 0 < R < \infty \).

By global topology is meant the study of the shape and structure of the potential energy surface over the entire range of the nuclear position coordinates. Certain kinds of structural features are well-known. For example, wherever two nuclei coincide the potential surface has a coulomb singularity. This singularity is easily removed by subtracting the nuclear-nuclear repulsion from \( U \) to get the "electronic energy" \( U_e \)

\[
U_e = U - e^2 \sum_{A \neq B} Z_A Z_B r_{AB}^{-1} \quad (3)
\]

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