# Symmetry Rules for Transition Structures in Degenerate Reactions

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**Abstract:** The work of Pechukas [*J. Chem. Phys.* **1976**, *64*, 1515−1521] on predicting transtion structure symmetry from reactant and product symmetries is extended to degenerate reactions. Pechukas showed that the group of the transition structure in a one-step nondegenerate reaction must be one of the Pechukas groups common to reactant and product. It is now shown that for a one-step degenerate reaction the transition structure symmetry must either be that of one of the Pechukas groups as predicted for a nondegenerate reaction or a group constructed from one of them by adding “extra” symmetry operations to double its order. Several examples are given to clarify these rules, and a table is presented to aid in their application.

## I. Introduction

Do the symmetries of reactant and product impose any restriction on the possible symmetry of a transition structure (TS) connecting them? A recent paper by Minyaev[1] gives a useful set of references to the early history of this problem. We shall not repeat these, but only note a key paper by Stanton and McIver[2] in 1975. Pechukas[3] followed with an elegant analysis of the problem and a rule for predicting possible TS symmetries in nondegenerate concerted reactions, i.e., one-step reactions where reactant and product are chemically distinct.

We extend Pechukas’ work to degenerate concerted reactions, i.e., one-step reactions in which reactant and product differ only by the interchange of identical atoms.[4] Both Pechukas[3] and Stanton and McIver[2] discussed degenerate reactions. They knew that the TS in these reactions may have extra symmetry operations not shared by the entire reaction path and that these extra operations interchange reactant and product paths. What is new here is the derivation of a rule restricting possible TS symmetry groups in degenerate reactions.

These rules for one-step reactions apply equally well to the individual steps in multistep processes. They can also be applied to the steps in the probably rather common situation in which the path up from reactant goes to a TS, then falls to a second TS from which two paths fall to two products, either degenerate or nondegenerate.

Two examples in section II show the application of these rules. Proof of the rule for degenerate reactions follows in section III. Section V gives further examples in more elaborate situations.

The work here is based on the use of Pechukas groups. There has also been a parallel development using Longuet-Higgins groups (= permutation-inversion groups = molecular symmetry groups).[5−10] In particular, although the two derivations are quite different, Nourse[5] has published a result for the Longuet-Higgins groups of degenerate reactions analogous to what will be presented here. Some comparisons of the two approaches are in section IV where the question of relative orientation of reactant and product is also discussed.

## II. Two Examples

**II.1. Assumptions.** The two examples in sections II.3 and II.4 will show how to predict TS symmetry without following the derivations upon which the methods are based. This can be done correctly if one keeps in mind the assumptions underlying these derivations. Beneath the special assumptions here is the usual supposition that the molecule is being treated by a method that produces a potential energy surface giving molecular energy as a function of nuclear positions. That is, the Born−Oppenheimer separation of electronic and nuclear coordinates[11] is assumed. An impossibly rigorous treatment would not make this approximation, and there would be no potential surface.

Additional assumptions needed to derive the TS symmetry rules are fortunately few. First, the conditions of the Murrell−Laidler theorem[12] are assumed so that two and only two steepest descents paths come down from the TS, one to reactant and one to product. Second, all second derivatives of the potential energy with respect to nuclear Cartesian coordinates are assumed continuous in the region of the two steepest descents paths. Thus regions containing surface crossings must be avoided. Third, it is assumed that the energy gradient with respect to nuclear coordinates, which determines forces on the atoms at each point on the potential surface, has the same symmetry as does the nuclear framework. For example, at a point on the $H_2O$ potential surface where both OH bonds are equally stretched, the restoring force on both must be equal. Potential surfaces constructed from symmetry-broken wave functions may not satisfy these conditions, and they are to be treated with caution.

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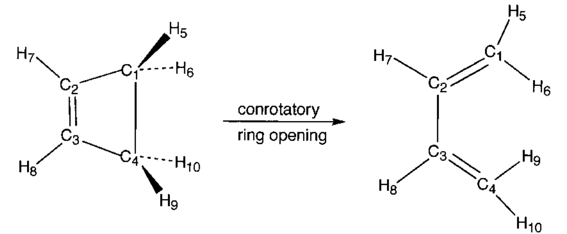

| $C_{2v}$ | $C_{2v}$ |
|---|---|
| E | E |
| (1,4)(2,3)(5,10)(6,9)(7,8) $C_2$ | (1,4)(2,3)(5,10)(6,9)(7,8) $C_2$ |
| (1,4)(2,3)(5,9)(6,10)(7,8) $\sigma_v$ | (1,4)(2,3)(5,10)(6,9)(7,8) $\sigma_v$ |
| (5,6)(9,10) $\sigma_v'$ | $\sigma_v'$ |

**Figure 1.** The ring opening of cyclobutene to planar *s-cis*-butadiene. Automer numbering and Pechukas symmetry groups are shown.

The predicted geometry of stable molecules and transition structures, of course, varies with the level of calculation. It is not rare for a TS at one level to become a minimum at another. However, as Stanton and McIver[2] point out, the TS symmetry rules here apply to all potential surfaces, not just the most nearly exact.

**II.2. Pechukas Groups.** Pechukas carried out his analysis using modified point symmetry groups that we shall call "Pechukas groups". These will also be used in the extension of his work to degenerate reactions. To construct such a group, start with the usual point symmetry group. For example, cyclobutene shown in Figure 1 has $C_{2v}$ point group symmetry with the identity, a 2-fold rotation axis, and two reflection planes. We shall interpret these symmetry operations in the active sense and let them operate on the molecule itself rather than on the coordinate system. Thus the point symmetry elements interchange various identical atoms (ignoring the atom numbering) in cyclobutene.

To obtain the operations in the Pechukas group, append to the point symmetry operation the permutation of identical nuclei that returns all numbered atoms in the molecule to their original positions. The cyclic notation for permutations will be used, thus $(i, j, k, ..., v, w)$ means atom $i$ is replaced by atom $j$, $j$ by $k$, ..., $v$ by $w$, and $w$ by $i$. Single-membered cycles such as $(i)$ in which $i$ is replaced by itself, i.e., is unchanged, are omitted. For example, reflection of cyclobutene in the plane of the page by $\sigma_v'$ interchanges atoms 5 with 6 and 9 with 10 in the reactant. Therefore, following $\sigma_v'$ by the permutation (5,6)(9,10) returns the reactant to its original configuration, and the operation of the Pechukas group corresponding to $\sigma_v'$ in the point symmetry group is $(5,6)(9,10)\sigma_v'$.

Let R be any point symmetry operation and P be the permutation of identical nuclei that cancels the effect of R. The Pechukas group {PR} and the point symmetry group {R} of a molecule are isomorphic with the obvious correspondence PR↔R.

In the following it will be convenient to define the "structure" of a molecule by the $3N - 6$ (or $3N - 5$ for linear molecules) internal coordinates. If $n_i$ is the number of identical atoms of type $i$, there are $\Pi_i n_i!$ ways of forming this structure that differ only in the interchange of identical atoms. These may be distinguished by numbering the atoms, and we shall use Balaban and Farcasiu's[13] term "automer" for these numbered structures. That is, each structure gives rise to $\Pi_i n_i!$ automers. Structures and automers can be oriented in space by fixing the three coordinates of the center of mass and the three (or two for linear molecules) rotational angles of the rigid molecule. An oriented automer of cyclobutene is shown in Figure 1.

**II.3. Nondegenerate Case.** The general procedure, illustrated below for the ring opening of cyclobutene, for predicting possible TS symmetries in a one-step nondegenerate reaction from a particular reactant automer to a particular product automer is the following.

1. Choose particular orientations of particular reactant and product automers.
2. Determine the Pechukas groups $\mathbf{G}_R$ of the reactant and $\mathbf{G}_P$ of the product automers.
3. Find the Pechukas operations common to reactant and product automers. These form a group $\mathbf{G}_0$, the largest common subgroup of $\mathbf{G}_R$ and $\mathbf{G}_P$. Let the subgroups of $\mathbf{G}_0$ be $\mathbf{G}_1$, $\mathbf{G}_2$, ..., $\mathbf{G}_k$.
4. Possible symmetries for the TS in a one-step reaction from the chosen oriented reactant automer to the chosen oriented product automer are $\mathbf{G}_{TS} = \mathbf{G}_0$, $\mathbf{G}_1$, $\mathbf{G}_2$, ..., or $\mathbf{G}_k$.
5. Repeat in the same way with all other orientations of the product automer to give further possible symmetries for the TS from the chosen reactant automer to the chosen product automer. Since only relative reactant and product orientations matter, it is not necessary to consider other reactant orientations. All this is not as onerous as it may appear since most additional oriented product automers contribute no new TS possibilities. Pechukas himself did not include this step. It is often not needed, but we shall see cases where it is.

Return now to the ring opening of cyclobutene to *s-cis*-1,3-butadiene shown with oriented automers of reactant and product in Figure 1. For simplicity we assume the product to be planar, contrary to the calculations of Bruelet, Lee, and Schaefer.[14] Consequences of the actual nonplanar geometry will be considered in section V.

The point symmetry groups are identical for reactant and product, but the Pechukas groups are not. Their largest common subgroup is {E, (1,4)(2,3)(5,10)(6,9)(7,8)$C_2$}, and the only subgroup of this is {E}. Therefore, the Pechukas group of the TS between these oriented automers, if the process is a one-step reaction, must be one of the two.

Next, all possible orientations of the product automer must be considered. In Figure 1, the product can be rotated by 180° about the $x$ or $y$ axis, or by any angle about the $z$ axis, to give the result we already have.

All other product orientations have only the operator E in common with the reactant, and hence predict $C_1$ symmetry for the TS.

Thus for the automers in Figure 1, the TS can have the Pechukas symmetry group {E} or {E, (1,4)(2,3)(5,10)(6,9)(7,8)-$C_2$}. This treatment cannot predict which of these two symmetries the TS will have, but it does say with certainty that the symmetry can be no other.

If one prefers to think in terms of the more familiar point symmetry groups, the permutation operations may now be dropped, and one can say the symmetry of the TS is either $C_2$ = {E, $C_2$} or $C_1$ = {E}. However, doing so does discard information that may be useful. That is, more is known than that if the TS has $C_2$ symmetry it has a 2-fold axis. Rotation around that axis must interchange atoms 1 and 4, 2 and 3, ..., 7 and 8. These predictions are consistent with MP2/6-31G* calculations that find a TS with $C_2$ symmetry.[15]

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[13] Balaban, A.; Farcasiu, D. *J. Am. Chem. Soc.* **1967**, *89*, 1958−1960.

[14] Breulet, J.; Lee, T. J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1984**, *106*, 6250−6253.

[15] Baldwin, J. E.; Reddy, V. P.; Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 8555−8556.

A similar analysis for the product as in Figure 1, but with $H_9$ and $H_{10}$ interchanged, predicts either a $C_1$ or a $C_s$ transition structure. In the same way it is shown that the product of Figure 1 with $H_5$ and $H_7$ interchanged can be reached in a one-step reaction only through a $C_1$ transition structure.

It is seen that these symmetry predictions are of a different nature than those from the Woodward–Hoffmann rules.[16] In the Woodward–Hoffmann treatment, symmetries are assumed for reactant, product, and all geometries, including the TS, along the reaction path. A correlation between reactant and product orbitals is then constructed, and from this it is predicted whether the reaction will be allowed (as for the conrotatory ring opening above) or forbidden (the disrotatory ring opening). The Pechukas analysis starts with the symmetry of reactant and product only and predicts the possible symmetry of the TS. More precisely, it states which symmetries of the nuclear framework are not possible for the TS, leaving all others as possibilities. It says nothing about relative activation energies for various reactant or product automers.

**II.4. Degenerate Case.** The general procedure is as follows.

1. Follow steps 1–5 as in the nondegenerate case. Suppose this gives the possibilities $\mathbf{G}_{\mathrm{TS}} = \mathbf{G}_0, \mathbf{G}_1, \mathbf{G}_2, ..., \mathbf{G}_k$ for the Pechukas group of the TS, assuming the reaction nondegenerate.

2. Suppose $\mathbf{G}_0{}^1, \mathbf{G}_0{}^2, ..., \mathbf{G}_0{}^\alpha$ are groups of twice the order of $\mathbf{G}_0$ that contain $\mathbf{G}_0$ as a subgroup; $\mathbf{G}_1{}^1, \mathbf{G}_1{}^2, ..., \mathbf{G}_1{}^\beta$ are groups of twice the order of $\mathbf{G}_1$ with $\mathbf{G}_1$ as a subgroup; ... ...; $\mathbf{G}_k{}^1, \mathbf{G}_k{}^2, ..., \mathbf{G}_k{}^\omega$ are groups twice the order of $\mathbf{G}_k$ with $\mathbf{G}_k$ as a subgroup.

3. Then possible Pechukas symmetry groups of the TS are any of $\mathbf{G}_0, \mathbf{G}_1, \mathbf{G}_2, ..., \mathbf{G}_k$; $\mathbf{G}_0{}^1, \mathbf{G}_0{}^2, ..., \mathbf{G}_0{}^\alpha$; $\mathbf{G}_1{}^1, \mathbf{G}_1{}^2, ..., \mathbf{G}_1{}^\beta$; ... ...; $\mathbf{G}_k{}^1, \mathbf{G}_k{}^2, ..., \mathbf{G}_k{}^\omega$.

4. Further, the "extra" Pechukas operations in $\mathbf{G}_0{}^1 ... \mathbf{G}_k{}^\omega$ that are not common to $\mathbf{G}_{\mathrm{R}}$ and $\mathbf{G}_{\mathrm{P}}$ have the property that they turn the reactant (product) automer into the product (reactant) automer.

The Feist rearrangement[17] of methylenecyclopropane by the Doering and Roth pivot mechanism[18] provides such an example. One possible set of automers for reactant and product is shown in Figure 2. Since the reaction is degenerate, reactant and product must have the same point symmetry group, $C_{2v}$ in this case. However, the two Pechukas groups have only the element E in common. There are no permutation operations to drop here so the largest common Pechukas subgroup corresponds to the point symmetry group $C_1 = \{E\}$. This is one possible symmetry for the TS, but since the reaction is degenerate other possibilities are any group that is double the order of $C_1$ (i.e. any group of order 2) and containing $C_1$ as a subgroup (all groups do). Thus $C_2$, $C_i$, and $C_s$ as well as $C_1$ are possible point symmetry groups for the TS. No other orientation of the product gives additional symmetry possibilities.

A $C_s$ symmetry is found by MP2/6-31G* calculations for this TS, in agreement with these predictions.[19,20] The "extra" $\sigma$ operation of the TS passes through $C_1$ and the pivot $C_2H_5H_6$ methylene and is associated with the permutation (3,4)(7,10)(8,9). As seen in Figure 2 (**a**, **c**, and **d**), the resulting Pechukas operation does turn reactant into product, as required.

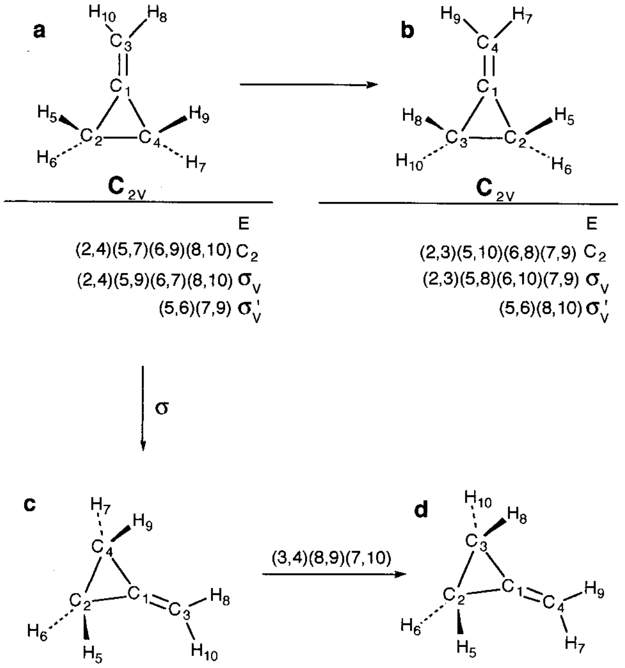

**Figure 2.** Feist rearrangement of automer **a** of methylenecyclopropane to automer **b**. Structures **c** and **d** show that the "extra" operation $\sigma$ of the Pechukas symmetry group of the transition structure does interchange reactant and product. See text for the definition of $\sigma$.

These results may be summarized in two rules, remembering that all relative orientations of reactant and product automers must be considered.

*Rule 1. The Pechukas group of the TS in a one-step nondegenerate reaction is either the largest common subgroup of the reactant and product Pechukas groups, or any subgroup of that.*

*Rule 2. The Pechukas group of the TS in a one-step degenerate reaction is one of the groups from Rule 1 for nondegenerate reactions, or any Pechukas group obtained from any of these by adding extra symmetry elements to double the group order.*

Table 1 is arranged to simplify these TS symmetry predictions. See footnote *a* for use of the table.

## III. Derivation of the TS Symmetry Rule for Degenerate Reactions

We first review, with additional comment on some points, the main steps in Pechukas' proof of Rule 1 since these are necessary to the extension to Rule 2.

Consider an $N$-atom molecule in 3-dimensional space with atomic Cartesian coordinates $\mathbf{x} = (x_1, x_2, x_3; x_4, x_5, x_6; ..., x_{3N})$ where $x_1, x_2, x_3$ refer to atom 1, etc. Let $V(\mathbf{x})$ be the potential surface (i.e., the surface of total energy in a fixed-nuclear calculation) in $3N + 1$ dimensions. Then the steepest-descents lines (=gradient lines) are given by

$$\frac{\mathrm{d}x_i}{\mathrm{d}s} = -\frac{\partial V/\partial x_i}{|\nabla V|}; \; i = 1, 2, ..., 3N \qquad (1)$$

where

$$|\nabla V| = \left[\sum_{i=1}^{3N} (\partial V/\partial x_i)^2\right]^{1/2} \qquad (2)$$

in the denominator of eq 1 normalizes the step size so that

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(17) Feist, F. *Chem. Ber.* **1893**, *26*, 747–764.

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(19) Skancke, A.; Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5315–5316.

(20) Nakamura, E.; Yamago, S.; Ejiri, S.; Dorigo, A. E.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 3183–3184. It is mentioned in footnote 3 of this paper that our MP2/6-31G* TS collapses to trimethylenemethane on geometry optimization in a CASSCF calculation. This is certainly an important observation, but does not affect our comments above that apply specifically to the MP2/6-31G* potential surface.

**Table 1.** Allowed Point Symmetry Groups for Transition Structures[a]

| | |
|---|---|
| $C_1$: | none $[C_2, C_s, C_i]$ |
| $C_2$: | $C_1$ $[C_4, S_4, C_{2v}, C_{2h}, D_2]$ |
| $C_s$: | $C_1$ $[C_{2v}, C_{2h}]$ |
| $C_i$: | $C_1$ $[C_{2h}]$ |
| $C_3$: | $C_1$ $[C_6, S_6, C_{3v}, C_{3h}, D_3]$ |
| $C_4$: | $C_1, C_2$ $[C_8, S_8, D_4, C_{4h}, C_{4v}]$ |
| $S_4$: | $C_1, C_2,$ $[ D_{2d}, C_{4h}]$ |
| $C_{2v}$: | $C_1, C_2, C_s$ $[D_{2h}, D_{2d,} C_{4v}]$ |
| $C_{2h}$: | $C_1, C_2, C_s, C_i,$ $[D_{2h}, C_{4h}]$ |
| $D_2$: | $C_1, C_2$ $[D_{2h}, D_{2d}, D_4]$ |
| $C_5$: | $C_1$ $[C_{5h}, C_{5v}, D_5]$ |
| $C_6$: | $C_1, C_2, C_3$ $[C_{6h}, C_{6v}, D_6]$ |
| $S_6$: | $C_1, C_i, C_3$ $[C_{6h}, D_{3d}]$ |
| $C_{3v}$: | $C_1, C_s, C_3$ $[C_{6v}, D_{3h}, D_{3d}]$ |
| $C_{3h}$: | $C_1, C_s, C_3$ $[C_{6h}, D_{3h}]$ |
| $D_3$: | $C_1, C_2, C_3$ $[D_{3h}, D_{3d}, D_6]$ |
| $C_7$: | $C_1$ [none] |
| $C_8$: | $C_1, C_2, C_4$ $[D_8]$ |
| $S_8$: | $C_1, C_2, C_4$ $[D_{4d}]$ |
| $D_{2h}$: | $C_1, C_2, C_s, C_i, C_{2h}, C_{2v}, D_2$ $[D_{4h}]$ |
| $D_{2d}$: | $C_1, C_2, C_s, S_4, D_2, C_{2v}$ $[D_{4h}]$ |
| $D_4$: | $C_1, C_2, C_4, D_2$ $[D_{4h}, D_{4d,} D_8]$ |
| $C_{4h}$: | $C_1, C_2, C_s, C_i, C_{2h}, C_4, S_4$ $[D_{4h}]$ |
| $C_{4v}$: | $C_1, C_2, C_s, C_{2v}, C_4$ $[D_{4h}, D_{4d}]$ |
| $C_{5h}$: | $C_1, C_s, C_5$ $[D_{5h}]$ |
| $C_{5v}$: | $C_1, C_s, C_5$ $[D_{5h}, D_{5d}]$ |
| $D_5$: | $C_1, C_2, C_5$ $[D_{5h}, D_{5d}]$ |
| $C_{6h}$: | $C_1, C_2, C_s, C_i, C_3, C_{2h}, C_{3h}, S_6, C_6$ $[D_{6h}]$ |
| $C_{6v}$: | $C_1, C_2, C_s, C_3, C_{2v}, C_{3v}, C_6$ $[D_{6h}, D_{6d}]$ |
| $D_{3h}$: | $C_1, C_2, C_s, C_3, C_{2v}, C_{3v}, C_{3h}, D_3$ $[D_{6h}]$ |
| $D_{3d}$: | $C_1, C_2, C_s, C_i, C_3, C_{2h}, D_3, C_{3v}, S_6$ $[D_{6h}]$ |
| $D_6$: | $C_1,C_2, C_3, D_2, D_3, C_6$ $[D_{6h}, D_{6d}]$ |
| $T$: | $C_1, C_2, C_3, D_2$ $[T_d, T_{h,} O]$ |
| $D_{4h}$: | $C_1, C_2, C_i, C_s, D_2, C_{2h}, C_{2v}, S_4, C_4, C_{4v}, C_{4h}, D_4, D_{2d}, D_{2h}$ $[D_{8h}]$ |
| $D_{4d}$: | $C_1, C_2, C_s, D_2, C_{2v}, C_4, C_{4v}, D_4, S_8$ $[D_{8h}]$ |
| $D_8$: | $C_1, C_2, C_4, D_2, C_8, D_4$ $[D_{8h}]$ |
| $D_{5h}$: | $C_1, C_2, C_s, C_{2v}, C_5, D_5, C_{5v}, C_{5h}$ [none] |
| $D_{5d}$: | $C_1, C_2, C_s, C_i, C_{2h}, C_5, D_5, C_{5v}$ [none] |
| $D_{6h}$: | $C_1, C_2, C_s, C_i, C_3, D_2, C_{2h}, C_{2v}, D_3, C_{3h}, C_{3v}, S_6, C_6, D_{2h}, D_6, D_{3d}, D_{3h}, C_{6v}, C_{6h}$ [none] |
| $D_{6d}$: | $C_1, C_2, C_s, C_3, D_2, C_{2v}, S_4, D_3, C_{3v}, C_6, D_{2d}, D_6, C_{6v}$ [none] |
| $T_d$: | $C_1, C_2, C_s, C_3, S_4, C_{2v}, D_2, C_{3v}, D_{2d}, T$ $[O_h]$ |
| $T_h$: | $C_1, C_2, C_s, C_i, C_3, D_2, C_{2h}, C_{2v}, S_6, D_{2h}, T$ $[O_h]$ |
| $O$: | $C_1, C_2, C_3, D_2, C_4, D_3, D_4, T$ $[O_h]$ |
| $D_{8h}$: | $C_1, C_2, C_s, C_i, C_4, S_4, C_{2h}, C_{2v}, D_2, D_{2h,} D_{2d}, D_4, C_{4h}, C_{4v}, C_8, S_8, D_8, D_{4h}, D_{4d}$ [none] |
| $O_h$: | $C_1, C_2, C_s, C_i, C_3, D_2, C_{2h}, C_{2v}, S_4, C_4, D_3, C_{3v}, S_6, C_{4v}, C_{4h}, D_4, D_{2d}, D_{2h}, D_{3d}, T, D_{4h}, T_d, T_h, O$ [none] |
| $I$: | $C_1, C_2, C_3, D_2, C_5, D_3, D_5, T$ $[I_h]$ |
| $I_h$: | $C_1, C_2, C_s, C_i, C_3, D_2, C_{2h}, C_{2v}, C_5, C_{3v}, D_3, D_{2h}, D_5, C_{5v}, T, D_{3d}, D_{5d}, T_h, I$ [none] |
| $C_{\infty v}$: | $C_1, C_2, C_s, C_3, C_4, C_{2v}, C_5, C_6, C_{3v}, C_7, C_8, C_{4v}, C_{5v}, C_{6v}$ $[D_{\infty h}]$ |
| $D_{\infty h}$: | $C_1, C_2, C_s, C_i, C_3, C_4, S_4, C_{2h}, C_{2v}, D_2, C_5, C_6, S_6, C_{3v}, C_{3h}, D_3, C_7, C_8, S_8, D_{2h,} D_{2d}, D_4, C_{4h}, C_{4v}, D_5, C_{5v}, C_{5h}, C_{6h}, C_{6v}, D_{3d}, D_{3h}, D_6,$<br>$D_{4d}, D_{4h}, D_{5d}, D_{5h}, D_{6h}, D_{6d}, D_{8h}, C_{\infty v}$ [none] |

[a] The point symmetry group $G$ corresponding to the largest common Pechukas group of reactant and product is shown before the colon. These are arranged in increasing order for 49 common groups, including the 32 crystallographic point groups. All subgroups of $G$ that are in the set of 49 groups are between the colon and left square bracket. The square brackets contain groups with twice the order of $G$ that have $G$ as a subgroup. For example, if $D_2$ corresponds to the largest common subgroup of reactant and product in a nondegenerate reaction, then possible symmetries for the TS are $D_2$ or either of its subgroups $C_1$ and $C_2$. If the reaction is degenerate additional possibilities are groups in the square bracket for $D_2$, i.e., $D_{2h}$, $D_{2d}$, $D_4$, and those in the square brackets for the subgroups $C_1$ and $C_2$, i.e., $C_2$, $C_s$, $C_i$, and $C_4$, $S_4$, $C_{2v}$, $C_{2h}$, $D_2$. The notation "[none]" means no group with required properties is in the set of 49 groups.

$$\sum_{i=1}^{3N}\left|\frac{\mathrm{d}x_i}{\mathrm{d}s}\right|^2 = 1 \tag{3}$$

As Pechukas[3] has pointed out, gradient lines are useful here because they lead to relations between the symmetries of the critical points they connect. Whether or not the reacting molecule actually moves along the gradient line is not directly relevant to these symmetry questions.

Eq 1 is almost analogous to the equations for the steepest path down a hill on the (approximately flat) earth where the hill height $z$ and the $x$ and $y$ directions all have units of length. The element of path length includes all three variables and is $[(dx)^2 + (dy)^2 + (dz)^2]^{1/2}$. In eq 1 the variable analogous to hill height has unit of energy instead of length as for the other $3N$ variables. Distance is therefore not defined in the $(3N + 1)$-space, and the element of path length is

$$\mathrm{d}s = \left[\sum_{i=1}^{3N}(\mathrm{d}x_i)^2\right]^{1/2} \tag{4}$$

in $3N$ rather than in $(3N + 1)$-space.

Equation 1 is a set of $3N$ first-order differential equations with independent variable $s$ and dependent variables $x_1, ..., x_{3N}$, but because of the additional constraint of eq 4 the usual proof[21] of the uniqueness of solutions does not apply. However, if all lines in eq 1 are divided by the last

$$\begin{gathered}\frac{\mathrm{d}x_1}{\mathrm{d}x_{3N}} = \frac{\partial V/\partial x_1}{\partial V/\partial x_{3N}} \equiv f_1 \\ \vdots \\ \frac{\mathrm{d}x_{3N-1}}{\mathrm{d}x_{3N}} = \frac{\partial V/\partial x_{3N-1}}{\partial V/\partial x_{3N}} \equiv f_{3N-1} \\ 1 = 1\end{gathered} \tag{5}$$

These $3N - 1$ first-order differential equations determine the $3N - 1$ dependent variables $x_1, ..., x_{3N-1}$ in terms of the independent $x_{3N}$, and hence determine a line in $3N$-dimensional space.

If all

$$\frac{\partial f_i}{\partial x_j} = \frac{\left[\left(\frac{\partial V}{\partial x_{3N}}\right)\frac{\partial^2 V}{\partial x_j \partial x_i} - \left(\frac{\partial V}{\partial x_i}\right)\frac{\partial^2 V}{\partial x_j \partial x_{3N}}\right]}{(\partial V/\partial x_{3N})^2};\ i, j = 1, 2, ..., 3N - 1 \tag{6}$$

are continuous in a region $R$ of $3N$-space, then eq 5 has a unique solution[21] at all points in any closed rectangular region $R'$ interior to $R$. Consequently, the gradient lines in $3N$-space determined by eq 5 cannot cross in such an $R'$. These conditions are sufficient, but not necessary, for the existence of unique solutions. They appear weak enough to cover the cases of interest on potential surfaces, but they are slightly stronger (i.e., more restrictive) than the more usual Lipschitz conditions.[21] Still weaker conditions are known,[22] but even they are only sufficient, not necessary.

Since these gradient lines in $3N$-space are projections of paths on the surface of $V$ in $(3N + 1)$-space, the paths in $(3N + 1)$-

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[21] Pennisi, L. L. *Elements of Ordinary Differential Equations*; Holt, Rinehart and Winston: New York, 1972; Appendix 2.

[22] Coddington, E. A.; Levinson, N. *Theory of Ordinary Differential Equations*; Krieger: Malabar, FL, 1987; p 49.

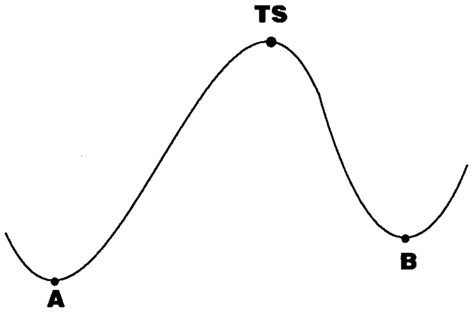

**Figure 3.** Gradient path for a one-step (= concerted) mechanism.

space cannot cross except at crossings of their projections. Conversely, since $V$ is a single-valued function of $x_1, ..., x_{3N}$, the potential surface does not fold back on itself; and the lines in $3N$-space cannot cross unless those in $(3N + 1)$-space cross. Thus there is a one-to-one correspondence between the crossings of the paths in $(3N + 1)$-space and of their projections in $3N$-space.

The potential $V$ becomes infinite wherever two nuclei coincide. Here gradient lines may cross, but such points are not met along ordinary reaction paths. The right sides of eq 6 will also become infinite at any point where $\partial V/\partial x_{3N}$ vanishes, but this difficulty can be avoided by dividing eq 1 by some line other than the last, except at critical points of $V$ (maxima, minima, transition structures, etc.) where all $\partial V/\partial x_i$, and hence $\nabla V$, vanish. For the moment we shall avoid consideration of cases where two potential surfaces cross leading to gradient lines that may not have a continuous slope. Consequently, on the surfaces considered there is no crossing of gradient lines along a reaction path except at critical points. We assume further that quadratic terms dominate the power series expansion of $V$ in the neighborhood of each transition structure so that the Murrell−Laidler result[12] holds, and hence only two gradient lines descend from each TS.

Let R be any rotation, including an improper rotation (reflection, inversion, rotatory reflection), of the molecule in 3-dimensional space. Let P be a permutation of identical atoms. The set {PR} includes all operations in the Pechukas group of the molecule. Both R and P also correspond to transformations of a point in the $3N$-dimensional molecular configuration space. The following results from Pechukas[3] and earlier papers will be useful.

1. The operations R and P transform a point on the potential surface $V$ to another of equal energy. This is apparent since R is an orthogonal transformation and therefore preserves angles and distances; P interchanges only identical atoms.

2. If $\mathbf{q}$ is a gradient line on $V$, so are $\mathrm{R}\mathbf{q}$ and $\mathrm{P}\mathbf{q}$.

3. Gradient lines terminate on critical points, and, excluding these termini, symmetry is conserved along gradient lines.

Pechukas' Rule 1 now follows quickly. By continuity of the gradient lines and their derivatives, any symmetry of the line is also a symmetry of the critical points at its ends. Consequently any critical point must have at least all symmetry of all gradient lines terminating on it. In particular, a TS must have at least the symmetry of the two gradient lines, $\mathbf{q}_\mathrm{a}$ leading down to reactant A and $\mathbf{q}_\mathrm{b}$ to product B (Figure 3). Consider a nondegenerate reaction, and suppose the TS has an extra element of symmetry PR not possessed by the gradient line $\mathbf{q}_\mathrm{a}$. Then $\mathrm{PR}\mathbf{q}_\mathrm{a}$ must be a gradient line, and it must terminate on the TS since PR is a symmetry element of the TS. Therefore, either $\mathrm{PR}\mathbf{q}_\mathrm{a} = \mathbf{q}_\mathrm{a}$ or $\mathrm{PR}\mathbf{q}_\mathrm{a} = \mathbf{q}_\mathrm{b}$. The first is impossible since by assumption PR is not a symmetry element of the entire line $\mathbf{q}_\mathrm{a}$. The second is impossible since PR must turn each point on $\mathbf{q}_\mathrm{a}$ to one of equal energy on $\mathbf{q}_\mathrm{b}$, but reactant and product at the ends of these lines are not of equal energy in most nondegenerate reactions. One might imagine rare cases where reactant and product are accidentally isoenergetic in a nondegenerate reaction, but the fact that R preserves angles and lengths and P interchanges only identical atoms prevents PR from transforming reactant into product in such a case. Thus for a nondegenerate reaction, the TS can have no symmetry element additional to those of the gradient line down to reactant. Exactly the same reasoning applies to $\mathbf{q}_\mathrm{b}$, and leads to the conclusion that in a nondegenerate reaction symmetry is conserved along all points on a gradient line from reactant to product, excluding reactant and product themselves but including the TS. Reactant and product might have more symmetry than this gradient line, but they cannot have less. Hence the TS can have only symmetry operations that are shared by reactant and product, and hence Rule 1 for nondegenerate reactions.

There are also gradient lines down to the TS from higher energies. Any symmetry along these lines will be brought to the TS, but, since these gradient lines and those coming up to the TS from lower energies cannot be interconverted by any PR, they can add no symmetry elements to TS in addition to those already allowed by Rule 1.

The degenerate reaction differs from the nondegenerate in that in the former the two paths are isoenergetic and so might be interchanged by some Pechukas operation. This might be imagined to occur by paths $\mathbf{q}_\mathrm{a}$ and $\mathbf{q}_\mathrm{b}$ each having certain Pechukas operations not common to the other. Such operations of $\mathbf{q}_\mathrm{a}$ might turn $\mathbf{q}_\mathrm{b}$ into $\mathbf{q}_\mathrm{a}$ while those of $\mathbf{q}_\mathrm{b}$ turn $\mathbf{q}_\mathrm{a}$ into $\mathbf{q}_\mathrm{b}$. All symmetry operations of $\mathbf{q}_\mathrm{a}$ and $\mathbf{q}_\mathrm{b}$ would, of course, also belong to the TS. It will be shown that this is not the case. Instead, $\mathbf{q}_\mathrm{a}$ and $\mathbf{q}_\mathrm{b}$ have identical Pechukas groups just as in the nondegenerate case, and the extra symmetry operations of the TS which interchange $\mathbf{q}_\mathrm{a}$ and $\mathbf{q}_\mathrm{b}$ belong to it alone (or more precisely, not to any downward gradient path from the TS).

Suppose for a degenerate reaction

$$\mathbf{G}_0 = \{\mathrm{X}_1, \mathrm{X}_2, ..., \mathrm{X}_n\} \tag{7}$$

where $\mathrm{X}_i = \mathrm{P}_i\mathrm{R}_i$, is the Pechukas group of $\mathbf{q}_\mathrm{a}$, excluding its end points A and TS which both have at least this much symmetry. Let

$$\mathbf{G}_\mathrm{TS} = \mathbf{G}_0 + \mathbf{K} = \{\mathrm{X}_1, \mathrm{X}_2, ..., \mathrm{X}_n; \mathrm{Y}_1, ..., \mathrm{Y}_m\} \tag{8}$$

be the Pechukas group of the TS so that

$$\mathbf{K} = \{\mathrm{Y}_1, ..., \mathrm{Y}_\mathrm{m}\} \tag{9}$$

is the set, perhaps empty, of "extra" Pechukas symmetry elements of the TS. Since these turn a gradient path down from the TS into an isoenergetic path also starting at the TS and since $\mathrm{Y}_j \notin \mathbf{G}_{0,}$ it must be that

$$\mathrm{Y}_j\mathbf{q}_{\mathrm{a}\,=}\,\mathbf{q}_\mathrm{b} \qquad j = 1,2, ..., m \tag{10}$$

while

$$\mathrm{X}_i\mathbf{q}_\mathrm{a} = \mathbf{q}_\mathrm{a} \qquad i=1,2, ..., n \tag{11}$$

Next suppose that $\mathbf{G}_0$ is not the Pechukas group of $\mathbf{q}_\mathrm{b}$. Then it must follow that at least for some $\mathrm{X}_i$

$$\mathrm{X}_i\mathbf{q}_\mathrm{b} = \mathbf{q}_\mathrm{a}$$

and since $\mathrm{X}_\mathrm{i}^{-1}$ is a member of $\mathbf{G}_0$

$$\mathrm{X}_i^{-1}\mathrm{X}_i\mathbf{q}_\mathrm{b} = \mathrm{X}_i^{-1}\mathbf{q}_\mathrm{a}$$

or

$$\mathrm{X}_i^{-1}\mathbf{q}_\mathrm{a} = \mathbf{q}_\mathrm{b}$$

which is contrary to the definition of $\mathbf{G}_0$. Hence

$$\mathrm{X}_i\mathbf{q}_\mathrm{b} = \mathbf{q}_\mathrm{b} \tag{12}$$

and $\mathbf{G}_0$ is the Pechukas group of both $\mathbf{q}_\mathrm{b}$ and $\mathbf{q}_\mathrm{a}$.

In a similar way $\mathrm{Y}_j^{-1}$ is a member of $\mathbf{G}_\mathrm{TS}$, and it must be that

$$\mathrm{Y}_j^{-1}\mathbf{q}_\mathrm{a} = \mathbf{q}_\mathrm{b} \tag{13}$$

since otherwise

$$\mathrm{Y}_j^{-1}\mathbf{q}_\mathrm{a} = \mathbf{q}_\mathrm{a}$$

$$\mathrm{Y}_j\mathrm{Y}_j^{-1}1\mathbf{q}_\mathrm{a} = \mathbf{q}_\mathrm{a} = \mathrm{Y}_j\mathbf{q}_\mathrm{a}$$

which is contrary to eq 10. Hence $\mathrm{Y}_j^{-1}$ belongs to $\mathbf{K}$. Then using eq 13

$$\mathrm{Y}_j\mathrm{Y}_j^{-1}\mathbf{q}_\mathrm{a} = \mathrm{Y}_j\mathbf{q}_\mathrm{b}$$

so that

$$\mathrm{Y}_j\mathbf{q}_\mathrm{b} = \mathbf{q}_\mathrm{a} \tag{14}$$

and the "extra" operations in $\mathbf{K}$ do interchange $\mathbf{q}_\mathrm{a}$ and $\mathbf{q}_\mathrm{b}$.

Next consider the products $\mathrm{X}_i\mathrm{X}_j$, $\mathrm{X}_i\mathrm{Y}_j$, $\mathrm{Y}_j\mathrm{X}_i$, and $\mathrm{Y}_i\mathrm{Y}_j$. All belong to $\mathbf{G}_\mathrm{TS}$ because of the closure property, and for the same reason $\mathrm{X}_i\mathrm{X}_j$ belongs to $\mathbf{G}_0$. To show that $\mathrm{X}_i\mathrm{Y}_j \in \mathbf{K}$, multiply eq 10 by $\mathrm{X}_i$ and use eq 12

$$\mathrm{X}_i\mathrm{Y}_j\mathbf{q}_\mathrm{a} = \mathrm{X}_i\mathbf{q}_\mathrm{b} = \mathbf{q}_\mathrm{b} \tag{15}$$

In the same way, multiplication of eq 12 by $\mathrm{Y}_j$, and use of eq 10 shows also that $\mathrm{Y}_j\mathrm{X}_i \in \mathbf{K}$. Again, multiply eq 10 by $\mathrm{Y}_i$ and use eq 14

$$\mathrm{Y}_i\mathrm{Y}_j\mathbf{q}_\mathrm{a} = \mathrm{Y}_i\mathbf{q}_\mathrm{b} = \mathbf{q}_\mathrm{a} \tag{16}$$

to show that $\mathrm{Y}_i\mathrm{Y}_j \in \mathbf{G}_0$. In summary

$$(\mathrm{X}_i\mathrm{Y}_j \text{ and } \mathrm{Y}_j\mathrm{X}_i \in \mathbf{K}) \text{ and } (\mathrm{X}_i\mathrm{X}_j \text{ and } \mathrm{Y}_i\mathrm{Y}_j \in \mathbf{G}_0) \tag{17}$$

Finally, multiply $\mathbf{G}_\mathrm{TS}$ on the right by $\mathrm{Y}_j$

$$\mathbf{G}_\mathrm{TS}\mathrm{Y}_j = \mathbf{G}_0\mathrm{Y}_j + \mathbf{K}\mathrm{Y}_j = \{\mathrm{X}_1\mathrm{Y}_j, ..., \mathrm{X}_n\mathrm{Y}_j; \mathrm{Y}_1\mathrm{Y}_j, ..., \mathrm{Y}_m\mathrm{Y}_j\} \tag{18}$$

By the rearrangement theorem which says that multiplication of all members of a group by any particular member gives back the group in a perhaps rearranged order, each of the elements in this set is distinct and each is a member of $\mathbf{G}_\mathrm{TS}$. By eq 17, each member of $\mathbf{G}_0$ is turned into a member of $\mathbf{K}$, and each member of $\mathbf{K}$ into a member of $\mathbf{G}_0$ by this postmultiplication by $\mathrm{Y}_j$. Thus $m = n$, and any allowed group for the TS in a degenerate reaction that contains symmetry operations that are not shared by reactant and product must be twice the order of one of the groups allowed by Rule 1 and must contain that group as a subgroup. Hence Rule 2 holds for transition structure symmetries in one-step degenerate reactions.

Since the set of all elements common to any two groups $\mathbf{G}_1$ and $\mathbf{G}_2$ (i.e., $\mathbf{G}_1 \cap \mathbf{G}_2$) is itself easily shown to be a group, Rule 1 can alternatively be stated: "The symmetry group of the TS in a one-step nondegenerate reaction is one of the subgroups common to the reactant and product Pechukas groups."

## IV. Discussion

**IV.1. The Problem of Rotation.** Because the energy of a molecule is unchanged by rotation or translation, each gradient path in 3*N*-space has associated with it a 6-fold infinity of equivalent paths. Along each of these, symmetry is preserved. If symmetry elements are defined relative to the three Cartesian axes of laboratory space (e.g., a 3-fold rotation around the *z* axis, or a reflection in the *xy* plane), then it is clear that the symmetry elements may vary from one equivalent path to another. Since the derivation of Rules 1 and 2 made use of the symmetry conservation along a gradient path, to apply these rules one must imagine the reaction carried out without sliding from one equivalent path to another, that is, without overall rotation or translation of the reacting molecule.

Holding the center of mass fixed in the laboratory space prevents translations, but since the molecule is not rigid, it is not always easy to see how to avoid rotation. The permutation operators attached in the Pechukas group to the point symmetry elements help to overcome this problem. As the molecule is transformed from reactant to product, symmetry elements of the reactant may disappear and new ones appear for the product. It is necessary to know whether a particular $C_2$ axis (say) in the product is the same as one in the reactant. For example, in the conrotatory ring opening of cyclobutene in Figure 1, the rotation of the two $\mathrm{CH_2}$ groups makes an overall rotation (i.e., a motion requiring an external torque) about an axis through the $\mathrm{C_2{=}C_3}$ and $\mathrm{C_1{-}C_4}$ bonds. To cancel this, the entire molecule must be rotated in the opposite direction. Thus the $\sigma_\mathrm{v}$ plane of the reactant is different from that of the product; but since the former permutes atoms 5 and 9 while the latter permutes 5 and 10, the permutations of the Pechukas symmetry elements make it clear that these two operations are different even without considering overall rotation of the molecule.

However, these permutation operators alone are not always sufficient, as the *cis*−*trans* isomerization of ethylene by rotation about the C═C bond shows. Start with ethylene lying in the *xy* plane as **a** in Figure 4. If the $\mathrm{C_2H_5H_6}$ group is rotated clockwise by 90° and the $\mathrm{C_1H_3H_4}$ group counterclockwise by 90°, the rotations about the C═C bond cancel, and the resulting Berry pseudorotation[23] gives the product **b** in the *xz* plane shown in Figure 4. There is a reflection plane in both reactant and product that induces the permutation (3,4)(5,6), but they are not the same plane. Thus the two Pechukas operations are not identical. The largest common Pechukas group of reactant **a** and product **b** in Figure 4, taking account of spatial orientation of **a**, **b**, and all symmetry elements, is {E, (3,4)(5,6)$C_{2x}$, (1,2)(3,5)(4,6)$C_{2y}$, (1,2)(3,6)(4,5)$C_{2z}$} which is isomorphic with the point group $D_2$ containing (see Table 1) subgroups $C_1$ and $C_2$. These are possible TS symmetries. Doubling the order of these gives (again, see Table 1) the additional possible symmetries: $C_1 \rightarrow [C_2, C_s, C_i]$; $C_2 \rightarrow [C_4, S_4, C_{2v}, C_{2h}, D_2]$; $D_2 \rightarrow [D_{2h}, D_{2d}, D_4]$. Thus 12 point symmetry groups are possible for the TS of this reaction. Note, however, that the $C_2$ group arises in two ways that correspond to different Pechukas groups: first, as a subgroup of the largest common subgroup of reactant and product Pechukas groups so that the $\mathrm{C_2}$ operation

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[23] Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933−938.

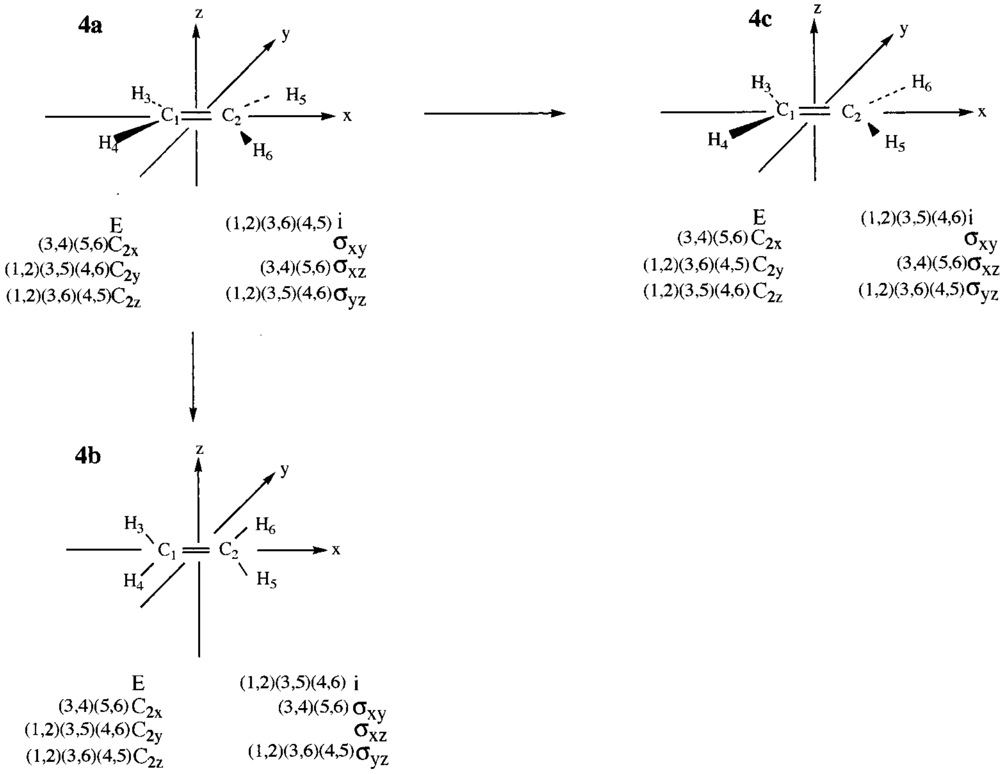

**Figure 4.** Pechukas groups for the rearrangement of the automer **a** of ethylene to two orientations (**b** and **c**) of the product automer.

must be one of the 2-fold rotations with associated atom permutations in that group. Second, $C_2$ may arise by doubling the common subgroup $C_1$. In this case the atom permutations associated with the 2-fold rotation are not specified. Similar remarks apply to the $D_2$ symmetry.

If instead the $C_2H_5H_6$ group is rotated by 180° while holding the $C_1H_3H_4$ group fixed, the isomerized product is in the *xy* plane (**c** Figure 4). The largest common Pechukas group of this reactant and product is $\{E, (3,4)(5,6)C_{2x}, \sigma_{xy}, (3,4)(5,6)\sigma_{xz}\}$ which is isomorphic with the point group $C_{2v}$ containing subgroups $C_1$, $C_2$, and $C_s$. From Table 1 additional possible TS symmetries are: $C_1 \rightarrow [C_2, C_s, C_i]$; $C_2 \rightarrow [C_4, S_4, C_{2v}, C_{2h}, D_2]$; $C_s \rightarrow [C_{2v}, C_{2h}]$; $C_{2v} \rightarrow [D_{2h}, D_{2d}, C_{4v}]$.

The TS symmetry predictions given by orientations **b** and **c** in Figure 4 differ in that the first allows $D_4$ while the second allows $C_{4v}$. This $C_{4v}$ possibility is excluded by the following reasoning. The largest common Pechukas subgroup of **a** and **c** is isomorphic with $C_{2v}$ and contains the operation $\sigma_{xy}$. Should the actual TS be of this symmetry or of symmetry gotten by doubling the order of this group (i.e., $D_{2h}$, $D_{2d}$, or $C_{4v}$), the symmetry operation $\sigma_{xy}$ must be preserved all along the gradient path. Since this operation interchanges no atoms, the molecule must remain planar. In the same way, the operation $(3,4)(5,6)\sigma_{xz}$ must also be preserved. This requires that atoms 5 and 6 move symmetrically with respect to the *xz* plane. They must therefore meet on the *x* axis and pass through each other. Such infinite-energy paths are of no practical interest and so must be excluded. It is true that a $C_{2v}$ TS structure is also possible for path **a** to **b** (Figure 4), but this occurs by doubling the common subgroup $C_2$ so that the exact symmetry planes are not specified, and neither a $C_{2v}$ nor a $D_{2d}$ (which does not arise from $C_{2v}$ for this path) TS causes difficulties.

It might seem more natural to attach the point symmetry elements to molecule-fixed rather than laboratory-fixed coordinates. After all, there is nothing to prevent the actual reacting system from translating and rotating. The difficulty is that we see no way to be sure that a symmetry plane, for example, that permutes certain atoms in the reactant and another that permutes the same atoms in the product is actually the same plane and is conserved along the reaction path. For example, **a** and **b** in Figure 4 both have some reflection plane that permutes no atoms and another that exchanges atoms 3 and 4, and 5 and 6. Similarly, they both have three $C_2$ axes that cause the same permutations in reactant and product. It might then be said that the Pechukas groups of **a** and **b** have 6 elements (E, three $C_2$ axes and 2 reflection planes) in common. This is impossible since the set of all elements common to two groups forms a subgroup of both, and hence its order must be an integer divisor of the order of both groups, but 6 is not an integer divisor of 8.

The example of Figure 4 is a degenerate reaction, but the same problem can occur in nondegenerate cases. Replace $H_4$ and $H_6$ in this figure by Cl atoms, and consider the resulting *cis*−*trans* isomerization of 1,2-dichloroethylene. The resulting modified structures **a** and **b** then have $\{E, (1,2)(3,5)(4,6)C_{2y}\}$ as the largest common subgroup while modified **a** and **c** have $\{E, \sigma_{xy}\}$.

Since in Figure 4 one can go from **a** to **b** by a Berry pseudorotation, i.e., by vibration of the two halves of the molecule moving against each other with no external torque, while **c** can be reached from **a** by rotating the right methylene group, which would require an external torque, we can exclude the product orientation **c** in this case. In fact, any degenerate reaction, except the interconversion of enantiomers, along a gradient path with no external force or torque must be describable as a Berry pseudorotation. The case of enantiomer interconversion is excluded since reactant and product, although of equal energy, are distinguishable.

It is further true that the extra TS symmetry allowed by **c** is shown to be impossible because it requires motion of atoms through each other. However, we do not see, in general, any way to choose a unique orientation of product, or even to recognize those orientations that cannot be reached without

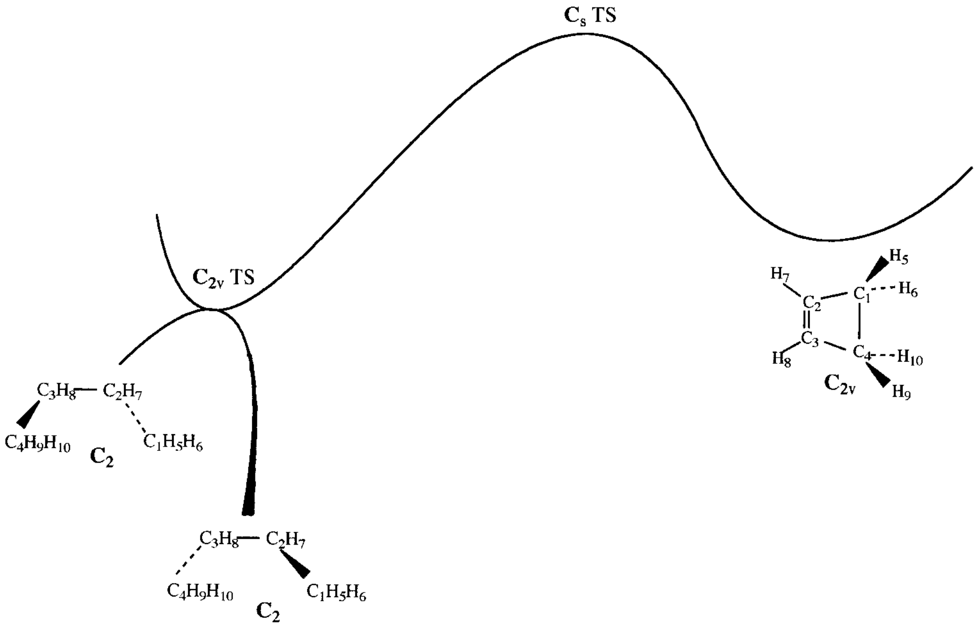

**Figure 5.** Sketch of the potential surface showing the ring opening of cyclobutene to gauche butadiene. The $C_{2v}$ transition structure here is the planar *s-cis*-butadiene shown in Figure 1.

rotation of the system as a whole. The only safe procedure appears to be to choose some spatial orientation of reactant (or product) and then to examine all relative orientations of product (or reactant). All distinct TS symmetry predictions from all orientations are then possible TS symmetries unless they can be excluded by further considerations. For the ethylene example of Figure 4, we have found no further TS symmetries not allowed byproduct orientations **b** and **c**.

**IV.2. Comparison with the Use of Longuet-Higgins Groups.** In 1963 Longuet-Higgins[24] introduced the group consisting of all "feasible" permutations in the molecule plus all "feasible" inversions of permuted configurations. A "feasible" permutation is one obtainable under the conditions of the experiment considered during the time of the experiment. Longuet-Higgins called this group the "molecular symmetry group", but we shall follow others including Balaban and Brocas[25] and use the name, "Longuet-Higgins group". Although this group was developed to understand the spectra of nonrigid molecules, it can be applied to rigid molecules as well where it and the point symmetry group are isomorphic.

Consider again the reaction **a** to **b** in Figure 4. The Longuet-Higgins symmetry operators for both **a** and **b** are

$$\begin{array}{rr} E & E^* \\ (3,4)(5,6) & [(3,4)(5,6)]^* \\ (1,2)(3,5)(4,6) & [(1,2)(3,5)(4,6)]^* \\ (1,2)(3,6)(4,5) & [(1,2)(3,6)(4,5)]^* \end{array} \qquad (19)$$

This group is isomorphic to the $D_{2h}$ point group, and using Table 1 as above this gives all the 13 possibilities for TS symmetry predicted by the Pechukas group above for orientations **a** and **c** and the two additional possibilities $D_{4h}$ and $C_{4h}$. Since the Longuet-Higgins group contains no information about spatial orientation of reactant or product, it predicts the same TS symmetries for the reaction **a** to **c** as for **a** and **b**.

Again, because of the lack of spatial information in the Longuet-Higgins group, it is not surprising that its predictions are less restrictive than those of the Pechukas group. It is only surprising that the difference is as small as it is with 15 possible TS symmetries predicted by the Longuet-Higgins group and 13 by the Pechukas group.

The Longuet-Higgins group avoids the troublesome problem of relative orientation of reactant and product. On the other hand, the Pechukas group is more selective and the isomorphism with the familiar point group is more immediately obvious.

## V. Further Examples

All of the examples below, like the two above, are unimolecular rearrangements. Multimolecular steps may also be treated with the additional complication of considering various relative orientations of the reactant and of the product components.[3]

**V.1. The Ring Opening of Cyclobutene.** We return to the cyclobutene ring opening discussed in section II.3. This proceeded from cyclobutene with $C_{2v}$ symmetry to planar $C_{2v}$ *s-cis*-butadiene through a $C_s$ transition structure. However, the $C_{2v}$ butadiene is actually not an energy minimum, but rather a transition structure between two enantiomeric forms of gauche butadiene, each with $\boldsymbol{C_2}$ symmetry. When the gradient along the $C_1-C_4$ bond lengthening, $C_1-C_2$ bond shortening, etc., direction reaches a minimum, it meets a pair of downward gradients in an orthogonal direction (rotation of the terminal methylene groups about the central $C_1-C_3$ bond) that lead to the gauche products. These points on the potential surface are sketched in Figure 5 where, for clarity, the scale is distorted.

None of this affects our previous prediction of the symmetry of the TS between cyclobutene and *s-cis*-butadiene since our reasoning required only that we consider a TS between, and higher in energy than, two points where all first derivatives vanish, as they do at transition structures as well as at minima. However, the question of whether this new $C_{2v}$ TS has proper symmetry to mediate the reaction between the two gauche forms of butadiene should be considered. These gauche forms have identical Pechukas groups which are isomorphic to $C_2$.

The reaction is degenerate, and Table 1 shows the observed $C_{2v}$ TS symmetry to be in the allowed list ($C_1$, $C_2$, $C_s$, $C_i$, $C_{2v}$, $C_{2h}$, $C_4$, $S_4$, $D_4$) of possibilities.

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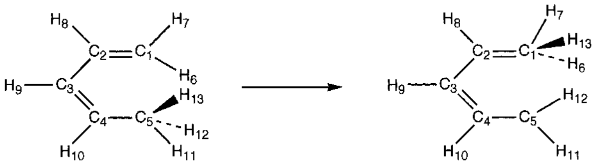


| $C_s$ | $C_s$ |
|---|---|
| E | E |
| (12,13)σ | (6,13)σ |

**Figure 6.** The hydrogen shift in 1,3-pentadiene.

Situations such as this where the gradient path from one TS falls to another TS are probably not uncommon. The gradient path for the Diels–Alder endo addition of *s-cis*-butadiene to cyclopropene has been followed at the STO-3G level,[4] and is like Figure 5. The gauche butadiene flattens to the same $C_{2v}$ TS as in Figure 5 which then adds to cyclopropene to give a $C_s$ transition structure.

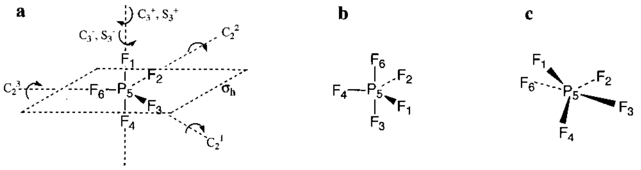
The last part of the computed gradient path for the combination of silene and ethylene to form silacyclobutane is another example.[26] Silene and ethylene first react to form a trans diradical which then rises to a $C_s$ TS. This in turn falls to a $C_{2v}$ TS in the degenerate interchange of an enantiomeric pair of puckered silacyclobutene rings. In this example, the symmetry rules were a considerable practical aid in connecting the various stationary points on the potential surface.

It is a minor point of nomenclature that, if one follows a gradient path such as above down from the first to the second TS, and then down to product, it might be said that the reaction path has bifurcated to two products. It seems to us clearer to say that the original gradient path reaches its minimum at the second TS from which it begins to rise. At the second TS two other gradient paths go down to product.

**V.2. The [1,5]-Sigmatropic Hydrogen Shift in *cis*-1,3-Pentadiene.** In 1982 Kwart and his colleagues[27] proposed a $C_{2v}$ transition structure in the degenerate concerted hydrogen shift reaction shown in Figure 6. This TS was later shown by computation to have $C_s$ symmetry instead.[28−30]

It will be shown now that with the rules above, the $C_{2v}$ TS can be excluded without computation. Figure 6 lists the Pechukas groups of reactant and product in this reaction. The largest common subgroup is isomorphic with $C_1$. No other relative orientation of reactant and product automers give additional symmetry; nor do any other pair of automers with a single hydrogen transferred from the methyl to the methylene group. Table 1 shows that the only possibilities for the TS symmetry in this degenerate reaction are $C_1$, $C_2$, $C_s$ (as calculated), $C_i$. $C_{2v}$ is not a possibility.

**V.3. Rearrangement of PF$_5$ by Berry Pseudorotation.** The rearrangement of the phosphorus pentahalides by the pseudorotation mechanism proposed by Berry[23] in 1960 is an interesting example where the obvious relative orientation of automers does not give the correct symmetry prediction. Suppose the automer **a** of PF$_5$ shown in Figure 7 is rearranged to automer **b**. It seems natural, if one imagines not knowing the Berry mechanism, to align the two automers so the $C_3$ axes coincide as in **b**. With this relative orientation **a** and **b** share only the two underlined Pechukas operations E and (1,4)(3,6)-$C_2{}^2$. From Table 1, nine possible symmetries for the TS are then $C_1$, $C_2$, $C_s$, $C_i$, $C_4$, $S_4$, $C_{2v}$, $C_{2h}$, and $D_2$.



| $D_{3d}$ | $D_{3d}$ | $D_{3d}$ |
|---|---|---|
| E | $\underline{E}$ | $\underline{E}$ |
| $(2,3,6)C_3^+$ | $(1,4,2)C_3^+$ | $(1,2,4)(C_3^+)'$ |
| $(2,6,3)C_3^-$ | $(1,2,4)C_3^-$ | $(1,4,2)(C_3^-)'$ |
| $(1,4)(2,6)C_2^1$ | $(3,6)(2,4)C_2^1$ | $(3,6)(2,4)C_2^4$ |
| $(1,4)(3,6)C_2^2$ | $\underline{(3,6)(1,4)C_2^2}$ | $\underline{(3,6)(1,4)C_2^2}$ |
| $(1,4)(2,3)C_2^3$ | $(3,6)(1,2)C_2^3$ | $(3,6)(1,2)C_2^5$ |
| $(1,4)\sigma_h$ | $(3,6)\sigma_h$ | $\underline{(1,4)\sigma_h}$ |
| $(1,4)(2,3,6)S_3^+$ | $(3,6)(1,4,2)S_3^+$ | $(3,6)(1,2,4)(S_3^+)'$ |
| $(1,4)(2,6,3)S_3^-$ | $(3,6)(1,2,4)S_3^-$ | $(3,6)(1,4,2)(S_3^-)'$ |
| $(2,6)\sigma_v^1$ | $(2,4)\sigma_v^1$ | $(2,4)\sigma_v^4$ |
| $(3,6)\sigma_v^2$ | $(1,4)\sigma_v^2$ | $\underline{(3,6)\sigma_v}^2$ |
| $(2,3)\sigma_v^3$ | $(1,2)\sigma_v^3$ | $(1,2)\sigma_v^5$ |

**Figure 7.** The Berry pseudorotation rearrangement of PF$_5$ from automer **a**. The Pechukas operations underlined for the two orientations **b** and **c** of the same product automer are those common with the Pechukas group of the reactant automer **a**.

However if the automer in **b** Figure 7 is rotated around the P–F$_2$ bond until F$_3$ and F$_6$ are in the $\sigma_h$ plane of **a**, **c** is obtained. The largest Pechukas group common to **a** and **c** then consists of the four operations underlined in the Pechukas group of **c** and is isomorphic with the point group $C_{2v}$. This adds, using Table 1, the three additional possibilities $D_{2h}$, $D_{2d}$, and $C_{4v}$ for the TS symmetry. There is also an orientation of the product automer in which the P–F$_4$ bond lies along the original $C_2{}^2$ axis and in which F$_3$–P–F$_6$ is in the $\sigma_h$ plane. This has a Pechukas group isomorphic with $C_s$ in common with **a**, but it adds no new possibilities for the TS symmetry.

Since the Berry pseudorotation mechanism and the $C_{4v}$ TS are already known, automer orientation **c** in Figure 7 would probably be one's first choice. Of course, if the TS is known, there is no point in predicting its possible symmetry. Our purpose was to show that had the TS not been known, the methods here would correctly have predicted a $C_{4v}$ structure as a possibility. Although 37 of the 49 symmetries in Table 1 are rigorously eliminated in this case, 12 still remain. Further techniques that eliminate six more possibilities, still leaving $C_{4v}$, have been developed by Bytautas.[31] Their application requires a little more effort than the methods here, and their results cannot be summarized as in Table 1.

**V. 4. The Bond-Shift Rearrangement in Cyclooctatetraene.** By the methods above, Table 1 gives the 15 possibilities, $D_{4h}$, $D_{2d}$, $C_{4h}$, $C_{4v}$, $D_{2h}$, $D_4$, $S_4$, $C_{2v}$, $D_2$, $C_{2h}$, $C_4$, $C_2$, $C_s$, $C_i$, and $C_1$, for TS symmetry in a one-step ring inversion (**1** to **2** or **3** to **4**, Figure 8) of cyclooctatetraene where reactant and product have identical Pechukas groups isomorphic with $D_{2d}$. In the same way, the largest Pechukas group common to reactant and product for a one-step bond-shift rearrangement (**1** or **2** to **3** or **4**, Figure 8) is isomorphic with $S_4$, and there are 11 possible TS symmetries, $S_4$, $D_{2d}$, $C_{4h}$, $C_{2v}$, $C_{2h}$, $D_2$, $C_4$, $C_2$, $C_s$, $C_i$, and $C_1$. These do not include the planar $D_{8h}$ structure that might perhaps be expected.

In 1992 Hrovat and Borden[32] published CASSCF results demonstrating the three-step mechanism shown in Figure 8

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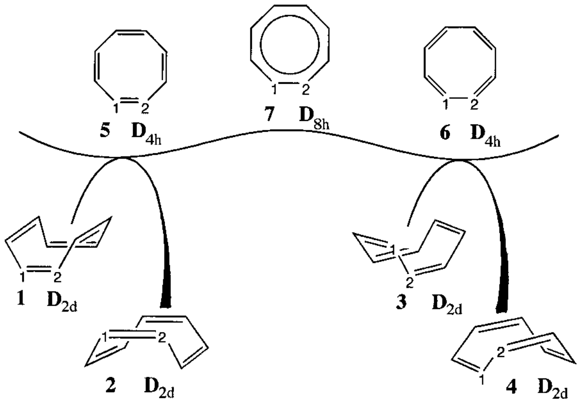

**Figure 8.** Sketch of the potential surface showing the ring-inversion (**1** to **2** or **3** to **4**) and the bond shift (**1** or **2** to **3** or **4**) automerization of cyclooctatetraene as calculated by Hrovat and Borden.[32]

where all structures are singlets. The first step is a ring inversion between **1** and **2** or **3** and **4** with calculated $D_{4h}$ transition structures **5** and **6** as allowed above. Transition structures **5** and **6** also have identical Pechukas groups, and Table 1 shows $D_{8h}$ to be an allowed symmetry for TS **7** connecting them. The bond-shift reaction as followed along gradient paths is thus a three-step process: up from **1** or **2** to TS **5**, then up again to TS **7** and down to TS **6**, then down to the bond-shifted products **3** and **4**.

However, the reacting molecule may not follow a gradient reaction path.[32] If the descending gradient line from **7** goes along the floor of a valley whose sides become less and less steep so that the descending valley becomes a descending ridge, the gradient becomes unstable and the molecule will fall from the ridge along a gradient extremal as defined by Ruedenberg[33] in his extensive study of the ring opening of cyclopropylidene to allene. In this case, cyclooctatetraene will bypass TS **5** on the way to structures **1** or **2**. Consequently, what we have called a three-step reaction for bond shifting by following the gradient through three transition structures, might equally well be considered a one-step reaction if transition structures **5** and **6** are avoided. This emphasizes Pechukas' point[3] that gradient lines are useful here not because the actual reaction must always move along gradient, but because the symmetry conservation along gradients imposes symmetry constraints on critical points connected by gradients. The symmetry rules are therefore helpful in mapping the potential surface whether the actual reaction path follows gradient lines.

The mechanism calculated by Hrovat and Borden has been strengthened by the spectroscopic observation of their $D_{4h}$ transition structure.[34,35] They also give an estimate of 12 ± 1 kcal/mol for the antiaromatic destabilization of planar cyclooctatetrene. This is in fair agreement with the simple Hückel result, using a Dewar reference, of 15.7 kcal/mol.[36,37]

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