

by what looks like a bend of $B_1-A-(B_2B_3)$ to a planar structure, and thence by repetition of these motions, in reverse order, to the mirror image form.

Least motion analysis predicts that the direct inversion path is to be preferred, if extrapolations of distortions to the planar forms are justified. (*N.b.*, the necessary use of transition state structures to characterize final end-point states for this, and for that matter any other mechanistic distinction.) Spectroscopic results for many AB_3 system indicate the symmetrical bend (direct inversion) mode to be very soft (NH_3 and PH_3 , for example, invert in average times of $\sim 10^{-11}$ and 10^{-7} sec, respectively)²² and extrapolation would appear relatively safe here. For the other mode, which follows a composite of motions, various intermediate structure effects may enter to complicate the extrapolation, although not likely to change the ordering determined.^{23,24} In the following paper, detailed examination is made of such complicating effects as they can

(22) Reference 12, pp 220–225.

(23) Inversion in pyramidal AB_3 molecules, as importantly influenced by changes in ν_2 and the angle β , is discussed by G. F. Koepl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967).

(24) R. F. W. Bader, *Mol. Phys.*, **3**, 137 (1960), has employed D_{3h} and C_{3v} symmetry AB_3 molecules undergoing distortion in illustration of the "pseudo-Jahn-Teller" effect which rationalizes the sign of interaction constants for vibration in terms of symmetry and energetics of low lying molecular electronic states. Others have invoked related arguments in rationalization of preferred structures and relative reactivities.^{25,26} Such concepts it appears may be usefully combined with force constant weighted least motion analysis to extend the domain and comprehensibility of the PLM.

(25) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968); L. S. Bartell and B. Anderson, *J. Chem. Soc., Chem. Commun.*, 786 (1973).

(26) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969); L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

influence reactivity correlation by least motion analysis based on end-point structural information.

Conclusions

To the extent that simple chemical reactions can be viewed as processes where the geometric deformations which characterize them are extensions of the small structural changes which give rise to their vibrational spectra, the principle of least motion for correlation of relative reactivities appears to be satisfactorily rationalizable. With the appropriate weighting of the individual atomic motions by masses and force constants, the harmonic model least motion deformations parallel the vibrational energies within symmetry selected modes. Even in the absence of such weighting, least motion paths for a given amount of collective atom movement usually correlate with those modes which are the softest in energy requirement, although exceptions must certainly be anticipated, notably for deformation of such unstable structures as those which characterize transition states. Along reaction paths, incremental motion perpendicular to the vector directed toward the molecular center of gravity appears to be generally favored over motion along the vector in either direction, a situation analogous to the stable molecule (vibration) results noted.

When applied to the large molecular deformations which are experienced over the entire course of conventional chemical reactions, a number of effects can enter which may mitigate the least motion–vibration theory analogy. A variety of these effects, both of external and internal origin, are examined in detail in the following report, employing the formalisms developed here.

Application of Analytic Least Motion Forms to Organic Reactivities¹

S. Ehrenson

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973. Received October 16, 1973

Abstract: The analytic expressions previously derived to evaluate least motion distortions undergone during reaction are applied to a number of chemically interesting organic molecule systems. Consideration is given to differential changes along reaction pathways as well as to the gross geometry changes which accompany reactant conversions to product or transition states. Adopting the previously demonstrated analogy to the theory of small vibrations, the value of considering these differential changes within the principle of least motion is stressed. As well as reexamining a number of previously correlated reaction systems, some relatively simple examples are considered where dissections of the over-all motions are easily made and where good theoretical structure and energy information are available. These studies reveal least motion and enthalpies of activation usually produce the same ordering of reactivities. In all cases examined, where disagreement with experiment or other more firmly grounded theory is encountered, successful rationalization of the discrepancies appears possible.

Hine's harmonic springs ensemble model used for correlation of organic reactivities within the framework of the principle of least motion (PLM) was examined in detail in the preceding paper.² Closed

forms were presented for computation of least motion distortions for systems of fairly broad generality. Employing these, especially for differential motions around end-point states (reactant, product, and transition states), revealed a number of details of strong correspondence between the PLM and conventional theory of molecular vibrations. Similar and potentially useful

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. Ehrenson, *J. Amer. Chem. Soc.*, **96**, 3778 (1974).

connections with dynamical properties of reaction systems between such end points were also obtained.

In the present paper, these analytic forms will be applied to a number of organic chemical reactivities, and attempts will be made to extend the correspondences with alternative theoretical methods. The extent to which such correspondences may be shown to hold in comparisons of reactivity, and why they fail when they do, provide important insights into the physical basis of the least motion concept and its ultimate utility as a correlation tool.

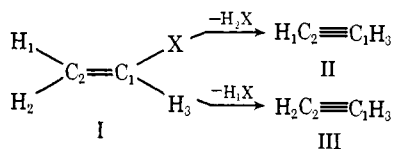
Systems of Chemical Interest

General Remarks. It is clear from the results of ref 2 that least motion measures of molecular distortion exactly parallel potential energy differences upon appropriate weighting of the individual nuclear motions (by masses within a particular vibrational mode and with force constants among modes). Further, at least in the conventional cases examined, it also appears that even without such weighting, least motion generally corresponds to that distortion which is the softer. That is, bends are lesser motion distortions for the molecule than stretches, given equal displacement of the individual nuclei.

In application to reactivities which depend upon gross differences between rather different states (reactant to transition state for rates, reactant to product for equilibrium product distribution), a number of potentially mitigating effects on the differential displacement analogies with vibrational theory must be considered. These are most conveniently examined in terms of examples of the groups of reactivities in which they are most likely to enter.

Reaction Systems Exhibiting a Net Gain or Loss of Atoms. The first chemical reactivity systems examined by Hine not involving predominant π -electron resonance effects were hydrogen halide elimination reactions from ethyl and vinyl halides.³ Tee has reexamined these reactions in greater detail.⁴ They are chosen here to illustrate the considerations involved when reactant and product differ in number of constituent atoms and as well to introduce the useful distinction among systems which differ only in long-range interactions, as contrasted to those which exhibit short-range interaction differences.

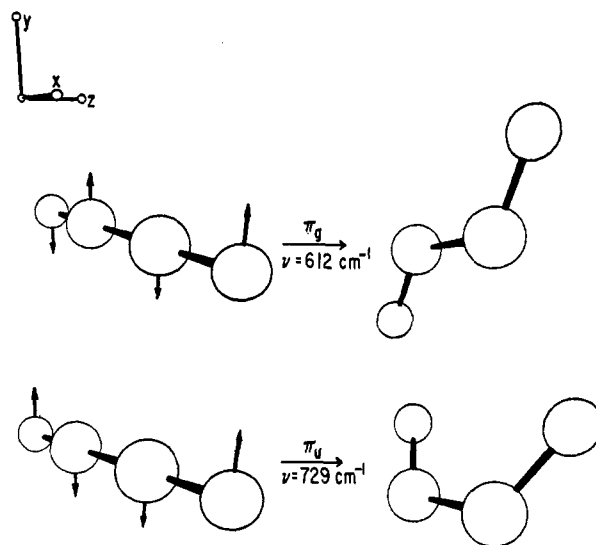
The dehydrohalogenation reactions of vinyl halides are known to proceed preferentially by trans (I to II), rather than by cis (I to III), elimination.⁵ The reactant



is common to both pathways; the products are identical except for hydrogen labeling, which in experimental systems may be accomplished by use of deuterium. Excluding differential effects of the medium, whether exerted in the removal of HX or in solvation of the transition states, the trans to cis rate preference is

attributable to the difference in transition state free energies (II[‡] vs. III[‡]).

Vibrational normal coordinate analysis includes differential distortion modes for acetylene to bent structures,⁶ which would approach, in the limit of large deformations, reasonable expectations of the respective transition state structures for these pathways, *viz.*



It is important to note that just such structures as these, with HX assumed completely removed and HCC angles $\sim 120^\circ$, are used as the initial states for computation of the respective D^2 values. Acetylene is the final state structure. The vinyl halide bond lengths, involved in specification of the initial state, of course, require other (stretch-type) distortions, but the same stretch deformations apply to both the cis and trans skeletons. Furthermore, as in ref 2, it should be stressed that the vibrations as pictured in the normal coordinate framework correspond exactly, with respect to maintenance of center of mass position and rotation to conserve angular momentum, to the positional optimization procedure involved in calculation of the D^2 values.

From the quoted frequencies, it is quickly seen that bending into the cis form requires more energy than into the trans form and, consequently, if the harmonic approximation and others, discussed immediately below, hold, the trans reaction would be expected to be favored. Force constants for the picture displacements, which render the vibrational energy change directly comparable to D^2 , even more strongly illustrate the relative stiffness of the cis vibration. In symmetry coordinate terms where ω_1 and ω_2 are respectively the left and right HCC angle deformations, for π_u ($\propto [\omega_1 - \omega_2]$) the force constant is 0.270 mdyn/Å and for π_g ($\propto [\omega_1 + \omega_2]$) 0.122 mdyn/Å.⁷

The harmonic approximation, and to what point it holds, is but one of the assumptions involved in the above extension to reactivity. Another which connects follows from the question of why the product state rather than the reactant state is used to evaluate the relative transition state energies. It is clear for the least motion model that structural information for

(3) J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

(4) O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969).

(5) D. V. Banthorpe, "Elimination Reaction," Elsevier, New York, N. Y., 1963, pp 142-144.

(6) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1945, Chapter III 3b.

(7) E. Meisingseth and S. J. Cyvin, *Acta Chem. Scand.*, **15**, 2021 (1961).

vinyl halide with stretched CH and CX bonds is lacking and difficult to hypothesize. If it were available, displacements of equilibrium vinyl halide to these structures could have been computed. In the vibrational analysis framework, no reason other than the complexity of mixing the proper normal coordinate vibrations to yield satisfactory representations of the eliminations prompted the procedure adopted.

What has been done, then, in application of the least motion model, from the perspective of the theory of small vibrations, is (a) assume the transition states for the reactions lie close enough to product (here acetylene) that the difference in potential energy obtained from the harmonic approximation for small distortions persists upon enlargement of these distortions; (b) assume the free energy difference parallels the potential energy difference; and (c) since the end-point states employed in the computation of D^2 relate more directly, conceptually, to the reverse reaction, assume the equilibrium constants for the compared reactions are the same, as they are here, or, generally, that they are sufficiently similar so that if $k_{-11}/k_{-1} > 1$ then $k_{11}/k_1 > 1$.

It is important to note, for reactions where atoms are gained or lost, that the least motion model, as presently formulated, implicitly assigns greater similarity of the transition state to one or the other end-point states. That is, the transition state more closely resembles the molecular state having fewer nuclei. However, it is also useful to recognize that proportionality only between the vibrational distortion energy difference and transition state energy difference is required in assumption a. Hence, similar but not necessarily identical positions of the transition states as regards the sizes of the individual normal-coordinate distortions of the end point are acceptable in the comparison of theories.⁸ In the event the same ordering of reactivities is obtained for differential distortions from both end points (here by distortion of vinyl halide and of acetylene), it appears likely the least motion model would correctly order simple reactivities independent of how well or poorly it represents, in a normal coordinate vibration sense, the true character of the transition state.

An important effect, not likely to be contained in the end-point structural information used in the motion calculations, is the differential short-range force requirements for entering the different transition states. This effect, which bears crucially on assumption b, also may play a role in how correctly pictured from end-point information the transition states are with respect to potential energy.⁹ Systems which differ solely in long-range interactions, as do the present, should be less susceptible to large entropy of activation differences and short-range force differences. Vibrational deformations corresponding to bends, which themselves involve β neighbors, taken in different combinations, as here, would appear to provide the most satisfactory candidates for successful least motion correlation. The differences between the over-all

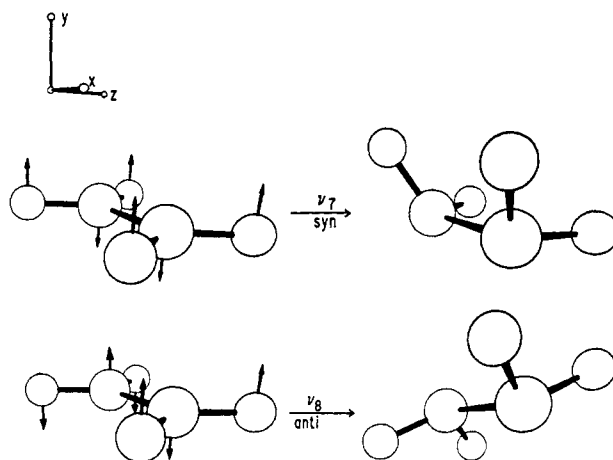
(8) The greater the degree of blurring due to such differences, the less pertinent become the force constants derived from vibrational analysis, (see ref 2).

(9) Included within this effect are the nonbonded repulsions often called steric effects but as well such interactions as conjugative stabilization not present at one or the other end point. As an extreme case, a large difference in interaction for the contrasted paths among two or more departing atoms could conceivably invalidate the transition state structures assumed upon neglect of such atoms.

(combination) modes are then due to γ - or more distant neighbor interactions.

For the present purposes, the elimination of hydrogen halides from ethyl halide to form ethylene may be considered a similar reaction. It has at least two additional features of importance, however. The first involves the relatively low energy of interconversion among energetically nonidentical rotameric states of the reactant. The second concerns mixing of normal modes of vibration to model the eliminations occurring from other than the extreme reactant conformations (staggered and eclipsed, relative to the leaving hydrogen and halide atoms).

Corresponding to these extreme conformations, the appropriate normal coordinate vibrations leading to the anti and syn transition states from ethylene are



where ν_7 is of B_{1u} symmetry and ν_8 is of B_{2g} symmetry. Examination reveals that even though the frequencies for these vibrations are very similar (947 and 949 cm^{-1} , respectively), the force constants for the symmetry coordinate displacements, which normalize the energy terms for equal increments of angular distortion,¹⁰ are not. This syn vibration is found to be substantially stiffer, *i.e.*, 0.206 *vs.* 0.155 $\text{mdyn}/\text{\AA}$,¹¹ in force constant terms.

To this point, analysis resembles that for the vinyl halides, *i.e.*, trans favored over cis elimination. It must, however, be recognized that explicit neglect of the reactant structures here obscures a feature not present in the vinyl halide case. The eclipsed conformations of the ethyl halides are known to be 3–4 kcal/mol higher in energy in the gas phase than their staggered counterparts.¹² Nothing in the least motion model and “reactant” geometry input thereto, or in the analogous vibration distortion model employed, recognizes this difference explicitly.¹³ From the previous analysis it is apparent, then, that the least motion results will only correctly order the rates of the present reactions occurring from rotationally “frozen” reactants if the transition state energy difference (syn

(10) In symmetry coordinates, the displacements for the B_{1u} vibrations are $(RD/2)^{1/2}(\omega_1 + \omega_2)$ and for the B_{2g} $(RD/2)^{1/2}(\omega_1 - \omega_2)$, where the ω 's are the distortions of the left and right hand CCH_2 (bisector) angles and R and D are respectively the CC and CH distances.

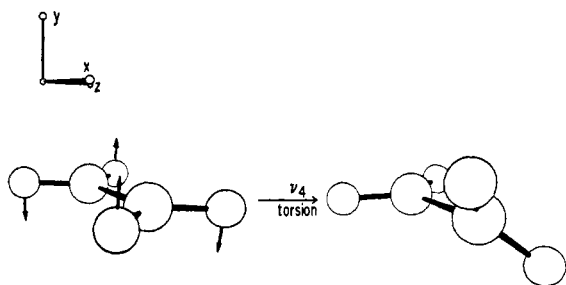
(11) B. N. Cyvin and S. J. Cyvin, *Acta Chem. Scand.*, 17, 1831 (1963).

(12) Cf. J. P. Lowe, *Progr. Phys. Org. Chem.*, 6, 36 (1968).

(13) Even if the structures for the staggered and eclipsed rotamers were known, all the least motion model could recognize are the minor (two) eclipsing H–H interactions. The more important HX interaction could not be incorporated within the present common atom model approach.

relative to anti) is larger than the energy corresponding to the rotation barrier in the ethyl halide. This is equivalent to returning to assumption c, above, and positioning the equilibrium constants, here quite different, to have greater similarity than the rates of the reverse reactions. Such a position may, in fact, often be unrealistic, suggesting that least motion comparisons of reactions different in either end-point state is risky where the difference is not explicitly recognized for all constituent nuclei.

Where one or another β hydrogens may be removed from a given alkyl halide rotamer, and their relative rates of removal are at issue, the above complication does not of course occur. For these cases, or for that matter any others involving intermediate energy alkyl halide rotamers, modeling in terms of normal coordinate vibrations requires consideration of the following twist mode for ethylene



This vibration is of A_u symmetry and has been identified from Raman combination bands as having a frequency of 825 cm^{-1} . Equal and small displacements of the reactants from their extreme (staggered and eclipsed) conformations should require equal mixing of this mode with the appropriate bending modes discussed before in representation of the transition states.

Reference to the least motion D^2 values for these eliminations again shows how the motion and vibrational analysis results connect. PLM predicts product from staggered ethyl chloride to be formed more easily than from the eclipsed reactant form (0.185 vs. 0.421 \AA^2)⁴ and that small twists from these reactant conformations should have essentially equal effects (ΔD^2 equals $0.237 \pm 0.005\text{ \AA}^2$ for 30° twist in each case). This suggests that (pure) cis elimination would be substantially favored over trans-like (60° from pure trans) elimination from the eclipsed C_2H_5X conformer but that the (pure) trans elimination would be even more favored than the cis-like elimination from the staggered reactant conformer.

As in the vinyl halide reactions, the PLM difference between the extreme reactant forms may be traced principally to the greater efficacy in reducing D^2 by the in-plane rotational adjustment (by γ , eq 9)² than by the center of gravity adjustment (eq 5).² Skewing of the reactants, here, involves rotation in another dimension (*e.g.*, by β) but similarly from both extremes. For larger twists of the reactant (or for that matter, unrealistically, of the product, accounting for the second elimination mode per reactant conformer), simple mixing of normal coordinated in representation of the distortions may be unjustified. Significant interaction terms among the symmetries must then be considered; similar nonadditivity effects are noted to enter concomitantly into the D^2 dependence on twist.⁴

The real molecule cases to which this analysis properly extends are those where conformation may be held (*e.g.*, as in a ring structure) and where one or the other β hydrogens are removed along with halide. Consistent with correct mixing of the normal coordinates of vibration, the same conditions for successful application of least motion analysis as outlined previously for the vinyl halides may be expected to apply but with even greater stress on steric requirements. The latter can now be more than short-range dependent because of the over-all rigidification of structure.

Molecular Rearrangements. Reactions wherein atoms are neither gained nor lost but merely subjected to intramolecular repositioning have been the most thoroughly studied, as a group, by nuclear least motion methods. Even so, the number of cases studied is small, especially in comparison to those of a similar type examined in terms of electronic motion (conservation of orbital symmetry, COS) rules. Since rearrangement reactions promise in the future to be important subjects for continued application of least motion analysis, it is useful at this point to reexamine a typical set and compare results with COS analysis. Employing the closed form equations, agreements and disagreements and reasons therefore may be usefully explored.

The particular set of reactions chosen is the electrocyclic ring opening-closing reactions. Tee and Yates¹⁴ have examined a small number of these cases and contrasted their results with those of Woodward and Hoffmann.¹⁵ Of those systems examined, three in number (cyclopropyl-allyl cation, butadiene-cyclobutene, hexatriene-cyclohexadiene), only for the latter did predictions as to stereochemical course (conrotatory *vs.* disrotatory motion accompanying rearrangement) disagree. Tee and Yates correctly analyzed the discrepancy as being due to overriding importance of orbital symmetry in the formation of the new σ bond. For this reason, the disrotatory path is the preferred one, despite the greater motion involved.

This effect can be recognized as one of the mitigating effects discussed previously and can be incorporated into the vibration analogy model upon force constant weighting. From either ground state end point, and either is equally acceptable here in light of conservation of nucleus number, conrotatory motion would be accompanied by an incremental increase in antibonding character as the primary bonding decreases, whereas for disrotatory motion, bonding of one type (σ or π , depending on the reaction direction) replaces the other. Consequently, the force constant for conrotatory motion would be larger, reflecting a greater energy change for equal twist, for this as well as for all other $4n + 2$ π -electron systems. Conversely, in $4n$ π -electron systems, ground state electrocyclic transformation should proceed by conrotatory paths since disrotatory motion here would be accompanied by antibonding terminus interactions.

Unweighted least motion does not explicitly recognize these effects. From the analytic forms developed in ref 2 it may be shown, in fact, that the unweighted analysis will generally predict conrotatory paths favored as long as the rotational motions of the CH_2 groups occur about axes normal, or close to normal, to the

(14) O. S. Tee and K. Yates, *J. Amer. Chem. Soc.*, **94**, 3074 (1972).

(15) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

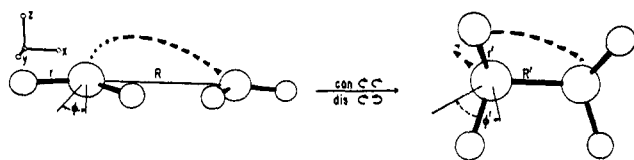


Figure 1. Coordinate system and variables for electrocyclic ring opening-closing reactions.

vector describing the newly forming (or breaking) CC σ bond and, as well, that most of the over-all intramolecular motion is due to these CH₂ groups.

From eq 9 of ref 2, it may easily be shown that for linear structure and rings disposed as in Figure 1

$$\Delta(D^2)_{R\gamma} [\text{dis} - \text{con}] = 2[(\{xx'\}^2 + \{xz'\}^2)^{1/2} - (\{yy'\}^2 + \{yz'\}^2)^{1/2} + \{yy'\} - \{xx'\}] \quad (1)$$

where

$$\begin{aligned} \{pq'\} &= \sum_{i=1}^N p_i q_i' \\ \{xx'\} &= \frac{3}{2}RR' + 2Rr' \cos \theta \sin \varphi' + \\ &\quad r \sin \varphi [R' + 2r' \cos \theta \sin \varphi'] \\ \{yy'\} &= \frac{2}{3}rr' \cos \theta \cos \varphi' + \text{ring contribution} \quad (2) \\ \{xz'\} &= -2\sqrt{3}rr' \sin \theta \cos \varphi \\ \{yz'\} &= -2\sqrt{3}rr' \sin \theta \sin \varphi \end{aligned}$$

Here, θ is half the focal HCH angle in the ring structure; this HCH angle in the linear structure is assumed to be 120°. It is apparent that only in the event φ departs significantly from zero (the amount necessary dependent upon the ring contribution to $\{yy'\}$) will the disrotatory mode be favored.¹⁶

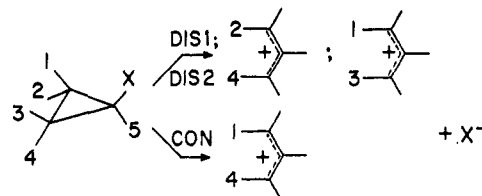
Numerical results obtained for real molecule cases completely support the foregoing analysis.¹⁴ Of those considered, only for the small ring system, cyclopropyl cation, where φ and φ' are large, and where $\{yy'\}$ is small, is the disrotatory mode favored. The conclusion, it should be noted, is valid for planar chain structures as well as for the optimal symmetric distortions of the larger chain structures examined, the latter serving mainly to minimize the distortions necessary at the nonreactive molecular sites in transformations to the ring structures. Only in the event of considerable dissymmetry in either the chain or ring structures is this angular (φ -) dependence generalization likely to break down.

Two other features of cyclopropyl-allyl systems are also pertinent to the present analysis. The first concerns extension to the radical and anion cases. COS (and associated results from semiempirical MO methods)¹⁵ suggests that in these rearrangements the conrotatory mode will be favored. From eq 1 and 2, it may be concluded that least motion should not reproduce this reversal, unless rather extreme structural

(16) An extreme yet easily visualized model case is with two CH₂ groups. If $\varphi = 0$, conrotatory motion is favored because rotational adjustment by $\tan \gamma = \{xz'\}/\{xx'\}$ effectively reduces D^2 . When $\varphi = 90^\circ$, it is a rotation by $\tan \gamma' = \{yz'\}/\{yy'\}$ that makes the disrotatory mode more favorable. The latter case, $\varphi = 90^\circ$, resembles the twisting process, for example, in ethylene (see the ν_2 associated motion in the ethyl halide elimination section). Disrotatory motion turns the whole molecule without twisting the CH₂ groups with respect to each other, unquestionably a more favorable process.

differences, especially in φ , which are not expected, occur. As in the hexatriene comparison, the deficiency of the conventional least motion analysis in recognizing orbital interaction constraints can again be cited.

The second feature involves ring opening of X-substituted cyclopropane, with concerted loss of X⁻, where two distinguishable disrotatory modes and one conrotatory mode are to be considered.



DIS2 is favored by least motion, in agreement with semiempirical MO and more exact calculations, because of a reinforcing term in $\{yz'\}$ (a negative term due to the nonplanar H5 in the ring). D^2 for DIS1, on the other hand, is increased because $\{yz'\}$ is decreased, becoming, for reasonable structural choices of the ring and chain cations, about the same size as for the conrotatory process.

The results obtained for the electrocyclic reactions may be usefully summarized at this point as follows, prior to presentation of some other rearrangements and related reaction processes where transition state structures and differential pathway motions are explicitly examined.

It is apparent that unweighted least motion analysis, as conventionally applied, fails to explicitly recognize important quantum mechanical effects, except as these may parallel gross structural effects operative at the reaction end points. These effects may, however, often be incorporated through force constant weighting upon recognition of analogous small vibration effects. It further appears that the least motion method, conversely, may be sufficiently unselective about the relative importance of various structural features of the end-point states to fail in correlations of series of related reactions. The previous analysis for the electrocyclic reaction, where strong contributions of the term $\{yy'\}$ relative to $\{yz'\}$ were inferred, presents an example where the effect of increasingly larger group substitution at sites removed from (and having little if any influence on the geometry or other properties of) the reaction sites could reverse the predicted reactivity order.

Exchange and Substitution Reactions. There are a number of chemical systems wherein substitution and abstraction pathways are competitive and which contain many of the elements of structure and reactivity discussed previously, as well as several novel ramifications. The reactions chosen here are between CH₄ and hydrogen atoms and CH₄ and protons. While certain details are presently lacking, both from the experimental as well as *ab initio* molecular orbital and other theoretical studies on these systems, they represent good compromises in simplicity for the purposes of theory and yet have details of mechanism and structures of intermediates among which least motion analysis might reasonably be expected to distinguish. They further possess the qualities of pertinence, especially the H-atom reactions; active experimental and trajectory theory program on the hot atom and

thermal aspects of these and closely related reactions are currently going on in several laboratories¹⁷⁻¹⁹

A. Separated Reactants Forming CH₅ Species. The exchange reactions of hydrogen atoms, above thermal energies, and protons (in the presence of a third body), with CH₄, to reproduce CH₄ are believed to involve intermediate structures of the type shown in Figure 2.

In the ion-exchange reactions, all pertinent structures are stable with respect to H⁺ + CH₄ and all have the same total energies within a very small range, as computed by relatively good theoretical treatments.²¹ If any structure is to be favored for a transition state (arising in the reaction CH₄ + MH⁺), it is that of C_s symmetry, more from steric considerations (there are more edges and face diagonals available than unoccupied corners of the methane containing cube) than from its slightly more favorable energy. Experimental stereochemical support of C_s-type transition states for gas phase proton exchanges (by HeT⁺) on halogenated alkanes has recently been reported.²²

In contrast, for the atom substitution reaction, the D_{3h} structure is the most energetically favorable of the three; it is predicted to be ~40 kcal²³ less stable than isolated H and CH₄. Because this theoretically obtained result (by CI-double ζ STO MO methods) is satisfactorily in agreement with the experimental threshold reaction energy (~35 kcal/mol),²⁴ the exchange reaction is presumed to go through a transition state with this structure.

Accepting the theoretically obtained geometric parameters for these structures with the same confidence as their energies, we may compare what the PLM method suggests as the most favorable transition state structures.

Table I contains the results for both reaction types and as well for the different positions in these structures which the entering hydrogen can occupy. Several comparisons may be immediately drawn from this table. In all intermediates, the least motion quantities for formation are in agreement with empirical steric arguments as to which is the most favorable entry mode for the incoming hydrogen. For example, formation of the D_{3h} complex by axial attack, the Walden inversion mode (which involves approach to the methane cube at an unoccupied corner), is supported by PLM measures to be more facile than approach to a face (equatorial attack). In the formation of the eclipsed C_s complexes, both modes involve direct approach to an edge, but one (entrance into an H_b position) involves very large internal hydrogen movements.

(17) Cf. R. Wolfgang, *Progr. React. Kinet.*, **3**, 97 (1965); *Accounts Chem. Res.*, **2**, 248 (1969); **3**, 48 (1970).

(18) D. L. Bunker and M. D. Pattengill, *Chem. Phys. Lett.*, **4**, 315 (1969); *J. Chem. Phys.*, **53**, 3041 (1970).

(19) Various details of the least motion analysis of these reaction systems have already been presented.²⁰ They are reexamined, expanded upon, and interpreted here consistent with the evaluation of the merits of the original and improved least motion models.

(20) S. Ehrenson, "Chemical and Biochemical Reactivity," Proceedings of the International Jerusalem Symposium, 6th, 1973, in press.

(21) W. Th. A. M. van der Lugt and P. Ros, *Chem. Phys. Lett.*, **4**, 389 (1970).

(22) F. Cacace and M. Speranza, *J. Amer. Chem. Soc.*, **94**, 4447 (1972).

(23) K. Morokuma and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1060 (1972).

(24) C. C. Chow and F. S. Rowland, *J. Chem. Phys.*, **50**, 5133 (1969), and references contained therein.

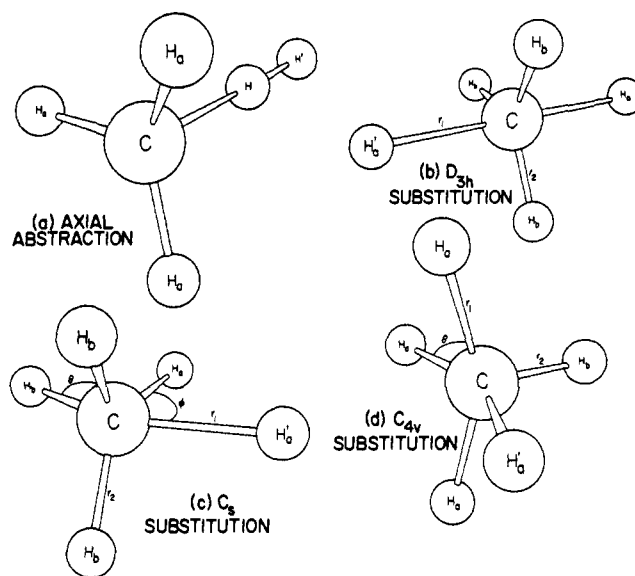


Figure 2. Intermediate structures for hydrogen-methane substitution and abstraction reactions.

Table I. (D^2)_{R_γ} Values for the Production of Various CH₅ Structures^a

Structure	Entering position ^b	Cation ^c	Radical ^d
D _{3h}	Axial H _a	0.171, 0.298	0.108, 0.291
	Equatorial H _b	0.689, 0.814	0.998, 1.116
C _s (eclipsed)	H _a	0.139, 0.174	0.269, 0.332
	H _b (I)	0.492, 0.756	0.359, 0.686
	(O)	1.124	1.128
C _s (staggered) ^e	H _a	0.139, 0.174	0.269, 0.332
	H _b (I)	1.862	2.036
	(O)	0.653	0.555
C _{4v}	H _b	1.859	1.778
	H _a	0.314, 0.428	0.331, 0.456

^a In Å², obtained with unit weighting; secondary entries, following commas, obtained with mass weighting. The experimentally determined distance, 1.106 Å is the value taken for r_{CH} in methane.

^b Hydrogen positions as labeled in Figure 2. I and O refer respectively to entering positions in and out of the xy plane. The out-of-plane species do not have C_s symmetry and hence cannot be evaluated with the closed form expression. ^c Geometries from the SCF-MO calculation of ref 21. ^d Geometries from the SCF-CI-MO calculations of ref 23. Geometries and (D^2)_{R_γ} values computed therefrom are substantially the same as from the extended basis set Gaussian calculations of ref 29. ^e Structure where H_aCH_a group twisted π/2 to lie normal to the xy (C_s symmetry) plane.

This distortion difference is certainly verified by the D^2 quantities computed.

The analytic forms developed allow inquiry into the geometric features which produce the noted effects. Application of eq 9, ref 2, for example, yields the following difference relationship for the D_{3h} structures formed in the different entry modes

$$\Delta(D^2)_{R\gamma}(\text{eq} - \text{ax}) = (6/5)(r_a^2 - r_e^2) - r_m[(8/\sqrt{6}) - 2)r_a - 2(\sqrt{2} - (1/\sqrt{3}))r_e] \quad (3)$$

This equation reveals the order of preferred entry to be unchanged for any reasonable D_{3h} structure; viz., for r_a > r_m, (r_e/r_m) would have to be greater than 1.35 for equatorial entry to be preferred.

All discussion on the methane exchange reactions thus far, it should be noted, is based on the unweighted least motion results. Mass weighting would be ex-

pected to have minor effects on the entry mode comparisons, which are generally characterized by large D^2 differences, mainly because carbon lies fairly near the centers of gravity for the distorted methane final state structures. This may be verified from the limited mass weighted results contained in Table I. Only in the case of the D_{3h} radical where a very long axial CH bond pertains is a large effect noted. Force constant weighting would even more strongly favor the preferred modes, as they correspond to the lowest energy paths into the respective CH_5 structures (see below, remarks on CH_5 interconversions).

The results for the formation of the D_{3h} compared to the C_s symmetry structures are even more pertinent, here bearing on the over-all mechanism for the exchange. For the preferred modes of entry, in the ion, PLM predicts the C_s structure to be mildly preferred, while in the radical the D_{3h} structure is favored, but substantially more strongly. These relative preferences, which are substantially unaffected by mass weighting, are in excellent agreement with those obtained from consideration of the theoretically obtained energies and steric arguments as previously discussed. Recent trajectory studies by Valencich and Bunker on an all-(6)-atom potential surface appear to verify the predominance of T-atom exchange on methane through D_{3h} structures at moderate energies.²⁵ Other substitution channels are predicted to become very important at higher energies, *i.e.*, $\gtrsim 100$ kcal tritium.

In the present PLM calculations, these relative preferences may be traced mainly to the differences between the lengths of bonds, CH_a for both structures, between the ions and radicals. For both structures, the CH_a distances are increased considerably in the radical (1.35 and 1.36 Å, for the D_{3h} and C_s structures, respectively, *vs.* 1.13 and 1.17 Å in the ion). This increase is such that in the D_{3h} radical the H_aH_b distances are essentially the same as are the interhydrogen distances in CH_4 , which accounts for the small D^2 value calculated. That these lengths should be so extended is entirely reasonable on bonding arguments relating to plivalence of carbon and the extra electron in the radical. The CH_b bonds for both species, on the other hand, are theoretically predicted to change little from the methane length; their relative constancy explains the considerably larger D^2 values obtained for the less favorable modes of entry (where two axial and two equatorial bonds are identifiably formed from four methane bonds *vs.* one axial and three equatorial bonds in the preferred mode).

For both the ion and radical, the C_{4v} structure is predicted by PLM to be the least preferred of the three exchange structures. Little should be made of this in the way of comparison with theory at this point, although the role played by such forms in the pseudorotation process will be considered below.

While attention has been mainly directed toward the substitution reactions, it is also of interest to consider the abstraction reaction. In the neutral reactions (producing $\text{CH}_3 + \text{H}_2$), this is known experimentally^{24,26} and supported theoretically to be the preferred channel at low energy.²³ Employing the computed

saddle point parameters,²³ corresponding to the axial (C_{3v}) structure shown in Figure 2, (D^2)_{RY} values of 0.037 unweighted (0.086 mass weighted, Å²) are obtained, considerably and not surprisingly smaller than that obtained for the preferred mode of substitution (0.108 unweighted, 0.291 mass weighted, Å²). Here we note that although one CH bond is noticeably longer than in CH_4 (1.365 Å²), and even more extended than in the D_{3h} structure, the rest of the molecule is essentially unchanged. Least motion again appears able to correlate the observed reactivity ordering (abstraction preferred over exchange).

At this point it is again useful to raise the question of whether PLM ordering among reactions which produce substantially different products can be expected to be meaningful. While generally a negative response would be in order as previously concluded, especially when the different products are the compared end points, when both reactions are simple and presumably characterized by at least roughly similar transition states which constitute the end points of the motions, the comparison would appear to be safer. This transition state approach has been used here; its extension, as follows, reemphasizes the similarities assumed for both reactions (abstraction and exchange) in the vicinity of the respective transition states.

Another postulated mechanism for abstraction is through a knockout or stripping type mode,¹⁷ as a result of a glancing approach of H, which may be imagined to proceed through a structure of the C_s symmetry type. We may on the basis of the PLM reject this mode, at least as far as a comparison at thermal energies with the head on attack by hydrogen to form the C_{3v} transition state structure goes. Here, a very substantial difference in D^2 values exists (0.269 to 0.037 Å² unweighted, 0.332 to 0.086 Å² mass weighted); the arguments, as concern structures for the transition states, exactly parallel those which may be drawn purely on energy grounds.

B. Pseudorotations and Similar Rearrangements among CH_5 Species. Among the most interesting observed or potentially observable details of the exchange reactions undergone by alkanes and substituted alkanes with hydrogen and MH^+ involve accompanying stereochemical changes. Assuming the methane reactions as prototypes, we may label the hydrogens and follow various reaction channels by least motion analysis in a way similar to theoretical energy surface analyses previously carried out.^{27,28}

1. Rearrangements Involving D_{3h} Symmetry Structures. Formation of a D_{3h} symmetry structure transition state, Figure 2b, is reasonably expected on all empirical and heretofore obtained theoretical grounds to lead to inversion upon exchange. The Walden pathway certainly represents a smooth route for exchange as far as continuity of motion is concerned. Moreover, only for the asymmetric stretch corresponding to this motion is the force constant negative.²⁹ It seems useful to inquire whether unweighted as well as force constant weighted least motion analysis supports this conclusion and how other intramolecular shifts carry out of this structure on the way to product.

(27) S. Ehrenson, *Chem. Phys. Lett.*, **3**, 585 (1969).

(28) R. E. Weston and S. Ehrenson, *Chem. Phys. Lett.*, **9**, 351 (1971).

(29) S. Ehrenson and M. D. Newton, *Chem. Phys. Lett.*, **13**, 24 (1972).

(25) T. Valencich and D. L. Bunker, *Chem. Phys. Lett.*, **20**, 50 (1973).

(26) R. N. Walker, *J. Chem. Soc. C*, 2391 (1968); M. Kurylo and R. B. Timmons, *J. Chem. Phys.*, **50**, 5076 (1969).

Retention of configuration is possible if the D_{3h} structure undergoes five successive pseudorotations (where the incoming and outgoing hydrogens both occupy axial positions at the onset and finish of the process, to guarantee microscopic reversibility). Tee has calculated the D^2 values for these intraconversions for a hypothetical structure with $r_{\text{CH}_a} = 1.1$ and $r_{\text{CH}_b} = 1.0$ Å and found them to be large (between 1.22 and 6.00 Å², over the various steps).⁴ From the analytic forms, we may easily confirm these results and, further, predict that for the theoretically obtained structures they are even larger for the ion (1.35 to 7.47 Å²) and the radical species (1.85 to 7.08 Å²). The first number in each case refers to a single pseudorotation; for multiple pseudorotations the D^2 value steadily increases.

Examination may also be made of the motion required to get to the optimized C_{4v} structure, which represents the midpoint, or what might correspond to a transition state, for the single pseudorotation process. The analytic least motion equations are respectively for pseudorotation (Ps: $D_{3h} \rightarrow D_{3h}$) and intermediate pseudorotation (IPs: $D_{3h} \rightarrow C_{4v}$)

$$(D^2)_{R\gamma}(\text{Ps}) = 4(r_b^2 + r_a^2 - \sqrt{3}r_b r_a) \quad (4)$$

$$(D^2)_{R\gamma}(\text{IPs}) = 3(r_b^D)^2 + 2(r_a^D)^2 + (r_b^C)^2 + 4(r_a^C)^2 - \frac{(r_b^C + 4r_a^C \cos \beta)^2}{5} - 2\{r_a^C r_b^D (\sqrt{3} \sin \beta - \cos \beta) + 2r_a^C r_a^D \sin \beta + r_b^C r_b^D\} \quad (5)$$

The species labeling conforms to Figure 2 with superscripts D for D_{3h} and C for C_{4v} ; β is the angle H_aCH_b in the C_{4v} structure. For the ion and radical we find D^2 values for conversion to the C_{4v} structure of 0.35 and 0.49 Å², respectively, only a small fraction of that for the entire pseudorotation. Nevertheless, for all these D_{3h} interconversion processes, the distortions as measured by the PLM are large compared, for example, to those for decomposition back to methane by the Walden mode. They must be judged therefore as representing an unlikely process *independent of the use of force constant weighting*, with the reservation that a comparison between intermediate intraconversion and product formation involves vastly different end points and hence is open to the question of validity raised before.³⁰

Another pertinent comparison of such processes is available through examination of the relative differential motions upon departure from the common state, *i.e.*, here, by considering the normal mode vibrations of D_{3h} CH_5 leading toward pseudorotation *vs.* (Walden-like decomposition to $\text{CH}_4 + \text{H}$).

From eq 12 and 13 of ref 2 we find that for the two vibrations of A_2'' symmetry³¹ which resemble Walden

(30) Interestingly, pseudorotation is intramolecularly discontinuous only as regards the motions of the Walden formation mode. It represents, however, a smooth continuation of the motions accompanying equatorial attack, and, moreover, has D^2 values ($D_{3h} \rightarrow C_{4v}$) which are favorable compared to formation by this, itself a disfavored mode.

(31) The symmetry coordinate vibrations related to the Walden inversion (A_2'') and pseudorotation (E') types of distortions of D_{3h} structures follow.^{29,32} For A_2'' vibrations: $R_3, (\Delta r_{a1} - \Delta r_{a2})/\sqrt{2}$; $R_4, r_a \Sigma(\Delta \beta_{a1b_j} - \Delta \beta_{a2b_j})/\sqrt{6}$. For E' vibrations: $R_{5a}, (2\Delta r_{b1} - \Delta r_{b2} - \Delta r_{b3})/\sqrt{6}$; $R_{5b}, (\Delta r_{b2} - \Delta r_{b3})/\sqrt{2}$; $R_{6a}, r_a \Sigma(2\Delta \beta_{a_j b_1} - \Delta \beta_{a_j b_2} - \Delta \beta_{a_j b_3})/\sqrt{12}$; $R_{6b}, r_a \Sigma(\Delta \beta_{a_j b_2} - \Delta \beta_{a_j b_3})/2$; $R_{7a}, r_b (2\Delta \phi_{b_2 b_3} - \Delta \phi_{b_1 b_2} - \Delta \phi_{b_1 b_3})/\sqrt{6}$; $R_{7b}, r_b (\Delta \phi_{b_1 b_2} - \Delta \phi_{b_1 b_3})/\sqrt{2}$. The variables, r , are as labeled in Figure 2 and the angles β and ϕ are respectively H_aCH_b and H_bCH_b , with H_{b_1} the equatorial hydrogen lying in the xy plane. All summations are with index j over 1 to 3.

inversion-like departure from the D_{3h} structure

$$(\Delta D^2)_{R\gamma} = \frac{5}{6}\{(\Delta r_{a1})^2 + (\Delta r_{a2})^2\} + \frac{1}{3}\Delta r_{a1}\Delta r_{a2} + r_b\{\frac{3}{2}r_b(\Delta \beta)^2 + (\Delta r_{a1} - \Delta r_{a2})\Delta \beta\} \quad (6)$$

where β is the angle H_{a1}CH_b ($\pi/2$ in the D_{3h} structure), and negligible change in r_b is assumed.

The vibrations distorting the D_{3h} structure in the direction of pseudorotation are of E' symmetry and are described by the following analytic least motion equation

$$(\Delta D^2)_{R\gamma} = \{2(\Delta r_a)^2 + (\Delta r_{b2})^2 + r_a^2(\Delta \beta)^2 + (r_{b2}^2(\Delta \phi/2)^2)\} - \frac{1}{6}(\sqrt{3}r_{b2}(\Delta \phi/2) - 2r_a\Delta \beta - \Delta r_{b2})^2 \quad (7)$$

where ϕ is the angle $\text{H}_{b2}\text{CH}_{b3}$ (involving the out-of- xy -plane equatorial hydrogens, 120° in D_{3h} structure), and again negligible change in r_{b1} is assumed.

If we now adjust the deformations for these equations to conform to the processes as we understand them, *i.e.*, for eq 6

$$\Delta r_{a1}(\text{outgoing H}) = \Delta R > 0$$

$$\Delta r_{a2}(\text{remaining H}) = -C_a \Delta r_{a1}; 1 \geq C_a \geq 0 \quad (8)$$

$$r_b \Delta \beta = C_b \Delta R; 0 \geq C_b \geq -1$$

then the minimax conditions for $(\Delta D^2)_{R\gamma}/(\Delta R)^2$ are respectively $1/2$ (with $C_a = -C_b = 1/2$) and $4/3$ (with $C_a = 0, C_b = -1$ or $C_a = 1, C_b = 0$).

For eq 7, the differential minimum motions are much larger. Even if equal changes in the CH_a and CH_b bond lengths, equal to Δr_{a2} for the Walden inversion process, are assumed, which seems reasonable for comparison between the two modes, the $(\Delta D^2)_{R\gamma}/(\Delta R)^2$ value is substantially greater than 23/24 (by an amount determined by the sizable angular contributions). Mass weighting only reduces the difference somewhat, principally by increasing the value for the inversion process which has a greater relative displacement (uncorrected) of the center of gravity.

Again, we are presented with confirmation by the least motion analysis with or without mass or force constant weighting that deformation of the D_{3h} structure is most easily accomplished in the axial attack-departure mode to product. Considerably more confidence it would appear is justified for this type of comparison than any involving substantially different product end points.

2. Rearrangements Involving C_s Symmetry Structures. CH_5 structures of C_s symmetry might, it has been speculated, undergo intramolecular shifts through generally lower symmetry structures but returning to their original symmetry form, processes which could profound implication on the stereochemical outcome of the exchange.^{27,28} Because of the relative energetics, (*i.e.*, C_s symmetry forms are at least competitive with other likely intermediate forms in the ion formation, and low energy barriers are predicted for C_s intraconversions), this seems a more important consideration for the ions at thermal energies but may also be of real concern for the radical reactions above thermal energies.²⁸ In ref 27, the theoretical energetic and structural arguments which lead to the postulation of racemization, rather than retention, out of C_s symmetry ion intermediates are detailed. The least motion

(32) P. C. Haarhoff and C. W. F. T. Pistorius, *Z. Naturforsch. A*, **14**, 972 (1959).

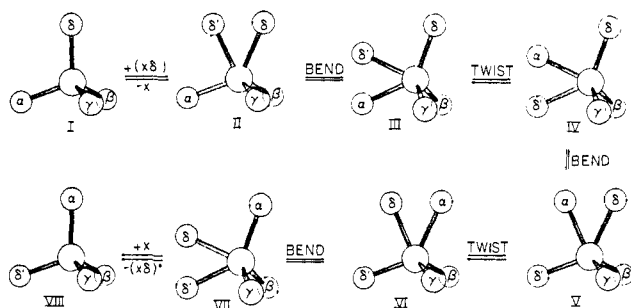


Figure 3. Interconversion scheme among C_s symmetry species.

implications of these rearrangements may be usefully compared.

Figure 3 depicts the formation of CH_5^+ , and the subsequent series of five bends and twists leading to the ion which returns inverted CH_4 with full obedience to the principle of microscopic reversibility. In Table II,

Table II. $(D^2)_{R\gamma}$ Values for Intraconversion of C_s Symmetry^a

Structures ^b (initial, final)	Equivalent ^c motions	Cation ^d	Radical ^e
II, III	B	0.163	0.082
II, IV	BT, TB	3.479	4.790
II, V	BTB	4.433	4.422
II, VI	BTBT, TBTB	5.867	6.214
II, VII	BTBTB	6.336	6.315
III, IV	T	2.574	5.014
III, VI	TBT	5.205	6.115
E, S'	$\frac{1}{2}$ T	1.087	2.027
C_s, C_{2v}^o	$\frac{1}{2}$ B	0.306 ^h	0.248 ^h
		0.058 ⁱ	0.031 ⁱ

^a In \AA^2 . ^b Numbering conforms to Figure 3. ^c B and T stand for bend and twist motions, respectively; a series of these symbols implies successive motions as depicted in Figure 3. ^d Geometries from the SCF-MO calculations of ref 21. ^e Geometries from the SCF-CI-MO calculations of ref 23. ^f For the torsional motion converting the eclipsed C_s structure to the staggered, which is the midpoint in the full T motion. All other geometric parameters are unchanged. ^g For the bending motion to a C_{2v} structure, which represents the midpoint in the full B motion. *E.g.*, in the II, III transition, δ' , β , γ , and C are in a plane and α , δ' , δ , and C are in another, perpendicular to the first, with β and γ and α and δ occupying symmetric positions. In this structure it is assumed that $r_{C\alpha}$ ($=r_{C\delta}$) is the average of these distances in II; the angle $\beta C \gamma$ is 120° and $r_{C\beta} = r_{C\gamma}$ unchanged from the C_s structure. ^h Angle $\alpha C \delta$ equals 180° , $r_{C\delta'} = r_{C\beta}$. ⁱ Angle $\alpha C \delta$ and $r_{C\delta'}$ have the same values as in II.

the least motion $(D^2)_{R\gamma}$ values connecting all possible unique shifts within this scheme, from one C_s structure to another, are given, both for CH_5^+ and CH_5^\cdot , employing their theoretically determined geometries. Values are also given for the distortions required to get to the midpoints of the individual single intraconversion. For these latter calculations, some geometric assumptions are of course necessary.

In contrast to the pseudorotations considered previously, at least the first isomerizations (II-III type), which superficially appear to require rather large angle deformations as well as expansions of one and contractions of another bond, are characterized by least motion measures as reasonably likely processes, both on the basis of absolute D^2 values and in comparison with those obtained for formation of the C_s symmetry

structures. Close examination reveals that really rather small distortions have taken place in the bend (II-III), especially when viewed from the position of superimposed centers of gravity. The twist (III-IV), on the other hand, which has been verified for the ion to be a process requiring little energy,²⁷ in agreement with energy results obtained for many other sixfold barriers¹² has very large D^2 values associated with it; *i.e.*, the D^2 values are more than an order of magnitude greater than for the corresponding bends, do not vary with geometry changes between the ion and radical as do the bends, and as a matter of fact are characterized by even larger values than pseudorotations. The half-twists, while having considerably smaller values, are still predicted to be more unfavorable than the full bends.

This result presents the first major conflict between predictions based on unweighted least motion analysis and potential energy (enthalpy) differences for the CH_5 systems, and, interestingly, the motion analysis appears to better model the reaction system. The HeT^+ exchange reactions with halogenated alkanes are the closest, albeit imperfectly analogous, systems studied. These reactions, reasonably assumed to go through C_s transition states, are characterized almost completely by retention of configuration, with very little racemization observed.²²

The barrier energy-motion disagreement observed here is probably a general one in that n -fold torsions (especially where n is large) are usually low-energy processes, but because of the interatomic distance changes accompanying full group rotations will be characterized by large D^2 values. Again restoring to analogy with the vibrational analysis model, some amelioration of this disagreement will accompany weighting. The force constants for the twist torsions will be small, even in comparison with those for the bends, which are, themselves, apparently quite soft.³³

Dimerization Reactions

Another and final example of the utility of the closed form least motion equations is useful; the dimerization reaction of methylene to form ethylene seems particularly appropriate. Hoffmann, *et al.*,³⁴ have examined this system by means of semiempirical MO methods and concluded that, upon separation, singlet methylene fragments would prefer, early on, a C_{2h} symmetry configuration (methylene planes parallel) and then, upon further separation, a C_s conformation (with methylene planes perpendicular to each other), rather than maintain a D_{2h} conformation (methylenes coplanar) as in ethylene. This result is claimed to be in disagreement with what least motion analysis would predict.

The unweighted closed form results for the end-point cases (corresponding to large separation) are easily

(33) Perhaps, significantly, the twists are recognizable as intramolecularly disconcerted motions when viewed in terms of continuity of the formation process (edge attack on the methane cube). Recall as well the similar analysis for pseudorotation. On the other hand, bends of the sort which intraconvert hydrogens between the twofold and threefold symmetric positions represent a continuity of motion and appear to be favorable, both absolutely and in comparison with the formation process. Inspection reveals the source of the D^2 value similarity; very similar sorts of bends are involved in the (II-III) interconversion and in the formation process from isolated hydrogen and methane.

(34) R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Amer. Chem. Soc.*, 92, 1460 (1970).

obtained. They are

$$(D^2)_{R\gamma}(D_{2h}) = \frac{3}{2}(\Delta R)^2$$

$$(D^2)_{R\gamma}(C_s) = \frac{3}{2}(\Delta R)^2 - r\Delta R - \frac{1}{3}r^2 - W(R, r, r') \quad (9)$$

where ΔR is the difference in the C-C distance between the separated methylenes and the original ethylene systems, and r is the CH bond length (assumed unchanged with stretching, as are the CH_2 angles, 120°). W is a small positive sum of fractions, all with R' , the methylene carbon separation, in the denominator, a remainder in the expansion of the square root quantity of eq 9, ref 2 for large R' .

It is apparent from this result that, ultimately upon separation, the methylenes would prefer to adopt the C_s conformation by least motion considerations. This may have been qualitatively anticipated since the rotational possibilities inherent in the superposition of the C_s and ethylene structures, which, with all other things being equal, diminish the least motion distortions relative to those which appear to develop upon coplanar stretching.

It is even more instructive to examine the closed form differential least motion equation for this system. In terms of the separation parameter, ΔR , we obtain from eq 12 and 13 of ref 2

$$\frac{(\Delta D^2)_{R\gamma}}{(\Delta R)^2} = \frac{3}{2} - \frac{((r/2)[\cos(\theta + \epsilon\theta) + \cos\theta])^2}{\frac{3}{2}R^2 + \frac{2}{3}r^2 + Rr \sin(\theta + \epsilon\theta) + (r/3)[3R \sin\theta + r \cos(\epsilon\theta)]} \quad (10)$$

where the notation for distances are as above, and the angles θ and $\epsilon\theta$ following Hoffmann's notation are as shown in perspective Figure 4. From eq 10 it may be quickly gathered that the *maximum* motion accompanying extension or contraction of the C-C distance occurs from ethylene-like (D_{2h}) conformations, *i.e.*, where $\theta = \pi/2$ and $\epsilon\theta = 0$, but that at large R the minimum motion occurs from the C_{2h} symmetry structure ($\theta = \epsilon\theta = 0$) rather than from the C_s structure predicted by Hoffmann from MO considerations. It should be stressed, however, that at these distances the differences are small, due to the large denominator in eq 10, but that deformation of the ethylenic D_{2h} structure remains the costliest. These results may be usefully rationalized by reference to the general reaction path dynamics analysis contained in the preceding paper.² From the D_{2h} , C_{2h} , and C_s structures respectively the reaction path motions are seen to occur at increasingly greater angles to the vector connecting the centers of gravity of the dissociating species (the CH_2 groups).

Hoffmann attributes charge transfer as a stabilizing feature for the C_s structure; this factor, of course, does not enter into the unweighted least motion analysis. Nor is it apparent how force constant weighting could be introduced without intimate knowledge of the energetics of the transient, partially dissociated structures involved. The interesting possibility exists of including lone pairs (and perhaps even empty orbitals, appropriately weighted) into the motion analysis, since these describe important, albeit nucleus-independent, bonding potentialities for the separate fragments.

However, whether it is appropriate to be concerned about such refinements at this time is questionable. More recent and exact theoretical studies³⁵ have re-

(35) H. Basch, *J. Chem. Phys.*, **55**, 1700 (1971).

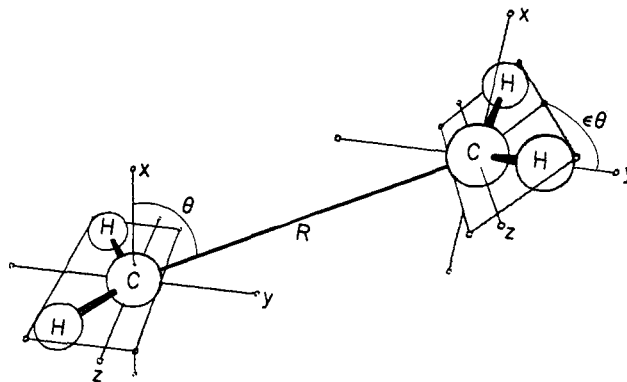


Figure 4. Coordinate system and variables for the methylene dimerization reaction.

vealed coplanar triplet, rather than singlet, methylenes correlate with the ground state of ethylene and that for closed shell, singlet state methylenes the coplanar reaction path is repulsive. As with charge transfer from filled to empty orbitals, the least motion method recognizes no such multiplicity differences beyond their influences on geometry.

Conclusions

In this paper, analytic formalisms for the harmonic springs least motion model have been applied to a number of systems of chemical interest. Examination of the individual atom and group contributions to the over-all motions, and comparison with energy effects forthcoming from vibrational analysis and other theories, have presented a better understanding of why the PLM works to correlate reactivities when it does and under what circumstances it is likely to fail.

In particular, when comparisons of rates for similar reactions are to be made, PLM calculations will be successful when the end-point structures reflect all important bonding effects which determine the nature of the respective transition states. In this event, even in the absence of weighting by masses and/or force constants, the model is very often capable of distinguishing among the relative energetics of various distortion modes. When effects such as orbital symmetry constraints and other bonding or antibonding requirements are not reflected in the end points chosen, invocation of weighting, particularly by force constants, and knowledge of transition state structures may, however, be necessary for successful correlation of rates by the motion analysis method.

If a generalization may reasonably be drawn from the limited number of cases examined here and elsewhere, it appears that there is sufficient firm theoretical ground and easily obtained successful or rationalizably deficient correlational utility to justify further application of least motion to reactivities. Both extended application to other systems from a pragmatic point of view, and further analytic comparison to other theories for reactivity is desirable. Comparisons with theories of molecular dynamics, as regards the latter, seem particularly appropriate, since there are aspects of reaction probability as well as energetics to correlate with the motions of reacting systems. At present, there is no information on how they correspond or in fact if the vibrational model can, even with weighting, encompass them.